SCOPE UNEP

PHOSPHORUS CYCLES IN TERRESTRIAL AND AQUATIC ECOSYSTEMS

REGIONAL WORKSHOP 1: EUROPE

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Edited by Holm Tiessen

SASKATCHEWAN INSTITUTE OF PEDOLOGY

PHOSPHORUS CYCLES IN TERRESTRIAL AND AQUATIC ECOSYSTEMS
REGIONAL WORKSHOP 1: EUROPE

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Preface

In 1974, the SCOPE Executive Committee initiated the biogeochemical cycles project to focus on the study of the cycles of carbon, nitrogen, sulphur and phosphorus separately one after another. It was understood from the beginning that none of these cycles operates in isolation from the others and that there are many linkages and mutual interactions to be understood. Hence, over the intervening 15 years the biogeochemical cycles focus has been two-fold; (1) to understand the individual cycles and (2) to understand their linkages with one another. Studies on nitrogen, carbon, sulphur and some heavy metals have been underway for some time and it was not until the General Assembly in 1985 that SCOPE launched a study aimed at better understanding the nature, sources and fluxes of phosphorus in terrestrial and aquatic ecosystems and its global environmental effects through interactions with the cycles of other elements.

Shortly after the Washington General Assembly in 1985 the SCOPE Executive asked C.V. Cole to take the leadership in developing this project and together with a Scientific Advisory Committee consisting of J.R. Freney, S. Kempe, V. Subramanian, J.K. Syers, J.D. Beaton, H.L. Golterman and J.W.B. Stewart (ex officio), a proposal was formulated which received initial financial support from the United Nations Environment Program and from the Andrew W. Mellon Foundation. The proposal adopted by UNEP envisaged three levels of activity; (a) the organization of four regional workshops to synthesize data on the P cycle in major ecosystems of each area, (b) the development of conceptual and simulation models of P cycling in major ecosystems to the world and (c) integration of this information on a global basis at a final international workshop, this would lead to the publication of these findings as a book in the SCOPE series.

The first workshop was held in Poland following an invitation from the Polish Academy of Science. The Department of Agro-Biology and Forestry of the Polish Academy of Sciences hosted the meeting at Czerniejewo on May 1-6, 1988.and Professor Lech Ryszkowski and his staff looked after the local arrangements. Professor J.K. Syers (chairman), L. Ryszkowski and H. Golterman organized the scientific program and subsequently, on May 1-6, 1988 the first phosphorus cycling workshop, held in a former palace at Czerniejewo, discussed phosphorus sources and fluxes between various pools in the environment, using Central Europe as a focus. Draft contributions presented and discussed at the workshop were later revised by authors and edited by H. Tiessen.. These proceedings will hopefully serve to provide an up-to-date critical survey of our present knowledge of phosphorus cycling, fluxes and transfers in a densely populated area under intensive agriculture. It will provide a format and direction to later workshops and will be invaluable for later synthesis. SCOPE is most grateful to Dr. Cole and his Scientific Advisory Committee for getting this ambitious project underway. SCOPE is also greatly indebted to all those who in one form or another have contributed to these proceedings and for the financial support of UNEP, the Andrew W. Mellon Foundation and the French Ministry of Environment.

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INTRODUCTION

Phosphorus occupies a key place among the major nutrients because of its relative scarcity among the light elements and its essential role in energy transformations in all life forms. Man's use of phosphate reserves has produced both desirable and undesirable effects on the environment. Widespread fertilizer phosphate applications have greatly increased food and fiber supplies for an expanding world population. On the other hand, phosphorus associated with eroded sediments from agricultural lands, as well as phosphorus discharges from urban and industrial areas in sewage effluents and other wastes, are major causes of eutrophication of water bodies.

Scientific information is increasingly needed to guide the use of phosphorus to obtain maximum benefits without producing undesirable impacts on the environment. To this end, information on the phosphorus cycle needs to be summarized and then integrated with knowledge of other nutrient elements and their interactions. Phosphorus differs from carbon, nitrogen and sulphur, since it does not have a significant gaseous atmospheric transfer. However, phosphorus has significant indirect global effects on the environment through its effects on carbon, nitrogen and sulphur transfers. Extensive data are available in a number of regions of the world on (a) mineral phosphate deposits, (b) fertilizer production and usage, (c) detergent, pesticides and other industrial production and usage, (d) soils and plant communities in various ecosystems, (e) river transport, and (f) lake sediments. There have been few attempts to integrate this information.

Although on a global scale there is no shortage of phosphate rock for use in industry and fertilizers, reserves of high quality ores are being rapidly depleted. This will result in the need for new technology to utilize lower grade ores with high contents of silica and sesquioxides. High costs of production of soluble fertilizer products together with indications of lower residual value have stimulated the development of alternative approaches including more direct application to the rooting zone of crops or the use of reactive phosphate rock and partially acidulated products. Also, there is an urgent need to develop improved methods for recycling phosphorus in wastes, particularly human and animal wastes. Research is underway to investigate these concerns in several countries.

Recent studies on phosphorus transformations focus on microbial activity and the importance of both inorganic and organic forms, as organic phosphorus forms are both a significant source and sink for biologically active phosphorus in ecosystems (Cole and Sanford, this volume, Tate 1984, Stewart and Tiessen 1987). New methods have helped quantify levels of biologically active phosphorus and relatively inert physically and chemically occluded forms in ecosystems. Key processes of phosphorus interactions with carbon, nitrogen and sulphur have been identified and incorporated into computer models to guide interpretation of phosphorus data (Parton et al. 1988, Sanford et al. this volume). These models need to be extended to a wider range of ecosystems so that, in addition to the data base, they will provide a mechanism for the evaluation of the short- and long-term impact of man's manipulation of phosphorus in the biosphere. A realistic understanding of elemental cycles is not possible in isolation from other nutrients and a holistic approach to global biogeochemistry is needed.

SCOPE project in general

In response to the above noted concerns, SCOPE launched a major new study aimed at better understanding the nature, sources and fluxes of phosphorus in

terrestrial and aquatic ecosystems and into the global environmental effects of P through interactions with cycles of other elements.

The objectives of the project are:

1) To critically assess knowledge of the nature, sources, sinks and fluxes of phosphorus in the biosphere.

2) To identify mechanisms of supply of biologically active phosphorus in terrestrial and aquatic ecosystems.

3) To provide the information required to more effectively meet worldwide phosphorus requirements for sustainable food and fiber production while minimizing adverse effects on the environment.

4) To evaluate the environmental effects of current and projected use of phosphorus in relation to the biogeochemical cycles of carbon, nitrogen, sulphur and metals.

5) To evaluate the transfers of phosphorus from terrestrial to aquatic and marine environments and the relationship to the cycling of other elements.

6) To assess current and likely future economic trends in phosphorus use.

The primary focus of this project will be to integrate and synthesize information on phosphorus in diverse environments with emphasis on the flows of phosphorus between terrestrial systems, ground waters, rivers, lakes, estuaries, and oceans. Both natural and anthropogenic fluxes in the phosphorus cycle will be assessed in a study of the biogeochemical processes. Particular attention will be paid to phosphorus interactions with other elements (carbon, nitrogen, sulphur and metals).

The project comprises three levels of activity:

1) Organization of regional workshops in Africa, Asia, Europe and South America; these workshops will synthesize data on the phosphorus cycle in major ecosystems of each area.

2) Development of conceptual and simulation models of phosphorus cycling in major ecosystems of the world; these models will identify gaps in knowledge, and areas where careful management of phosphorus resources will be required to optimize food and fiber production and minimize hazards in various environments.

3) Integration of the information from the four regional workshops and presentation of the results at a final international workshop to be held in India. Every attempt will be made at this workshop to link these findings on a global scale including oceanic fluxes; it is expected that this will provide a global perspective on the economic and environmental consequences of the use of phosphorus resources.

This information is required to develop management strategies and policies for an important and potentially limiting resource. In addition, it will provide understanding of the interrelationship of nutrient elements in a changing world environment. It will develop insights into the mechanisms and processes involved in phosphorus cycling, in addition to addressing major agricultural and environmental issues. It is anticipated that the project will stimulate further investigations by UNEP, SCOPE, and other scientific organizations.

Specific objectives of this meeting

This, the first meeting will attempt to integrate and synthesize information on phosphorus in Central Europe, a densely populated area with intensive mixed farming systems, which is largely drained into the enclosed Baltic Sea as well as the North Sea, both of which have a considerable net primary production. Specifically, a number of questions must be addressed, these relate to:

1) The nature of the phosphate reserves in parent material. As these are transformed by biogeochemical cycling to other phosphorus forms are there loss processes that occur in natural ecosystems?

2) What types of phosphorus transformations and translocations occur in rolling topography where erosional and soil development cause difference in the accumulation of phosphorus forms? For instance, what is the function of meadow land as a receptor of and accumulator of phosphorus? What is the significance of shelter belts? Do processes differ under forest vegetation as opposed to grassland?

3) It is generally recognized that fertilizer phosphorus is needed to supply enough nutrients in agroecosystems, what are the sources of phosphate and how long will they last? What are the guidelines for use of chemicals in soil and what if any, are the effects on the natural processes of phosphorus translocation and movement? What is the relative importance of natural and anthropogenic phosphorus flows?

4) What are the major forms of movement of phosphorus to surface waters? Can one quantify the natural processes and the changes brought upon these processes by different management systems? How does the management of cattle in small areas affect phosphorus transfers? What are the beneficial and detrimental effects of using land for waste disposal? Is the environment adequately protected under this system?

5) What is the acceptable loading capacity of phosphorus in rivers and lakes? What are the processes involved in lake eutrophication and to what extent can control of phosphorus or other inputs affect this?

6) In estuaries and river deltas, what do we know about phosphorus movement and transformation in these areas? And finally, in an enclosed sea area such as as the Baltic, what are the current loading rates of phosphorus and what is the net result of these rates on the marine environment?

Many of these individual questions have been addressed in the papers presented at this first workshop. However gaps in knowledge still exist in many areas. In particular, although data exists on P inputs and exports from ecosystems even to the documentation of phosphorus deposition in dust and rain there is little concrete information on the extent to which the original parent material has been transformed, how much has been lost or on the quantity left to be used. The question of the degree of weathering and transformation of phosphate in parent material has received scant attention. Greater emphasis on documenting this question must follow particularly as soils become excessively weathered and the important phosphorus reserve is used up (as has occurred in many tropical areas where crop production depends on strategies for minimising loss of active phosphorus fractions and reserves). Recent methods such as the "pedogenic index" approach that have been used to quantify losses and transformations in temperate regions (St. Arnaud et al. 1988) should be extended to other regions.

The challenge of the workshop is integration of the data for a complete region through discussion and analysis among experts to see if the complete picture can be understood.

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The contributions to this workshop

Much of the European expertise on phosphorus transformations has been contributed to this present volume, and to the task of mapping the P cycle in this continent of intensive land use and industrialisation under a humid temperate climate. The contributions to this volume all address important facets of the P cycle, so that together they serve as a framework for a synthesis of the available knowledge on the P cycle:

The first two chapters give an overview over the organic and inorganic transformations in P cycling, and chapter three introduces a means of synthesising these components into a general ecosystem model.

The following three chapters concentrate on forest and grassland ecosystems, then natural and agricultural systems are compared in two contributions from Poland.

Phosphorus transformations and budgets under intensive grazing and arable agriculture are summarised for western Europe in the contributions by Sibbesen and Johnston, followed by a more detailed examination of fertiliser P transformations in Swedish long-term trials.

The chapters by Kahnt and Jäger, Postinkov, Sdobodnikova and Yefremov permit an insight into the agricultural P balance and attempts to improve plant P supplies in large areas of eastern Europe. These contributions point to a growing awareness of the importance of ecologically balanced agricultural P supplies, and the associated problems of monitoring not only total but active P levels across landscapes.

The importance of landscape relationships in P cycling is further emphasised in the following three papers from Lithuania and Poland. These contributions clearly show that there are net-loss and net-accumulator sites in hilly landscapes, and that the flows of P through such landscapes can be greatly modified by land management, the presence of meadows, shelterbelts and a patchy distribution of arable and other land uses. In this landscape analysis, the land is also recognised in its role as the major natural contributor of P to surface waters.

The three following chapters give a brief overview on total P fertiliser use, other anthropogenic P sources and attempts to remove P from anthropogenic effluents before discharge into surface waters.

The freshwater environment is the central theme of the following 4 chapters, with an emphasis on biotic P transformations in lakes in Blazkas' and their manipulation in Kajaks' chapters. This is followed by chemical equilibria and transport in rivers.

The final destination of all "leaks" in terrestrial and freshwater P cycles are the coastal seas of Europe, the Baltic and North Sea, whose P loads and routes of transport and transformation are summarised in the final chapters.

No separate synthesis of the knowledge presented has been attempted, but the sequence of contributions in this volume attempts to point out the interconnectedness of the ecosystems. It will be the object of a later meeting (and much effort before) to construct a framework of conceptual and mathematical models that will permit a better integration of the wealth of information presented, and at the same time point to the weaknesses in our understanding of the global P cycle.

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BIOLOGICAL ASPECTS OF THE PHOSPHORUS CYCLE

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Phosphorus is second only to nitrogen in limiting primary production in most temperate aquatic and terrestrial ecosystems, and is the first element limiting primary production in many tropical ecosystems.Because P has a central role in the energetics and productivity of the biosphere, information on the distribution and flows of P can provide valuable indices of biological activity. Knowledge of the biological transformations of phosphorus is essential not only for an understanding of P cycling, but also for an understanding of the cycling of the other major nutrient elements, carbon, nitrogen and sulfur. Earlier research on P focused primarily on budgets and little consideration was given to; (1) interactions with other major elements, (2) cycling through vegetation and (3) organic forms. Similarly, much of the earlier agronomic research on P was limited to inorganic forms and direct crop responses to P fertilization. Ecosystem level studies of nutrient budgets and fluxes in the 1970's began to direct attention to the importance of phosphorus cycling in relation to other elements and to biological transformations of P. In particular, the biome studies of the International Biological Program developed P budgets for grassland and forest ecosystems (Halm et al. 1972, Harrison 1978, Clark et al. 1980). There have been major developments in the understanding of the biological aspects of P cycling and interactions with other nutrient elements in the last twenty years. This paper will briefly summarize these developments to provide a perspective for analyses of regional and global phosphorus cycling.

Chronosequence studies in New Zealand first documented control of productivity and accumulations of carbon and nitrogen in ecosystems by the supply of P in parent materials (Walker and Adams 1957, Syers and Walker 1969). These studies stimulated comparative research in other ecosystems which have led to examination of linkages of P with other elements on both the pedologic and biological time scales.

Cole and Heil (1981) reviewed the evidence for linkages between organic carbon and nitrogen accumulations in mature soils and the P contents of the original parent materials. They focused on microbial growth processes as the arena for the adjustment of the supply of nitrogen (and carbon) to the supply of P. They also emphasized the need or better estimates of cycling rates of these and other elements as a basis for examining nutrient cycling processes across a wide range of ecosystems. The comparative aspects of cycling of organic C, N, S and P through soil organic matter were reviewed by McGill and Cole (1981). They proposed a conceptual model to explain the wide variations in elemental ratios across chrono-, climo-, and toposequences. In the model organic P (Po) and sulfate esters are hypothesized to stabilize independently, while C and N are stabilized through their interaction with each other. Hunt et al. (1983) adapted these concepts to examine variability in the composition of decomposer organisms. Differences in nutrient cycling patterns among C, N, S and P were discussed in relation to; (1) their chemical properties, (2) information from microbial physiology, and (3) theories about the formation and decomposition of organic matter. Their model distinguishes fungi from bacteria and features a trophic structure with amoebae feeding on bacteria

and nematodes feeding on fungi. Five chemical bond classes were identified in each of the organic substrate pools and patterns of variation in the C/N, C/S and C/P ratios were related to the relative proportions of structural components, synthetic machinery and stored material in the biomass of soil organisms. The model yielded qualitative predictions about the relative rates of turnover of C, N, S and P and the constraints on variations in element ratios of living organisms.

In a companion paper, Stewart et al. (1983) examined controls on nutrient cycling processes within the framework of ecosystem properties and driving variables. Their general hypothesis was that the driving variables of an ecosystem such as climate, geological parent material etc..control the rates of chemical, physical and biological processes.

Tate (1984) assessed those biological transformations of P in soil most likely to influence the P nutrition of plants. He summarized the evidence for rapid transfers through microbial biomass and emphasized the need for better means of characterizing forms of P in soil. Smeck (1985), in a review of P dynamics in soil and landscapes, contrasted transformations along long term pedologic pathways versus P dynamics in rapid biological pathways. He identified relationships between soil taxonomy at the order level and P distribution among various forms and C/Po ratios. Levels of leaching, weathering, secondary mineral formation, and organic matter accumulation along a sequence of soil orders from relatively unweathered Entisols to highly weathered Ultisols were good predictors of the forms of P found in these soils. Stevenson (1986) gave a comprehensive review of the P cycle in a summary of soil nutrient cycling that emphasizes the importance of P cycling in relation to other element cycles. In the most extensive compilation of world literature on soil organic phosphorus, Harrison (1987) prepared statistical relationships that describe the relationships of Po with; (1) soil properties, (2) effects of climate, (3) vegetation, (4) parent material (5) distribution in soil profiles, and (6) the effects of land management practices.

Finally, the review by Stewart and Tiessen (1987) is organized around a conceptual model that focuses on the central role of microbial uptake of P and its subsequent release and redistribution. They note that, "The dynamic nature of soil Po is masked by the fact that only a small portion of the total soil organic matter may be biologically active." They conclude that the factors that control transformations of soil Po are the solution Pi concentration in combination with soil biomass activity and that "Mineralization of Po is controlled by the balance of P availability and P demand of microbial biomass and plants, and by the mineralization of organic matter which releases Po as a by-product."

Phosphorus cycling concepts have been developed from the observation of long term effects across climatic gradients and parent materials as well as from numerous short term studies of individual processes. Incorporation of these concepts into mathematical simulation models (Cole et al. 1977, Jones et al. 1984, Parton et al. 1987, 1988) has exposed gaps in information and has provided a means of testing hypotheses that integrate nutrient interactions in ecosystems. Subsequently, these efforts encouraged the development of new methodologies for characterizing P forms and P dynamics, which have stimulated the current round of very exciting experimental studies. A brief description of the methodological advances over the past 10 years is important for understanding the direction of current research.

The importance of microbial immobilization and mineralization of P in

soil was recognized in early work (Thompson et al. 1948), but it was not until the development of methods for directly estimating microbial P that quantitative evaluations of microbial pools as sinks and sources for P could be made. These methods (Hedley and Stewart 1982, Brookes et al. 1982, McLaughlin and Alston 1986) are based on differences in extractability of organic and inorganic P after lysis of microbial cells by either chloroform or hexanol with appropriate corrections for the fraction of microbial P extractable and adsorption of released P onto mineral surfaces.

Application of isotopic techniques has also made significant contributions to the evaluation of P dynamics. In our early studies of P cycling in semiarid grasslands (Clark et al. 1980), gross P mineralization rates were determined by following the changes in specific activity of labile Pi in soil cylinders in the field. The results indicated P mineralization of over 5 $g \cdot m^2$ in the surface 18 cm over a thirty day period at the peak of the growing season. This information together with detailed budgets of P in soil and vegetation pools in Colorado and Saskatchewan grasslands was used to supply quantitative information for the simulation model of P cycling (Cole et al. 1977). In a complementary study, Harrison (1982) used ^{32}P labeled RNA in an incubation method to measure the mineralization rates of labile Po in soil. More recently, McLaughlin and Alston (1986) have made use of isotopic techniques to trace the flow of labeled P from plant residues into microbial biomass and organic forms. Their most recent work (McLaughlin et al. 1988a and 1988b), made use of dual isotopes, ^{32}P and ^{33}P, to estimate rates of organic P turnover and quantify the role of microbial biomass in P cycling in wheat pasture rotations.

Some of the most revealing evidence for the importance of P cycling processes comes from a series of investigations on P transformations in plant rhizospheres. The rhizosphere is an especially active site because it is the focus of interactions between root and soil and has a much higher abundance of bacteria and fungi than bulk soil. Jungk and Classen (1986) based their work on the earlier studies of Helal and Sauerbeck (1984) who examined the influence of plant roots on carbon and P metabolism in soil. Quantitative radioautography with ^{33}P was used to determine the depletion of soil P around individual roots. Isotopically exchangeable P was reduced to 50% of the initial concentration over a three day period within a depletion zone extending 1.5 mm from the root surface (Fig. 1). The corresponding drop in solution P concentration in the 1.5 mm zone (as estimated from desorption isotherms) was twenty-six fold. The extent of the depletion zone corresponded to the length of root hairs. In related experiments Tarafdar and Jungk (1987) measured the distribution of phosphatase activities in the soil around plant roots to evaluate the role of Po mineralization in the rhizosphere of several plant species and found up to seven-fold higher concentrations of acid phosphatase within the same zone that was depleted of inorganic P (Fig. 2). Similar results were obtained for the alkaline phosphatases that are believed to be produced only by microorganisms. Acid phosphatase activity was increased over levels in the bulk soil up to distances of 2 to 3 mm while alkaline phosphatase showed an increase in activity up to a distance of 1.2 to 1.6 mm for all plant species and soils tested. Both fungal and bacterial populations were significantly increased in the rhizosphere and organic P was strongly depleted at the root surface. The results confirmed Sharpleys's view (1985) that plants utilize soil Po by means of an increased phosphatase activity in the rhizosphere.

Mycorrhizal fungi are an important component of rhizospheres of some plant species and recent work by Dodd et al. (1987) documents phosphatase activity of roots and rhizospheres of plants infected with vesicular-

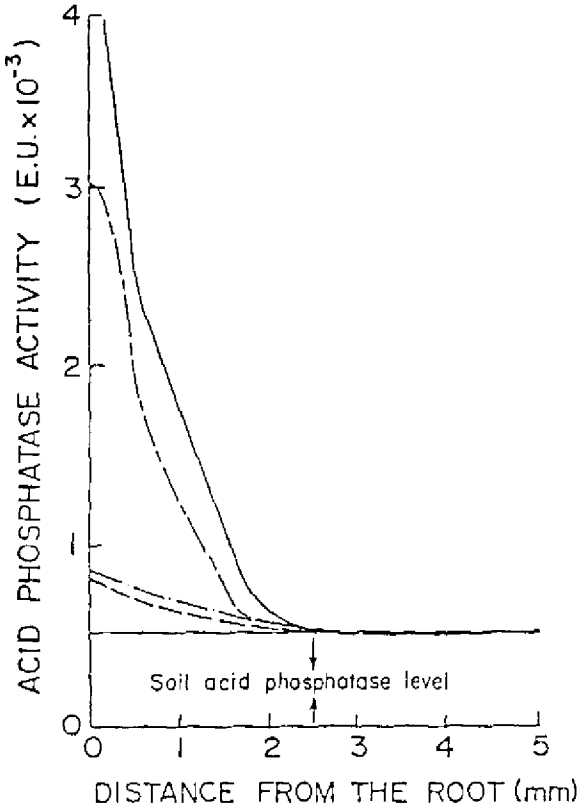

Figure 1. Concentration of isotopically exchangeable phosphorus and soluble inorganic phosphorus in the vicinity of a 3-day-old corn root. Redrawn from Jungk and Classen (1986).

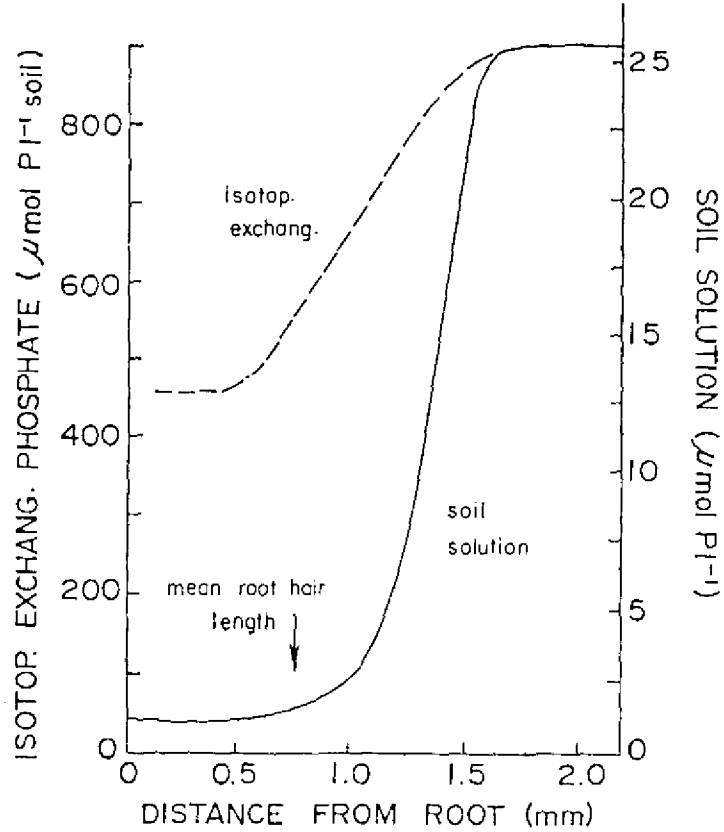

Figure 2. Distribution of acid phosphatase activity in the rhizosphere of four different plant species. Redrawn from Tarafdar and Jungk (1987).

arbuscular mycorrhizal fungi. Rhizosphere phosphatase activities were higher for onion and wheat plants infected with G. mosseae and G. geosporum compared with control plants. They also noted high phosphatase activities associated with the roots and rhizospheres of non-mycorrhizal rape compared to mycorrhizal onions or mycorrhizal wheat and speculated that phosphatase activity is inversely related to mycorrhizal dependency of a crop species.

The future directions of research on the biological aspects of the phosphorus cycle will be determined by advances in three related areas: (1) improved methods to assess P pools, flows between pools and uptake rates, (2) conceptual models that extend current understanding of P transformations into new ecosystems, and (3) modeling the results of new research (the products of new methodological approaches) to identify gaps in understanding of P transformations. Advances in area one (above) are especially needed for understanding P cycling in tropical ecosystems. Improvements in isotope methods for measuring gross and net P mineralization in acid soils are badly needed. As P cycling processes are better understood the next challenge involves questions of scaling and regional analysis. This area of future research depends on the development of robust conceptual and mathematical models that integrate processes across large, diverse regions. Development and application of such models for temperate grasslands has begun (Parton et al. 1987, 1988), however, considerable research is needed for such efforts to be successful in other ecosystems.

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INORGANIC REACTIONS CONTROLLING PHOSPHORUS CYCLING

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Introduction

Phosphorus (P) plays a vital role in energy transformations and is essential for the growth and development of plants and animals. The widespread use of P fertilisers, prepared by the chemical processing of naturally-occurring phosphate rock (PR) materials, has had an enormous impact on agricultural production in many countries of the world, particularly in tropical regions where the soils are frequently P deficient, and has contributed to a relatively secure food supply for an expanding world population. Although there is no shortage of PR on a global scale, higher-grade deposits are being depleted.

At the same time, P runoff from agricultural land and P discharges from urban areas, principally in domestic sewage, can result in the P enrichment of surface waters, with deleterious effects on water quality through the growth of aquatic nuisance plants.

Although a substantial amount of work has been directed towards increasing the efficiency of P fertiliser use, progress has been rather limited because of the complexity of the problem. Further studies are required to maximise the benefits of fertiliser P and to minimise the undesirable effects on the environment. In this regard, an improved knowledge of P cycling in terrestrial and aquatic ecosystems is seen to be essential for obtaining an adequate understanding of the behaviour of P in the environment and to the development of management strategies and policies for the use of this vitally important and potentially-limiting resource.

The present paper is concerned with a discussion of the inorganic reactions which control P cycling. In singling out those reactions which are inorganic in nature it is fully recognised that biochemical reactions (Tate, 1984; Smeck, 1985; Stewart and Tiessen, 1987) are equally, if not more important in influencing the dynamics of P in soils and waters.

A cycle for inorganic P

A simplified inorganic P cycle for soils is shown in Figure 1. Solution P is the focal point of such a cycle, with several transfer processes operating to control the concentration of inorganic P in the soil solution.

By far the most important reactions in the inorganic P cycle are dissolution-precipitation reactions and sorption-desorption reactions and these will be considered in some detail. For the sake of completeness, however, brief mention will be made of the very limited extent to which phosphate leaches in most soils, because of the high affinity of phosphate ions for oxide surfaces (Parfitt, 1978; Barrow, 1985). Consequently, it is only in sandy soils having a very low capacity to remove phosphate ions from

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solution by sorption reactions that the leaching of phosphate occurs to any significant extent, at least over short periods of time. Over pedological time, however, leaching constitutes a major P loss mechanism.

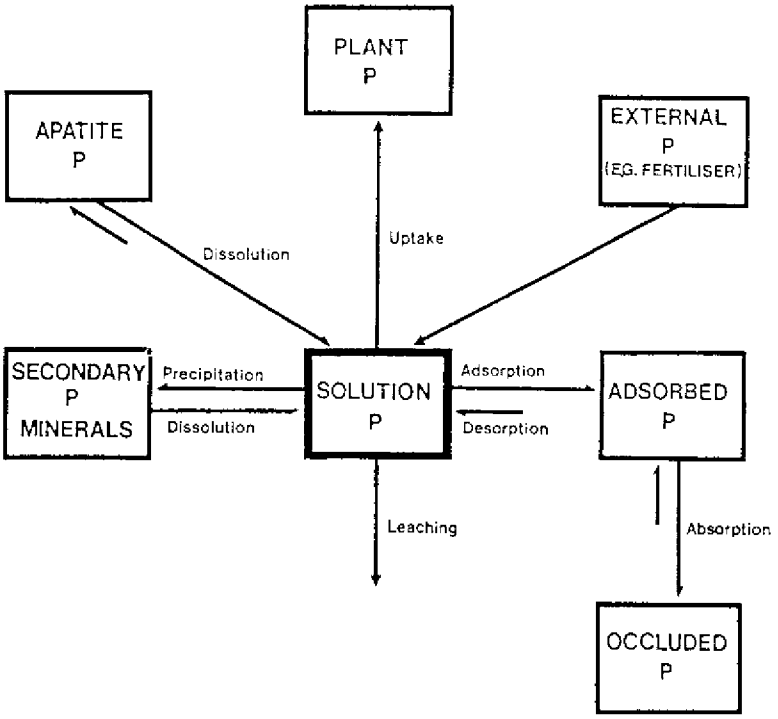


Figure 1. A simplified inorganic P cycle for soil

Also, plant roots remove phosphate ions from solution and, in the case of certain species, can also enhance the dissolution of calcium phosphate minerals (Hedley et al., 1982) by decreasing the pH near the root surface (Grinsted et al., 1982).

External sources of P, such as fertiliser and sewage sludge, may contribute to man-modified ecosystems, such as intensively-farmed land. However, it should be emphasised that P is the one major element in soil organic matter which must be supplied almost entirely by the parent material of unfertilised soils (Walker and Syers, 1976).

Dissolution-precipitation reactions

In discussing dissolution-precipitation reactions it is convenient to consider systems in which calcium (Ca) is the dominant controlling cation, usually in neutral or calcareous environments, separately from those in which iron (Fe) and aluminium (Al) are the dominant controlling cations, usually acidic environments.

Ca Systems. Minerals of the apatite group, usually referred to simply as apatite, are by far the dominant phosphate minerals in rocks, soils, and sediments. These are calcium phosphates having the general formula

$Ca_{10}(PO_4)_6X_2$, where x= F, Cl, OH, or $1/2CO_3$.

Fluorapatite is the most stable and the most abundant (McConnell, 1979).

Apatite is least stable under acid conditions and dissolves, releasing constituent ions:

$$Ca_{10}(PO_4)_6 X_2 + 12H^+ = 10Ca^{2+} + 6H_2PO_4^- + 2X^-$$

The chemical reactivity of an apatite increases as the degree of carbonate substitution increases (Lehr and McClellan, 1972) and this influences the rate of dissolution. Information on the rate of dissolution of apatite in soils has been obtained from chronosequence studies. Apatite decreases during soil development due to weathering as shown in Figure 1. Other forms of P increase, at least initially, but there is an overall decrease in total P, due primarily to leaching.

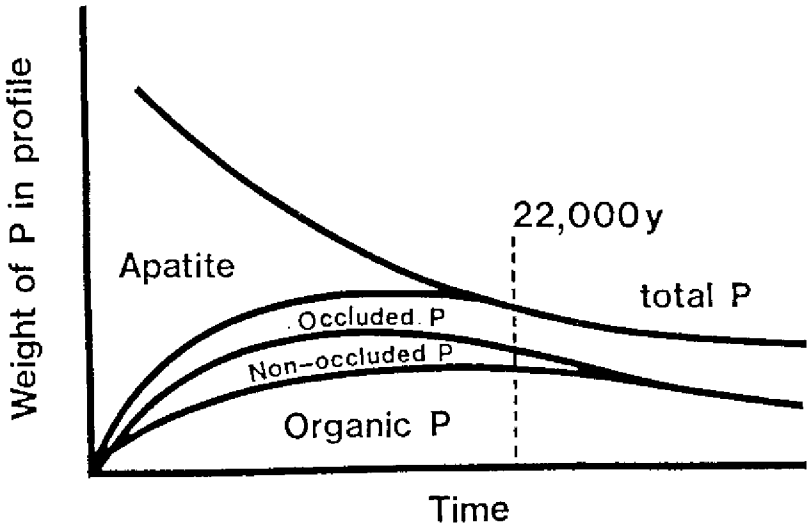


Figure 2. Changes in forms and amounts of soil P with time (redrawn from Walker and Syers, 1976).

In a chronosequence of soils developed under a humid climate in New Zealand, apatite had disappeared from the upper 60 cm of the profile in 22,000 y (Walker and Syers, 1976). The decline was more rapid in the surface than in the lower horizons, reflecting the higher degree of weathering and lower soil pH in the surface horizons.

Although the rate of weathering of apatite will vary with rainfall and temperature, in particular, it is very difficult to predict the rate of disappearance of apatite in different environments. There is an acute shortage of information on this important, first-step in the P cycle. Recent studies of the kinetics of dissolution of PR added to soils, and the factors which influence dissolution (Mackay and Syers, 1986; Mackay et al., 1986) are providing useful information relevant to apatite dissolution in natural environments.

The formation of calcium phosphates by precipitation following an initial adsorption of phosphate on to calcite has been studied extensively (e.g., Cole et al., 1953; Griffin and Jurinak, 1973; Freeman and Rowell, 1981). In a comprehensive study, involving an assessment of phosphate exchangeability using ^{32}P, Freeman and Rowell (1981) showed (Figure 3) that

phosphate adsorbed on calcite was completely exchangeable ($P_E/P_S \cdot 100$) during Stage 1 but with further additions of phosphate (P_i) exchangeability decreased abruptly during Stage 2. The rapid formation of dicalcium phosphate during Stage 2 was followed, in Stage 3, by the slow change to octacalcium phosphate, the reaction products being identified by x-ray diffraction analysis.

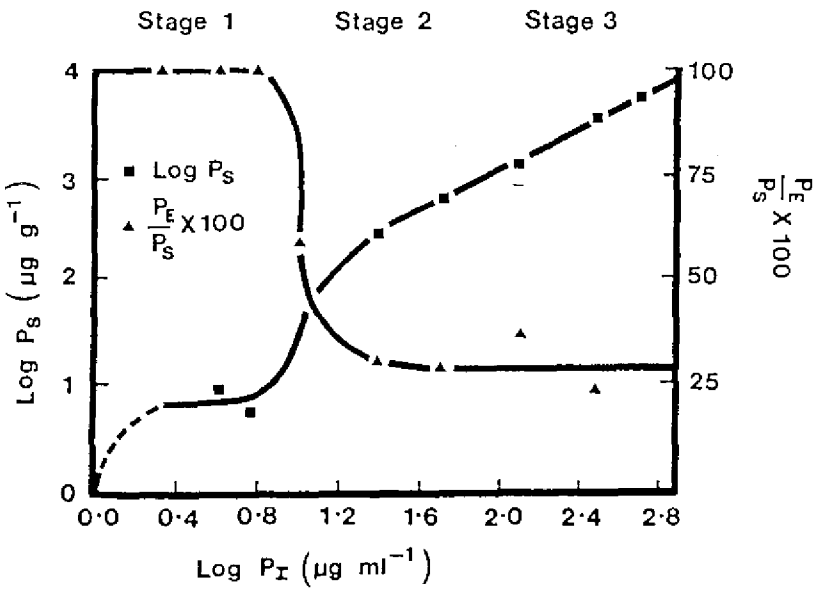


Figure 3. Amount of reacted phosphate (P_S) and percentage of reacted phosphate which is exchangeable ($P_E/P_S \cdot 100$) for a range of solution phosphate concentrations (P_i) in contact with calcite (redrawn from Freeman and Rowell, 1981).

Ion-activity product data have been used to indicate the formation of calcium and other metal phosphate compounds in soils (e.g., Murrmann and Peech, 1968). Solubility isotherms for several calcium phosphate minerals are shown in Figure 4. Largely based on this approach, Larsen (1967) has argued that "impure" hydroxyapatite controls the chemical mobility of P in soils, even down to soil pH values as low as 4.

Although dicalcium phosphate and dicalcium phosphate dihydrate can form as reaction products in soils to which monocalcium phosphate (MCP) is added as a fertiliser (Lindsay et al., 1959) these compounds are unlikely to persist, even in weakly acid soils (Probert and Larsen 1970). It further seems doubtful that such compounds will form in unfertilised soils or in sediments because phosphate concentrations are not sufficiently high.

Fe and Al systems. Short-range order iron and aluminium phosphates appear to form in soils when MCP is added (Lindsay et al., 1962; Taylor et al., 1963). The strongly acid (pH approximately 1.5) solution diffusing out of an MCP particle may liberate iron and aluminium ions from soil components which could interact with the high concentration of phosphate (approximately 4.0 moles l^{-1}) present. It has been suggested that the short range order phosphate compounds crystallise slowly to strengite ($FePO_4 \cdot 2H_2O$) and

variscite ($AlPO_4 \cdot 2H_2O$). However, such metal phosphates are unlikely to be stable in soils and sediments because congruent dissolution, which appears to be required for stability of strengite and variscite, is restricted to pH values below 1.4 and 3.1, respectively (Bache 1963). The levels of P sustained in solution by hydrous ferric oxide gel, a common and important component for P sorption, have been shown to be lower than those sustained by strengite (Bache, 1964; McLauglin and Syers,1978) and short-range order ferric phosphate (McLaughlin and Syers, 1978) it seems unlikely that such compounds will persist, even if they form in soils and thus their likely importance as a controlling influence in P cycling seems to be limited.

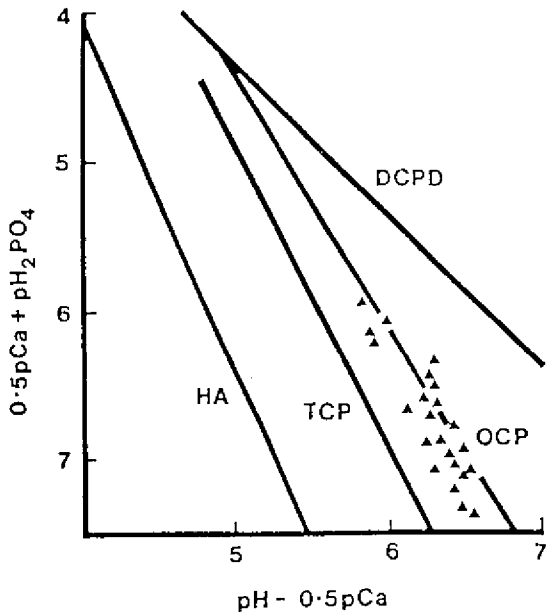


Figure 4. Solubility isotherms for hydroxyapatite (HA), tricalcium phosphate (TCP), octacalcium phosphate (OCP), and dicalcium phosphate dihydrate (DCPD) (redrawn from Olsen et al., 1983).

As with calcium phosphate systems, ion-activity data have also been used to assess the formation of iron and aluminium phosphates in soils (Clark and Peech, 1960; Murrmann and Peech, 1968). Comparison of the ion-activity product (pFe + 2pOH + pH_2PO_4) for iron phosphate, for example, with that predicted from the solubility product (pK_{sp}) has been made. It is reasonably clear that the solubility of phosphate compounds does not satisfactorily explain the observed soil solution P concentrations (Wild, 1954; Bache, 1963), Wild (1954) clearly showed that the concentration of P in the soil solution did not correspond with the solubility of several P compounds in the pH range 4 to 7.5. More recently, Ryden and Pratt (1980) showed that, over the same pH range, the P concentrations and pH values of soil extracts were independent, being undersaturated with respect to all P compounds between pH 5.5 and 6.5.

Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) occurs sporadically in strongly reducing environments, such as waterlogged soils and certain lake sediments (Mackereth, 1966). The dynamics of vivianite formation and its persistence are not at all well understood but its presence is always associated with organic-matter rich zones.

Dissolution-precipitation theory is still used to describe the interaction of P with soil and sediment components, although good evidence for the participation of such reactions in P cycling is rarely forthcoming. It is now generally accepted that, with the possible exception of recently fertilised soils, the uptake and release of P by soils and sediments can be described better by sorption-desorption reactions.

Sorption-desorption reactions

If the phosphate ions removed from solution by soil and sediment components are restricted to the surface then this implies an "adsorption" reaction. This reaction may or may not be followed by the diffusive penetration of P into the retaining component and this is considered to be an "absorption" reaction. In reality, it is very difficult to distinguish between these two reactions and the generic term "sorption" is usually used (Glasstone, 1960).

Sorption isotherms. The relationship between the amount of P sorbed and that remaining in solution at constant temperature is given by a sorption isotherm. Typical sorption isotherms for three soils which vary appreciably in their ability to sorb P are shown in Figure 5.

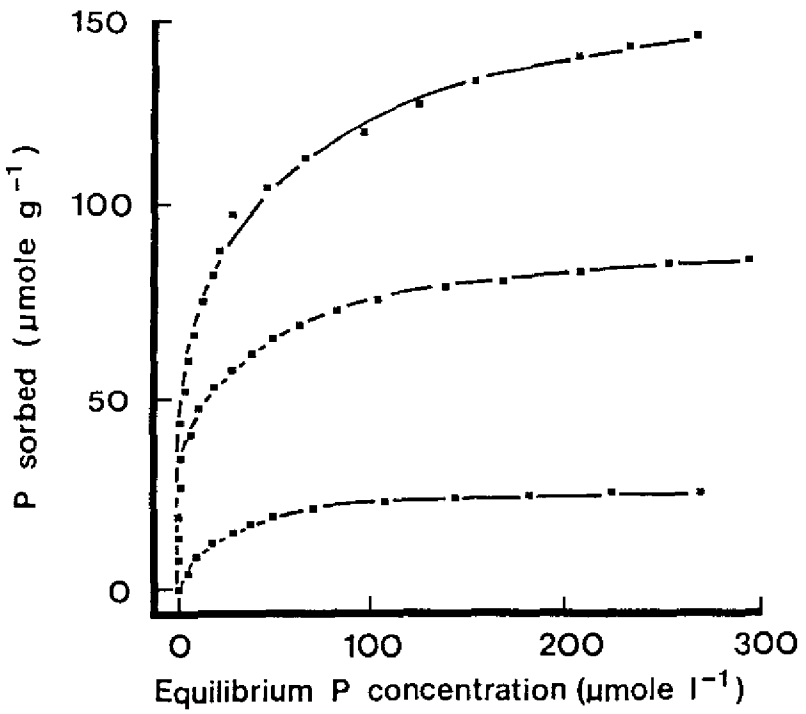


Figure 5. Isotherms for P sorption by three contrasting New Zealand soils (redrawn from Tyden et al. (1977)

Despite the considerable differences in the amounts of P sorbed at a particular solution P concentration, the overall shape of the isotherms is remarkably similar. Giles (1970) has classified isotherms similar to those shown in Figure 5 as "high affinity" or "H-type" isotherms.

There is an important practical distinction between sorption and precipitation reactions in terms of the control over solution P concentrations. Whereas sorption theory requires that the amount of P sorbed is largely determined by solution P concentration, precipitation theory requires that the solubility product of the least-soluble P compound controls the solution P concentration. At high saturations of the sorption complex, the concentration of P maintained in solution is higher.

Desorption. The reverse reaction of sorption, namely desorption, describes the release of sorbed P into solution. It is well established that P is not reversibly sorbed by soil and sediment components: That is, the sorption and desorption isotherms are not coincidental. This is illustrated by the isotherms in Figure 6. Here the desorption isotherm is displaced to the left of the sorption isotherm.

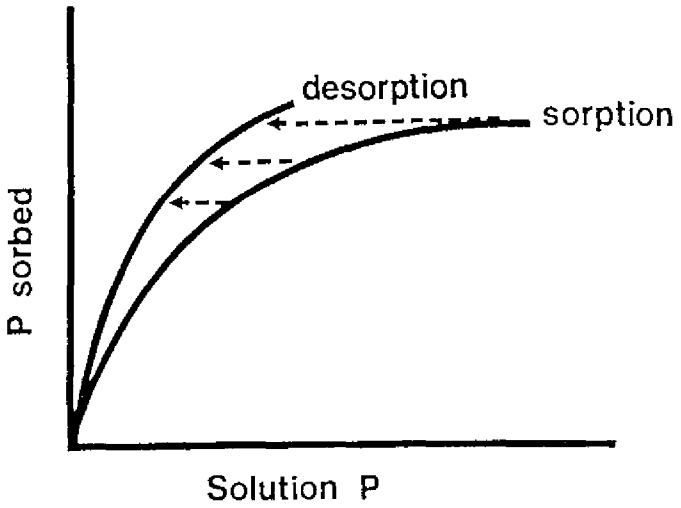


Figure 6. Isotherms for the sorption and desorption of P by a soil showing lack of reversibility.

Barrow (1985) has questioned the use of the word "irreversible" to describe P sorption. According to Barrow (1985), if desorption differs from adsorption then either desorption is slower and insufficient time has been allowed, or a further process follows the initial adsorption so that a part of the "adsorbed" P is no longer in equilibrium with the solution. The diffusive penetration of initially adsorbed P, in fact an absorption process (Figure 1), explains the lack of reversibility of P adsorption (Barrow, 1983a) and this in fact can be modelled (Barrow, 1983b), discussed below.

Factors affecting sorption-desorption reactions. Several factors influence the sorption and desorption of P by the components of soils and sediments. These include the amount and nature of the components involved, other ions, pH of the system, and kinetics of the reaction. These have been discussed in detail in recent reviews (Parfitt, 1978; Barrow, 1985).

It is commonly accepted that hydrous metal oxides of Fe and Al are particularly important in the sorption of P by soils (Parfitt, 1978) and there

is reasonable evidence to also suggest that hydrous ferric oxide largely controls the sorption of P by lake sediments (Shukla et al., 1971, Syers et al., 1973). Short-range order components usually have a much larger capacity to sorb P than do their crystalline counterparts (Bache, 1963), a finding related to surface area and the number of participating functional groups in surface positions. Even in calcareous soils, it seems likely that small amounts of hydrous ferric oxide dominate the P sorption complex (Holford and Mattingly, 1975a) and the same may be the case for calcareous lake sediments (Shukla et al., 1971). This is consistent with the very low capacity of calcium carbonate to sorb P (Griffin and Jurinak, 1973), unless it contains hydrous ferric oxide impurities (Holford and Mattingly, 1975b).

Under reducing conditions in soils and lake sediments, P is released to solution and this is related to the reduction of ferric iron to ferrous iron and the partial elimination of P sorption sites (Syers et al., 1973). The release of P from contrasting soils following submergence is shown in Figure 7.

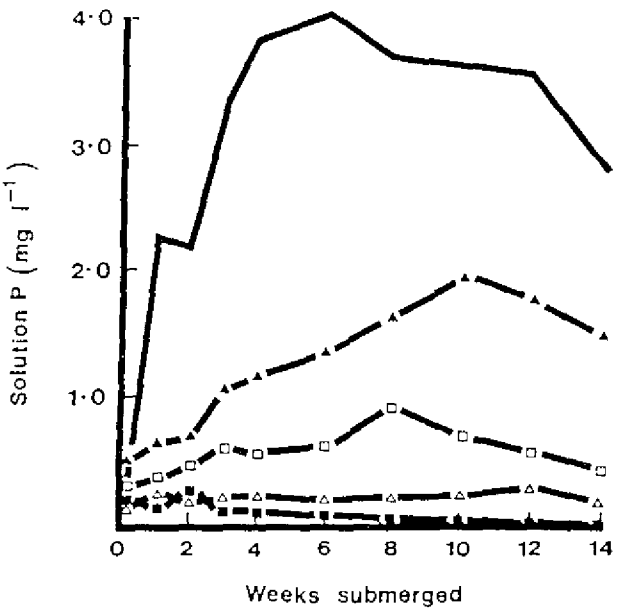


Figure 7. Release of P from contrasting soils as a function of time following submergence (redrawn from Ponnamperuma, 1972).

Other ions influence P sorption to a varying extent, and there is an interaction here with the effects of pH on P sorption. It is well recognised that more P is sorbed from a Ca system than from a Na system. Explanations for this range from the formation of insoluble Ca phosphates (Wild, 1950) to the effect of the divalent cation on the screening of surface negative charge (Ryden et al., 1977b) or of surface potential (Barrow, 1985). The decrease in P sorption with an increase in soil pH (Figure 8) of an Na-saturated soil contrasts with that for the same soil but saturated with Ca. The essentially constant isotopic exchange ability of sorbed P (varying only between 57 and 45%) suggests that it is unlikely that the formation of a calcium phosphate is responsible for the increased amounts of P sorbed in a Ca system above pH 6.0.

A recent study (Ryden et al., 1987) has shown that with the exception of OH^-, inorganic anions have a limited ability to compete with P for sites on

hydrous ferric oxide gel. The practical significance of this is that no inorganic anion is likely to be present in sufficient concentration to affect P sorption, other than OH^-. Also, this work showed that there is no need to postulate the existence of sites specific to the sorption of particular anions by hydrous ferric oxide gel, in contrast to the suggestion of Hingston et al. (1971).

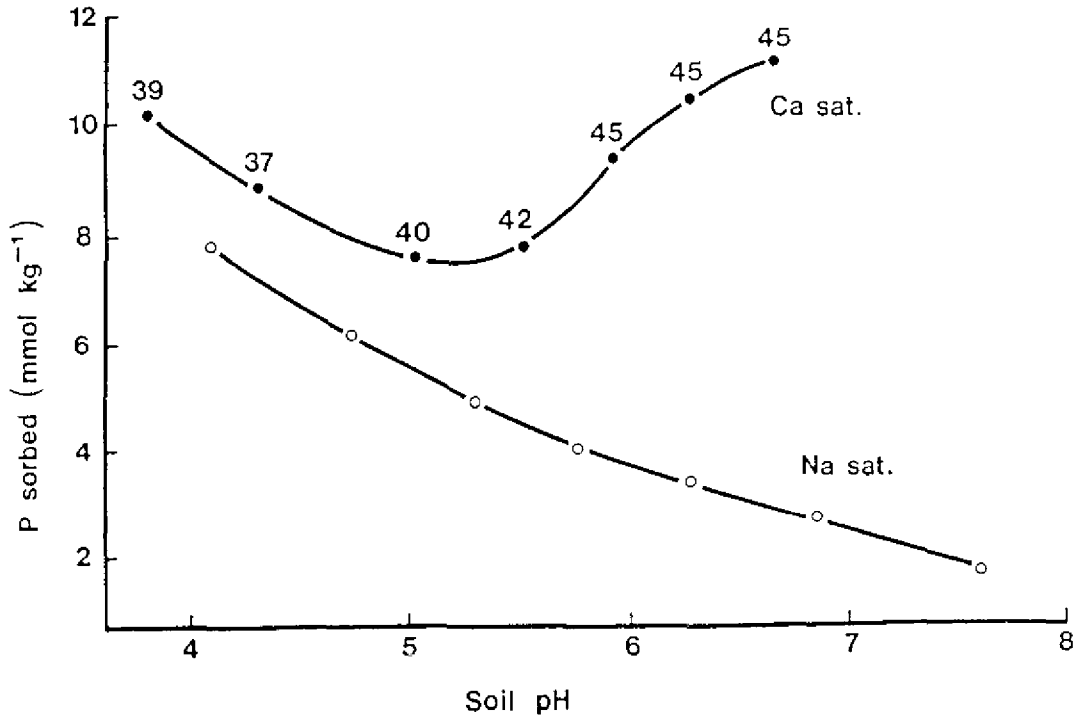


Figure 8. Amount of P sorbed by Ca- and Na-saturated soils as a function of soil pH. Isotopic exchangeability of sorbed P is indicated by the number above the curve for the Ca-saturated soil.

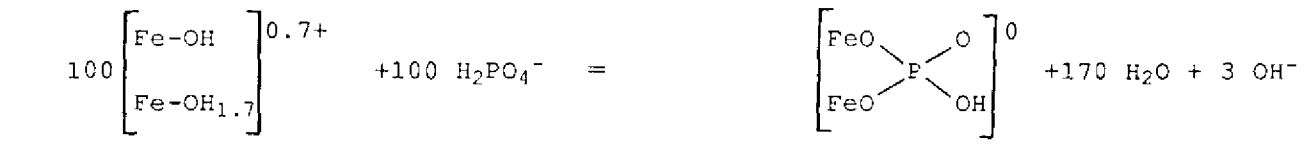
Mechanisms of P sorption. Several mechanisms have been proposed to describe the sorption of P at a hydrous metal oxide surface and these invariably involve ligand-exchange. The formation of mononuclear complexes, with or without an increase in negative charge, has been described (Ryden et al., 1977a) as follows:

$$\begin{matrix} \text{Fe-OH}_2 \\ \text{Fe-OH} \end{matrix}\Big|^{1+} + H_2PO_4^- = \begin{matrix} \text{Fe-H}_2\text{PO}_4 \\ \text{Fe-OH} \end{matrix}\Big|^{0} + H_2O$$

$$\begin{matrix} \text{Fe-OH} \\ \text{Fe-OH} \end{matrix}\Big|^{0} + H_2PO_4^- = \begin{matrix} \text{Fe-OH} \\ \text{Fe-H}_2\text{PO}_4 \end{matrix}\Big|^{0} + OH^-$$

Evidence obtained from infrared absorption studies with a range of hydrous metal oxides suggests that a binuclear or bridging complex is formed and that HPO_4^{2-} is the form of phosphate sorbed (Parfitt et al., 1976). At pH

5.1 (the pH of net zero charge at half coverage of goethite with phosphate) the following mechanism can be written:



Modelling. Good progress has been made in recent years in modelling the sorption and desorption of P by goethite. The model initially developed by Bowden et al. (1977) has been extended by Barrow (1983b) to describe the reaction between divalent phosphate ions and a variable charge surface, and the solid-state diffusion of initially adsorbed phosphate towards the interior of the particle.

The model takes the form:

$$\theta = \frac{(K_i a_i \exp(-Z_i F\Psi_a/RT)}{1 + K_i a_i \exp(-Z_i F\Psi_a/RT)}$$

Where θ = Proportion of sites occupied

K_i = Binding constant for HPO_4^{2-}

a_i = Activity of HPO_4^{2-} in solution

Ψ_a = Surface potential

F = Faraday constant

R = Gas constant

T = Temperature

Z_i = Valence

A difficulty in applying this equation is that the electrostatic potential (Ψa) cannot be measured. Values have been assigned to it for well-defined materials, such as goethite, but this is not possible for soils and an alternative approach (Posner and Barrow, 1982) is required.

The mechanistic model extended and tested by Barrow (1983b) provides a close description of the effects on P sorption of P concentration, pH, time of contact, and temperature. In particular, it accommodates the diffuse penetration of absorption of P into soil particles which can explain the lack of reversibility of sorption and the continuing, slow removal of P from solution over time.

Rationalisation of retention reactions in different environments.

Although sorption-desorption reactions are considered to provide a better description of the chemistry of P in terrestrial and aquatic environments, the role of dissolution-precipitation reactions in certain situations must be recognised. In particular, the dissolution of apatite in soils and sediments is clearly an important starting point in the cycling of P. Also, over geological time, the formation of apatite occurs, as in marine phosphorites, through the phosphatisation of calcium carbonate. Secondary Ca,

Fe, and Al phosphates may form in fertilised soils but their persistence seem unlikely, given their instability in most situations. Vivianite can form in strongly-reducing environments in soils and sediments. However, it is with sorption-desorption reactions that the best prospects of understanding the inorganic controls on P cycling lie. These are by no means fully understood, because of the complexity of the systems.

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SOIL PHOSPHORUS INTERRELATIONSHIPS WITH CARBON, NITROGEN AND SULPHUR: A MODELING APPROACH

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Introduction

The amounts and fluxes of phosphorus, carbon, nitrogen and sulfur are important parameters for assessing the conditions of both aquatic and terrestrial ecosystems. Within an ecosystem these elements are linked and their transformations depend on the linkages as well as external driving variables such as climate. These complex interactions have been examined for terrestrial systems within a conceptual framework that encompasses primary production, decomposition and nutrient cycling (Stewart et al. 1983). This paper describes a simulation model which offers a means of testing such concepts of ecosystem function by integrating available quantitative data on nutrient interactions and their driving variables into the conceptual framework. The objective of our modeling approach is to test hypotheses concerning controls on nutrient cycling. Such hypotheses serve as a basis for relating nutrient cycling to environmental conditions which then allows extrapolation of information for regional analyses.

The interaction of phosphorus transformations in soils with transformations of other elements is shown in studies of soil organic matter (SOM) formation because SOM integrates changes in production and decomposition over time, and is central to the cycling of plant nutrients. The modeling of nutrient cycling relies on the systematic organization of element interactions with the acknowledged goal of reducing the complexity of the interactions to a minimum level required for results that compare well with observed data. The utility of this approach is not necessarily in extrapolative or predictive power (though this is often instructive) but in determining the key interactions between phosphorus and other elements that ultimately determine the rates of primary plant production and decomposition. Additionally, modeling almost inevitably leads to identification of misunderstood subject areas that are important for a more complete understanding of nutrient interactions.

In this paper we will explain the basic function of a model that simulates soil organic matter with particular emphasis on the phosphorus cycle. It will become readily apparent that a complete description of phosphorus cycling is not possible without integrating interactions with other

elements. Finally, we will show results of a new interaction term that successfully simulates N-P interaction effects on plant production.

Model Description

A simulation model called the `CENTURY Soil Organic Matter model' has been developed that simulates primary productivity, soil nutrient dynamics and soil water, but that focuses on soil organic matter (Parton et al. 1987, 1988). The model emphasizes SOM because SOM integrates changes in production and decomposition over time. To do this, the model simulates labile (rapid turnover) and stabilized (slow and passive turnover) fractions of soil organic matter. This simulation tracks both the nutrient-supplying capacity of SOM as well as the absolute quantity (Fig. 1). The CENTURY model was originally designed to simulate long-term (5-5000 yr) dynamics. Accordingly, the plant production submodel simulates maximum aboveground production and belowground production (g m^{-2}) as a function of precipitation (appt in cm) and temperature on a monthly time step during the growing season. Plant production is then reduced if there is insufficient mineral N, P or S. For a complete description of the plant growth submodel see Parton et al. 1987.

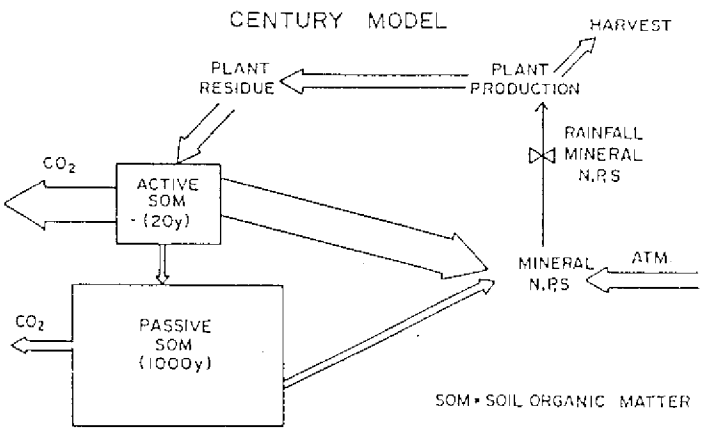

Figure 1. A conceptualized diagram of the main components of the CENTURY soil organic matter model.

Phosphorus submodel. The phosphorus submodel is a logical extension of earlier simulation models of the P cycle (Cole et al. 1977). The results of research on phosphorus cycling by Chauhan et al. (1981), Stewart and McKercher (1981) and Tiessen et al. (1984) have been incorporated into the current version of the model. As is the case for C, N and S, phosphorus flows in the model are generated by monthly time steps (Fig. 2). The primary mineral source of P in soils is the weathering of apatite in the parent material. Fertilizer P inputs can also be simulated. Physical and chemical weathering transforms primary P to secondary and occluded forms. Simultaneously, plant roots and soil organisms take up P from the soil solution. At this point the P submodel becomes tightly linked to the carbon and nitrogen submodels (see below). Carbon assimilation and fixation into plant and microbial biomass (and subsequent plant residue) is suppqrted by phosphorus incorporation into plant and microbial biomass. Organic matter

accumulation may be a direct function of the P available for biological consumption because as more P becomes fixed via plant and soil microbial uptake, larger amounts of P become immobilized in organic matter (Cole and Heil 1981). Plant residue P is subdivided into structural and metabolic flows. These flows are determined by the C:P ratio. The structural P box receives low P content material as determined by a fixed C:P ratio of 500. The metabolic P box receives the remainder of the plant residue P such that the C:P ratio varies from 80 to 150. It is important to recognize that it is not possible to proceed up to or past this step in understanding modeling of P flows unless both carbon and nitrogen flows have been estimated. This is because C residue content is a function of both C:N and C:lignin ratios. Redistribution of organic P compounds in soils is mediated by microbial activity which decomposes plant residues. The polymerization of the products of microbial decomposition results in compounds that bond physically and chemically with clay particles as well as amorphous mineral colloids. However, the mechanisms involved in the stabilization of these compounds are only partially understood and are the subject of current research. Functionally, stabilization appears to be related to soil texture. Hence soil texture is used in the model as one of the controlling factors that determines organic matter stabilization (see Carbon Submodel description). Once carbon flows are estimated, phosphorus flows can be modeled on the basis of C:P ratios. In the model, structural and metabolic products are divided into three fractions based on the turnover time of the various fractions. Microbial biomass and metabolites with C:P ratios ranging from 30 to 80 constitute the active soil P fraction. The passive soil P fraction is made up of stable organic P forms with C:P ratios ranging from 20 to 200. Finally, the slow soil P fraction, which is intermediate with regard to turnover time, has C:P ratios ranging from 90 to 200. Tiessen et al. (1982, 1983) provide the P fractionation data that indicates the viability of the three fractions.

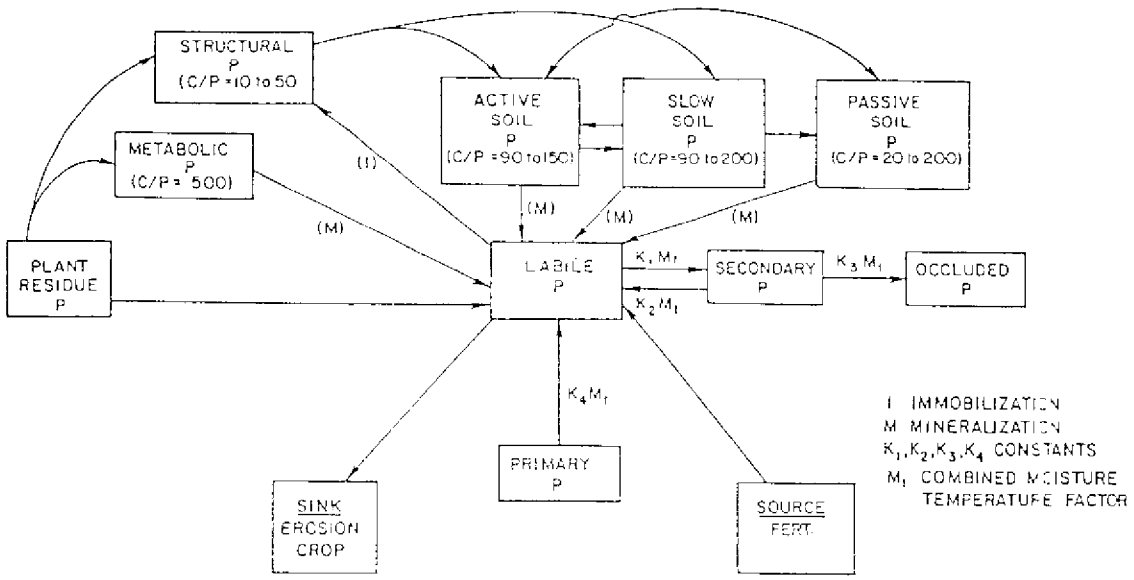

Figure 2. Flow diagram for the phosphorus submodel (after Parton et al. 1988).

The labile P level is defined as orthophosphate that is extractable with anion exchange resin (Sibbesen 1977) or as isotopically exchangeable orthophosphate (Sibbesen 1984). In their review article, McGill and Cole

(1981) report that under low levels of labile P, phosphatase enzymes mineralize P directly from the system. They also state that C:P ratios of microbes vary as a function of the labile P levels, which is a key assumption of the phosphorus submodel. Direct mineralization of P when labile P is low, in combination with varying C:P ratios of microbial biomass (also dependent on labile P levels), results in formation of new soil organic matter with a C:P ratio that varies as a function of the current labile P level. Ultimately, the C:P ratio of active, slow and passive SOM pools varies as a function of the labile P level. Further evidence for this assumption is provided by a comparison of C:P ratios in soils with differing available-P levels (McGill and Cole 1988). In soils with low C:P ratios (~60 to 120), available-P levels are high while high C:P ratios reflect low available-P levels.

The decomposition of metabolic plant material and active, slow, and passive SOM (with low C:P ratios) usually results in the mineralization of labile P. This is because the phosphorus attached to carbon that is lost as microbial respiration (ranging from 30 to 80% of the carbon flow) is assumed to be mineralized. In contrast, immobilization of P from labile P is required for decomposition of structural plant material which has a high C:P ratio.

Additional flows in the phosphorus submodel are: (1) weathering of primary P, (2) formation as well as solubilization of secondary P and (3) formation of occluded P. These flows are controlled by the combined moisture-temperature decomposition parameter (Mt) times the value of a constant (K_1 through K_4). It is important to recognize that the weathering rate of parent material P is regulated by soil moisture as influenced by texture. Hence, sandy soils weather more slowly than clay soils. The value of Mt is calculated as the ratio of monthly precipitation (ppt) to potential evapotranspiration rate (PET) times the effect of monthly soil temperatures on decomposition. The values of K_1, K_2, K_3, and K_4 are 0.05, 0.0022, 0.000001, and 0.0001 per month, respectively.

The carbon submodel. Given our conceptual framework (Stewart et al. 1983) the functioning of the phosphorus submodel is incomplete without repeatedly linking it to the carbon submodel. The carbon submodel is similar to the P submodel in that plant residue C is divided into metabolic and structural forms, and then partitioned into active, slow and passive pools based on residence time (Fig. 3). The lignin to nitrogen ratio of plant residue is the basis for the division into structural (2-5 yr turnover time) and metabolic (0.1 to 1.0 yr turnover time) pools. The structural, metabolic, active, slow, and passive pools are state variables. The dynamics of C (in each of the state variables) are calculated by multiplying the decay rate specified for each state variable times the combined effect of soil moisture and temperature on decomposition (Parton et al. 1987). The soil temperature term is a function of the average monthly soil temperature at the soil surface, while the soil moisture term is a function of the ratio of monthly precipitation to monthly potential evapotranspiration (Parton 1984). The decay rate of active pool material is further modified to change as a function of soil texture with low rates for silty and clayey soils and high rates for sandy soils.

Soil tillage is an optional modeling step in the CENTURY model. When soil tillage is invoked, the decomposition rates for the month when tillage

occurs are increased by 25%, 50% and 50% for the active, slow and passive pools, respectively, based in part on data of Tisdale and Oades (1982).

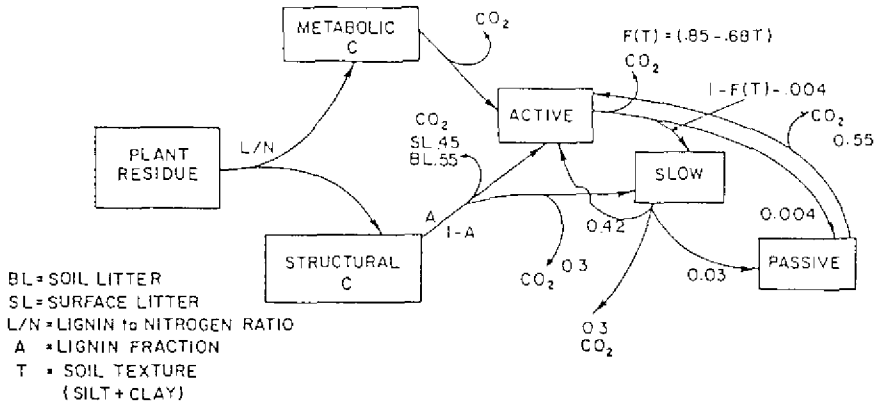

Figure 3. Flow diagram for the carbon flows in the CENTURY model (after Parton et al. 1987).

Except for the active pool, each carbon flow has a fixed respiration loss. The active SOM pool respiration loss varies as a function of soil texture, with respiration losses decreasing with greater amounts of silt and clay. Further explanation of the carbon submodel (including equations that describe decomposition of the state variables) can be found in Parton et al. (1987). A key concept that serves as the foundation of the CENTURY model is that the flows of P, N and S are calculated by multiplying the carbon flow rates by C:P, C:N and C:S ratios of the state variables. Our assertion, and the assertion upon which this model is based, is that P, N and S cycling cannot be understood nor modeled unless the elements are linked with each other and with carbon flows.

The nitrogen submodel. Most nitrogen is assumed to be bonded to carbon and the N attached to carbon lost in respiration (30 to 80% of the carbon flow) is assumed to be mineralized. The structure of the nitrogen submodel is similar to the carbon flow diagram in that plant residue N is subdivided into structural and metabolic pools initially, and subsequently into active, slow and passive pools (Fig. 4). In contrast to the phosphorus submodel where the C:P ratios are variable, the C:N ratios in the nitrogen submodel remain fixed: structural C:N = 150, active C:N = 8, slow C:N = 11, and passive pools C:N = 11. The metabolic N pool varies as a function of N content of plant residue. The nitrogen that is in excess of the amount needed to create the structural pool (with its fixed C:N ratio of 150) becomes part of the metabolic N-pool.

Nitrogen flows are assumed to be stoichiometrically related to the carbon flows. Nitrogen flow rates are determined by multiplying the corresponding carbon flow rate by the fixed N:C ratio of the pool (state variable) that is to receive the carbon. Decomposition of metabolic residue and active, slow, and passive fractions results in a net mineralization of nitrogen because of the C:N ratios of these state variables and the CO_2 losses associated with each flow. For the same reasons, decomposition of structural residue results in immobilization of N. For a further description of the N

submodel and explanation of the equations used to represent N inputs and N losses see Parton et al. 1987.

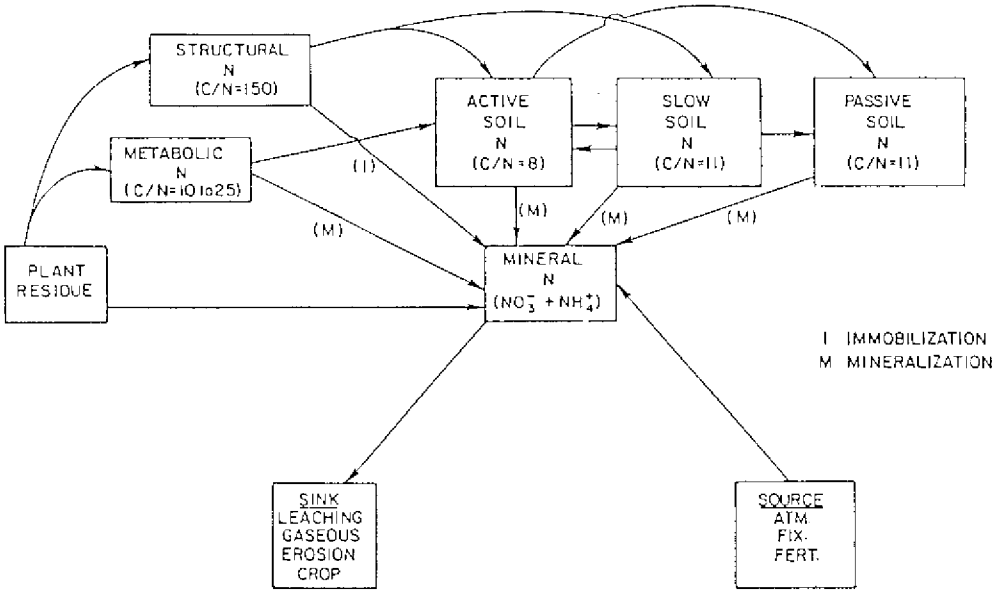

Figure 4. Flow diagram for the nitrogen submodel (after Parton et al. 1987).

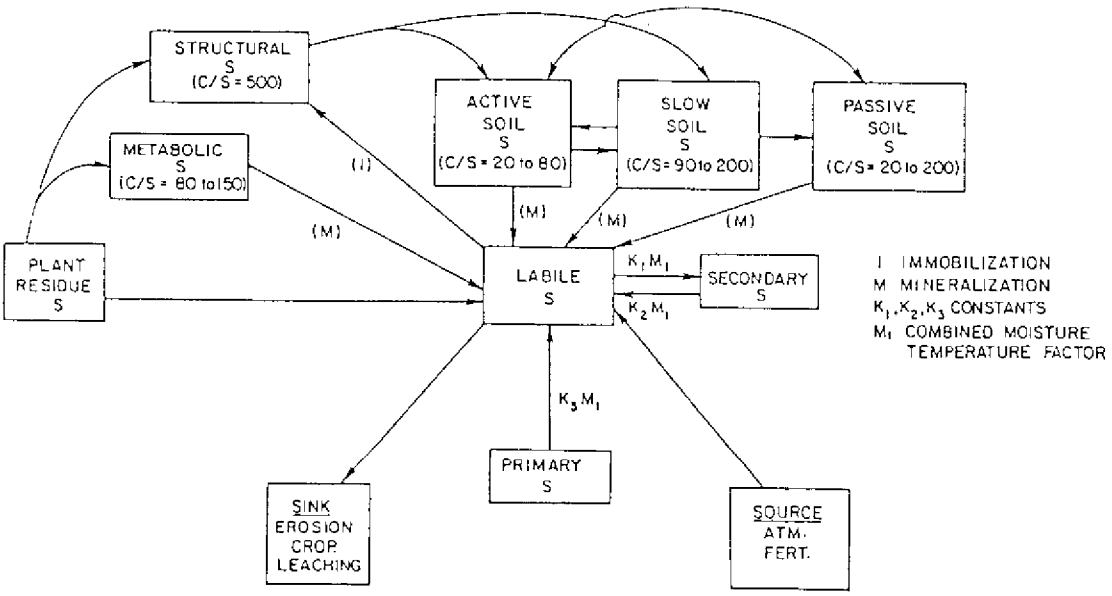

Figure 5. Flow diagram for the sulphur submodel (after Parton et al. 1988).

The sulphur submodel. Only in this decade has there been sufficient progress to develop a conceptual soil sulphur model that is useful for understanding the effect of soil sulphur on SOM composition (Bettany et al. 1980, Freney and Williams 1983). This work has been complemented by laboratory studies that focus on processes important to the transformations of S in soil ecosystems (Maynard et al. 1985, Saggar et al. 1983). Building on existing data and earlier computer models, the CENTURY sulphur submodel is a simplified sulphur model that operates on monthly time steps (Fig. 5). Similar to the phosphorus submodel, the S submodel has a fixed C:S ratio defining the structural pool, and C:S ratios in the metabolic, active, slow

and passive pools that vary as functions of plant residue C:S, microbial biomass C:S, microbial metabolite C:S and labile S soil solution concentration, respectively. The variation in the C:S ratios for different SOM fractions are based on the observed C:S ratios for different particle size SOM fractions (Anderson et al. 1981, Anderson and Paul 1983).

The same algorithm used to calculate the split between structural and metabolic pools in the N and P submodels is used to determine metabolic and structural S. It is interesting to note that the S submodel has several characteristics similar to the N and P submodels. This is because the S cycle is similar to both the N and P cycles in that some organic matter S has carbon bonds (similar to the N cycle) while other organic matter is bonded by esters (similar to the P cycle). For a more complete description of the S-submodel (including justifications for the C:S ratios and more exact definitions of weathering and labile S) see Parton et al. (1988).

Phosphorus-nitrogen interactions in the CENTURY SOM model. Building on the earlier work of Hutchinson (1944, 1970), Cole and Heil (1981) hypothesize that "the levels of biologically active nitrogen in any living system come into balance with the supply of biologically active phosphorus". Cole and Heil (1981) cite numerous examples of the N-P balance hypothesis including nitrogen fixation by plants (Andrew 1976, Gates 1974), by blue-green algae (Nawawy 1974) and by lichens (Tansley 1977) where the nitrogen supply adjusts to the phosphorus supply. The inverse also occurs, for example, when phosphorus limitation reduces photosynthetic efficiency and ultimately reduces the supply of photosynthate available to associative bacteria (Bowen and Cartwright 1977).

An additional factor to be considered is the interaction of nitrogen and phosphorus on plant phosphorus uptake. Many agronomic studies have shown increased absorption of phosphorus by plants when nitrogen is added to the soil (Scarseth et al. 1942, Robertson 1954, Grunes 1959). The mechanism for this interaction is partially attributable to the physiological reaction of the plant (Miller 1974), and partially due to a link between the synthesis of N intermediates such as glutamine and the energy supply needed for anion uptake (Cole et al. 1963, Thien and McFee 1970). Recent research has begun to unravel the details of these mechanisms and has uncovered a complex set of physiological interactions that control the nature of P uptake, translocation of P and the sustenance of these processes via materials from the endosperm (Jackson et al. 1980, Smith and Jackson 1987a, 1987b).

Under the current model structure there is no procedure for simulating the effect of added N on P uptake and resultant plant production. The long term (20 yr) experimental manipulation of agricultural fields in Sweden (see Ivarson, this volume) reveal a pronounced effect of N addition on plant production via increased P uptake. For example, at Orja, Sweden the effect of nitrogen addition on plant production is poorly modeled because there is no N-P interaction term that allows for greater P uptake due to N input (Fig. 6a,b). To simulate the effect of nitrogen on phosphorus uptake we inserted an equation whereby an increase in soil mineral N results in an increased amount of phosphorus available for plant uptake (Fig. 7). This addition to the model has the effect of improving the simulation of plant production where N is added but no P is added. The net effect is a sort of `mining' of organic P forms from the soil over a 20 yr period. The model with the N-P interaction

term simulates production well for situations where both N and P are added over a 20 yr sequence (Fig. 8).

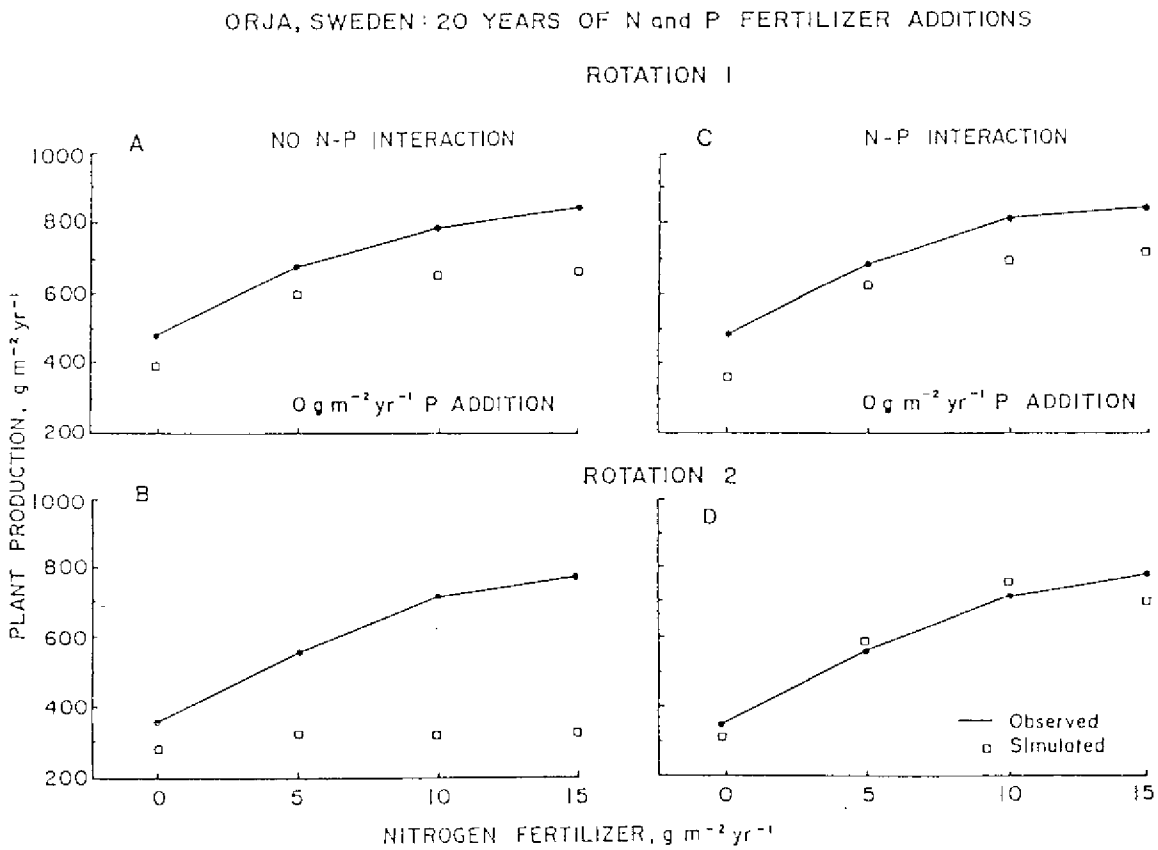

Figure 6. Observed and simulated results for rotations at Orja, Sweden where no phosphorus has been added but where nitrogen has been added on an annual basis. Model simulations do not approximate field results (A,B) until an N-P interaction term is inserted into the CENTURY model (C,D).

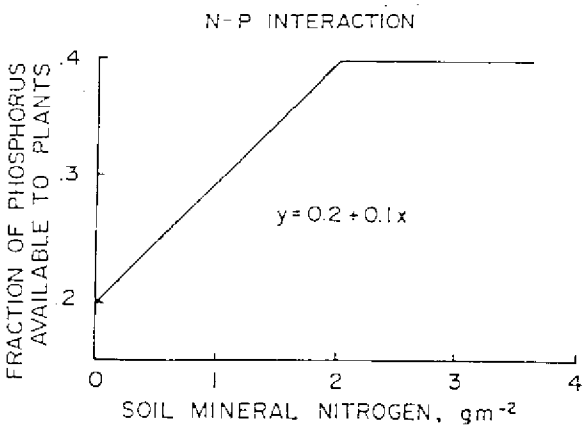

Figure 7. The N-P interaction term is a linear function that increases the fraction of labile P available to plants in a given time step as a function of soil mineral N.

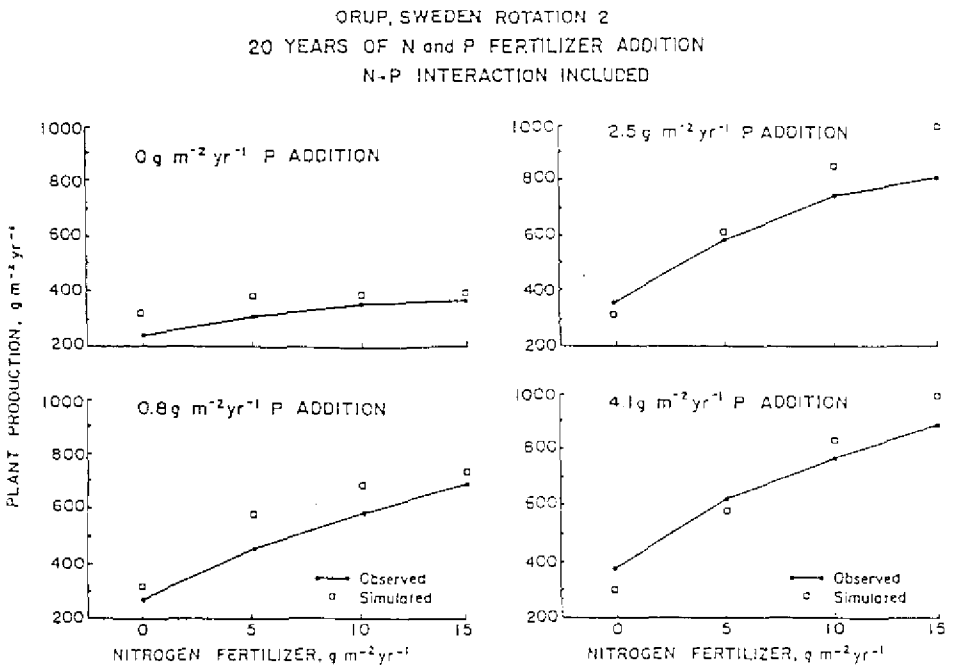

Figure 8. Validation of N-P interaction for four levels of N addition and four levels of P addition. Model simulations agree well with field data at most levels of fertilizer application.

Conclusions

There are at least four good reasons to model soil organic matter and elemental cycles. First, modeling is useful as a logical framework to organize concepts, transform concepts into mathematical equations, and rigorously examine complex interactions within the rubrick of that logical framework. Tests of complex hypotheses, with multiple interacting factors, are most efficiently accomplished by models. Second, models are important for generating spatial patterns based on empirical data. The extrapolation of soil C, N and P, and of aboveground plant production for the United States Great Plains Region serves as an example of this use (Parton et al. 1987). Third, models provide a method useful in predicting changes. For example, the results of the CENTURY model for 100 yr, 1000 yr and 10,000 yr runs show the accumulated costs and benefits of element capital and availability, for grassland soils (Parton et al. 1987). Finally, and most importantly, model failure leads to new ideas, new hypotheses and new experiments. An example is the interaction of N fertilization on P uptake. Although the exact mechanism is not modeled in detail, the net effect is a successful simulation based on a utilizable simplification.

The CENTURY SOM model has been shown to simulate complex interactions in a verifiable manner for both long time periods and extensive spatial scales. The ultimate utility of the model occurs when empirical results disagree with model simulation runs because this leads to explicit questioning of assumptions and changes or additions to the model.

Acknowledgements

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PHOSPHORUS DISTRIBUTION AND CYCLING IN EUROPEAN FOREST ECOSYSTEMS

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Introduction

Phosphorus deficiency is a major, if not dominant factor, limiting the productivity of forests in various parts of the world including many areas of Europe. To improve or at least maintain the productivity of European forests, it is therefore essential to understand how forest management and environmental factors affect P cycling and the P nutrition of the trees. For example, P is lost from sites when trees are harvested particularly when whole-tree and complete-tree harvesting methods are practiced. This loss may not be replaced 'naturally' by inputs from rain and rock weathering, especially since drainage losses after felling may be significant. Changes in the physico-chemical form of P in soils may occur when organic matter accumulates under trees and this may slow the rate of P cycling and induce P deficiency. Acid rain, because of its potential to reduce soil pH, organic matter decomposition and soil biological activity, and mobilise iron and aluminium in soils, may further exacerbate these problems. Yet the distribution and cycling of P in forest ecosystems receives far less attention in research programmes than nitrogen, such that in forest modelling and acid rain studies, P nutrition of trees and P cycling have hardly featured at all. Clearly there is a need to put more emphasis on research programmes dealing with the distribution and cycling of P in forests. In this paper, I will therefore review some of aspects of P cycling in European forest ecosystems.

The P cycle of forest ecosystems

Figure 1 provides details of the P distribution and the main annual transfers between the compartments within an ecosystem of a mixed deciduous forest containing: coppice-with-standards oak (*Quercus petraea* Mattushka. Liebl.), ash (*Fraxinus exelsior* L.), birch (*Betula pubescens* Ehrh. and *B. pendula* Roth) and sycamore (*Acer pseudoplatanus* L.) with an understorey of hazel (*Corylus avellana* L.), sited in an oceanic climate on an acid brown earth soil on the northern side of Morecambe bay, Cumbria, England (Harrison 1985). The woodland has had a long history of coppice-with-standards management and was the British IBP woodland site.

P Reserves and distribution

The total P reserves of mature forests of northern Europe range up to 5.5 thousand $kg \cdot ha^{-1}$, but the majority of forests, particularly those on sandy podzolics, peats or the heavily-weathered soils of southern Europe, would contain only 300 to 1000 $kg \cdot ha^{-1}$. Ninety-five to 98% of this P occurs in the soil down to the base of the main rooting depth, usually 50 cm (Duvigneaud and Denaeyer-de Smet 1970, Nykvist 1971, Harrison 1978, Heinrichs and Mayer 1977, Ulrich and Ellenberg 1981, Nys et al. 1983).

Quantities in trees. Most of the 2 to 5% of the total P reserves which are in the vegetation occurs in the tree component. The content of the tree component is related broadly to the forest biomass (Table 1). Total (per hectare) biomass and P of the trees are related both to the number and size

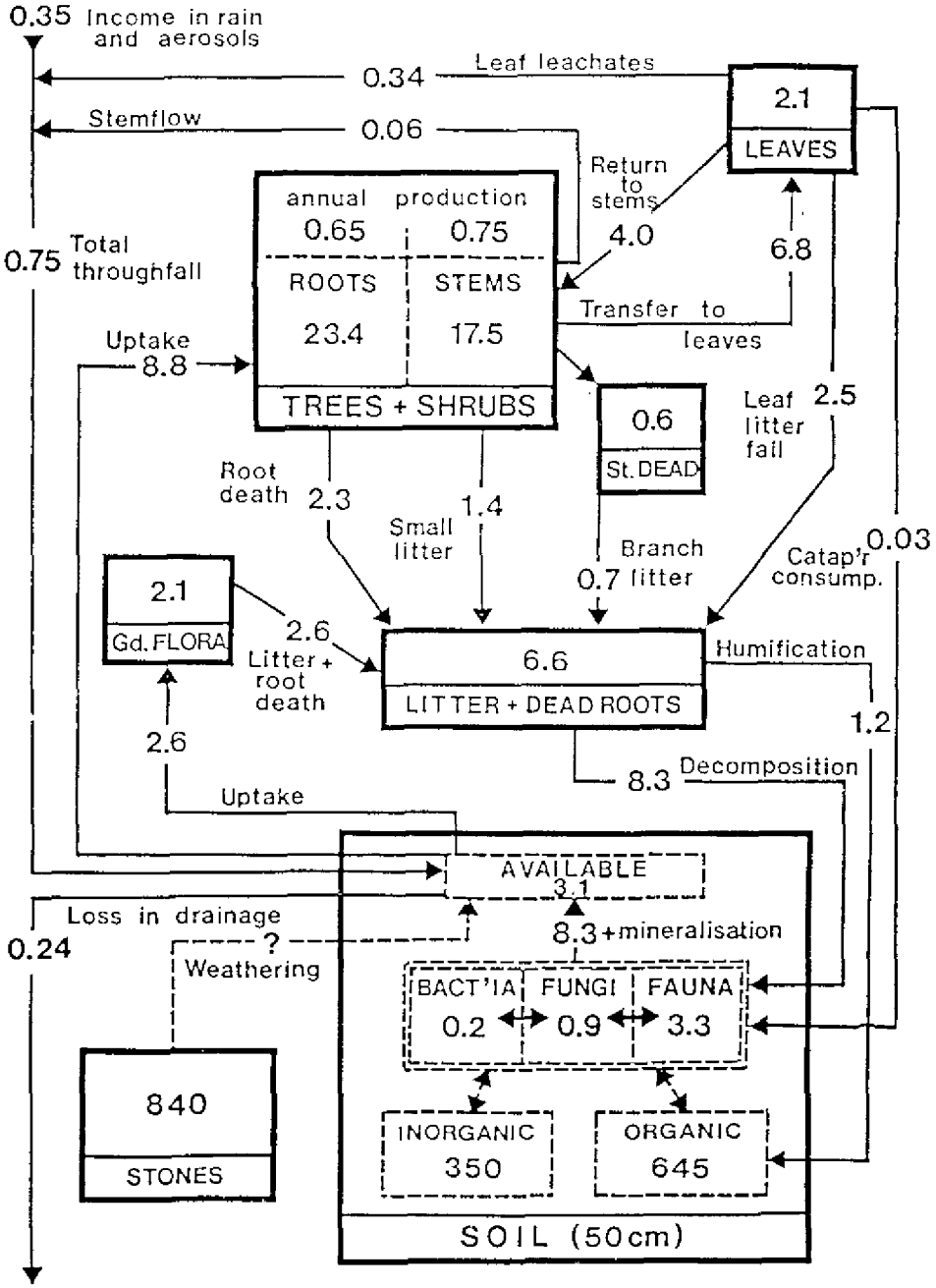

Figure 1. Phosphorus cycle of a mixed deciduous woodland (Meathop Wood, Cumbria, U.K.): contents in kg P ha^{-1} and transfers in kg P ha^{-1} yr^{-1}. (from Harrison 1985).

distribution of stems and to the species composition of the forest. Conifers usually contain greater weights of P than hardwoods of the same age grown under similar conditions (Ovington and Madgwick 1958). However, biomass broadly governs P content of an individual tree irrespective of species and growing conditions (Ovington and Madgwick 1958), as shown in an analysis of the data contained in Table 1 for forests of varying age and species across Europe (Figure 2). Any possible 'species' effect in the relationship appears to be small in relation to the importance of the biomass factor.

Table 1. Tree biomass ($t \cdot ha^{-1}$) and amounts of P ($kg \cdot ha^{-1}$) in forest stands

Forest type	Age (yr)	Biomass (t)	Total P (kg)	Reference
Pines	18-64	26-118	12-25+	Wright and Will (1958)
Fir	47	264	62+	Ovington (1968)
Pine	47	176	43+	"
Spruce	47	165	56+	"
Oak	47	134	40+	"
Pine	55	365	86	Ovington (1959a)
Pine	20	88	30	Miller et al. (1980)
Pine	70	293	49.8	"
Spruce	33	371	95	Carey and O'Brien (1979)
Pine	33	186	41	Ovington and Madgwick (1959a)
Birch	6	1.7	2.1	Ovington and Madgwick
Birch	55	214	61	" (1959b,c)
Spruce	45-132	213	40.5	Nykvist (1971)
Pine	120-150	81	13.6	Bringmark (1977)
Spruce	34	143	59+	Ulrich and Ellenberg
Beech	80	181	47	" (1981)
Beech	45-130	375	99.4	Nihlgård (1972)
Spruce	55	367	92.7	"
Beech	90-100	263-358	55-85	Nihlgård and Lindgren (1977)
Mixed/Oak	70-75	156	44	Duvigneaud and
Mixed/Oak	115-160	380	95	Denaeyer-de Smet (1970)
Oak/Ash	80	198	41	Harrison (1978)
Pine	33	146	87.1	Rapp and Cabanettes (1980)
Pines	28-47	25-95.2	10.3-21.1	Mälkönen (1974)
Spruce	50	187	36.1	Nys et al. (1983)
Birch	40	114	31.7	Mälkönen (1977)
Pine$	18	128	40.6	Ranger (1981)
Pine	18	56	8.6	Ranger (1981)
Pine	59	89.5	39.8	Weiner and Grodzinski (1984)
Oak/Hornbeam	72	129.4	22.1	Weiner and Grodzinski (1984)

+ Above ground only.
$ Fertilised.

For plantations, at least, the accumulation of P in the trees occurs relatively rapidly for the first 20-30 years but then tends to slow down (Ovington 1959a, Miller et al. 1980). This is because P initially accumulates in the P-rich, rapidly forming foliage and roots early in forest development, with the progressive production of low-P woody tissues occurring later (Table 2) (Ovington 1959b, Albrektson 1980, Miller et al. 1980, Miller

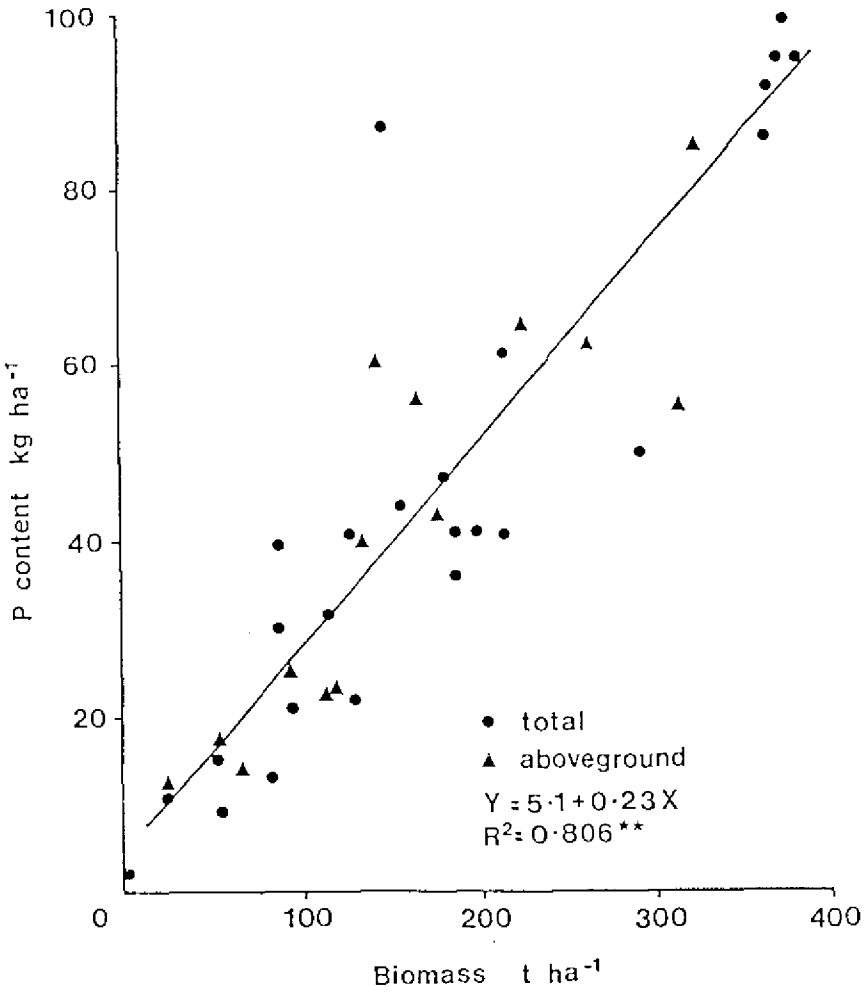

Figure 2. Relationship between total P content and total tree biomass for forests of varying age and species across Europe (sources of data Table 1).

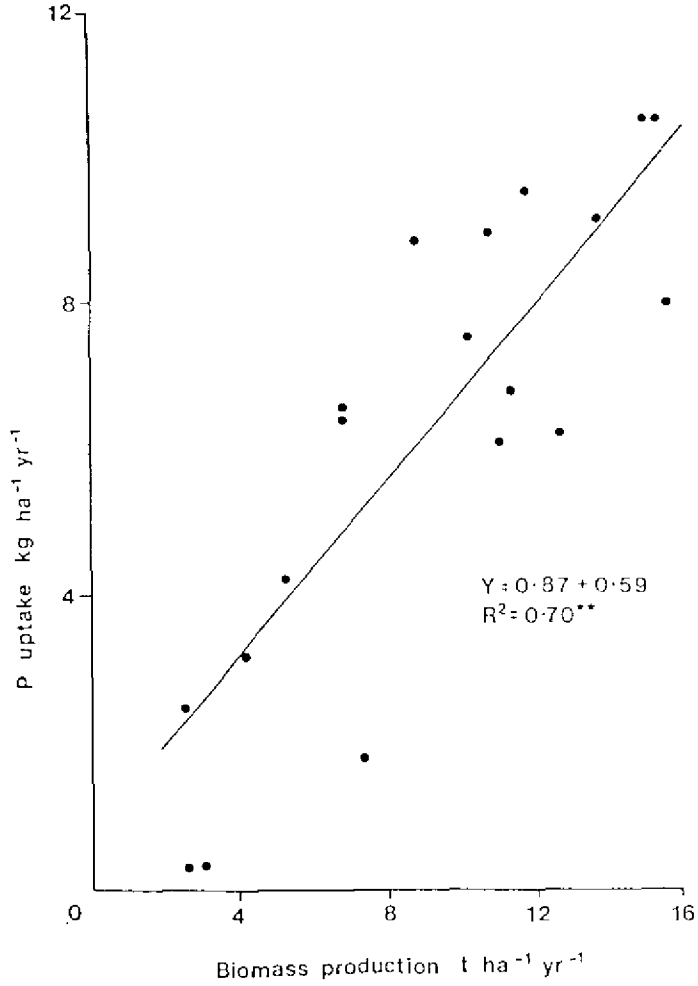

Figure 3. Relationship between P uptake and total production for forests of varying age and species across Europe (sources of data Table 6).

1984b). In established forest, the distribution of P between the various components shows considerable variation; only the root system appears to have consistently a low proportion of the P but this may well be due to an underestimation of the biomass because of the difficulties in attaining complete recovery of root systems and other problems (Persson 1984, 1989).

Table 2. The distribution of P ($kg \cdot ha^{-1}$) between tree components within the forest

Forest type	Age (yr)	Foliage	Branches and Twigs	Stem	Roots	Reference
Birch	42	2	4	6	4	Ovington and Madgwick (1959c)
Beech	45-130	-	61.4	22.4	15.6	Nihlgård (1972)
Spruce	55	21.8	30.2	28.5	5.7	Nihlgård (1972)
Pine	50	11.4	8.6	14.9	10.9	Miller et al. (1980)
Pine	55	13.7	3.3	7	17	Ovington (1959b)
Mixed deciduous	30-75	4.7	11.4	11.6	10	Duvigneaud and Denaeyer de-Smet (1970)
Pine	120-150	4.8	3.0	2.8	3.0	Bringmark (1977)
Pine	33	15.3	23.3	37.5	11.0	Rapp and Cabanettes (1980)
Spruce	33	18.9	47.5	18.9	9.9	Carey and O'Brien (1979)
Beech	45-130	5.2-6.2	26-55	20-22.4	-	Nihlgård and Lindgren (1977)
Pine+	18	24.1	9.3	15.4	2.3	Ranger (1981)
Pine$	18	5.5	2.4	3.3	0.4	Ranger (1981)
Pines	28-47	2.7-5.8	1.9-4.0	1.6-5.2	3.2-6.2	Mälkönen (1974)
Spruce	50	19.1	12.9	4.4	-	Nys et al. (1983)
Birch	40	5.63	4.42	11.2	10.4	Mälkönen (1977)
Spruce	45-132	14.4	10.7	9.9	4.4	Nykvist (1971)
Pine	59	4.33	5.5	24.6	5.3	Weiner and Grodzinski (1984)
Oak Hornbeam	72	6.93	1.93	7.11	6.11	Weiner and Grodzinski (1984)

+ Fertilised; $ non-fertilised.

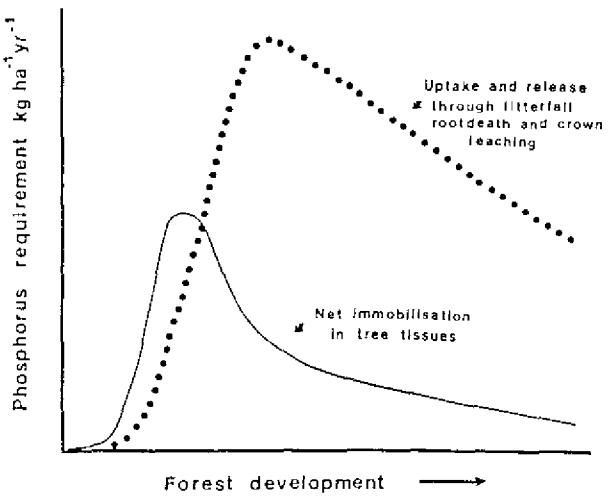

Figure 4. Changes in amounts of P i) immobilised in tree tissues and ii) uptake and release through litterfall, root death and crown leaching, during forest development (based on Miller 1981).

Quantities in the ground flora. The amount of ground vegetation, and consequently its P content (Table 3), generally depends on the stage of development of the forest canopy and the level of light penetration through it. In the early stages of stand development or after coppicing, the ground flora is most abundant, diminishing as the canopy becomes more dense, to increase again at later stages (Ovington 1959a), particularly after thinning. Soil pH also has an influence on the abundance of the ground flora, with higher pH's resulting in better growth (Nihlgård and Lindgren 1977); pH will therefore partially determine the amounts of P contained within the ground flora.

Quantities in the soil litter layer. The amounts of P within the forest litter layer varies considerably from near nothing to perhaps more than those in the tree component (Table 4). Generally, the mass of this layer, and therefore its P content varies with tree species, the type and decomposability of the litter components produced, soil type, environmental conditions and the stage of development of the forest ecosystem (see Figure 4).

Table 3. Biomass ($t \cdot ha^{-1}$) and P ($kg \cdot ha^{-1}$) content of the ground flora of forest ecosystems

Forest type	Age (yr)	biomass (t)	P content kg	Reference
Pine	7	11.58	7.88	Ovington (1959a)
Pine	23	0.15	0.25	Ovington (1959a)
Fir	47	4	6	Ovington (1965)
Beech	45-130	<.01-.9	0-1.9	Nihlgård and Lindgren (1977)
Pine	120-150	7.76	5.05	Bringmark (1977)
Mixed deciduous	30-75	0.79	5.1	Duvigneaud and Denaeyer-de Smet (1970)
Spruce	45-132	0.52	1.15	Nykvist (1971)
Spruce	55	.01	0.02	Nihlgård (1972)
Mixed deciduous	80	1.4	2.1	Harrison (1985)
Pines	28-47	1.37-2.03	3.7-7.2	Mälkönen (1974)
Birch	40	2.3	3.9	Mälkönen (1977)
Pine	59	.92	1.2	Weiner and Grodzinski(1984)
Oak/Hornbeam	72	1.12	3.55	Weiner and Grodzinski (1984)

Forms of the P in forest soils. Phosphorus in forest soils occurs in many complexed states which can be divided broadly into inorganic and organic forms. Particularly in the surface accumulations of organic matter but also in the surface mineral horizons, the majority (up to 90% or more) may be bound in organic forms (Sauerlandt et al. 1959, Floate 1962, James et al. 1978, Nômmik 1978, Harrison 1979, 1981, Wilke 1979). In temperate forest surface soils, the amount of organic P (P_o; $\mu g \cdot g^{-1}$ soil) can be predicted (Harrison 1987) from estimates of soil total P (P_t; $\mu g.g-1$), pH, organic carbon (C; %) and soil depth (D; cm) by the following equation ($R^2 = 0.85$, $P<0.001$):

$$P_o = 0.839P_t + 0.8*10^{-4}P_t^2 - 135pH + 8.76pH^2 + 9.1C - 0.11C^2 + 17.3D - 0.52D^2 + 165$$

The amount of organically-bound P declines with depth in the soil profile (Sauerlandt et al. 1959, Floate 1962, Brogowski 1966, Harrison 1987), though the Po concentration in the organic matter increases with depth (Harrison, 1987). Total amounts of Po in the rooted layers of the soil may be considerable ranging from 560 to 2990 $kg \cdot ha^{-1}$ (Floate 1962, Jenkinson 1971, Harrison 1978). Inorganic P, usually a much smaller proportion of the total P in a forest soil, is mostly insoluble and associated with iron and aluminium, or calcium (depending on soil pH) and the fine particle fractions clay and silt (James et al. 1978, Wilke 1979, Harrison 1981).

A few percent, but sometimes less than one percent, of the P in the surface soil is in labile organic and inorganic forms. The labile pool can undergo fairly rapid transformations and is often determined by extraction in Olsen's bicarbonate solution at pH 8.5 (Harrison 1981, 1982). The percentages of the total P in the labile organic and inorganic forms are strongly negatively related to pH, and aluminium and iron extractable by 3% oxalic acid (Allen et al. 1974, Harrison 1981). Though water-soluble P can be a significant proportion of the P in forest litter layers (Wilke 1979), it is usually a very small part of that present in the mineral soil (Wilke 1979, Harrison 1982).

Table 4. Litter layer (including H-layer material) P content and P input

Forest type	Age (yr)	P content ($kg \cdot ha^{-1}$)	P input ($kg \cdot ha^{-1} \cdot yr^{-1}$)	Reference
Oaks	130-150	-	.7-9.6	Rapp (1969a)
Beech	-	-	1.0-1.75	Lemée and Bichaut (1971)
Pine	120-150	4.14	0.38	Bringmark.(1977)
Beech	45-130	5.80	5.00	Nihlgård (1972)
Spruce	55	15.40	4.80	Nihlgård (1972)
Pine	14	6.76	8.14	Ovington (1959b)
Pine	55	27.56	9.31	Ovington (1959b)
Pine	29	-	4.5	Aussenac et al.
Fir	33	-	2.1	" (1972)
Spruce	24	-	1.5	"
Mixed hardw.	30	-	5.3	"
Spruce	34-47	47-51	2.3-7.8	Carey and Farrell (1978)
Mixed oak	70-75	2.41	4.7	Duvigneaud and Denaeyer-de Smet (1970)
Spruce	45-132	57.6	-	Nykvist (1971)
Beech	-	-	2.7-5.4	Gloaguen and Touffet (1974)
Mixed oak	80	3.3	7.2	Harrison (1978)
Spruce	115	98	3.7	Ulrich and Ellenberg (1981)
Beech	59	62	4.2	"
Beech	-	110*	-	Bulgen et al. (1983a)
Spruce	-	110*	-	"
Pines	20	-	3.5-6.4	Gloaguen and Touffet (1976)
Firs	20	-	4.1-5.7	"
Pines	28-47	18.9-30.7	.22-.85	Mälkönen (1974)
Spruce	50	40	4.0	Nys et al. (1983)
Birch	40	15	2.8	Mälkönen (1977)

* excluding roots.

Inputs to and losses from forest ecosystems

Inputs to forest ecosystems occur through three processes, i) in precipitation from the atmosphere ii) from bird droppings, and iii) from rock weathering. Losses occur through the leaching and runoff from soils and removal of timber.

Inputs. Inputs of P from the atmosphere in precipitation has been widely studied and the results show that generally little P enters forest ecosystems from the atmosphere (Table 5). Inputs as dry deposition in the form of dust is usually considered to be small and is included with the estimated precipitation input, though dry deposition is difficult to estimate as a separate entity because of the problem of distinguishing this from canopy leaching of P.

Table 5. Atmospheric inputs and soil leaching losses

Forest type	Age (yr)	Inputs ($kg \cdot ha^{-1} yr^{-1}$)	Losses ($kg \cdot ha^{-1} yr^{-1}$)	Reference
Beech	30-200	.285	-	Lemée (1974)
Beech	125	.48	.01	Ulrich and Mayer (1972)
Oak	40-120	.43	-	Carlisle et al(1966)
Oak/Pine	-	.1-1.9	-	Rapp (1969b)
Spruce	24	.04	-	Aussenac et al(1972)
Beech	125	.5	.04	Mayer and Ulrich (1974)
Beech	80	.8	.1	Heinrichs and Mayer (1977)
Spruce	34	.8	.17	Heinrichs and Mayer (1977)
Pine	34-40	.08	-	Miller et al(1976)
Oak,Ash/Birch	80	.35	.24	Harrison (1978)
Spruce/Beech	55-100	.066	-	Nihlgård (1970)
Spruce	20	.25-.4	.094-.15	Harriman (1978)
Spruce*	20	.25-.4	.33-2.5	Harriman (1978)
Pine/Spruce	-	0-.13	0-.07	Rosen (1982)
Birch	-	.2	-	Miller (1984a)
Spruce$	35	.1	.021-.421	Adamson et al. (1987)
Pine/Spruce+	5-75	-	-	Mälkönen (1974)
Spruce/Mixed	-	.08-.09	.03-04	Paces (1985)
Oak/Hornbeam	72	1.8	0.5	Weiner and Grodzinski (1984)
Pine	59	1.8	0.2	Weiner and Grodzinski (1984)
			0.39	Stauffer and Furrer (1984)
Spruce	0-.55	0.6	0.3	Roberts et al. (1983)

* Fertilised with 47 kg $P \cdot ha^{-1} \cdot yr^{-1}$.
$ Some plots clearfelled 1-3 years previously.
+ Mean of three years after clearfelling.

Inputs of P through bird droppings are thought generally to be insignificant, but where there are bird roosts significant quantities are added to the soil, and availability of P can be markedly increased (Gilmore et al. 1984).

Though inputs of P into the P cycle from rock weathering are potentially significant, there are no measurements (because of the difficulties of determination) of rates at which P is produced from these sources and captured into the P cycle by roots. Deep-rooting trees have long been thought to take up nutrients from lower soil horizons and recycle them to the surface soil (Schneider 1940, Dimbleby 1952, Hartmann 1967, Duvigneaud and Denaeyer-de Smet 1970). However, in an investigation of P 'accumulations' in surface soils under Birch using a ^{32}P injection technique, this process was thought unlikely to be significant (Harrison, Miles and Howard, 1988). Estimates of elements released through rock weathering in catchment studies often do not include P (e.g. Rosén 1982, Creasey et al. 1986).

Losses. Many of the earlier nutrient budgets of forests have tended to consider the inputs of P as real gains without considering the losses through runoff and leaching. There may indeed be net gains of P in standing, undisturbed, non-fertilised forests (Table 5) but net inputs are not always found (Viro 1953). Inputs of fertiliser (Harriman 1978), especially to peat soils (Kuntze and Scheffer 1979, Malcolm and Cuttle 1983, Ahti 1984) and clear-felling, particularly during the years immediately following (Grip 1982, Adamson et al. 1987), may result in significantly increased losses of P. Generally losses of P from forest catchments are very small, often at concentrations below detection limit (Hornung et al. 1986, Hornung, pers comm). Because of the low level of losses, P is frequently not mentioned in reports (e.g. Bringmark 1980).

Losses of P in timber removal can be significant (Nys et al. 1983, Ranger 1981), particularly if whole tree (all above ground biomass) or complete tree (above and below ground biomass) methods of harvesting are practiced. In such cases replacement of P by fertiliser application would be a necessity (Mälkönen 1979, Carey 1980, Krapfenbauer and Buchleitner 1981, Klimo 1984, Andersen 1985). In a study of nutrient removal from mixed hardwood coppice during a 15 year coppice cycle, P has been considered the most critical element (Sykes and Barr 1973).

Cycling within the ecosystem

Plant uptake of P. It is quite evident from the large amount of published data, that forest trees often take up considerably more P than is actually required for tree growth. A significant proportion of the total annual uptake is returned to the soil in canopy leachings and litter. The amounts taken up are, nevertheless, linearly related to the annual biomass production, irrespective of age and species of tree (Figure 3), the amounts ranging from less than 1 to over 10 $kg \cdot ha^{-1}\ yr^{-1}$ (Table 6). The P uptake from the soil is greatest in the early stages of forest development i.e. before maximum tree canopy formation. Thereafter, much of the demand is for the production mainly of woody tissues less rich in P, and this together with increased recycling of the element within trees, results in a declining P requirements (Figure 4) (Miller 1981, 1984b). The annual uptake of P by the forest ground flora will largely be determined by the overwintering biomass present and the light intensity under the forest canopy.

Internal recycling of P within trees. The concentration and total quantity of P in tree foliage generally reaches a peak in spring or early summer (Bunce and Sykes, pers comm, Miller et al. 1976, Rapp 1984) with often substantial amounts of P being transferred to the foliage from other parts of the tree (Bunce and Sykes, pers. comm., Bringmark 1977). Prior to leaf or

needle fall, significant proportions (41 - 68.4%) of the P in the mid-summer canopy are transferred back into the stems (Fries 1952, Harrison 1978, Ranger 1981, Staaf 1982, Miller 1984b, Rapp 1984, Carlyle and Malcolm 1986a). The chemical form of P also changes at leaf senescence, with much of the organic P being converted to inorganic (Fries 1952). Much of the P is transferred between foliage, twigs, bark and stem wood (Mutoh 1968, Ranger 1981, Rapp 1984, Carlyle and Malcolm 1986a), and some, in the case of conifers, between new and older needles (Ranger 1981, Rapp 1984). This is a well developed mechanism to conserve P already acquired by trees. Whether there is a similar reabsorption from roots prior to their death and decay is not known.

Phosphorus in trees may be distributed in two pools, the mobile and the structurally bound. The size of the former pool may determine the rate of formation of foliage biomass, as Fagerström and Lohm (1977) have suggested for nitrogen. More research needs to be carried out to demonstrate this potential parallel between P and nitrogen.

Table 6. Uptake and retention* of P ($kg \cdot ha^{-1} \cdot yr^{-1}$) by the aboveground tree component of forest stands

Forest type	Age (yr)	Production ($t \cdot yr^{-1}$)	Uptake ($kg \cdot ha^{-1} \cdot yr^{-1}$)	Retention	Reference
Beech	45-130	15.1	10.5	3.5	Nihlgård (1972)
Spruce	55	13.8	9.1	1.6	Nihlgård (1972)
Beech	45-130	10.6-15.8	8.0-10.5	2.3-3.5	Nihlgård and Lindgren (1977)
Pine	120-150	2.85	0.38	.15	Bringmark (1977)
Pine	28-47	2.4-5.1	2.5-4.2	2.2-3.2	Mälkönen (1974)
Spruce	48	11.2	6.1	1.4	Nys et al (1983)
Birch	40	6.9	6.5	0.9	Mälkönen (1977)
Pine	18	7.4-12.8	1.8-6.2	1.1-4.0	Ranger (1981)
Mixed Deciduous	80	6.9	6.4	1.4	Harrison (1985)
Mixed Deciduous	70-75	11.3	6.9	2.2	Duvigneaud and Denayer-De Smet (1970)
Spruce	87	8.9	4.7	1.4	Ulrich and Ellenberg (1981)
Beech	59	11.8	9.1	2.6	Ulrich and Ellenberg (1981)
Beech	122	10.4	6.7	2.1	Ulrich and Ellenberg (1981)

Leaching of P from the forest canopy. As rainfall passes through the forest canopy, it often becomes slightly enriched as a result of canopy branch and stem leaching (Table 7). Some of the increase may be due to the wash-off of aerosols trapped by the canopy (Nihlgård 1970, Mayer and Ulrich 1974). Decreases in amounts of P in rain on passing through the canopy have also been observed (Nihlgård 1970, Heinrichs and Mayer 1977), and this indicates that foliar absorption may take place. Changing the nitrogen status of trees may alter the amounts of P leached in throughfall and stem flow, though the amounts involved are small (Miller et al. 1976). Leaching of P may increase significantly during senescence of the foliage prior to leaf/needle fall (Schueller 1978, Carlyle and Malcolm 1986a). The amount lost through

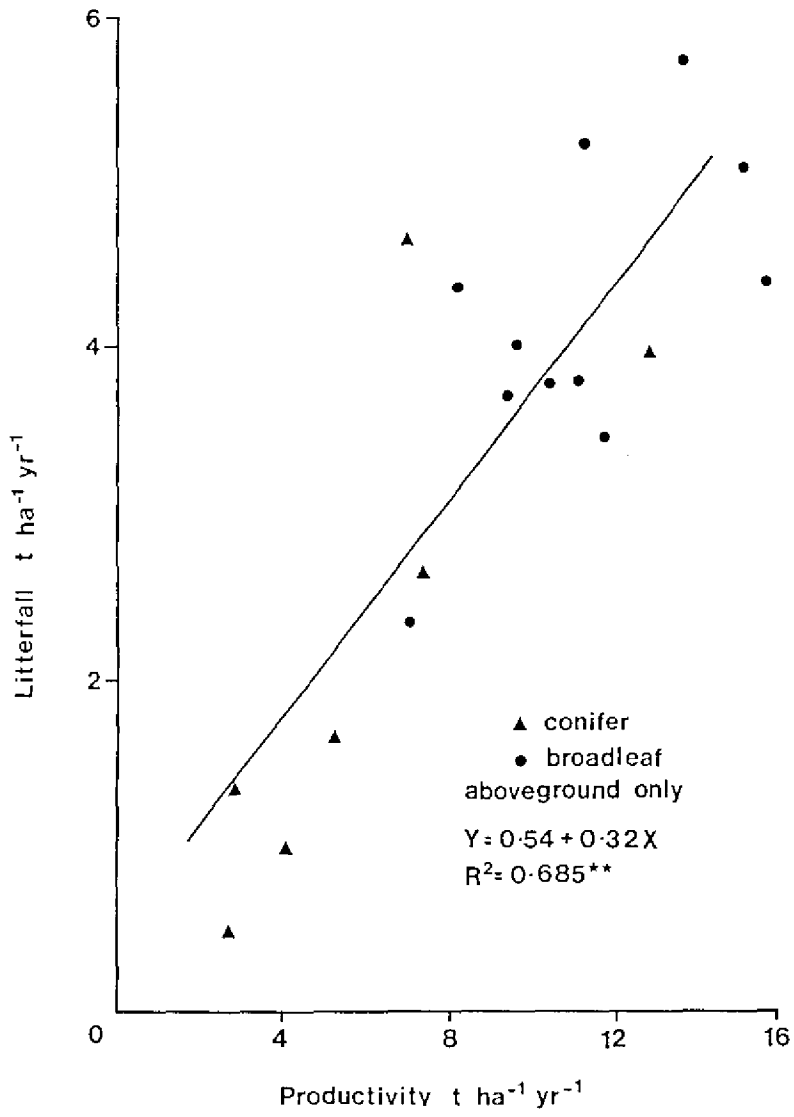

Figure 5. Relationship between total litterfall and total tree productivity for forests of varying age and species across Europe (sources of data Tables 4 and 6).

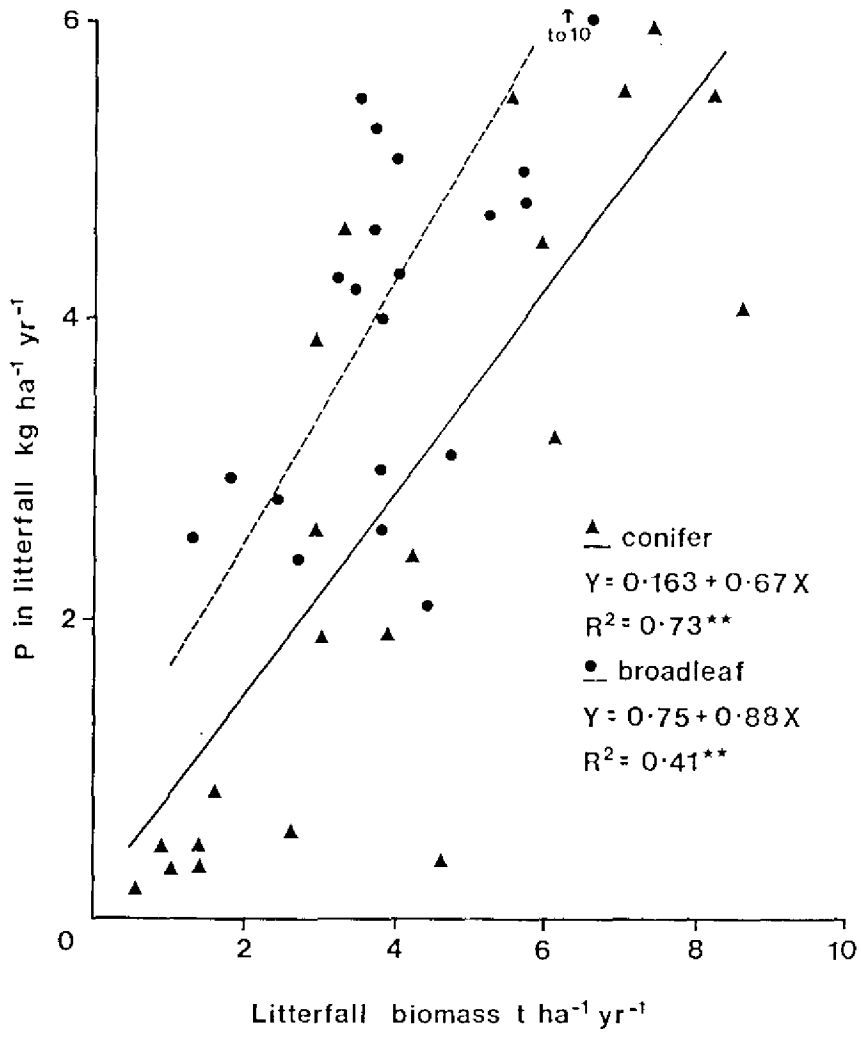

Figure 6. Relationships between the amount of litterfall and its P content for various conifer and broadleaved forests across Europe (sources of data Table 4).

leaching from the canopy probably also increases with age of the forest stand (Stevens 1987).

Table 7. Returns of P ($kg \cdot ha^{-1} \cdot yr^{-1}$) to soil in throughfall and stem flow

Forest Type	age (yr)	Throughfall + Stemflow	Net Gain ($kg \cdot ha^{-1} \cdot yr^{-1}$)	Reference
Oak	40-120	1.31	0.88	Carlisle et al. (1966)
Beech	100	0.048	0.022	Nihlgård (1970)
Spruce	55	0.222	0.195	Nihlgård (1970)
Spruce	24	0.31	0.26	Aussenac et al. (1972)
Oak	-	1.4-3.8	0.6-3.1	Rapp (1969b)
Pine	-	1.3	0.2	Rapp (1969b)
Pine	38	.13-.21	.04-.13	Miller et al. (1976)
Beech	125	0.3	-0.5	Heinrichs and Mayer (1977)
Spruce	85	0.7	-0.1	Heinrichs and Mayer (1977)
Spruce	48	1.1	0.7	Nys et al (1983)
Mixed deciduous	80	0.75	0.4	Harrison (1978)
Larch*	14	1.1	1.03	Carlyle and Malcolm (1986a)
Spruce*	14	0.99	0.92	Carlyle and Malcolm (1986a)
Spruce	5-48	0.36-0.79	0.33-0.76	Stevens (1987)

* During the period of foliage scenescence (Aug-Nov).

Recycling through litterfall. A major pathway for recycling of P in forest ecosystems is through the transfer of litter to the soil. The litter produced ranges from leaf, twig, branch and root material together with small debris of bark, flowers, fruits and even frass from leaf-eating larvae. The annual total production of this litter appears to relate to the total annual tree productivity (Figure 5), though it must be emphasised that there is in most cases an absence of root litter production values in these estimates because of the difficulties of measurement of this process. On the basis of the data sets examined here, it does not appear that there is any difference in the regressions for conifers and broadleaves. The quantity of P returned in the litter also appears to be related to the mass of litter returned, but with these parameters, there does appear to be a significant difference between coniferous and broadleaved trees. The broadleaf trees seem to return more P per unit litter mass than conifers (Figure 6); this means that conifer litter has a higher C:P ratio which has potential consequences for P cycling as discussed below. The quantity of litter and therefore the amount of P it contains, may decline as forests age (Figure 4) (Miller 1981).

Phosphorus returned to soil in ground vegetation litter is generally assumed to be equal to the amounts required for uptake and annual production, as usually there is little net production. There will be small changes in the balance between stages of forest development, as light intensity, to which the ground vegetation responds, decreases or increases (Ovington, 1959a).

Decomposition and P release from litters. The rate of decomposition of litters is governed largely by three factors, climate, soil microbial activity and litter quality, which varies with tree species (Swift

et al. 1979). Branch and bole wood decomposes much more slowly than foliage litters. However, with the majority of tree species the proportion of foliage litter to woody litter is high, with leaf litter accounting for about 70% of the total litter on a world-wide scale (Meentemeyer et al. 1982). Within European forests, the proportion tends to be higher (Sykes and Bunce, 1970, Mälkönen, 1974, Gloaguen and Touffet, 1976, Miller et al. 1976). The proportion of foliar litter in the total litter fall also increases generally with the above-ground net primary production (O'Neill and DeAngelis 1981). Since foliar litters contain a higher percentage of P, they provide a major source of P for recycling. Placement studies using ^{32}P can confirm the surface litter and soil as the most active zones for P uptake by trees (Harrison et al. 1988). The other important source is the fine root litter about which there is relatively little data.

Phosphorus is released for recycling from litters by leaching and decomposition (Berg 1986a). Some of the P in litter and the L/F horizon is water-soluble and can be leached (Table 8) (Bulgen, Dubois and Remacle 1983a, Malcolm and Titus 1983, Granhall and Slapokas 1984, Sevink et al. 1986) and this 'mobile' P is a major source of P for tree uptake (Ulrich and Mayer 1972, Malcolm and Titus 1983, Carlyle and Malcolm 1986b, Stevens et al. in press b). Some studies of leaching of P from the organic soil layers under different tree species in adjacent sites have shown the rates to be similar (Heinrichs and Mayer 1977, Buldgen Dubois and Remacle 1983a), whilst others have shown significant differences between species and even interactions between the litters of these different species resulting in enhanced P release (Chapman 1986, Chapman Whittaker and Heal, in press).

Table 8. Leaching of P ($kg \cdot ha^{-1} \cdot yr^{-1}$) from the litter and surface humus layers of the soil

Forest type	Age (yr)	Depth of organic layer (cm)	Water flux ($l\ m^{-2}$)	Amount of P leaching ($kg \cdot ha^{-1} \cdot yr^{-1}$)	Reference
Beech*	125	-	722	4.6	Heinrichs and Mayer (1977)
Spruce*	85	-	726	5.1	Heinrichs and May r (1977)
Beech	-	4-6	812	2.6	Bulgen et al. (1983)
Spruce	-	4-6	867	2.9	Bulgen et al. (1983)
Spruce	35	c 6	394	0.8	Adamson pers. comm
Spruce+	35	uneven	568	7.8	Adamson pers. comm
Oak	28	-	-	0.6	Chapman (1986)
Pine	28	-	-	2.2	Chapman (1986)
Spruce	28	-	-	2.1	Chapman (1986)
Spruce/Pine	28	-	-	3.2	Chapman (1986)
Spruce/ oak	28	-	-	0.2	Chapman (1986)
Spruce	50	2	1730	3.25	Stevens et al. (in press b)
Spruce$	50	uneven	-	1.4-2.6	Stevens et al (in press a)
Spruce$$	50	uneven	-	7.1-11.7	Stevens et al. (in press a)

* Non-rooted lysimeters.
\+ 1 year after being clearfelled.
$ 1 to 2 years after wholetree harvesting.
$$ 1 to 2 years after conventional harvesting.

The majority of the litter P is released through the decomposition of the organic matter. The main factors governing the decomposition rate are litter quality and climate, the latter mainly determined by the actual evapotranspiration rate (Berg 1986a, Berg Jansson and Meentemeyer 1984, Meentemeyer and Berg 1986). A model for litter decomposition suggests that the whole process may be divided into two phases (Berg and Staaf 1980a, Berg 1986a). In the first phase soluble substances and non-lignified carbohydrates are decomposed (Nykvist 1963, Minderman 1968, Berg and Staaf 1980a, Berg 1986a). The rate of mass-loss from the litter is largely controlled by concentrations of nutrients which limit microbial activity, such as N, P and S. In this early phase of decomposition P, along with other nutrients, can become immobilized by microbes. The amount of nutrients 'tied up' in microbial biomass is often only a minor part of those contained in litter (Wessen and Berg 1983) but other studies have shown that between 7 and 43% of the P in litters or organic layers is microbial (Frankland et al. 1978, Bååth and Söderström 1979, Frankland 1982 and pers. comm.), with variations depending on the type of forest ecosystem (Buldgen, Dubois and Remacle 1983b). However, P immobilisation in microbes is generally followed by release later in the decay processes when the easily decomposable carbon sources diminish. Generally, once a net release of nutrients has started, the rate is proportional to litter weight loss (Berg and Staaf 1981, Staaf and Berg 1982). Decomposition rate of litter and initial nutrient concentrations including that of P, are not always related however (Johansson 1986). The second phase of decomposition is largely governed by the the weight-loss of the lignin components and again net release of P with other nutrients, is broadly related to the mass-loss of the litter component (Berg 1986a).

Overlying this general pattern or model of decomposition, there are variations between tree species or litter qualities (Mikola 1955, 1960, Granhall and Slapokas 1984, Berg and Staaf, 1987), and regional and site variations in decay rates (Berg et al. 1984, Johansson 1986).

A particularly successful approach for obtaining an integrated estimate of organic matter turnover rate, and therefore the release of P (and nitrogen) in woodland soils, is the measurement of ^{14}C-bomb carbon incorporation from the atmosphere via photosynthate into the soil organic matter (Harkness, Harrison and Bacon 1986). Making the assumption that P turn over 'in tandem' with the carbon, estimates of P (and N) release from soil organic matter for a mixed deciduous woodland have been derived which closely match the estimated annual uptake by the trees and ground vegetation (Harrison 1987, Harrison, Harkness and Bacon 1989).

There have been many attempts to fit a negative exponential relationship to the pattern of organic matter decomposition (Jenny et al. 1949, Olson 1963), where k represents the rate constant treating mass-loss as a first-order reaction:

$$W_t/W_o = e^{-kt}$$

This model implies that the value k is constant over the whole time course of the decomposition. It appears that this relationship may be reasonable for the early stages of the decomposition process (to about 50-60% weight loss) but that the decay rate decreases during the time course of decomposition (Johansson 1986). This slowing of the decay rate tends to lead to a build up of organic matter with consequences for the cycling of P and its state within the soil.

Accumulation of organic matter in soil. In long-established or primary forest, the rate of decomposition and the rate of litter fall to the

soil surface reach an equilibrium, so that the amounts of litter on the soil surface remains approximately constant with time, unless there is some disturbance through management, climate change or pollutant input. In many plantation forests, however, there is a tendency for substantial amounts of decomposing litter to accumulate on the soil surface, as they develop (e.g. Ovington 1959a, Nykvist 1971, Nihlgård 1972, Adams and Dickson 1973, Carey and Farrell 1978, Buldgen et al. 1983a, Ogden 1986). The accumulation tends to peak (Figure 7) in mid-rotation (Page, 1968, Dighton 1987, Dighton and Harrison, unpublished) at around maximum canopy development, when litter production is probably at its highest (Miller 1984b). After this, the litter production declines and litter decomposition rate increases (Berg and Staaf 1980b). In addition to litter accumulations on the soil surface, large quantities, up to 45 t ha^{-1}, of humus can accumulate in the surface mineral horizon (Ovington 1959a, Page, 1968), particularly if afforestation takes place on old agricultural land (van der Drift 1971, Jenkinson 1971). Accumulations of humus in the surface soil horizons may be offset by reductions in organic matter lower in the soil profile and these changes may be quite difficult to detect because of high natural or site-preparation-induced soil heterogeneity (Ogden 1986). There can also be net reductions in organic matter and increases in soil bulk density under some tree species (Miles and Young 1980, Miles 1981). Coppice with standards management of a forest may mitigate against organic matter buildup (Bonneau and Ranger 1984). These findings are all based on studies in forests of northern Europe, with cooler climates. Whether such organic matter buildup occurs in soils under plantation forests under warmer southern European climates is not clear.

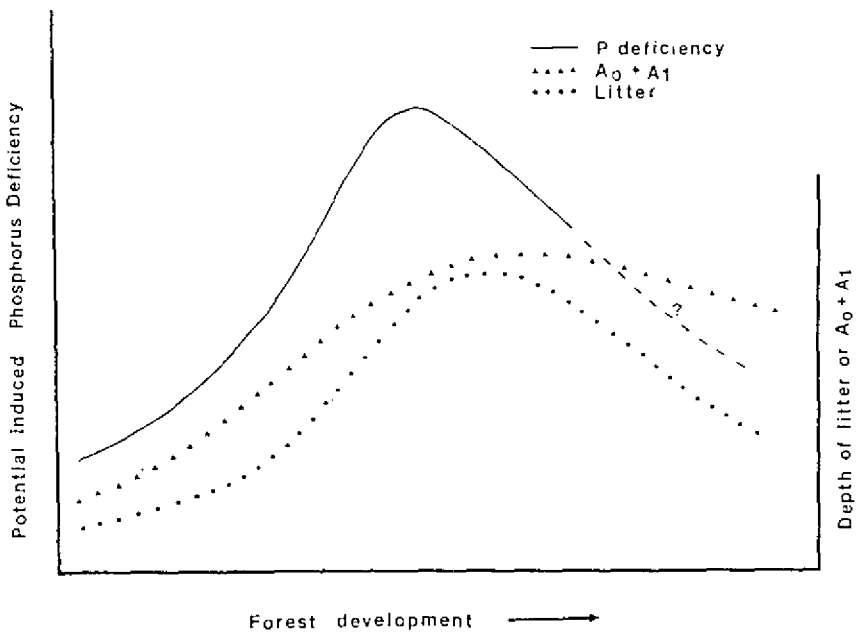

Figure 7. Trends in litter and humus accumulation under spruce and the potential induction of P deficiency in the trees.(based on Page, 1968, Harrison et al. 1986, Dighton 1987, Dighton and Harrison, unpublished).

Changes in the form and turnover rates of P. Changes in the quantity and form of the organic matter in soils affect the state and turnover of P. Increases in organic matter, as will be predicted from the equation quoted in an earlier section, will result in an increased proportion of the

organic P. This prediction is confirmed from detailed studies of the changes resulting from the natural conversion of agricultural land to woodland rates of conversion of inorganic to organic P ranged from 2.3 to 5.9 kg P ha^{-1} yr^{-1} in the surface 23 cm of soil over a period of 83 years (Jenkinson 1971). Increases in organic matter are often accompanied by increases in the C:P ratio of the soil organic matter (von Zezschwitz 1980) and the C:Po ratio tends to be twice as high under forests as under grasslands and agriculture (Harrison 1987), suggesting changes in P forms similar to those which occur during pedogenesis (Walker 1965, Harrison 1978).

Similar conclusions can be drawn from the changes in soil pH and cation contents of forest soils such as reduced pH, losses of Ca and Mg and the mobilisation of Fe and Al upon afforestation (Jenkinson 1971, Nihlgård 1971, Heinrichs and Mayer 1977, Buldgen et al. 1983a, Bonneau and Ranger 1984, Lysikov 1985, Johnston et al. 1986, Rasmussen 1986, Stevens et al. in press b). The reverse increasing of pH and Ca with significant lowering of organic matter can occur under some tree species, particularly birch (Gardiner 1968, Miles 1981).

The P chemistry and behaviour in forest soils is strongly linked with pH and extractable or mobile iron and aluminium (Harrison 1975, 1981, James et al. 1978, Wilke 1979) because these properties govern the soils P-fixation capacity. Extractable Ca and soil pH are dominant factors affecting the rate of mineralisation of organic to inorganic P in woodland soils, slower rates of mineralisation and hence P recycling are associated with low levels of extractable Ca and low pH (Harrison 1982). Extractable Mg is important as the enzyme co-factor affecting phosphatase activity (Harrison 1983). Hence the increase in organic matter content of forest soils, together with a reduction of soil pH, lowering of extractable Ca and Mg and the mobilisation of Al and Fe has a strong potential for slowing of the P cycle.

Relationships between phosphatase activity and P turnover in surface soils. Much of the P returned to soil in litters is bound in organic forms or is temporarily converted to organic forms in early stages of litter decomposition by microbial activity. Mineralisation of the organic P to inorganic P is mediated by phosphatase enzymes, which are most active in the organic matter rich surface horizons (Harrison 1979, 1983), and thus partly determine the leachability of P, as shown by lysimeter studies. The seasonal changes in the 'availability' of P are closely associated with the seasonal pattern of the phosphatase activity in surface soils of forests (Harrison 1981, 1983). Phosphatase activity varies with soil humus condition and its physico-chemical properties and there are strong complex interactions with soil type, site geology and forest vegetation type (Harrison 1979, 1982, 1983).

The role of mycorrhizae in P turnover and uptake. The development of mycorrhizae on the roots of forest trees enhances the ability of trees to obtain P by extending the root surface area available for uptake (Harley and Smith, 1983). The degree of mycorrhizal development on tree root systems is itself controlled by the 'availability' of P, with high levels tending to suppress development (Bjorkman 1970, Frankland and Harrison 1985). The diversity of mycorrhizae appears to peak with litter buildup on the soil surface and the induction of P-deficiency in mid-rotation stands (Dighton, 1987, Figure 7). Roots (Doumas et al. 1983) and mycorrhizae (Bartlett and Lewis, 1973, Alexander and Hardy, 1981, Dighton, 1983) produce higher levels of phosphatase activity under conditions of P-deficiency. Mycorrhizae can also enhance organic matter decomposition (Berg and Lindberg, 1980, Dighton et al. 1987), further aiding the release of P for root uptake.

Effects of acid rain

The effects of 'acid rain' on P cycling are less studied than its effects on cycling of N and base metals, probably because there are significant amounts of N in the atmospheric pollutant inputs whereas they contain little extra P. The acidifying effects of SO_2 and NOx inputs are likely to enhance the reductions in soil pH, Ca and Mg contents and mobilise Al and Fe and, theoretically at least, may slow the P cycle, through the mechanisms outlined above. Such effects do not appear to have been directly looked for in atmospheric pollution and 'Waldsterben' research programmes. However, simulated acid rain and SO_2-fumigation studies have found that rates of litter decomposition can be significantly reduced (Hagvar and Kjøndahl 1981, Berg 1986b and c, Ineson pers. comm.). The amounts of live fungal and bacterial biomasses decrease both in relation to the amounts of sulphuric acid applied and the reduced decomposition rates of litters (Bååth et al. 1980, 1984). Furthermore, it has been shown that the rate of $^{14}CO_2$ from ^{14}C-glucose added to soil is slower (Lohm et al. 1984), so micro-organism activity is affected as well as the biomass. Reductions in the rate of decomposition of organic matter induced by 'acid rain' can be expected to decrease rates of nutrient release, as the rate of release is proportional to mass-loss of litter (Staaf and Berg 1982, Berg 1986c). Mycorrhizal development on roots of trees is also changed substantially (Dighton and Skeffington 1987, Göbl 1986) potentially affecting P uptake by trees.

The effects of 'acid rain' on the P nutrition of trees is less clear. Damage to various physiological processes in trees have been reported, but coverage of these is beyond the scope of this review. Nevertheless, any change in the growth patterns or vigour of trees will affect the total demand for phosphorus by trees. There are a number of reports which indicate that the amounts of P in tree needles increases under the influence of 'acid rain' (Tveite 1980, Katainen and Heikkilä 1984, Blank and Roberts 1985, Skeffington and Roberts 1985), but it is not clear whether these increases are due to increased uptake by the trees or a redistribution of P reserves within trees. Significant reductions in seedling growth, both shoots and roots, can be brought about by fumigation with SO_2 (Blank and Roberts 1985). There can be increases in growth of non-fertilised trees but quite marked reductions in growth after NPK fertilisation, if the simulation is carried out by applying sulphuric acid (Tamm and Wiklander 1980). Increases in P concentrations of needles under the influence of acidic pollutants may be explained since P contained in acid affected trees has less biomass 'in which to be diluted'. The reduction of P-deficiency by acidic pollutants through lowered tree growth and reduced P demand has been confirmed using a P-deficiency bioassay on SO_2 fumigated trees (Dighton 1985). Atmospheric pollutant inputs of nitrogen have been found to induce P deficiency in trees (Mohren et al. 1986).

Tree P nutrition

Foliar analysis is generally used for diagnosing the nutritional status of trees (e.g. Bonneau 1972, Everard 1973, McIntosh 1984, Clement and Gessel 1985, Ferm and Markkola 1985, Guzman et al. 1985, Mohren et al. 1986, Hüttl 1986). Foliar concentrations of P show seasonal and between-year variations, and interactions with other elements which may be deficient (Bengtson and Holstener-Jørgensen 1971, Miller, Cooper and Miller 1976, Clement and Gessel 1985, Guzman et al. 1985, Ferm and Markkola 1986). These variations need to be taken into account in diagnosing changes in nutritional status. In some instances deficiencies and potential tree growth responses to applied fertiliser may not be detectable using foliar analysis (Dighton and Harrison

1983, McIntosh 1984). A laboratory bioassay based on the rate of metabolic uptake of ^{32}P by feeder roots from a standardised solution, has been found more sensitive than foliar analysis at detecting P deficiency in pine and spruce. The rate of uptake is negatively related to P status, with roots from trees of poorer status showing a 'hunger response' (Harrison and Helliwell 1979, Dighton and Harrison 1983, Harrison et al. 1986).

The close link of P cycling with the dynamics of organic matter means that changes in soil organic matter may indicate changes in the P status and thus the potential productivity of trees, particularly on poor soils.

Increased productivity of spruce when grown in mixture with pine or alder, compared with its growth in mono-culture, has been demonstrated to be linked to improved P nutrition using the root bioassay discussed above (Brown and Harrison 1983). The improved P nutrition appears to be associated with increased potential for organic matter decomposition in soils under tree mixtures compared with those under the mono-cultures (Chapman 1986, Brown 1988, Brown and Howson 1988, Chapman, Whittaker and Heal in press).

P deficiency induced during the development of spruce stands has been shown to be linked to the accumulation of litter on the surface soil (Figure 7). The deficiency was detectable with the root bioassay discussed above but not by needle analysis, and was confirmed by significant stem diameter growth in response to P fertiliser (100 $kg \cdot ha^{-1}$) application (Harrison et al. 1986, Dighton 1987, Harrison et al. 1989).

Driving variables of the P cycle

Clearly, the main variable driving both tree growth and the organic matter decomposition processes is the climate through the influences of temperature and moisture. An analysis of temperature and precipitation variations across Europe has been carried out (Jones and Bunce 1985) and eleven classes of area with distinct climatic attributes were identified (Figure 8). Attempts to relate both tree productivity and P cycling to these classes of climate is not yet possible. However, it is possible to identify some generalised trends in both.

Tree Productivity. Many attempts have been made to model forest productivity over large geographical areas (e.g. Paterson 1956, Esser et al. 1982). Scots pine is the most widely distributed conifer and it has a natural range covering much of Europe. As such it can provide a simplified basis for comparisons of productivity, and Ineson et al. (1985) using yield class data of Christie and Lines (1979) have attempted a first approach at this (Figure 9). Working with data from Cannell (1982) for various pure Scots pine sites for Europe, Ineson et al (1984) showed that above-ground biomass was linearly related to the log of stand age and a combination of log(age) plus distance from the Atlantic ocean. The latter was correlated with the hours of bright sunshine and the maximum temperature for several months of the year. They suggested that the "oceanity" of sites influences biomass accumulation of Scots pine and that "oceanity" is a complex variable related to the interactions of temperature and moisture. White (1982) supported this conclusion by showing that variations in growth of Scots pine in the UK were primarily associated with solar radiation and soil texture and moisture. However, the interaction between productivity and climate varies markedly between forest tree species, and Ineson et al. (1984) illustrated this variation by presenting regional productivity maps for Sitka spruce and Scots pine across the UK derived from data of Nicholls (1981). For Sitka spruce

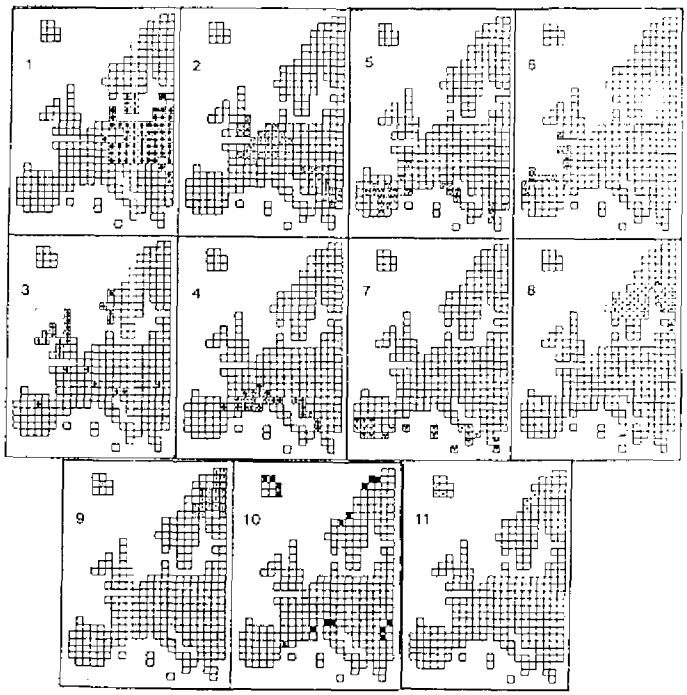

Figure 8. Distribution of the eleven climatic classes across Europe (taken from Jones and Bunce 1985).

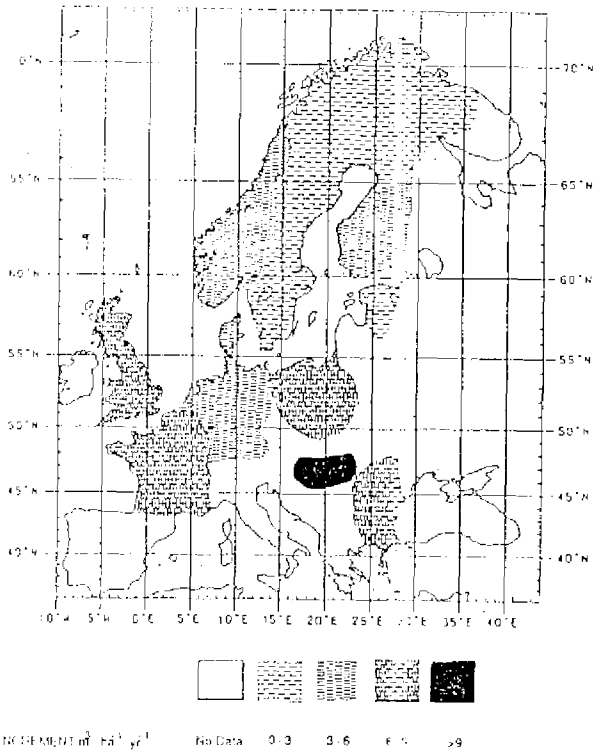

Figure 9. Regional productivity (m^3 ha^{-1} yr^{-1}) of Pinus sylvestris in Europe as indicated by yield tables. Data was extracted from Christie and Lines (1979) and shows the mid-value of the range of mean annual increment for individual countries.(from Ineson et al. 1984).

Figure 10. Calculated litter pools of Europe (redrawn from Esser et al. 1982). The estimates were derived by dividing predicted litter production by depletion rate. The map shows combined results for both woody and herbaceous litter.

longer growing season and high site moisture are more critical than accumulated site temperature (Christie and Lines 1979).

In broad terms, the demand for P by forest stands will be directly related to their productivity, which in turn is related to climatic factors but modified by local conditions such as soil type. Hence, rates of P uptake by trees and the return of P in litters to soil will also be related to productivity and indirectly to these same environmental factors.

Decomposition of organic matter. With regard to climate, temperature and moisture are critical factors influencing the rate of decomposition of litter. The rate of decomposition of Scots pine litter has been correlated with an integrated measure of temperature and moisture, the actual evapo-transpiration rate (AET) (Berg, Jansson and Meentemeyer 1984, Meentemeyer and Berg 1986). The same conclusion was reached by measuring the tensile strength loss (a function of decomposition) of cotton strips buried for varying periods in surface soils over a number of sites extending far beyond Europe (Ineson et al. 1988). Clearly, therefore, the rate of release of P from litters and its recycling will be linked to AET.

Climate and forest P nutrition. The cycling of P is linked to the production and decomposition of organic matter. Esser et al (1982) have attempted to model the balance between organic matter production and decomposition using their litter pool model and the results for Europe are presented in Figure 10. Unfortunately, no analysis has been carried out to see how far this model output matches the distribution of the climatic classes as demonstrated by Jones and Bunce (1985).

Under climatic conditions where the rate of release of P from organic matter is low, e.g. cold and acidic soil conditions, P deficiency in forests may occur. In a wide range of British soils, it has been found that the proportion of the total P reserves in organic form in the surface rooting depth of soils is positively correlated to altitude and rainfall and negatively correlated to temperature (Harrison 1985). Plant productivity was also found to be negatively correlated to the proportion of P in the organic form.

The rate of P recycling from organic matter is, in itself, no direct predictor of P deficiency in a forest, which depends on the balance of recycling and actual P demand of the tree crop. Thus in a situation where the climatic conditions are favourable for active tree growth, yet do not favour decomposition to allow release of P, P deficiency is likely to occur. An example of this situation may be the afforestation of the high rainfall areas of north and north-west Britain where Sitka spruce, a potentially highly productive tree species introduced from the northwest coast of North America, is extensively planted on acidic often highly organic soils with slow organic matter decomposition rates. To enable this species to become established, fertilisation with phosphate fertiliser is essential, and fertiliser is routinely applied at planting. Complete failure of the plantings, because of P deficiency, often occurs if fertilisation is not carried out.

The response to nitrogen fertiliser by trees is related to latitude and altitude implying a climatic interaction (Moller 1982). Is this interaction related to a direct effect of climate on the trees or through an indirect effect through soil organic matter turnover? Is there a similar interaction between tree response to applications of P fertiliser and climate? There are also interactions between the types of mycorrhizae on roots and the environmental factors associated with altitude and latitude (Read 1986). How

does the type of mycorrhizal association with tree roots affect tree growth response and how do these associations interact with P cycling, tree P nutrition and climatic factors? There are clearly many such questions which need to be answered, if we are to understand the complex interactions between climate, soils and tree growth and therefore learn how to optimise management for sustained forest productivity across Europe.

Conclusions

Much research is being carried out on the fine details of the complex and dynamic processes of P cycling but few studies are taking a broader approach. These latter studies are also important if we are to understand forest growth and the interacting effects of management and pollutants within Europe. Two major conclusions can be drawn from the above review of P cycling in European Forest Ecosystems:

a) A trans-European survey needs to be carried out to show where P deficiency in trees has been found to occur through the responses to trees to added P fertiliser.
The association of deficiency with factors such as climate class, tree species, tree yield class, tree age, soil organic matter input/decomposition balance, atmospheric pollution, soil type, site altitude and other nutritional deficiencies should be examined. Much could be done in outlining the likely associations from the analysis of existing data, topped up with additional specially instigated studies.

b) As the P cycling processes in forest systems are dynamic, growth and P cycling models need to be developed. Models probably need to be developed at three levels, i) the soil input-loss-turnover level ii) whole forest ecosystem level and iii) the regional climatic level. At each level however, P should not be examined in isolation; interactions between P cycling and the cycling of other nutrients, particularly nitrogen, need to be taken into account.

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PHOSPHORUS CYCLING IN SOILS OF FOREST ECOSYSTEMS IN NORTHERN POLAND

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1. Introduction

For the study of phosphorus (P) cycling forest ecosystems are more favourable objects than agricultural ones because of their limited anthropogenic disturbance. In this paper we intend to present our data on selected P transformation processes, especially of the biological cycle, for some forest ecosystems in Northern Poland. Most forests in the region are coniferous (mainly pine monoculture) growing on sandy podzolic soils. Some of these soils show distinct evidence of degradation caused by raking away of litter, pasturing of cattle and cultivation in the past. On the other hand, on similar soils there occur scattered fragments of forests showing much richer species composition, which probably occupied much wider areas in the past.

Experimental areas were located on several different sites, which facilitated comparisons between different ecological conditions. The studies evaluated: 1. P return to forest soils with litterfall, 2. release of P during litterfall decomposition, 3. changes of P content in different forest humus types, and 4. geochemical transformation of P in podzols.

2. Study areas

Studies on P return to soil with litterfall and P release during litter decomposition were conducted in different forest associations: in the reserve "Las Piwnicki" near Torun under Tilio-Carpinetum typicum (T-C) (hornbeam-oak-pine forest), and in Tuchola Forest under Leucobrio-Pinetum (L-P) (moss-pine forest) and Cladonio-Pinetum (C-P) (lichen-pine forest). All these forest associations grow on poor sandy soils. Soils under C-P are strongly degraded. To improve the functioning of the ecosystem, mineral fertilization is proposed. A nitrogen fertilized (C-P/N) and unfertilized (C-P/O) area were included in our studies.

Studies of P content in forest humus of different types included 7 sites, out of which No. 2 corresponds to C-P/O in Tuchola Forest, and Nos. 4 and 5 are situated in the reserve "Las Piwnicki". Other sites were included to collect all different types of forest humus. Site No. 1 is on a podzol developed on loose sand, Nos. 2 - 5 on other sandy soils, No. 6 - 7 on soils of other texture. Studies on P differentiation in podzols were conducted on dune sands all over Poland (Pokojska 1979a).

3. Materials and methods

Litter fall was collected in traps 1m above the soil surface. The material was divided into leaves, twigs, bark, fruits and a "residue" consisting of bud scales, anthers, excrement, and non-identified plant remains

(Prusinkiewicz and Bigos 1978, Dziadowiec and Plichta 1985). The dominant litter fractions were taken for further studies on decomposition in litter bags. In the T-C site the leaves of three main species were taken into account: hornbeam (Carpinus betalus), oak (Quercus robur) and Scots pine (Pinus silvestris). In the pine forests (L-P and C-P) Scots pine needles were analyzed.

Samples of forest humus were taken from each subhorizon of forest floor and from the humus horizon according to Prusinkiewicz's (1988) taxonomy.

For chemical analyses all litterfall fractions and materials from litterbags were mineralized in conc. H_2SO_4 with H_2O_2, whereas samples of forest floor were mineralized in a HNO_3, H_2SO_4 and $HClO_4$ (20:5:1) mixture. Estimation of P in humus horizons was made after ignition at 550°C and extraction with 0.1 M H_2SO_4. In podzols total P (TP) was determined after fusion of samples with Na_2CO_3, and dithionite-extractable P (Pd) by Mehra-Jackson's method. In all samples P was determined by the molybdenum blue method.

Table 1. Phosphorus content, C/P and N/P ratios in different components of litterfall of Tilio-Carpinetum, Leucobrio-Pinetum and Cladonio-Pinetum forests (data for autumn maximum of litterfall)

Plant association	Component of litterfall	P $mg \cdot g^{-1}$ (d·wt)	C/P	N/P
Tilio-Carpinetum typicum	Hornbeam			
	- leaves	1.07	409	11.0
	- wood fall*	0.61	755	19.0
	- key fruits	1.23	353	10.2
	Oak			
	- leaves	1.64	280	6.7
	- wood fall*	0.65	702	13.5
	- acorns	1.18	355	8.1
	Scots pine			
	- needles	0.51	968	12.4
	- wood fall**	0.42	1182	14.8
	Residue	1.50	285	12.5
Leucobrio-Pinetum	Scots pine			
	- needles	0.53	1044	11.6
	- wood fall**	0.22	2366	15.9
	Residue	0.77	673	13.6
Cladonio-Pinetum	Scots pine			
	- needles	0.37	1482	11.9
	- wood fall**	0.17	3051	18.1
	Residue	0.93	565	15.3

* bark, twigs
** bark, twigs and cones

4. Results and discussion

4.1 Phosphorus in litterfall. The forest associations selected for study differ from each other in all the characteristics of litterfall: its chemical composition, seasonal dynamics and total weight. These differences affect the biological cycling of P in the forest ecosystem.

4.1.1. Phosphorus content in litterfall depending on plant species and site. In the multispecies association Tilio-Carpinetum the litterfall of hornbeam and oak contains more P than that of pine and has narrower ratios of C and N to P (Table 1). The greatest variation occurs in leaves, due to the differences in progressive P withdrawal during aging of leaves. Fresh pine needles and fresh leaves of hornbeam contain comparable amounts of P. Before dropping needles pine withdraws 60 to 70% (Table 2) or even 80% (Stachurski and Zimka 1981) of the nutrients. The withdrawing of nutrients from aging leaves of hornbeam is less intensive and reaches about 25%. Fresh leaves of oak show a higher P content than those of hornbeam or pine needles, and only 6.4% of P are withdrawn (Zimka and Stachurski 1976).

Table 2. Nutrient content in fresh and dead pine needles ($mg \cdot g^{-1}$) and percentage withdrawal

	N	P	K	Ca	Mg
			Tilio-Carpinetum		
Fresh needles	12.5	1.30	7.7	3.9	0.94
Dead needles	6.3	0.51	1.9	5.1	0.92
% of withdrawal	49.6	60.8	75.5	-30.8*	2.1
			Cladonio-Pinetum		
Fresh needles	12.1	1.25	5.9	3.2	6.9
Dead needles	6.1	0.37	1.4	5.8	0.68
% of withdrawal	49.4	70.4	76.3	-81.2*	1.5

* net gain

The influence of the site on P content in the litterfall can be exemplified for pine (Table 1). The highest P content is found in the litterfall of pine growing in T-C, and the lowest in that of pine growing in C-P. Phosphorus content in needles falling in C-P is on average 0.11 $mg \cdot g^{-1}$ (P=0.99) lower than in the needles from L-P. Both sites have very similar poor, sandy soils, but the soil under C-P is strongly degraded.

4.1.2. Annual phosphorus return to forest soils with litterfall. In deciduous forest 5.4 kg of P per ha is returned annually with the litterfall. In pine forests P return is only 1/2 or even 1/4 of this value (Table 3) due to both the lower P content (Table 1) and the lower total weight of the litterfall (Table 3). In all associations the most important fraction accounting for more than half of the P return are the leaves or needles. The "residue" fraction is responsible for about 30% and wood fall for about 10% of P supplied annually to the soil (Figure 1).

4.1.3 The effect of nitrogen fertilization on phosphorus in the litterfall of Cladonio-Pinetum. Despite the small amount of P in biological

cycling (1.27 $kg \cdot ha^{-1} \cdot y^{-1}$) the main factor limiting production in the Cladonio-Pinetum site is nitrogen (Prusinkiewicz 1982). Nitrogen fertilization of this forest resulted in a change of the edaphic conditions of the site associated with an increased production of litterfall mainly from increased needle weight. The average weight of a pair of needles in the litterfall of the unfertilized area was 0.165 g, in fertilized area it was 0.242 g.

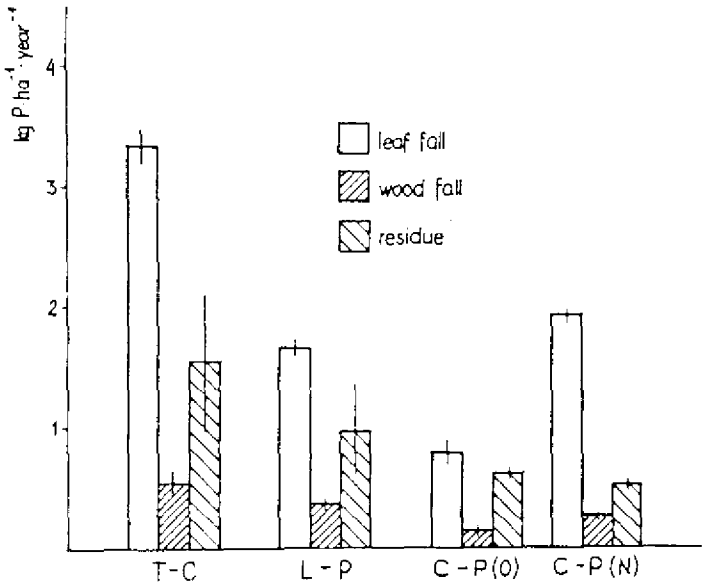

Figure 1. Phosphorus return to forest soils with different fractions of litterfall.

Table 3. Annual P return to forest soils with litterfall ($kg \cdot ha^{-1} \cdot y^{-1}$)

Plant association	Litterfall	Phosphorus
Tilio-Carpinetum	5489 ± 439*	5.44 ± 0.53
Leucobrio-Pinetum	3822 ± 492	3.00 ± 0.47
Cladonio-Pinetum (O)	2534 ± 100	1.27 ± 0.02
Cladonio-Pinetum (N)	3501 ± 57	2.60 ± 0.01

* Data from Prusinkiewicz and Bigos (1978)

The applied fertilization caused an increase in P content in the fallen needles by an average of 0.059 $mg \cdot g^{-1}$ (P = 0.9), even though this component was not supplied with the fertilizer. As a result of these changes both the weight of the litterfall and the amount of P return to the soil of the fertilized area (C-P/N) came close to the values of the L-P association growing on undegraded soil (Table 3, Figure 1).

4.2. Phosphorus release from decaying plant material. The second important link in the biological cycling of each element is the decomposition of plant material and the release of nutrients involved in this

process. Phosphorus release is of particular importance for forest ecosystems, since the small amounts of this element in the biological cycling limit equilibrium productivity of the ecosystem (Gosz et al. 1973). Dalal (1977) suggests that P may also play a significant role in the biological cycling of other nutrients.

Table 4. Chemical composition of the initial materials used in the study ($mg \cdot g^{-1}$ dry wt.)

Material	C	N	P	K	Ca	Mg	C/P
Hornbeam leaves	434.0	12.17	1.24	4.27	6.88	1.40	350
Oak leaves	468.2	10.48	1.62	4.28	9.65	2.42	289
Scots pine needles							
in T-C	503.2	12.50	1.30	7.72	3.90	0.94	387
L-P	538.0	10.47	1.44	3.96	4.38	0.78	374
C-P	553.7	12.05	1.25	5.87	3.18	0.69	443

4.2.1. Comparison of phosphorus release rates from different plant materials in one site. No essential differences in total P release from decaying hornbeam and oak leaves and pine needles were found during 3 year's experiments in the Tilio-Carpinetum association (Tables 5 & 6), where these three species occur together, despite the differences in morphology and chemical composition of the initial materials (Table 4). There are, however, significant differences in intensity of P release from the materials under study in particular years. The greatest intensity of P release from oak leaves was noted in the first year of decay, while from hornbeam leaves and pine needles it occurred in the second year (Tables 5 & 6).

Table 5. Weight loss and phosphorus release from decomposing hornbeam and oak leaves in T-C (% of initial weight)

Period of decay (years)	Hornbeam leaves		Oak leaves	
	weight	P	weight	P
0.0-0.5	31.33	18.04	25.07	35.71
0.5-1.0	14.84	11.63	10.72	9.20
1.0-1.5	7.60	21.49	6.21	16.83
1.5-2.0	6.23	12.39	10.81	11.86
2.0-2.5	3.89	11.12	0.55	3.19
2.5-3.0	-0.17*	-10.66*	1.55	-7.26*

* gain due to organic matter and P input from surroundings

4.2.2. Phosphorus release from decaying pine needles in different sites. During 5 year's investigations in T-C, 70% of the P in the pine needles was released; in L-P and C-P the respective values were 74% and 53% (Tables 5 & 6). No difference was found in the intensity of P release from decaying pine needles in T-C and L-P. There is, however, a distinct difference in the release rate between L-P and C-P/O.

4.2.3. The effect of nitrogen fertilization on the phosphorus release from decaying pine needles. Fertilizing degraded soil with nitrogen enhances

its biological activity which is reflected in increased intensity of decay and P release processes. During the 5 year investigations in C-P/N 72% of the P contained in the pine needle samples at the start of the experiment was released, i.e. by 19% more than in the unfertilized area (Table 6). This process is comparable to that in L-P and is distinctly different from the dynamics of P release in the unfertilized area.

Table 6. Weight loss and phosphorus release from decomposing Scots pine needles (% of initial weight)

Period of decay (years)	T-C		L-P		C-P(O)		C-P(N)	
	weight	P	weight	P	weight	P	weight	P
0-1	41.73	22.90	45.39	39.32	40.75	26.53	45.55	27.69
1-2	14.10	36.25	8.93	17.54	5.80	14.46	7.12	24.37
2-3	-0.71*	4.18	2.42	4.90	1.95	6.69	1.35	8.48
3-4	3.14	2.22	6.66	8.04	3.72	0.52	1.28	1.12
4-5	3.50	4.61	6.23	5.07	0.59	4.35	7.58	10.08

* gain due to organic matter inputs from surroundings

In the fifth year of the observations a rather unexpected increase in intensity of P release was observed in area C-P/N. This was probably the result of additional fertilization of the area with magnesium, which has been found to be the third factor after nitrogen and potassium, limiting the functioning of this forest ecosystem (Prusinkiewicz, 1982).

4.2.4 Mechanism of phosphorus release from decaying plant material. Two phases can usually be distinguished. Initially, loss of P proceeds more slowly than that of weight of organic matter, and later P content decreases more rapidly than weight (Table 5). An exception among the materials studied are oak leaves, in which P loss proceeds more rapidly than weight loss from the very beginning of decay. The initial phase generally lasts one year. In this phase the important factor of P release is leaching of both organic and inorganic P. Staaf (1980) has found that in the first months of decay of beech leaves, P losses are nearly equal to the amount of water soluble P in the leaves. Our studies have shown that during one-hour shaking of powdered pine needles with water 0.28 mg P g^{-1} (d.wt) passed into solution, which constituted more than 40% of total P content (Dziadowiec and Plichta 1985).

Despite the high C/P ratio, 289:1 to 443:1 in the initial materials (Table 4), P release was occurring in all cases from the beginning of decay. In the first phase the C/P ratio narrowed slightly, and in the second phase this ratio widened again to as much as 520:1 or more. If we accept the concept of critical values as the mechanism of P release from decaying materials (Gosz et al. 1973, Staaf 1980, Wessén and Berg 1983), then the critical value of C/P should be more than 500:1.

4.3. Phosphorus in forest humus of different types. Studies on P release in litterbags concerned only a relatively short period of time, in which the decomposition of plant remains was the most rapid. Further transformations can in many cases be examined in successive horizons of forest humus.

In all but one of the investigated humus subtypes the C/P ratio decreases as the degree of humification increases (Table 7). Ratios of C/N behave likewise, but the range of C/N values is not as large as that of C/P.

Table 7. The characteristics of forest humus of different types

Site No	Type of humus*	Subtype of humus*	Horizon	pH_{H_2O}	Hz** %	Corg. $mg \cdot g^{-1}$	C/N	C/P	Supply of O.M. $kg \cdot m^{-2}$	Supply of P $g \cdot m^{-2}$
1.	Mor	Drosomor	AoL	4.4	16.5	510	40	622	0.29	0.25
			AoF	4.1	23.9	486	36	640	2.08	1.67
			AoH	3.5	40.2	439	35	879	7.27	4.20
			Bh	4.1	n.d.***	12	32	22	0.54	14.28
2.	Mor	Kseromor	AoL	4.1	17.0	515	53	832	0.39	0.25
			AoF	4.0	21.0	494	39	727	1.67	1.22
			AoFH	3.7	32.1	414	38	691	4.23	3.30
			Ah	4.0	58.3	14	29	168	2.72	9.40
3.	Modermor	Droso-modermor	AoLf	5.5	15.8	461	35	457	0.99	1.11
			AofH	4.3	19.2	403	29	420	2.52	3.17
			Ah	4.0	35.8	19	25	143	3.11	12.59
4.	Moder	Drosomoder	AoL	4.4	14.2	469	28	447	0.66	0.74
			Aof	4.4	17.0	399	24	444	2.10	2.52
			Ah	3.8	41.1	27	20	120	3.36	16.20
5.	Detrito-mull	Hygro-detritomull	AoLf	4.4	13.5	442	35	574	0.35	0.31
			Ah	4.2	45.8	29	17	184	10.61	33.39
6.	Mull	Drosomull	AoL	4.9	n.d.	432	31	386	0.43	0.56
			Ah	4.8	n.d.	21	16	123	2.86	87.36
7.	Mull	Drosomull	AoL	5.9	n.d.	418	31	351	0.13	0.18
			Ah	6.8	n.d.	20	11	42	6.26	85.85

* Forest humus taxonomy according Prusinkiewicz (1988), ** degree of humification according Springer, Schlichting and Blume (1966), *** not determined.

According to Zezschwitz (1980), the wider variations of C/P ratios make them better suited than C/N ratios for the characterization of types of forest humus, and indirectly for the evaluation of the trophic conditions of forest ecosystems. The C/P ratios in our humus samples which correspond to those studied by Zezschwitz (i.e. mor and modermor in AoH horizon, and mull and mull-like in Ah) are within the ranges given by Zezschwitz (1980). Our data confirm the ranges given by Zezschwitz and confirm the value of C/P ratios for evaluating trophic conditions of forest soils. The variability of C/P ratios in different types and subtypes of humus underlines the flexibility of the soil P cycle and its processes which has been shown by many authors (Dalal 1977, McGill and Cole 1981).

An analysis of total P supplies in surface horizons of sandy soils confirms that different forest associations are supplied from similar P pools. The main factor differentiating these ecosystems are the different rates of biological cycling which are reflected in the development of differnt types of forest humus (from mor to detritomull) (Prusinkiewicz et al. 1974).

4.4 Phosphorus in podzol profiles. In the preceding sections some results concerning the biological cycling of P have been presented. In this section more attention is given to geochemical transformations of this element in podzols. All of the 7 podzols examined (Pokojska 1979a, 1979b) show differential levels of both total P and dithionite-extractable P in eluvial and illuvial horizons. The vertical distribution of these P fractions together with free sesquioxides and organic carbon has been drawn for profile No. 1 (Figure 2). The picture is typical of all podzols under study. The data point out that P is among the elements taking part in podzolization and may even serve as an indicator of this soil-forming process.

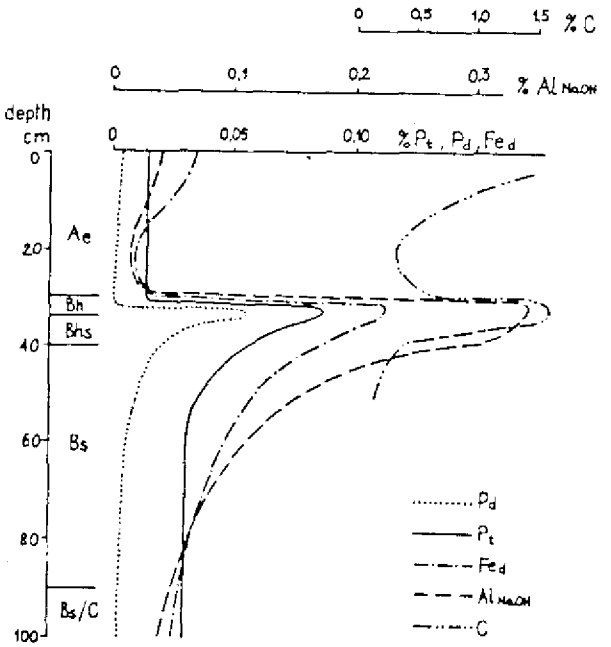

Figure 2. The distribution of phosphorus (P_t, P_d), free sesquioxides (Fe_d, Al_{NaOH}) and organic carbon in podzol profile No. 1.

The question arises whether P is leached from the surface horizons in the form of free phosphate ions or in combinations with other constituents of the soil solution. Studies carried out by Misterski and Loginow (1959), Levesque

(1969) and Sinha (1971) have shown the possibility of formation of soluble organo-metal-phosphate complexes, in which the phosphate ions are linked to fulvic and humic acids by Fe and Al ions. The migration of P in this form seems possible since all the components necessary to form the above-mentioned complexes are present in the upper part of podzol profiles. Migration of organic phosphates should also be taken into account. Large concentrations of inositol hexaphosphate may bring Fe, Al and organic matter into solution and may contribute to their movement down the profile (Anderson et al. 1974).

All these complexes of organic or inorganic P are fixed in the B horizon, where they are sorbed and occluded by excess Fe and Al. Great differences are observed in the proportions of the main P fractions in different podzol horizons (MacLean et al. 1971). For instance, P combined with free sesquioxides (Pd) ranges from 13% (C horizon) to 75% (Bh horizon) of total P (Table 8). In the parent material, where the amount of organic P is insignificant, the low values of Pd/TP can be interpreted as a predominance of Ca-phosphates. In the eluvial horizon, on the other hand, a low ratio of Pd/TP suggests the presence of greater amounts of organic P, since little of the highly weatherable Ca-P (Pokojska 1979a) is to be expected in this horizon. In the illuvial horizon both Fe and Al associated and organic P may be accumulated.

Table 8. The dithionite-extractable P as a fraction of total P in 6 podzol profiles

Horizon	Pd/Pt	
	Range	mean ± SD
Ae	0.09 - 0.47	0.19 ± 0.14
Bh	0.52 - 0.95	0.75 ± 0.17
Bhs	0.08 - 0.64	0.37 ± 0.22
Bs	0.10 - 0.40	0.24 ± 0.11
C	0.07 - 0.27	0.13 ± 0.07

The profile distribution of P fractions in podzols resembles the changes in proportion of these fractions in the different stages of soil weathering and development (Walker and Syers 1976, Tiessen et al. 1984). The parent material corresponds to the initial stage, and the illuvial horizon to the final stage of P transformation in soil.

The low plant availability of P fixed in the illuvial horizons is further reduced by high toxicity of Al accumulated there. Investigations carried out by Prusinkiewicz and Krzemien (1974) indicate that pine roots reaching the illuvial horizon become damaged and lose their capacity for water and nutrient uptake.

5. Summary

Sandy forest soils of Northern Poland are poor in total P because of low apatite content. Much of the P in these low pH soils has entered into the biological cycle. Our study of the successive stages of the cycle, i.e. P return to the soil with litterfall and P release from decaying litter and forest floor, point out that the cycling rates can be different which may

result in the formation of different forest associations on otherwise similar soils. If the biological cycling in the ecosystem is slowed down as a result of soil degradation and shortage of some nutrients, adequate fertilization can ameliorate the soil and accelerate the cycling rate. During soil development part of soil P is removed from biological cycling to nonavailable forms which in podzols and podzolic soils are accumulated mainly in the illuvial horizon.

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PHOSPHORUS CYCLE IN GRASSLANDS

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Introduction

Phosphorus (P) and nitrogen are fundamental limiting nutrients in all terrestrial ecosystems. The availability of labile inorganic forms of P is likely to be crucial for subsequent inputs and fluxes of N and C in the ecosystem (Cole, Heil 1981). That's why the attention of scientists is drawn to the transformations of organic P compounds in soils (Stewart, McKercher 1982; Stevenson 1986).

The initial accretion of P in the soil system from plant remains is not so well documented. The objective of this paper is to consider the dynamics of the P content in grassland phytomass components, distribution of P among these components and the P cycle between soil and plants.

Definitions and symbols for phytomass components

We use the following definitions and symbols: G-green phytomass, G_{max}-maximal standing crop of G, D-standing dead, L-litter, D+L-aboveground deadmass, G+D+L-aboveground phytomass; R-living roots or below-ground living phytomass, V-dead roots or below-ground deadmass, R+V-below-ground phytomass; G+R-living phytomass, D+L-V-deadmass, G+D+L+R+V-phytomass; Pl-plants, Sl-soil. NPP-net primary production, ANP-aboveground net primary production, BNP-below-ground net primary production. P_G-P stored in G, P_R-P stored in R and so on. P_{NPP}-uptake of P by the plants.

Methods

Sixty 0.25 m^2 sample plots were chosen at random within the grassland under study. In May, June, July, August, September, October and May of the following year ten plots were clipped and litter, L, was collected. The above-ground plant material was sorted into green phytomass, G and total standing dead biomass, D. Litter was washed on a sieve to remove soil particles.

Soil monoliths with a surface area of 100 cm^2 and length of 10 cm were collected on each sample plot with a special steel cylinder to a depth of 40 cm. From each monolith one tenth was cut off to analyse the composition of the below-ground plant material. The monoliths were washed and below-ground plant material was collected on a 0.5 mm sieve.

The below-ground plant material was sorted into living roots, R, and dead ones, V. In order to distinguish living roots from dead ones the following criteria were used. Living roots are far more resilient than dead ones and are not so easily broken if bent. Actively growing roots are light-coloured, succulent and covered by root hair. The share of living and dead material was estimated for each monolith.

All components of the above and below-ground plant materials were dried at 80°C for 24 hours and weighed. The P content was estimated in all components.

Leaching of P from above-ground phytomass by rainfall was estimated in a special field experiment (Titlyanova 1979).

The P fluxes were calculated using the system of balance equations, data on all component dynamics and concentration of P in each component (Titlyanova 1979).

Dynamics of the P contents in the phytomass components

The green phytomass of different grassland plants contains from 0.5 - 4 $mg \cdot g^{-1}$ of P (Titlyanova, Bazilevich 1979), the living roots from 0.5 - 2 $mg \cdot g^{-1}$ (Table 1). The P concentration in herbs is higher than that in grasses. The P content of the mesophytic meadow G was maximal at the beginning of the season and was decreasing during the season.

Table 1. Phosphorus content in the phytomass of mesophytic meadow, %

Component		May	June	July	August	September	October
Calamagrostis epigeios,	G	-	0.15	0.10	0.10	-	-
	R	-	-	0.12	-	-	-
Poa angustifolia,	G	-	0.08	0.07	0.10	-	
Eletrigia repens,	G	-	0.14	0.05	0.04	-	-
	R		-	0.12	-	-	-
Vicia cracca,	G	-	0.14	0.10	0.13	-	-
	G	-	-	0.10	-	-	-
Lathyrus pratenses,	G	-	0.32	0.18	0-.10	-	-
	R	-	-	0.10	-	-	-
Artemisia laciniata,	G	-	0.28	0.17	0.20	-	-
	R	-	-	0.14	-	-	-
Galatella biflora	G	-	0.29	0.20	0.14	-	-
	R	-	-	-	-	-	-
Green phytomass	G	0.27	0.19	0.19	0.17	0.17	-
Standing dead	D	0.05	0.08	0.05	0.07	0.07	0.06
Litter	L	0.10	0.13	0.10	0.12	0.12	0.12
Live+dead underground.phytom.	R+V	0.08	0.08	0.08	0.07	0.09	,0.08

In standing dead plant parts (D) the P concentration did not exceed 0.8 $mg \cdot g^{-1}$. In the litter the P content was estimated to be higher than that in the standing dead, with a range in L from 1.0 - 1.3 $mg \cdot g^{-1}$ and a maximum in June.

In below-ground phytomass (R+V) the P content varied from 0.7 -0.9 $mg \cdot g^{-1}$. The P concentration was the lowest in August at the moment of the maximal standing crop of R. In September when the living root phytomass decreased sharply the P content in the (R+V) increased by a factor of 1.3 (Titlyanova 1977, 1979). The P concentration was estimated by the balance method to be 0.6 $mg \cdot g^{-1}$ in R and 1.2 $mg \cdot g^{-1}$ in V. Hence an immobilization of P from soil solution into below-ground plant residues occurred.

The ratios of the average P contents in different phytomass components are as follows: $P_G/P_D=2.4$; $P_D/P_L=0.3$; $P_V/P_R=2.0$; $P_G/P_{R+V}=2.0$. Based on these ratios we may consider P an element which accumulates in green phytomass, is released from standing dead and concentrated in above- and below-ground deadmass again.

The P pools in grasslands

The total P pool of the phytomass including R+V in the 0 - 50 cm soil layer in steppes and meadows ranges from 1.5 - 4.7 $g \cdot m^{-2}$ (Table 2). The quantity of P in phytomass in Kazakhstan steppes and Siberian mesophytic meadow does not exceed 3 $g \cdot m^{-2}$ but is higher, up to 4 $g \cdot m^{-2}$, in the Siberian and Kursk natural meadow steppes. The P pool is very large in grassy swamps due to the enormous store of deadmass and high P concentration in it.

Grazing and haying affect the total pool of P in phytomass changing its distribution and structure. The P quantity is maximal in moderately grazed steppe where standing crop of V and its P content are high. The P pool in mown steppe is lower than that in a natural one due to the decrease of D and L when haying. The quantity of P in heavily grazed steppe is lowest because of the deminution of all phytomass components (Bazilevich, Semeniuk 1983, 1984). The P distribution between the phytomass components are influenced by the vegetation type and the kind of land use (Figure 1). From 65 up to 90% of P is accumulated in below-ground plant material due to the large stores of R+V in meadows and steppes. This value reaches 96% in grassy swamps.

The main reserve of P in phytomass is in living or dead roots. The R contains from 20% to 48% of P held in the total phytomass (G+D+L+R+V) while V accumulates from 22 - 46% of the total in different ecosystems. In the green phytomass even at G_{max} the share of the total P pool is no more than 20%. Moderate grazing and haying lead to the increase of the P share in V while intensive grazing results in the increase of the P share accumulated in the G and R.

Phosphorus stored in roots (R+V) diminishes with the depth. About 55% of the P held in the roots of the 0 - 50 cm layer are concentrated in the upper 10 cm. It should be noted that in every layer of soil the intermediate size fraction of R+V (2 - 0.5 mm) contains about 50% of all P accumulated in the roots (Figure 2).

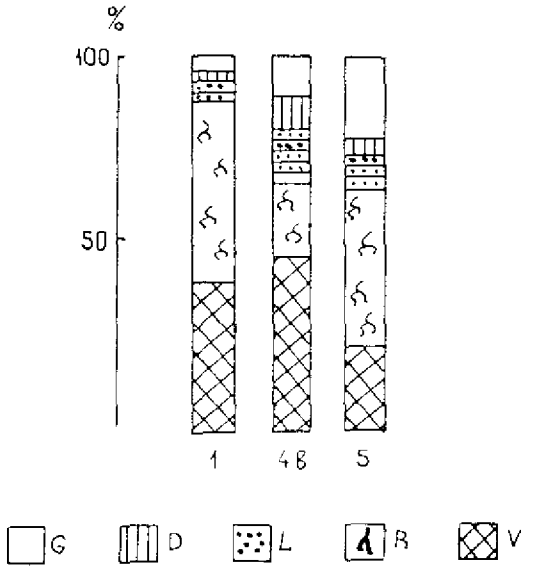

Figure 1 Phosphorus distribution between the phytomass components in grasslands. G - green phytomass, D - standing dead, L - litter, R - living roots, V - dead roots.
1 - dry steppe, 4B - meadow steppe, moderately grazed,
5 - mesophytic meadow.

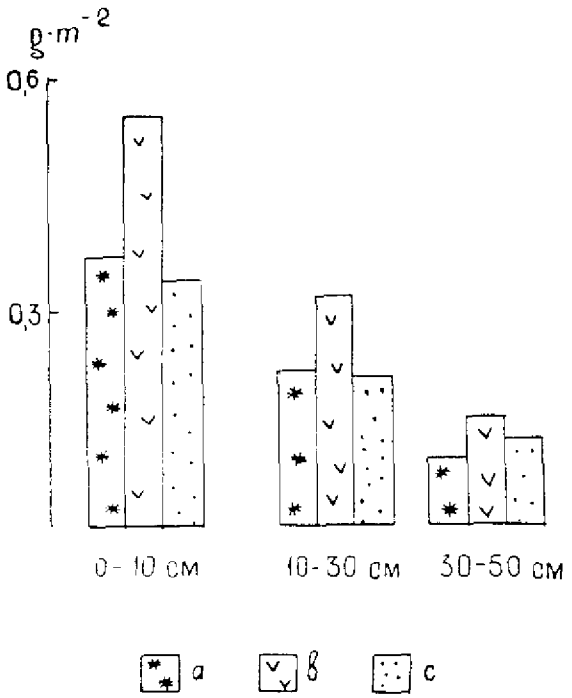

Figure 2 Mean storages of P in R+V in the soil layer - - 50 cm in true steppe.
Fractions of R+V: a - large / < 2 mm/, b - middle / 2 - 0.5 mm/, c - small / < 0.5 mm/

Table 2. Phosphorus stores in the components of grasslands, $g \cdot m^{-2}$

Index of grassland	Grassland-type, Locality	G_{max}	D	L	R	V	Sum of Components
					in the layer 0-50 cm		
	Kazakhstan						
1.	Dry steppe protected	0.08	0.05	0.20	1.37	1.17	2.87
2.	True steppe protected	0.19	0.09	0.34	1.38	0.97	2.97
	West Siberia						
3.	Meadow steppe protected	0.70	0.27	0.25	1.54	1.06	3.82
	Russian Plain						
4.*	Meadow steppe						
a.	protected	0.54	0.33	0.52	1.10	1.58	4.07
b.	moderately grazed	0.52	0.44	0.56	0.97	2.17	4.66
c.	heavily grazed	0.26	0.08	0.11	0.55	0.55	1.55
d.	mown	0.44	0.06	0.15	1.01	1.45	3.11
	West Siberia						
5.	Mesophytic meadow, protected	0.62	0.12	0.26	1.23	0.64	2.87

* Bazilevich, Semeniuk (1983,1984)

P budget in the system "soil-plant"

The annual uptake of P by meadow and steppe vegetation ranges from 2.0 - 3.5 $g \cdot m^{-2}$. In grassy swamps the uptake increases up to 17 $g \cdot m^{-2}$ (Table 3). From 30 - 45% of P taken by the roots is translocated into the above-ground phytomass in meadows and steppes while in grassy swamps the share of P translocated from R to G is only 3%.

In the second half of the season the intensity of P translocation from roots to shoots lessens and the direction of the flow may even be reversed. In autumn, part of the P accumulated in shoots can return to the roots. Simultaneous leaching occurs from G and D into the soil by rainfall (Table 3).

Table 3 Budget of P in grasslands

Index of grassland	Grassland-type	Uptake by roots from soil	Translocated		Output with harvest	Return to soil				
						total	leached	excreted	mineralized	
		Sl-->R	R-->G	G-->R	G_{out}	Pl-->Sl	G-->Sl	R-->Sl	L-->Sl	V-->Sl
3.	Meadow steppe, protected	3.33	0.78	0.21	0.00	4.40	0.12	0.18	0.35	3.75
4a	Meadow steppe, protected	2.92	1.24	0.00	0.00	3.05	0.10	0.00	1.25	1.80
4b.	moderately grazed	3.20	1.25	N.d.	0.12	3.08	N.d.	N.d.	N.d.	N.d.
4c.	heavily grazed	2.20	0.86	N.d.	0.43	1.77	N.d.	N.d.	N.d.	N.d.
4d.	mown	2.82	0.90	N.d.	0.38	2.44	N.d.	N.d.	N.d.	N.d.
5.	Mesophytic meadow protected	2.11	0.62	0.00	0.00	2.01	0.18	0.18	0.34	1.31
6.	Grassy swamp, protected	17.13	0.53	N.d.	0.00	20.20	0.25	N.d.	0.95	19.00
7a.	Alluvial meadows dry, mown	2.00	N.d.	N.d.	0.90	1.10	N.d.	N.d.	N.d.	N.d.
7b.	wet, unmown	3.30	N.d.	N.d.	0.00	3.30	N.d.	N.d.	N.d.	N.d.

3, 5, 6 - Titlyanova, 1977; 4 - Bazilevich, Semeniuk, 1983, 1984; 7 - Ulehlova, 1975.

The P content in the green phytomass during the season decreases due to back translocation and leaching. Senile plant tissues contain only 1/2 to 1/3 of the P in young ones. Leaching from the standing dead decreases the P content in this component even more (Table 1).

The uptake of P for the production of below-ground organs is directly proportional to the amount of the root production, BNP and ranges from 1.5 - 2.5 $g \cdot m^2 \cdot y^{-1}$. Excretion of P from roots into soil occurs sometimes in the second half of the season and can reach about 0.2 $g \cdot m^2 \cdot y^{-1}$. The main portion of P (50 - 60 %) taken up by roots from the soil returns from plant material to the soil due to the mineralization of the above-ground, L, and below-ground, V, plant residues. The rates of the uptake and release of P change during the season. The dynamics of these processes was assumed to be similar to the dynamics of the production and decomposition of the organic matter. However, the patterns of these dynamics do often not coincide.

In the season under study the NPP was maximal during the periods from May till June and from July till August while the plant residue decomposition was the same during the summer and increased from August till September (Figure 3). The dynamics of the P transformation was different. The main uptake of P by the plants occurred in the period June-July-August, having decreased by August. The release of P from the residues went on during the whole season decreasing only from June till September.

Immobilization of P on plant residues

Turnover of P through mineralization and immobilization follows a similar pattern as for N, both processes occurring simultaneously. The P content of the decomposing residues plays a key role in regulating the quantity of soluble P in the soil at any time. It has been shown that net immobilization of P occurs when the C/P_{org} ratio is 300 or more. Net mineralization results when the ratio is 200 or less (Stevenson 1986).

Table 4 shows that the C/P_{org} ratio is very high in the ecosystems investigated. It ranges from 500 - 900 for D and from 250 - 600 for R. In dead components the ratio decreases and varies from 220 - 380 for L and from 320 - 450 for V. Hence the P content of deadmass in grasslands increases before decomposition but the ratio C/P_{org} in decomposing residues is still above 200. This means that mineralization of P can occur when its content in litter and dead roots is less than 2 $mg \cdot g^{-1}$.

Table 4. C/P ratios of grassland components

Components	True steppe	Mesophytic meadow
Green phytomass	250-370	130-740
Standing dead	600-900	510-720
Litter	220-350	320-380
Live roots	470-570	230-600
Dead roots	320-450	300-360

Across the different particle size fractions of L and R+V P contents increase with diminishing size. In the large fraction of the litter (>7 mm) in Kazakhstan steppes the P content is about 0.7 $mg \cdot g^{-1}$ while in a small one (<1 mm) it is about 1.3 $mg \cdot g^{-1}$. In the large fraction of roots, R+V, where living roots are dominating, the P concentration is about 0.7 $mg \cdot g^{-1}$. In the small one where the bulk consists of the small dead roots the P content is about 0.9 $mg \cdot g^{-1}$.

The P concentration of R+V changes during the year at times increasing at times decreasing in all fractions simultaneously. The investigation of R and V dynamics and the P contents in the different fractions was carried out in the Kazakhstan steppes from 1978 till 1981 (Figure 4).

The production of roots in 1980 occurred from June till July and was accompanied by decreasing P content in all the fractions. The decrease of P content in R+V was due to the increase of the living roots which contain less P than the dead roots. After July R decreased with progressive root death and the concomitant increase of V as well as an increase of the P concentration in all the fractions of R+V. The increase of P content in V reveals the active immobilization of P on underground deadmass. During the autumn-winter-spring period the mass in V decreased and P content in all the fractions of R+V decreased due to the mineralization of organic matter and P release. From July till September immobilization of P on underground deadmass was found to be about 0.5 $g \cdot m^{-2}$ in the 0 - 50 cm soil layer. During the same period in a wheat agroecosystem located near the steppe 0.26 $g \cdot m^{-2}$ P was immobilized (Titlyanova 1984). In meadow steppe of Kursk immobilization of P was estimated to be 0.11 $g \cdot m^{-2} \cdot y^{-1}$ on the litter and 0.12 $g \cdot m^{-2} \cdot y^{-1}$ on the underground deadmass (Semeniuk 1986).

Conclusion

The behaviour of P and N in the system "soil-plants" is similar. Both elements are transferred in plants against a concentration gradient, from R to G, both of them translocate from senile tissues of plants to young ones, they are leached from G and D into the soil by rainfall and immobilized on deadmass from soil solution.

The P store in plant material of steppes and meadows is about 3 - 4 $g.m^{-2}$ and P uptake by plants is about 2 -3 $g \cdot m^{-2} \cdot y^{-1}$. The turnover time of P expressed as the ratio of its store to the uptake varies in grasslands from 0.4 - 1 y for G, 0.5 - 0.8 y for R and 0.4 - 1.7 y for V. The P turnover is characterized by high rates of the exchange processes and their great variability in different grasslands. It has been shown that the rates of N exchange processes are higher in the same ecosystems (Titlyanova 1979).

Net mineralization of P takes place when the P content in plant residues reaches 1.1 - 1.2 $mg \cdot g^{-1}$. Below that concentration net immobilization of P occurs. Immobilization can amount to 0.1 - 0.5 $g \cdot m^{-2} \cdot y^{-1}$.

The P store in the above and underground deadmass of steppes and meadows is about 1 - 2 $g \cdot m^{-2}$. Anderson and Domsch (1980) estimated the quantities of P held in microbial biomass as 7 - 8 $g \cdot m^{-2}$. According to these data the main pool of P in the soils are microorganisms. When one third of the microbial population dies they can release about 2.5 $g \cdot m^{-2}$ P or close to the annual uptake of P by the plants of grasslands.

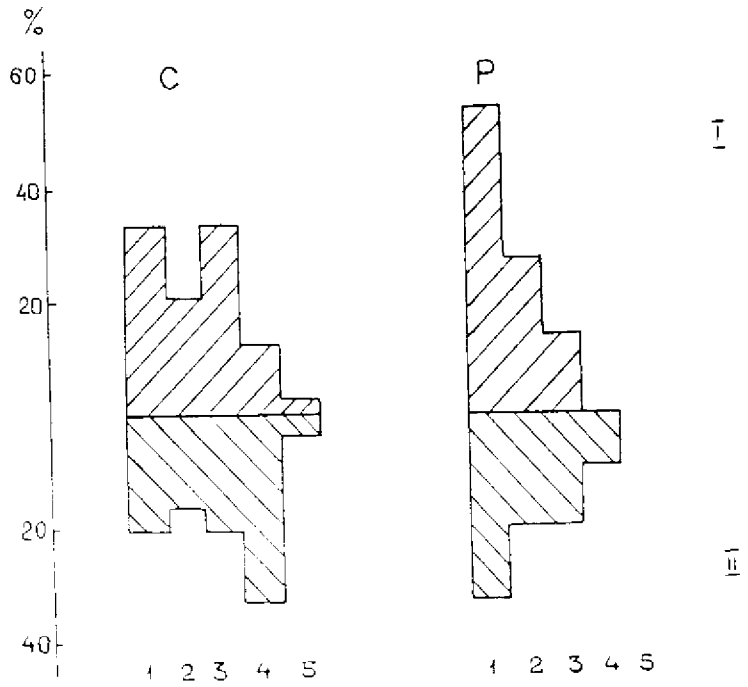

Figure 3 Dynamics of carbon production and phosphorus uptake by the plants /I/, mineralization of carbon and release of phosphorus/II/ in the mesophytic meadow.
The time periods: 1 - May-June, 2 - June-July, 3 - July-August, 4 - August-September, 5 - September-October.

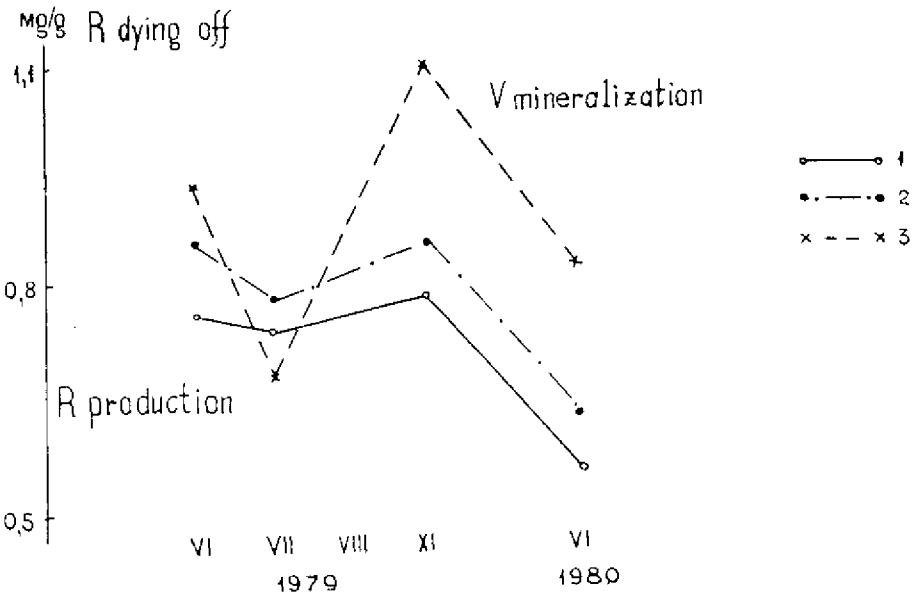

Figure 4 The change of the P content in the different fraction of R+V in the true steppe during a year.
1 - large fraction, 2 - middle fraction, 3 - small fraction.

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COMPARISON OF PHOSPHORUS CYCLES IN NATURAL AND AGRICULTURAL ECOSYSTEMS

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Comparative studies of the turnover and movement of biologically active elements in different ecosystems have shown that the natural biogeochemical cycles, particularly of phosphorus, show a more rational organization than those of agricultural sytems. This result can be used a basis for finding new ways to optimize mineral nutrition in agroecosystems, by using the organizational and functional principles of natural ecosystems.

Let us examine the P cycles in the forest and agriculture ecosystems on a heavy loam sod-podzolic soil (Figure 1). The natural ecosystem examined is a thin, mixed forest with a plantation age of 80 - 100 years. The topsoil is covered with a needle litter layer, as well as with green and bog (sphagnum) mosses and a scattering of grassy plants. The agroecosystem consists of a field of winter wheat grown in rotation with perennial grasses. The quantity of P involved in the annual biological cycle of the forest ecosystem was estimated from P content determinations of the surface soil, trees, plants and litter. In addition, an isotope tracer method was utilized to estimate P uptake by roots of grassy plants from various genetic horizons of the forest soil (CVs of this methodology were about 100%).

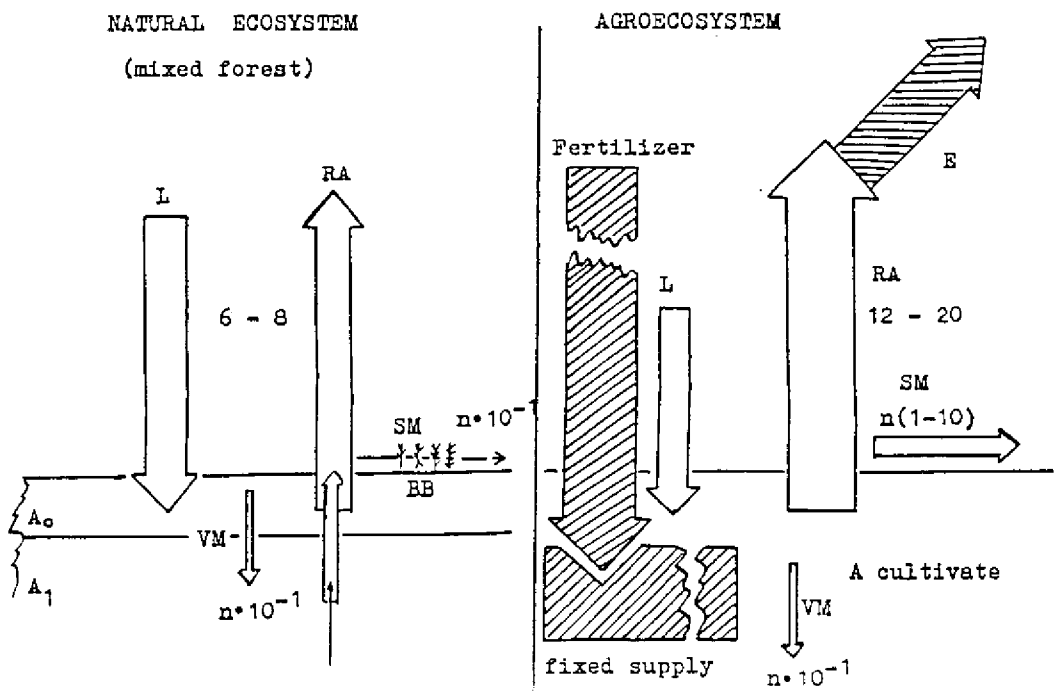

Figure 1. P cycles in forest and agricultural (shaded) ecosystems. Flows in $kg.10^4 m^{-2} \cdot y^{-1}$. Symbols: L-litter, RA-roots assimilation, BB-biological barriers, VM-vertical movement, SM-surface movement.

Vertical P movement within the profile was determined using a water permeable vessel which contained anion exchange resin and activated coal as sorbents and was inserted into the soil profile. ^{32}P and ^{33}P labels were used to trace vertical movements. Phosphorus transformations in the forest litter, surface movements and absorption by mosses from litter material were also studied using isotopic P. Components of the P cycle in the agroecosystem were established on the basis of surface soil contents, root biomass, P removal in plant yield, and the level of P fertilizers applied. Migration by surface runoff have been estimated using sorbents and P^{32} and P^{33} with methodology similar to that used in the natural ecosystem. The agroecosystem is distinguished by a considerable increase in the amounts of P involved in the cycle due to high levels of bioproductivity and the quantities of mineral fertilizers applied. However, this increase cannot be regarded as a general principle, since it is possible to find a number of cases in which the quantities involved in biogeochemical cycling were reduced during a transition from the natural to the agricultural ecosystem.

The following features should be noted based on the comparison of natural and agricultural cycles. In the mature natural ecosystem, the P cycle is nearly closed i.e. P supply from litter decomposition is practically equal to plant uptake. Indirectly, this is evidence for the high level of P re-utilization from plant residues. The closed nature of the P cycle is also enhanced by the presence of biological barriers formed by green and bog mosses, which prevent the export of this deficient element in surface flow of water (Fokin et al. 1979). Thus, the natural ecosystem examined functions according to the principle of "wasteless production" with minimum uneconomic P expenditures.

Unlike the natural ecosystem, the agrocenosis is characterized by a pronounced openness of the P cycle, because P is imported and exported in unbalanced amounts. The accumulation of insoluble products of the reaction of soil with mineral P fertilizers (fixed supply in the scheme) resulted in low coefficients of P utilization from fertilizers. In addition, P export with surface runoff was greatly increased, particularly under conditions of surface erosion, which were facilitated by the lack of biological barriers in the system. Thus, the comparison of the two systems shows that by many criteria, functioning and organization of trophic connectivity of the natural ecosystem is superior to that of the agroecosystem made and regulated by man.

The point of the investigation is to study the possibility of utilizing mechanisms of natural ecosystem function, and its rational organization, in the agroecosystem. In particular, we want to establish whether the high coefficients of P utilization from plant residue can be preserved in an agroecosystem, and what the underlying mechanisms of such recycling are. Results of our experiments show that in all cases absorption of labile P by different crops from plant residues was superior to the absorption of P from fertilizers. We examined the dynamics of P absorption by winter wheat, which was grown on a bed of perennial grasses (Figure 2). Uptake was best from grass root residues and less from mineral fertilizers likely due to the increased density of functioning roots within soil layers enriched with plant residue, and the more favourable physical properties and heightened biological activity, as well as a better nutrient balance in such layers.

Relative to mineral fertilization, higher coefficients of utilization of Ca and Zn have been found with plant residue recycling (Mishina 1984). These examples prove the advisability of creating favourable conditions for crop growth, by maintaining the greatest possible amount of after-harvest root residue in rotations, and particularly by including perennial grasses.

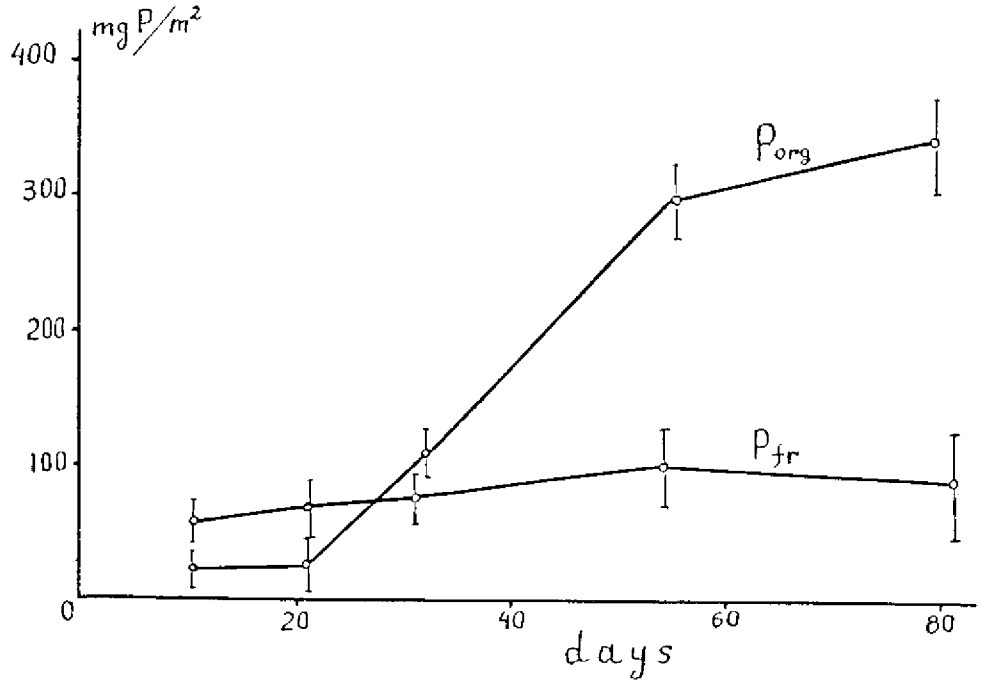

Figure 2. Dynamics of P uptake by winter wheat plants grown on a bed of perennial grasses from root plant residue of the preceding crop, and from mineral fertilizers.

A further reason for the efficiency of residue recycling is the increase in the coefficient of utilization of mineral fertilizers. This appears to be due to an increased utilization of several elements, and due to a longer retention of plant nutrients in plant available form. Attention should also be paid to the fertilization of grasses, because this practice results in a decreased need for high rates of fertilization to following crops, since the soil will be enriched with nutrient rich organic residues, and have an improved biological activity, which may increase its ability to detoxify pollutants. If fertilizers are applied to grass leys, leaching out of the rooting layer is minimized due to the abundant proliferation of roots. In addition, erosion losses are minimised. Consequently, subsequent grain crops grown on the residues of perennial grasses require smaller amounts of N fertilizers, which reduces the danger of lodging.

In the general practice existing in the USSR, however, much attention is paid to fertilization of cereal and tilled crops, while perennial grasses are ignored. Estimates based on experimental data show that in field rotations including perennial grasses on sod-podzolic soils, well aimed use of mineral fertilizers and agro technology can increase, post-harvest root residue accumulation in the soil to approximately 25 $t \cdot ha^{-1}$ of dry matter. Such amounts are equal to 100 - 120 t. of manure per ha. It appears that research directed into this field of agriculture might considerably improve bioproductivity and soil fertility. Microbiological mobilization of mineral nutrients from almost unavailable forms, are promoted by the energy released at the time of organic matter mineralization, and this important process is dependent on the presence of adequate levels of organic matter. Unfortunately, this process is not given its due attention in agroecosystems.

The different sources of elements (nitrogen from the air, non-hydrolysed forms of soil nitrogen, elements from soil minerals) are illustrated in the following.

Nonsymbiotic fixation of N_2 is known to be performed by microorganisms in connection with the decay of organic matter in soil (Emtsev et al. 1985). In our experiments with recently cultivated chernozems, hydrolyzed nitrogen content has been approximately doubled, as a result of the mineralization of starches (which basically contain no mineral nutrient elements) under optimum composting conditions (Figure 3). Acceleration of mineralization of labelled uracil, had been observed. This indicates that nitrogen from heterocyclic components in soil humic material can be transformed to labile forms. (The experimental quantities of N in labelled uracil was half as much as the total increase in hydrolyzed nitrogen).

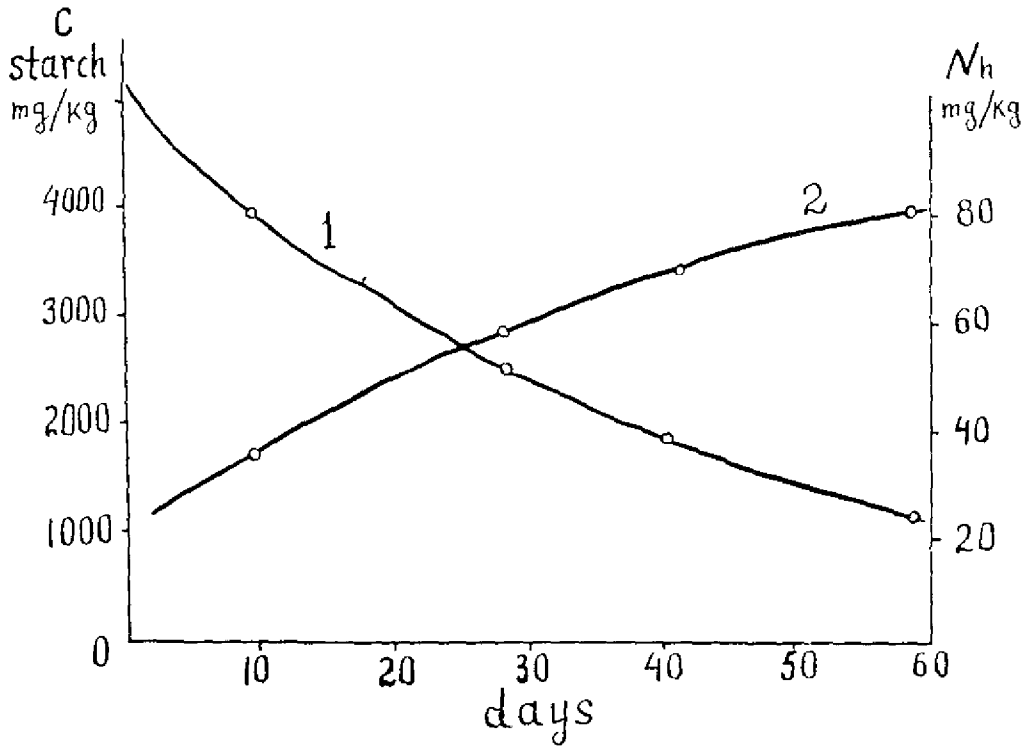

Figure 3. Transformation of non-hydrolyzed nitrogen into hydrolyzed N during the decomposition of starch in a black earth (laboratory experiment).

In contrast to popular opinion, experiments conducted with soluble three-substituted calcium phosphate with labelled P or Ca have shown that the mobilization of P is influenced not only by soil acidity, but also considerably accelerated by the presence of large quantities of decaying organic matter in the soil (Figure 4).

The results obtained, indicated the possibility of P mobilization apatites..for instance in irrigated serozems, by applying organic materials. Considering the high biological activity in serozems, and the exceptional conditions for decomposition of organic materials under high temperatures and irrigation in serozem areas, poorly decomposed organic materials may be applied, which may be imported from the northern parts of the non-chernozem

zones, such as various wastes from forest industries (lignin, hydrolysis products, etc).

Mobilization of any deficient element can probably be effected from different soil minerals in the presence of decaying organic substances. Such processes were likely very strongly pronounced in the initial stages of soil formation, when higher plants specialized in providing the ecosystem with available energy sources while microbes provided reserves of available mineral nutrient elements. In mature soils containing a created store of plant nutrients, such a "division of labour" between both groups of organisms will have a slightly different character.

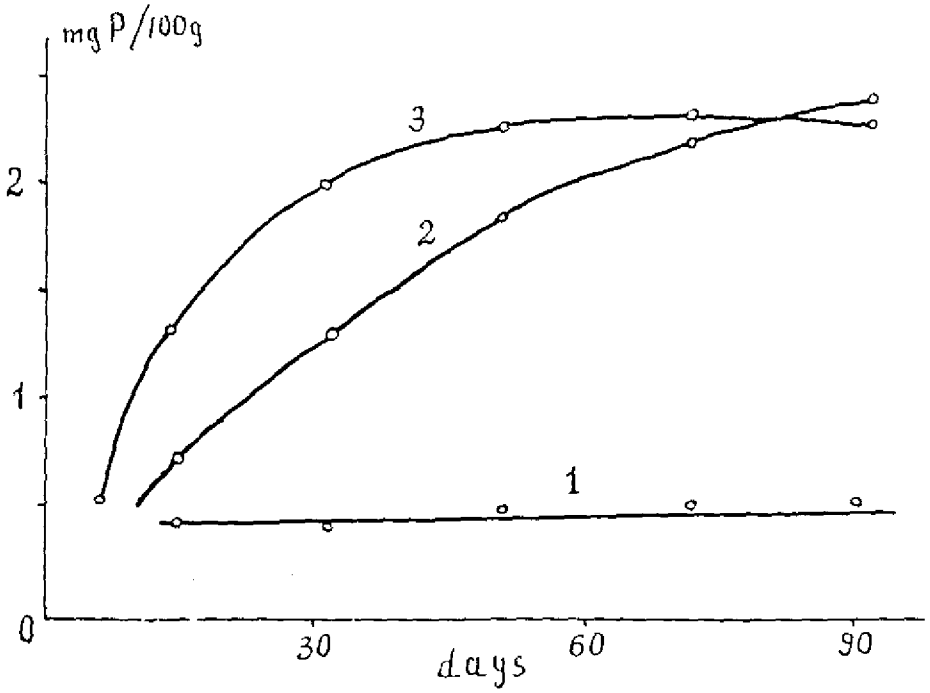

Figure 4. Influence of the decomposition of organic matter on transformations of sparing the soluble P (laboratory experiment: 1 kg soil + 20 g organic matter + 1.1 g Ca3(P04)2, 20% humidity by weight, t - 25° C).

Experiments and investigations in this direction promise to yield methodologies for restoring soil fertility in a natural way that use mechanisms typical for natural ecosystems. These could take the form of, for instance, not applying mineral fertilizers, but "mineral raw materials" as well as decayed organic substances which will be humified under cultivation and increase microbial activity.

The data presented on the rates of mobilization processes indicate that the methods proposed can satisfy the requirements of high productivity farming, and can be achieved with the use of appropriate agricultural technologies and organic materials. Such methodology will have definite ecological advantages in reducing the levels of mineral fertilization while also improving the balance of nutrient supplies. A nutrient supply, mediated by biological mobilization, is likely to contain all necessary nutritional elements in appropriate proportions for biological activity. In addition, pathogenic microflora may be suppressed on account of the abundant activity of

useful microorganisms. This may result in further lowered requirements for agricultural chemicals. There are a number of examples, especially under irrigated conditions, in which many tons of mineral and organic waste may be applied to the soil and, at least locally, solve waste disposal problems.

In order to realize the potential of this methodology in practice, it will undoubtedly be necessary to conduct complex research utilizing methods of biochemistry, ecology and soil biotechnology. At the scientific methodological level, such research should ensure an understanding of the mechanisms underlying the control of processes as well as forecasting of biological productivity and the future ecological condition of the agroecosystem.

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THE IMPACT OF AGRICULTURE ON THE PHOSPHORUS CYCLE IN POLAND

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The agricultural and geo-chemical transformations of phosphorus may be presented in the form of the model proposed by Russell (1977) and Fotyma et al. (1987) (Figure 1). This model is based on a kinetic equation of the first order:

$$\frac{dA}{dt} = F(t) + K_1T - (K_2 + K_3)\ A - U(t)$$

where: K_1 - soil phosphorus mobility factor
K_2 - phosphorus loss factor beyond the soil crop system
K_3 - phosphorus immobilization factor
t - time
the remaining definitions are given in Figure 1.

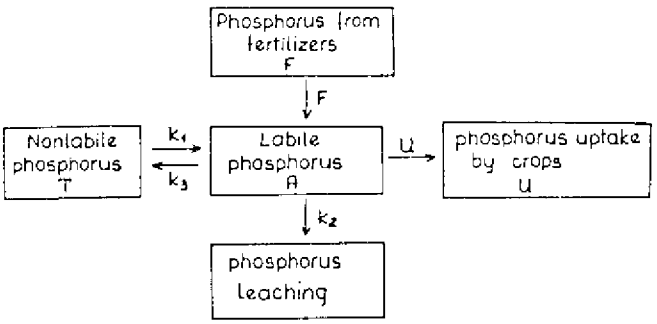

Figure 1. Long-term model of P transformations in soils according to Russell (Fotyma 1987)

In the present paper an attempt will be made to identify the elements of this model for Polish agricultural conditions.

The balance of phosphorus

The net balance of phosphorus (P) is taken to be the difference between the quantity of P in mineral and organic fertilizers and the uptake of P by crops. Two elements of the Russell model are thereby integrated:

$$dP(t) = F(t) - U(t)$$

where dP(t) - the P balance difference in time t. Values for different periods of the last 25 years are presented in Table 1.

In the period of 1961 - 1965 the quantities of P in fertilizers equalled the amount taken up by plants. In the last twenty years the P balance has been positive and until 1980 showed an increasing tendency. During the entire 25 year period about 250 kg more P was added to the soil than was taken up by crops.

The magnitude of the net balance varied in different regions of the country. In the northern and western voivodships of the country dP was in the

range of 20 - 25 $kg \cdot ha^{-1} \cdot y^{-1}$ (Figure 2). Highest values were recorded in the Poznań voivodship (which is hosting our meeting) with 27 kg of P $ha^{-1} \cdot y^{-1}$ and in the neighboring voivodships Leszno with 30 $kg \cdot ha^{-1} \cdot y^{-1}$. Organic fertilizers are produced on farms and, discounting fodder purchases, form part of the closed P cycle. Raw materials for fertilizer production are imported, and along with P significant quantities of heavy metals such as lead and cadmium are imported which can later become a danger for the agricultural environment (Table 2).

Table 1. Elements of the phosphorus balance in Poland 1961-1985 (Fotyma and Kesik 1978 and Fotyma and Kesik unpublished)

	Elements of the phosphorus balance in kg of P $ha^{-1} \cdot y^{-1}$			
	phosphorus in fertilizers			
Year	Mineral	Organic	Crop uptake	Net balance
1961 - 1965	5.6	5.4	9.5	1.5
1966 - 1970	10.3	5.9	11.1	5.1
1971 - 1975	17.5	6.8	12.9	11.4
1976 - 1980	21.8	8.6	11.2	19.2
1981 - 1985	20.2	7.7	13.7	14.2

Table 2. Quantities and origins of phosphorus imports to Poland in 1987

		Heavy metal content ppm		Amount of heavy metals t	
Country	Phosphate $t \cdot 10^6$	Pb	Cd	Pb	Cd
Algeria	77.0	40	80	3.1	6.2
Israel	65.7	30	20	2.0	1.3
Jordan	750.8	9-60	8-20	25.9	10.5
Morocco	861.6	6-80	10-40	9.0	14.9
Togo	276.9	600	10	166.1	2.8
Tunisia	94.0	6-60	10-50	3.1	2.8
USA (Florida)	589.7	15-110	8-10	36.9	5.3
USSR (Kola)	716.2	6	4	4.3	2.9
total	3431.9	-	-	250.4	46.7

The mobilization and immobilization of phosphorus

The concept of labile P (A in Figure 1) is defined in various ways. For plant nutrition purposes it is defined as the quantity of P in the solid phase of the soil which replenishes solution P and thereby becomes available for crops. In physical-chemical terms labile P is the quantity of the element with which ^{32}P released into the soil solution exchanges. For most practical purposes labile P is defined as the P extracted by some convenient extractant. Here, labile P or available P are understood as the element extracted by the Egner-Riehm method (0.4 N lactate extract) which is standard in Poland.

Dissolution and fixation of P occur simultaneously and in experiments must be defined in terms of net effect which is the loss or gain in the amount of labile P according to the equation:

$$dA = f(K_1T + K_3A)$$

where dA - the change in the labile P content, and the remaining symbols are defined in Figure 1. Two further elements of the Russell equation are then integrated in the value of dA.

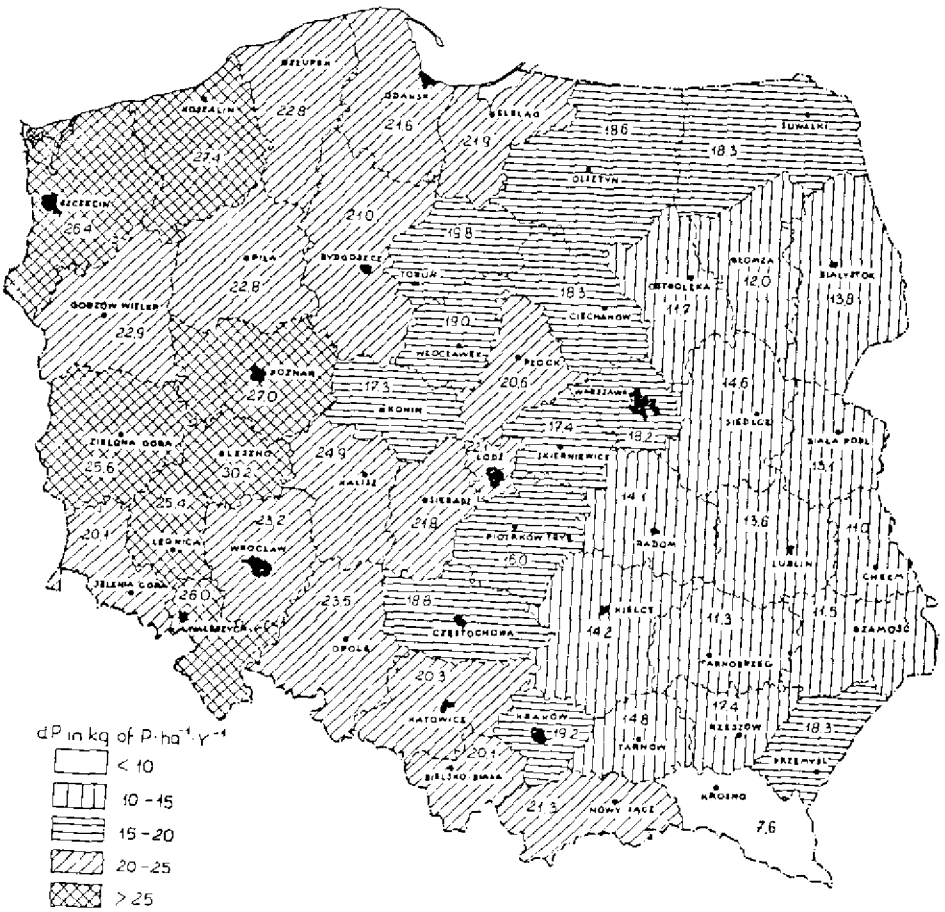

Figure 2. Net P balance in Poland in 1987

In 1962, 48 crop rotation experiments were begun in Poland with a range of P fertilization rates. Of these, 20 experiments were discontinued after three 4-year rotations (12 years) and the rest were carried out through 4 rotations (16 years). Labile soil P under each treatment was measured annually and used in the regression:

$$y = a + bx$$

where y - the labile P content in a given treatment after x years
x - the years of the experiment
a,b - coefficients of the equation

The regression coefficients for the series of 48 experiments conducted for 12 years (x = 12) and the series of 28 experiments carried out for 16 years (x = 16) are presented in Table 3.

The experiments were classified into four groups depending on the initial P content in the soil. A dose of 16 kg of P $ha^{-1} \cdot y^{-1}$, in which fertilizer

inputs and crop exports were balanced, caused an increase of labile P in the soil of about 1.0 $mg \cdot kg^{-1}$ of soil. It is interesting that in the soils of the control treatment no loss in labile P content was noted in spite of the negative P balance. This indicates that the nonlabile P (T in Figure 1) sustains crops, though with severely reduced yields. The increase of labile P content due to fertilization was greater in the soil with very low initial amounts than in the soil with high initial contents. The relationship y = f(x) was best represented by a linear function but closer analysis reveals that the increase in the labile P content was not equal during the entire 12 or 16 year period of the experiment. The most intensive accumulation of P took place in the first 4-course crop . The coefficients presented in the Table are then valid only for the period covered by the experiments (up to 16 years).

Table 3. Annual increase in P (coefficient b in a linear regression equation in mg $P \cdot kg^{-1}$ of soil per year) (Gosek et al. 1984)

Initial content	1st experimental series n=48				2nd experimental series n=28			
	Fertilizer doses in kg $P \cdot ha^{-1} \cdot y^{-1}$							
	0	16	32	64	0	16	32	64
very low	0.08	0.13	0.16	0.26	0.09	0.15	0.20	0.29
low	0.03	0.09	0.16	0.25	0.08	0.11	0.18	0.25
average	0.00	0.07	0.13	0.25	0.06	0.11	0.14	0.16
high	0.00	0.10	0.18	0.18	0.00	0.10	0.10	0.15
mean	0.03	0.10	0.16	0.25	0.07	0.12	0.17	0.24

For solving the Russell model the most interesting is the change in the labile P content dA integrating the elements K_1T and K_3A of the model. Using the results of the same experiments and the method worked by Kerschberger and Richter (1972, 1978) values for the stable P balance were calculated. The relationship between both variables is shown in the linear regression equation:

$$dA = 1600 + 0.076\ d\ P$$

where dA - the gain or loss in the labile P content in mg $P \cdot kg^{-1}$ soil
dP - the net total P balance in kg of P $ha^{-1} \cdot y^{-1}$

The P addition which is necessary for increasing the content of the element in the soil by 10 mg.kg-1 is calculated by transforming the regression equation:

$$dP_1 = \frac{10 - 1.600}{0.076} = 110\ kg\ P \cdot ha^{-1} \cdot y^{-1}$$

The average surplus of P necessary for increasing the labile form of the element in the soil by 10 $mg \cdot kg^{-1}$ came to 110 kg of $P \cdot ha^{-1}$. The mass of the plough layer with bulk density of 1.5 $kg \cdot dm^{-3}$ came to $3 \cdot 10^6$ $kg \cdot ha^{-1}$. Therefore 10 mg of $P \cdot kg^{-1}$ of soil corresponds to 30 kg of P in the plough layer per ha. The P balance ratio is then:

$$RP = \frac{dA}{dP_1} = \frac{30}{110} = 0.27 = 27\%$$

This means that 27% of the P surplus is found in the labile pool and 73% is probably bound in nonlabile forms. The value of the P surplus dP1 is supported by many other studies (Fotyma and Kesik 1978). It should be noted that the proportion of P from fertilizers contributing to the labile pool is quite large in comparison to the labile portion of native P. Therefore over the years of fertilizer application the share of labile P in the total P content continually increases (Fotyma and Kesik 1978).

The increases in labile P were confirmed in soil resource studies carried out nationally by regional agro-chemical stations. In Table 4 the number of negative soil evaluations for the labile forms of different periods are shown. The land evaluation (Riehm) number is the sum of the percent of the share of soils with low content of a given element and half of the share of soils with medium content. The lower the number the better the soils' state for any given element.

Table 4. Changes in soil acidity and content of the labile elements in Polish soils

Period of study	Number of negative land valuation (Riehm number)			
	acidity	potassium	magnesium	phosphorus
to 1966	71	48	71	79
1967 to 1976	71	61	62	67
1977 to 1982	72	61	55	63
since 1982	72	62	46	57

Soil reserves of P (and K) in contrast to magnesium reserves and soil acidity have systematically improved in Poland due to the above mentioned net surplus of fertilized P since the beginning of 1965 (Table 1).

Phosphorus leaching

The last part in the Russell equation is P leaching or losses of the component beyond the soil-crop system. These losses are measured in lysimeter experiments or by measuring the concentration of P in water and quantities of water from ditches leading away from individual fields and drainage areas. Summarizing the results of 17 years of lysimeter experiments conducted in central Poland in Pulawy it can be stated that the amounts of P in drain water are within the limits of the measurement error (Sykut 1988, Ruszkowska and others 1984). The experiments were conducted in lysimetres of 0.9 - 1.3 m depth filled with soil of varied texture. The P concentration in water from the ditches did not, as a rule, exceed 0.05 $mg \cdot dm^{-3}$ and was much lower than the concentration found in natural water courses (Pondel and Terelak 1981).

Using the results of all the studies conducted in Poland Fotyma et al. (1987) estimated the most probable P losses to ground waters at 0.1 - 0.2 kg of $P \cdot ha^{-1} \cdot y^{-1}$. These losses are very small in comparison to the P balance surplus in Polish soils, and that part of the Russell model may be disregarded.

Phosphorus from large applications of liquid manure (LM) has raised concerns about P leaching. In 8-year experiments carried out with a

monoculture of maize, mineral fertilizers and three doses of liquid manure were applied. Rodman wells were dug to depths of 100, 150 and 200 cm on experimental fields and the soil leachates were analyzed for the concentration of mineral elements including PO_4-P. In all the years of the experiments and in all the periods when samples were taken, the concentration of phosphates were found to be within the measurement error, and no relationship between P content and the doses or forms of fertilizer could be established (Table 5).

Table 5. Phosphorus balance for the years 1977 - 1984 (Warta 1987)

Treatment	Amount of phosphorus $kg \cdot ha^{-1}$			Labile P change in $mg \cdot kg^{-1}$ of soil in the layers (cm)			
	In fertilizers	uptake by crops	net balance	0-30	31-60	61-100	101-150
NPK	387	65	322	85	38	7	-13
LM 50 m^3	398	122	276	7	-19	-18	-47
LM 100 m^3	591	137	454	49	7	-6	-9
LM 150 m^3	1190	143	1047	96	31	6	-3

The accumulation of labile forms of P in the soil was limited to the A horizon (Table 5). In the subsoils even some P loss was found by the Egner-Riehm method which may be an error due to the lower number of samples. On the basis of the results obtained it may be stated that P from liquid manure applied every year even in large doses did not pollute ground and soil waters. An entirely different issue, of course, is soil surface erosion where soil is washed away along with the P contained in it.

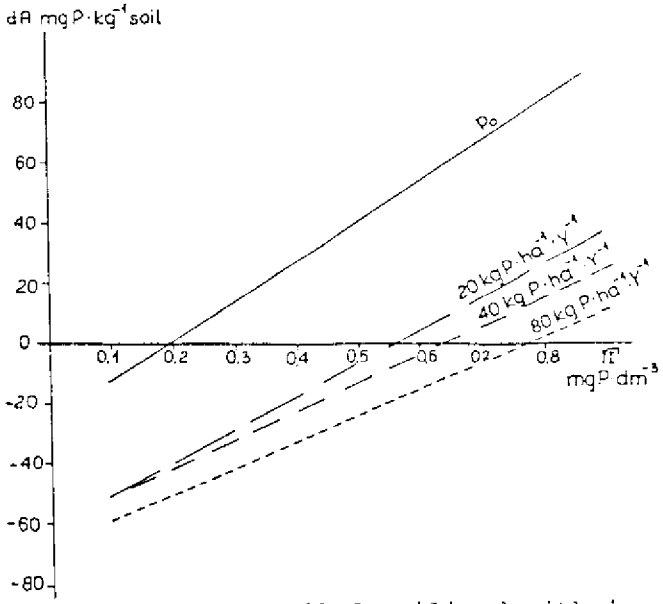

Figure 3. P sorption curves for soil fertilized with increasing doses of P

The phosphorus buffering capacity of soils

The accumulation of labile P in the soil leads to depletion of the soil buffer capacity in relation to this element. In the future this may cause the

infiltration of P further into the soil profile as the sorption capacity of each level is gradually exceeded. In order to build a layer model of the infiltration of P into the soil profile the sorption capacity of the individual layers of the profile need to be known. Studies designed to identify the parameters of the P adsorption equation (isotherm) for different soils with varied P contents were begun in Poland in the 1980s. Increases in P contents have come about as a result of the long term use of increasing doses of P fertilizers. Phosphorus sorption was described by an empirical equation proposed by Pagel (1981):

$$dA = n.V\ I + b$$

where dA - the change in the labile P content $mg \cdot kg^{-1}$ soil
I - the P concentration in $mg \cdot dm^{-3}$ in a 0.01 $mol \cdot dm^{-3}$ $CaCl_2$ solution
n - equation coefficient corresponding to the soil buffer capacity in relation to P, dA/I
b - equation coefficient corresponding to the theoretical quantity of P extracted by pure solution of 0.01 $mol \cdot dm^{-3}$ $CaCl_2$.

From this equation dA as a function of V I is linear, which makes identification of the equation parameters easier.

In Figure 3, curves of the adsorption equation are presented for a sandy loam heavily fertilized for a number of years with increasing doses of P fertilizers. Enriching the soil with P has increased the concentration of that element in the extracting solution (at equilibrium) and insignificantly decreased the soil P sorption capacity. An equilibrium P concentration with which crops are well nourished but which could also signal P leaching is accepted as being 0.8 $mg \cdot dm^{-3}$. From Pagel's equation (above) the necessary amount of P which should be applied to the soil (above the amount taken up by crops) in order to attain this equilibrium concentration in the extract may be calculated. The results of calculations for soils with varied textures and histories of P fertilization are shown in Table 6.

As shown in the Table 6, the sorption capacity (calculated for the concentration of 0.6 $mg \cdot dm^{-3}$) of soils fertilized for many years with doses of 20 $kg \cdot ha^{-1} \cdot y^{-1}$ has not been exceeded. Soils fertilized for 7 years at 40 $kg \cdot ha^{-1} \cdot y^{-1}$ are able to release sufficient quantities of P for plants even after discontinuation of fertilizer application for 1 to 2 years. The results of experiments shown in Table 6 should be treated as preliminary and have been presented as an illustration of the direction of work on P in Poland.

Table 6. The P balance difference dP necessary for increasing the equilibrium P concentration in solution to 0.6 $mg \cdot dm^{-3}$ (Kesik unpublished)

Soil type	dA in $kg \cdot ha^{-1}$ for soils fertilized with P for 7 years in doses of $kg \cdot ha^{-1} \cdot y^{-1}$			
	0	20	40	60
sandy loam	78.8	24.8	13.3	1.0
loam	20.3	1.2	-4.3	-22.7
silt	30.4	5.5	-27.1	-32.8

Conclusions

The balance of P in Poland over the last 20 years has been positive. The total surplus of P from 1965 to 1985 equals about 250 $kg \cdot ha^{-1}$.

The raw materials for fertilizer production in Poland are all imported. In the geo-chemical cycle of P Poland is a net consumer of that element.

The P surplus accumulates to about 30% in labile pools.

The transformation of P from fertilizers is limited to the upper 30 cm (in exceptions 60 cm) layer of the soil and leaching of the element is not significant.

Further studies on P, both on the agro-chemical and environmental protection aspects are being conducted to more exactly determine the course of sorption curves on P in soil.

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PHOSPHORUS CYCLING IN INTENSIVE AGRICULTURE WITH SPECIAL REFERENCE TO COUNTRIES IN THE TEMPERATE ZONE OF WESTERN EUROPE

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Introduction

The agriculture in the temperate zone of Western Europe is generally considered to be very intensive. The intensity, however, varies much between countries. The main variables are animal stocking rate, area use, and fertilizer use. These main variables govern the phosphorus (P) loads and flow rates in different portions of the agricultural system.

A P-flow chart covering the overall P-cycle of various agricultural systems will be presented and examples of P-flow rates under varying conditions will be given including the distribution of fodder-P on animal products and excreta. Furthermore, an attempt will be made to quantify the main average P-flow rates for seven Western European countries.

P-Flow chart

There are three main compartments through which phosphorus cycles in intensive as well as extensive agricultural systems, namely the soil, crop, and animals. Stable feeding of the animals, a characteristic of the intensive agriculture, however makes it necessary to divide the animal compartment into a confined and a grazing part. In addition, two storage compartments one for plant products, feeds, and mineral supplements and one for animal excreta are necessary (Figure 1).

Another characteristic of intensive agriculture is that many farms have both arable land, which is ploughed regularly, and permanent grassland. The P-flows to and from the two land types are different. For example the arable land usually receives more manure P than permanent grassland (van Beheemen, 1987, Breeuwsma, 1986) because the manure can be ploughed into the arable soil. Furthermore, losses of P by leaching, surface runoff and wind erosion seem to be different for arable land and permanent grassland. It is therefore convenient to divide each of the soil and crop compartments accordingly (Figure 1).

Compartments and flows

Soil. Intensively managed agricultural soils usually have a high P-content. For example Danish agricultural soils on average contain about 40 $\mu g \cdot g^{-1}$ Olsen-P (0.5 M $NaHCO_3$-soluble P) in the plough layer (Pedersen, 1988). This is a high or very high P-status, according to the Danish or English classification systems respectively and indicates that crop responses to further P application are not likely (Johnston et al., 1986). The average content of inorganic P in the plough layer of Danish soils is about 400 $\mu g \cdot g^{-1}$ equivalent to about 1 t of P per hectare in the plough layer. About two thirds of this originate from mineral fertilizers and imported feeds.

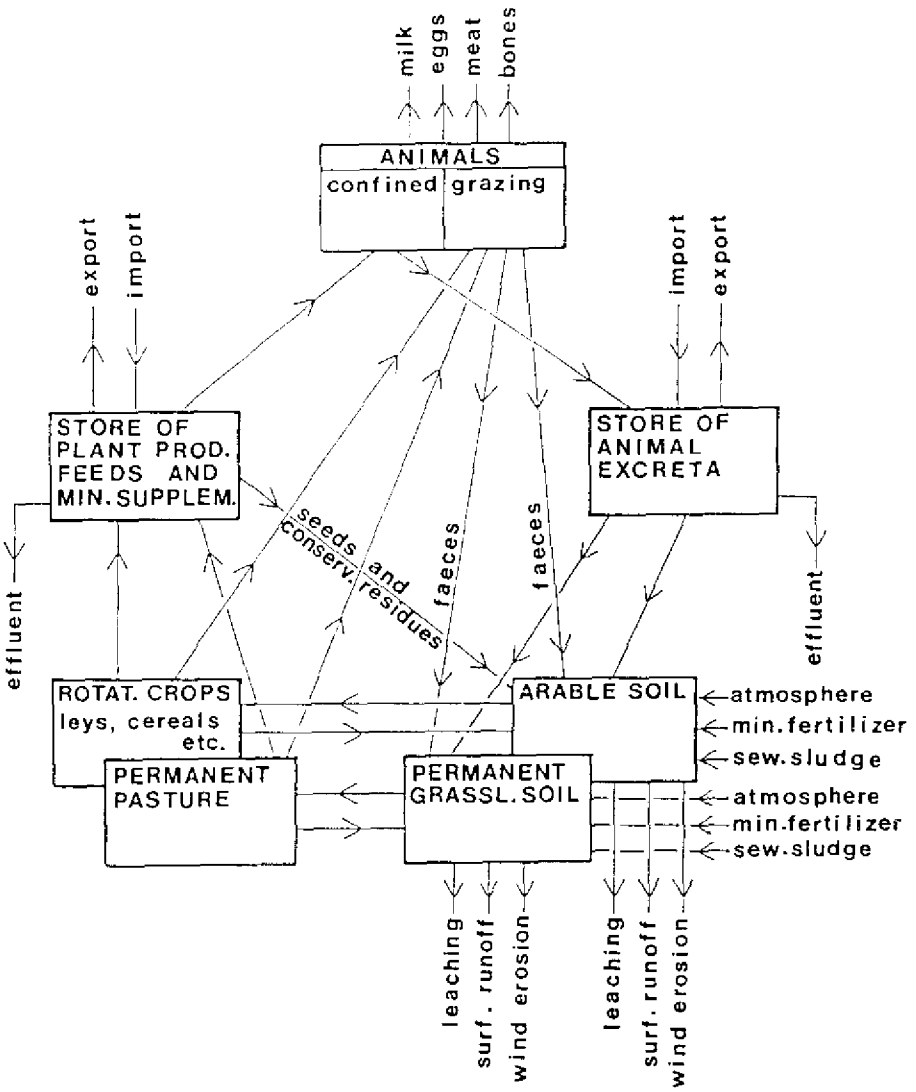

Figure 1. P-flow chart for farms growing both rotation crops and permanent pasture and feeding animals both confined and by grazing.

Crop-P. The amount of P taken up by crops is determined by the dry matter production and the concentration of P in the dry matter. Because of the generally high nutrient status of intensively managed soils, the dry matter production mainly depends on the nitrogen fertilization rate, water supply and irradiation. The P concentration of whole plants decreases with increased plant age (Table 1). General P-uptake rates are given in Table 6.

P in animal products and animal excreta. The fodder P is distributed on animal products (meat, bones, milk, eggs) and animal excreta (faeces and urine). Very little P is found in the urine (Table 2). The slaughter percentages given serve for calculation of the amount of P in whole animals from information about meat production.

Based on detailed information about fodder use and animal production in Denmark (Danmarks Statistik, 1987) I calculated the distribution of fodder-P

on animal products and excreta for cattle, pigs and poultry over a three year period (Table 3). About 1/5 to 1/4 of the fodder-P was exported from Danish agriculture with animal products and about 3/4 to 4/5 remained as animal excreta. The distribution coefficients calculated in this way are similar to results based on calculations for single animals made by Koefoed, (1988). He obtained the following fractions of the fodder-P in animal excreta: cows of 550 kg yielding 6150 kg milk per year with 4 % fat: 76 %; 1 years normal bread of calves and heifers: 83 %; cattle for slaughter (423 kg): 69 %; sows producing 21 piglets per year: 83 %; pigs for slaughter: 74 %.

Table 1. P-Concentration in crops ($g \cdot kg^{-1}$ dry matter)

	Before heading	Initial heading	Final heading	Flowering	After flowering	Reference
Perennial ryegrass	4.5	3.8	3.3	2.9	2.6	1
Timothe	4.4	3.7	3.0	2.4	2.0	1
Cocksfoot	3.6	3.0	2.6	2.3	2.1	1
Meadow fescue	4.8	4.0	3.4	2.8	2.4	1
Permanent pasture						
good population	4.6	3.9	3.4	3.0	2.7	1
bad population	-	2.6	2.2	1.9	-	1
Green maize					2.5	1, 2

	Before budding	Budding	Initial flowering	Flowering	Final flowering	
Red clover	3.4	2.9	2.7	2.5	2.2	1
White clover	4.2	3.6	3.2	-	-	1
Lucerne	4.1	3.5	3.0	2.7	2.5	1

	Initial heading	Final heading	Flowering	Grain	Straw	
Barley	3.8	3.4	3.0	3.9	0.8	1, 2
Wheat	3.4	2.7	2.0	3.8	0.8	1, 2
Oats	3.6	3.2	2.9	3.9	1.1	1, 2
Rye	3.7	3.3	3.0	3.4	1.0	1, 2

	Roots	Tubers	Top	
Potatoes		2.2	2.0	1, 2
Sugar beets	1.4		2.5	1, 2
Fodder sugar beets	1.8		2.5	1, 2
Swedes	3.5		4.3	1, 2

1) Nehring, Meyer and Hoffmann (1972). 2) Andersen and Just (1983).

Table 2. P in animal products and whole animals as well as slaughter percentages of various animals

		P conc. g/kg	Slaughter percentage 1)
Milk		0.97 2)	
Eggs w. shell		2.0 3)	
Cattle	100 kg	5.5 4)	51
	300 kg	6.3	52
	Cows	7.1	49
Pigs	90 kg	5.8 4)	73
Sheep	30 kg	4.8 4)	50
	50 kg	5.0	50
Poultry		6.2 4)	79

1) Weight of carcass relative to live weight, obtained from Nielsen (1988). 2) Andersen and Just (1983). 3) Simons (1986). 4) Günther (1972).

Table 3. Distribution of fodder P, on animal products and animal excreta based on average fodder use and animal production in Denmark during the years 1983/84, 84/85 (based on Danmarks Statistik, 1987)

		Cattle	Pigs	Poultry
Input of fodder P				
Vegetable fodder	T P	34182	26923	3776
Mineral supplements*	T P	4800	11200	1300
Total	T P	38982	38123	5076
Output				
Animal products	T P	8595	9009	1030
Relative to input	%	22	24	20
Animal excreta†	T P	30387	29114	4046
Relative to input	%	78	76	80

* Total input of P in mineral supplements from Fielsen (1988), distribution on animal groups from Koefoed (1988).
† Obtained by difference.

P-Losses from point sources. If storage facilities for excreta and silage of feed lot facilities are either too small or not suitably constructed P will sometimes be lost from these point sources and find its way to the

water environment via surface runoff and drain pipes. Such losses are difficult to monitor, but can locally be very large and harmful to the water environment.

Deposition of P from the atmosphere. Little P is deposited from the atmosphere. From 0.11-0.26 $kg \cdot ha^{-1} \cdot y^{-1}$ of P has been measured in Denmark and Sweden (Rebsdorf, 1981; Fleischer et al., P-deposition of 0.15 $kg \cdot ha^{-1} \cdot y^{-1}$.

Loss of P by leaching and surface runoff. The part of the precipitation which is not transpired by the crops or evaporated either leaches down through the soil profile or runs off along the soil surface. The water carries with it both dissolved P and particulate P, i.e. P bound to suspended inorganic and organic particles.

It is very difficult, may be impossible, to measure exactly the total loss of P by leaching under natural conditions. P losses measured in tile drain effluents are specific for the drainage system but give little information about the part of the precipitation which leaches between the drain pipes (about 60 %). Soil water samples with suction cells only contains dissolved P as the particulate P cannot pass the cell pores. Nevertheless, both types of measurements give information about the relative effect of various factors on the P-losses by leaching.

Leaching losses. Danish measurements made during the years 1971-81 of molybdate reactive soluble P (RSP) in tile drain effluents from 15 arable, sandy loam soils gave an average P concentration of 0.03 $mg \cdot l^{-1}$ (S.D. = 0.02) (Pedersen, 1983). Similar measurements on 7 peat soils gave an average RSP concentration of 0.09 $mg \cdot l^{-1}$ (S.D. = 0.06) (Hansen, 1986; Pedersen, 1985). Assuming a leaching of 300 mm per year then RSP leaching losses of 0.09 and 0.27 kg $P \cdot ha^{-1} \cdot y^{-1}$ are obtained for the sandy loam and peat soils respectively.

In Northern Ireland Jordan and Smith (1985) measured P losses in tile drain effluents from intensively managed permanent grassland on a medium heavy loam. For the years 1977, 1981 and 1982 they obtained annual RSP losses of 0.17, 0.45 and 0.70 $kg \cdot ha^{-1}$ and total -P losses of 0.41, 1.01 and 1.92 $kg \cdot ha^{-1}$ respectively. Furthermore, they found that slurry application and grazing during wet periods resulted in greatly increased losses of both soluble and particulate P. Similarly Sharpley and Syers (1979) found grazing to result in dramatic increases in the concentrations of RSP and particulate P of drain water from a New Zealand pasture.

The question is whether the P-leaching from permanent grassland is larger than from arable land. Results of Culley, Bolton and Bernyk (1983) obtained from a long-term drainage experiment on an Ontario clay loam showed that the leaching of RSP was more than 100 % larger from a permanent bluegrass sod than from any arable crop. Furthermore, they found the leaching of P from plots fertilized plots with 30 kg $P \cdot ha^{-1}$ to be much larger than from unmanured. The difference in P-leaching between arable land and permanent grassland may be caused by the presence of more continuous macropores down through the profile in permanent grasslands.

Surface runoff of P. Culley, Bolton and Bernyk (1983) found much larger P losses by surface runoff from plots with continuous corn than from plots with a bluegrass sod. Under Norwegian conditions, where most of the surface runoff takes place during snow melt, Uhlen (1986) found during an 8 year period much larger losses of RSP from permanent pasture plots (0.48-0.92)

than from spring cereals (0.09-0.13) or bare fallow (0.15). However, the corresponding losses of total P were largest from bare fallow (1.29) less from permanent pasture (0.59-1.16) and least from spring cereals (0.23-0.66) (all $kg \cdot ha^{-1} \cdot y^{-1}$). The P fertilization rate or form (organic, inorganic) had no influence on the P-losses by surface runoff from arable plots. On the permanent pasture plots P-losses increased with increased P-fertilization rate.However, P-losses by surface runoff from a field plot need not necessarily end up in the water environment but can be deposited in depressions down slope. The surface runoff of P to a stream depends very much on the geomorphology of the total landscape and the morphology and vegetation of the stream bank.

Wind erosion. Substantial amounts of soil and P can be lost due to wind erosion on susceptible land. Particularly sensitive are fine sandy soils located in open areas and without crop cover during spring time. The wind is able to carry soil particles smaller than 0.1 mm of diameter far away, whereas larger soil particles (0.1 to 0.5 mm) tend to be deposited in ditches and by hedges. Losses of about 2-3 cm soil sometimes occur in Denmark from land with a large proportion of fine sand (Kuhlmann, 1986). Two to three cm soil is equivalent to about 200-300 kg P/ha, which is a very large loss.

P-Balance for Danish agriculture

Based on information from Danmark Statistik (1987) about crop yields and import and export of plant and animal products I calculated an overall P-balance for Danish Agriculture. However, I was not able to obtain national figures for P-losses from leaching, surface runoff, wind erosion and effluents from excreta and plant product stores. Furthermore, for most P-flows it was not possible to distinguish between confined and grazing animals or permanent grassland and arable land. The results are therefore given in a simplified P-flow chart (Figure 2). On average Danish agricultural land receives about 40 $kg\ P \cdot ha^{-1} \cdot y^{-1}$ (22 + 16 + 1 + 1). About 20 $kg \cdot ha^{-1} \cdot y^{-1}$ is removed with the crops, leaving about 19 $kg \cdot ha^{-1}$ in the soil (if assumed that the input of P from atmosphere and sewage sludge balances the losses by leaching, wind erosion, and surface runoff).

P-Balances for other EEC-countries

As mentioned in the introduction the agricultural intensity of the countries in the temperate zone of Western Europe varies considerably. Some key figures for seven EEC-countries including Denmark are given in Tables 4 and 5. The permanent grassland area relative to the total agricultural area varies from 8 % in Denmark to 81 % in Ireland. Belgium and especially the Netherlands have much higher stocking rates of animals on concentrate feeds (pigs + poultry) than the other countries. This means, that the two countries have to import relatively large quantities of fodder-P in the form of cereals or cereal substitutes e.g. tapioca.

Based on information from Eurostat (1988) similar P-balances as the one made for Denmark were calculated for the six other countries. However, I was not able to get information about grass yields for Ireland, the Netherlands, and the UK and used estimates instead. The resultant, area weighted, average crop-P uptake rates are shown in Table 6 and Figure 2.

Table 4. Land use in 1986 of seven EEc-countries: Denmark (DK), Federal Republic of Germany (D), the Netherlands (NL), Belgium (B), France (F), Ireland (IRL) and the United Kingdom (UK), (Eurostat, 1988)

	DK	D	NL	B	F	IRL	UK
			10^6 ha				
Total land area	4.2	24.4	3.4	3.1	54.3	6.9	24.1
Agric. area	2.8	12.0	2.0	1.4	31.4	5.7	18.6
			% of agric. area				
Perm. grassl.	8	38	55	45	38	81	62
Arable land	92	60	43	53	57	19	37
Leys a.o. green fodder crops	12	10	12	11	17	10	9
Cereals	56	40	8	25	30	7	22
Root crops	8	6	15	14	4	2	3
Pulses and oilseeds	13	3	2	1	6	0	2

Table 5. Livestock and stocking rates in 1985 of seven EEC-countries (based on Eurostat, 1988). Note that the stocking rate of roughage eating animals (cattle, sheep, horses) is based on the roughage area whereas that of animals eating concentrated feeds (pigs, poultry) is based on the area with cereals and pulses.

	DK	D	NL	B	F	IRL	UK
			10^6 LU*				
Total livestock	4.6	19.6	8.6	4.2	25.0	5.3	16.3
			% of total LU				
Cattle, sheep, horses	48	65	55	61	80	93	78
Pigs	48	30	33	33	11	5	12
Poultry	4	5	12	7	9	2	10
			LU/ha				
Stocking rate							
Cattle, sheep, horses LU/ha RA†	3.3	2.2	3.6	3.1	1.2	0.9	1.0
Pigs, poultry LU/ha CA§	1.4	1.4	18.8	4.8	0.5	1.0	0.9
All animals LU/ha AA¶	1.6	1.6	4.3	3.0	0.8	0.9	0.9

*LU (livestock unit): 1 LU is equivalent to 1 dairy cow.
†RA (roughage area): grassland + leys + green fodder + fodder beets.
§CA (area with cereals and pulses).
¶AA (agricultural area).

Furthermore, I could not obtain information about the fodder use from grassland of the six other countries. I therefore calculated the P in fodder

and P in excreta by means of the distribution coefficients found for Denmark (Table 3) and from information about the animal production of the six countries. The results (Figure 2) are naturally open to debate. but nevertheless, illustrate that the overall P-cycling is very different from country to country.

It may be seen that Denmark and Germany produce less and Netherlands and Belgium much less fodder-P than eaten by their animals. Assuming that 1 kg $P \cdot ha^{-1}$ goes back to the soil with seeds and conservation residues then the net amount of fodder the four countries have to import each year is equivalent to 7, 8, 59 and 21 kg $P \cdot ha^{-1}$ respectively. France, Ireland and UK seem to produce enough fodder. France is actually exporting cereal grain equivalent to 3.6 kg $P \cdot ha^{-1}$ (Eurostat, 1988).

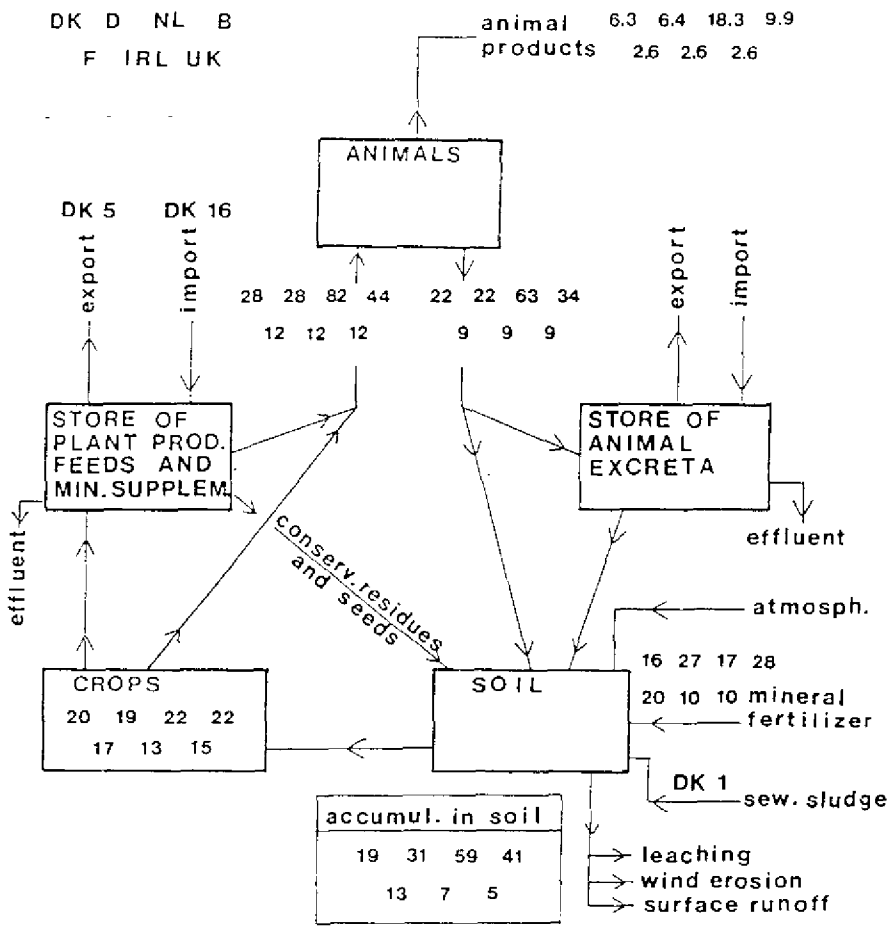

Figure 2. Overall, average P-cycling in the agriculture of seven EEC-countries expressed as kg P per ha agricultural area per year. P in feeds and excreta was calculated from P in animal products (see text). The annual accumulation of P in soil was calculated assuming i) a P return of 1 kg with conservation residues and seeds and ii) that the input from atmosphere and sewage sludge balanced the losses by manure outlet, leaching, surface runoff and wind erosion.

Assuming that P inputs from the atmosphere and sewage sludge balance the P-losses due to excreta effluents, leaching, surface runoff, and wind erosion, then the P accumulation in the soil of the seven countries should vary between 5 and 50 kg $P \cdot ha^{-1} \cdot y^{-1}$, i.e. by an order of magnitude.

Table 6. Average dry-matter yield, DMy ($t \cdot ha^{-1} \cdot y^{-1}$) and calculated P-uptake, Pu ($kg \cdot ha^{-1} \cdot y^{-1}$) of main crops in seven countries from 1983 to 86. The yields were obtained from EUROSTAT (1988) and converted to dry-matter yields assumming the following DM percentages: green maize: 20 %, potatoes: 25 %, beets: 20 %, cereal grain: 85 %. Furthermore, top DM-yield of beets was assumed to be 40 % of the root yield and the cereal straw yield 2/3 of the grain yield.

	P-conc. mg kg-1 DM	DK		D		NL		B		F		IRL		UK	
		DMy	Pu	DMy	Pu	DMy	Pu	DMy	Pu	DMy	Pu	DMy	Pu	DMy	Pu
Perm. pasture	2.6	5	13	5.9	15	8	21	7.8	20	4	10	4	10	4	10
Leys	3.3	9.5	31	8.4	28	11	36	10.7	35	9	30	9	30	9	30
Green maize	2.5	7.6	19	9.1	23	9.2	23	9.1	23	7.8	20	-	-	-	-
Potatoes	2.2	8.6	19	8.1	18	9.9	22	8.5	19	7.4	16	5.3	12	8.[illegible]	19
Beets															
Roots	1.6	10.7	17	11.8	19	10.4	17	9.9	16	11.3	18	8.7	14	8.[illegible]	13
Top	2.6	4.3	11	4.7	12	4.2	11	4.0	10	4.5	12	3.5	9	3.[illegible]	9
Cereals															
Grain	3.9	4.1	16	4.4	17	5.7	22	5.1	20	4.7	18	4.6	18	5.[illegible]	20
Straw	0.8	2.7	2	2.9	2	3.8	3	3.4	3	3.1	3	3.1	3	3.[illegible]	3
Average P-uptake weighted by crop average			20		19		22		22		17		13		15

It should be borne in mind that these are average figures and that some regions and individual farms produce considerably more manure-P. For example, in part of the Peel Region in the Netherlands the manure-P production amounts to about 200 kg $P \cdot ha^{-1} \cdot y^{-1}$ (van Boheemen, 1987). As a result, restrictions have been placed on the manure application in the Netherlands. From now until 1995 the maximum allowed application rates of manure P are reduced step by step from 153 to 76 kg $P \cdot ha^{-1} \cdot y^{-1}$ on arable land and from 104 to 76 $kg \cdot ha^{-1} \cdot y^{-1}$ on grassland (van Boheemen, 1987).

Conclusion

Based on the average net-input of P to the agriculture the following order can be drawn up for seven EEC-countries located in the temperate zone of Western Europe.: Netherlands: 59, Belgium: 41, Germany: 31, Denmark: 19, France: 13, Ireland: 7, and United Kingdom: 5 kg $P \cdot ha^{-1} \cdot y^{-1}$.

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PHOSPHORUS CYCLING IN INTENSIVE ARABLE AGRICULTURE

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Introduction

In 1842 J.B. Lawes of Rothamsted, England, patented a method for manufacturing superphosphate from rock phosphate and sulphuric acid and built the first artificial fertilizer factory in London. More important, scientifically, he together with J.H. Gilbert, started field experiments at Rothamsted in 1843 testing amongst other inorganic salts, superphosphate. This was to compare the plant nutrients, N P K Na Mg Si in these salts, singly and in various combinations with the effects of farmyard manure on a range of arable crops and grassland. Most of these experiments still continue, collectively they are known as the Classical experiments. Early results showed that crops responded to applications of phosphorus in excess of the quantity removed in the crop. Similar observations were subsequently made in other parts of the world. The fate of phosphorus not utilized by crops is of vital importance to the economics of using fertilizer P.

As a result of the foresight of Lawes and Gilbert and the efforts of others who followed them, a unique collection of crop and soil samples taken periodically throughout the Classical experiments has been built up. Data from them and from shorter-term experiments on the silty clay loam at Rothamsted, a sandy loam at Woburn and a sandy clay loam at Saxmundham are used here to illustrate our knowledge of phosphorus cycling in intensive agricultural systems under arable crops together with some reference, where appropriate, to grassland. Most of the soils have pHs (in water) ranging between 6.0 and 7.5. The discussion will center round the processes shown in Figure 1 and will concern mainly P added in superphosphate and farmyard manure (FYM).

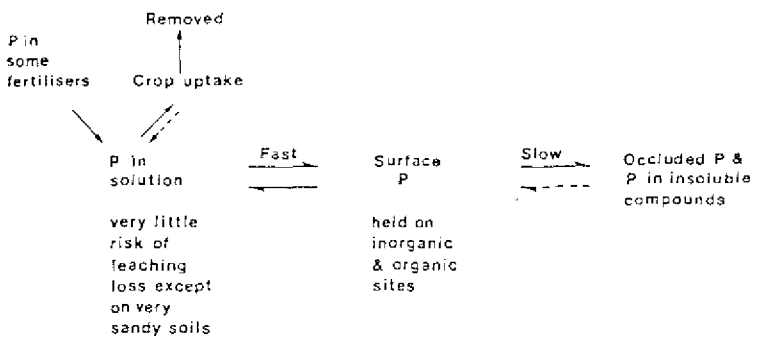

Figure 1. Schematic representation of changes taking place when water soluble phosphorus is added to soil.

Methods of analysis

Total P. Two methods for determining total P have been used at Rothamsted. Perchloric acid digestion is rapid and gives a good colorimetric finish with vanado molybdate. The use of perchloric acid was abandoned for safety reasons although no explosion ever occurred with soil digests. Sodium carbonate fusion in platinum crucibles is slower and more expensive and care is needed with the molybdenum blue finish in automated analytical systems. Mattingly (1970a) derived a factor to convert perchloric acid digest results to those obtained by fusion and data presented here are as by sodium carbonate fusion.

Readily-soluble P. It is important to have a reproducible, analytically convenient method of analysis to assess the phosphorus supplying power of soil and the likely response by crops to an application of P fertilizer. Many reagents have been tried. In 1872 Liebig tested various dilute acids to distinguish soils from the Rothamsted Classical experiments with and without P and K additions (Johnston 1969); Dyer (1984) later used 1% citric acid. Warren (1956) and Warren and Johnston (1965) tested six reagents on soils of known manuring history at Rothamsted on which crop responses to P had also been measured. By far the best method was that of Olsen (1954), using 0.5 M $NaHCO_3$ at pH 8.5 as the extractant. This method is now extensively used in both research and advisory work in England and Wales. Readily soluble-P data given here which were obtained by Olsen's method, will, for convenience, be referred to simply as soluble P.

Possible sources of error in P balance studies

Whilst it is usually possible to get reliable estimates of the P applied to and removed in crops, relating the difference or balance to changes in soil P content depends on a number of factors. In experimental work, especially on small plots, a major factor can be soil movement across plot boundaries, whilst on both an experimental and field scale the possibility of leaching and erosion losses must be considered.

Soil movement. In all the Classical experiments started by Lawes and Gilbert the amount of superphosphate applied each year was adjusted to supply 34 kg P ha^{-1}. In 1852 the Hoosfield Barley experiment commenced and 102 years later, in 1954 transects of closely spaced samples across and along the plots showed that the plot boundaries there was some loss of total P on P treated soils and a gain of P on plots without P fertilizer, (for some data see Warren and Johnston 1967). Later, Johnston (1975) was unable to reconcile a P balance in the Market Garden experiment on a sandy loam at Woburn. The reason (found subsequently, McGrath per comm.) was that much phosphorus had moved across plot boundaries (Figure 2). This can be a major source of error when relating nutrient balances to soil data.

In addition, discussion with Dr. E. Sibbeson also suggested that, even in carefully conducted field experiments, soil movement across plot boundaries was likely to occur when conventional farm machinery was used. Sibbeson and Andersen (1985) produced a "diffusion" or "transport" coefficient for soil movement on the sandy soil at Askov Experimental Station in Denmark. Applying the same concept McGrath and Lane (unpublished) have calculated a similar factor, but of smaller magnitude, using data for the total content of a number of trace elements in variously treated plots on the Woburn Garden experiment. Less soil movement would be expected on a sandy loam than a sand so the factor

should be smaller. It would be even smaller on heavier textured soils like those at Rothamsted.

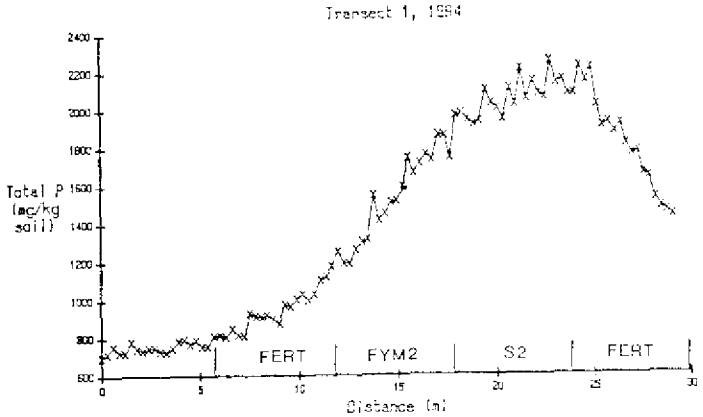

Figure 2. Changes in total P content of soil along a transect across plots receiving superphosphate (Fert), farmyard manure (FYM 2) and sewage sludge (S2). FYM2 and S2 received 7720 and 13130 kg P ha^{-1} in addition to superphosphate applied to all plots.

In the Woburn Reference experiment (Widdowson et al. 1982), which lasted 20 years and was also on a similar sandy loam soil to the Market Garden experiment, all cultivations were by hand and soil movement between plots prevented. The treatments included both superphosphate, FYM and FYM plus superphosphate. A complete P balance has been prepared and this can be related to changes in total P content in the top 25 cm of soil.

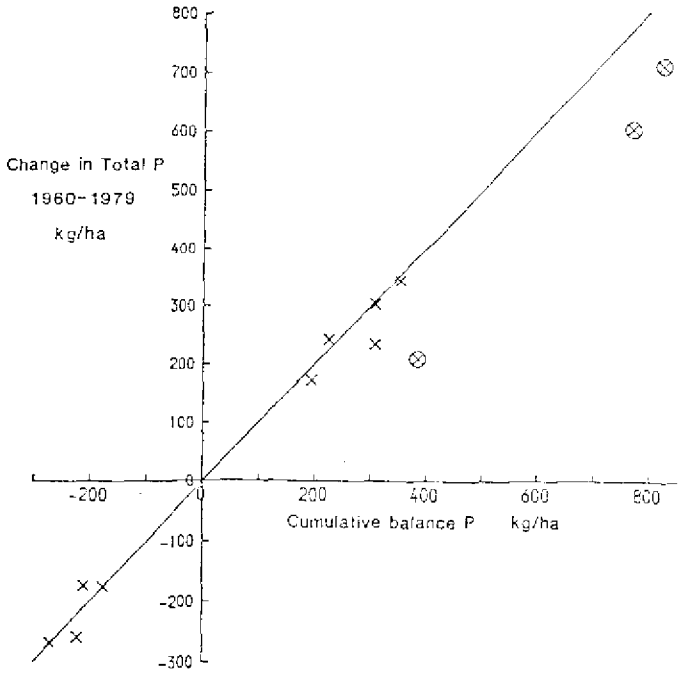

Figure 3. Relationship between change in total P, $kg \cdot ha^{-1}$, and cumulative P balance, $kg \cdot ha^{-1}$, in an experiment where soil movement between plots was prevented. Plots receiving farmyard manure ⊗ were excluded from the analysis.

A straight line relationship fitted to all the data accounted for 97% of the variance but the line was not 1:1 and did not go through the origin. However, when FYM-treated soils were excluded from the analysis a straight line relationship which was 1:1 and went through the origin, accounted for 98% the variance (Figure 3). The FYM-plots, circled, which have been added to Figure 3, were excluded because of the possibility that P had been leached below the top 25 cm which was the only horizon sampled and analysed.

Thus the possibility of soil movement must be considered seriously when assessing and interpreting results from experiments, especially on small plots, unless precautions have been taken to prevent movement as in the Woburn Reference experiment.

Leaching. Dyer (1894) used 1% citric acid to extract P from variously treated soils taken in 1889 from the Hoosfield Barley experiment, 38 years after it started. He showed that on this silty clay loam there was no increase in P soluble in 1% citric acid in the subsoils (below 23 cm) of P-treated plots. He confirmed this by estimating that, averaged over all treatments, 886 kg P ha^{-1} should have remained in the top soil whilst by analysis he found an extra 888 kg P ha^{-1}. This soil P content conceals values which ranged by ±7% of the average (see Johnston 1976) but well within the errors of sampling and analytical methods then available.

More recently and after many more years of P manuring, Johnston (1976) gave results from other long-term experiments on both a silty clay loam soil and a sandy loam and with treatments other than superphosphate. These data, some are in Table 1, showed that on a silty clay loam where arable crops given PK fertilizers have been grown, total P in the surface horizon has almost doubled compared with the unmanured soil and there has been no enrichment below 30 cm; apparent enrichment in the 23-30 cm horizon is probably because of occasional ploughing below 23 cm or perhaps to greater uptake of P from this layer on plots without P. Where FYM was applied total P in the uppermost horizon is the same as where PK fertilizers were given and there has been appreciable enrichment ob both the 23-30 and 30-46 cm layers. Movement of P into these two lower horizons was even larger when superphosphate and FYM were applied together. Where permanent grassland has been grown on a soil, with a pH a little over 7 in water, there has been P movement into the 23-30 cm horizon where superphosphate has been applied even though there has been no ploughing.

At Woburn horticultural crops were grown on a sandy loam soil and all plots received the same application of superphosphate, some had organic manures supplying much P in addition. There has been much P enrichment of the sub-surface horizons where FYM was applied but not where much larger quantities of P were applied in sewage sludge (Table 1). The sludge used between 1942 and 1963 has been anaerobically digested and lagoon dried so it is probable that much soluble phosphorus had been removed at the treatment works.

Sewage now tends to be treated in different ways, which may have other effects on P mobility. If iron and aluminium salts are used this could lead to the residual P having low solubility when applied to soil. Conversely the application of undigested sludges could lead to a greater movement of P down the profile. Very similar problems may arise from the spreading of animal slurries especially to soils in autumn when deep cracks, worm holes and large pores may lead to much P moving down the profile.

Table 1. Effect of cropping and form in which P was applied on movement of P into the subsoil - total P mg kg^{-1}

	Soil type and treatment								
	Silty clay loam						Sandy loam		
	Arable crops				Permanent grassland		Horticultural crops		
Depth cm	No P	PK	FYM	FYM + P	No P	NP	PK	FYM	Sewage sludge
0-23	777	1350	1376	1971	573	1425	1120	1780	3000
23-30	464	541	649	781	557	785	-	-	-
30-46	413	446	525	579	500	600	850	960	850
below 46	401	396	442	411	-	-	790	860	770

Adapted from Johnston (1976)

The downwards movement of P where FYM had been applied for many years suggests that P may be transported as water-soluble, low molecular weight organic P compounds. In permanent grassland P enrichment of the 23-30 horizon where P was applied as superphosphate again may have occurred following the movement of similar compounds released on the death of roots near the surface.

Leaching of P applied in superphosphate can be much greater from lighter textured soils. Mattingly (1970b), found only 7% of the residual phosphate was retained in the top 15 cm of a sandy podzol after superphosphate applications lasting for eight years. Interestingly, much of the leached phosphorus was found in the B1 and B2 horizons (Bolton and Coulter 1966) and deep rooted crops might have benefited from this phosphorus. On this soil much more of the P applied in rock phosphate was retained in the surface soil and, judged by the uptake of P by ryegrass grown in pots in the glasshouse, it was available to plants.

The possibility that phosphorus may have moved down the profile must be considered when relating soil P balances to changes in soil P content.

Erosion and movement over the soil surface. Whilst leaching of phosphorus may be relatively unimportant in many soils, erosion and surface movement may need to be considered. A long-term phosphate experiment on the sandy loam at Woburn (Johnston, Mattingly and Poulton 1976) had to be abandoned later because there was much erosion during one winter.

Both erosion and movement of slurry and sewage over the soil surface, especially when applied to frozen or very dry ground, can lead to appreciable transfer of P into aquatic ecosystems from intensively managed arable and grassland.

Relating P balance to soil P data

P balance and total P in soil. If there is little soil movement across plot boundaries and no loss of P by leaching or erosion, then the balance of phosphorus remaining in the soil and total soil P should be well related. Figure 3 gives one example for a long-term experiment on a sandy

loam. Mattingly, Johnston and Chater (1970) showed it to be true also for large additions of phosphorus during four years on a sandy clay loam at Saxmundham and Johnston and Penny (1971) for a long-term experiment at Rothamsted.

Relationship between total and readily-soluble P in soil. It is important to know the extent to which total phosphorus accumulates in soil because this relates to its transfer to other ecosystems. However, for agricultural soils, whether arable or grassland, it is essential to know whether these residues are available to plants. In our experiments and many others elsewhere, P soluble in 0.5 M $NaHCO_3$ has been found to be a good index of plant availability (see later). Figures 4 and 5 show relationships between the increase in total P and the amount of soluble P for soils at Rothamsted, Woburn and Saxmundham. For soils to which P has been added regularly (Figure 4) the percentage variance accounted for was 93%. Without exception the lighter textured soils at Woburn were above the line. The relationship suggests that about 13% of the increase in total P remains soluble in the sodium bicarbonate reagent. Because the data in Table 1 and Figure 1 show that some P has leached below the surface 23 cm where FYM was applied the data for fertilizer - and FYM -treated soils was analysed separately. For fertilizer treated soils (not shown) the % variance accounted for increased to 96%, and 15% of the increased total P remained soluble. For FYM-treated soils (also not shown) the variance accounted for was 95%, and 13% of the increased total P remained soluble. Thus after many applications of FYM and superphosphate over many years the solubility of the residual P in 0.5 M $NaHCO_3$ at pH 8.5 was very similar irrespective of the form in which the P was added.

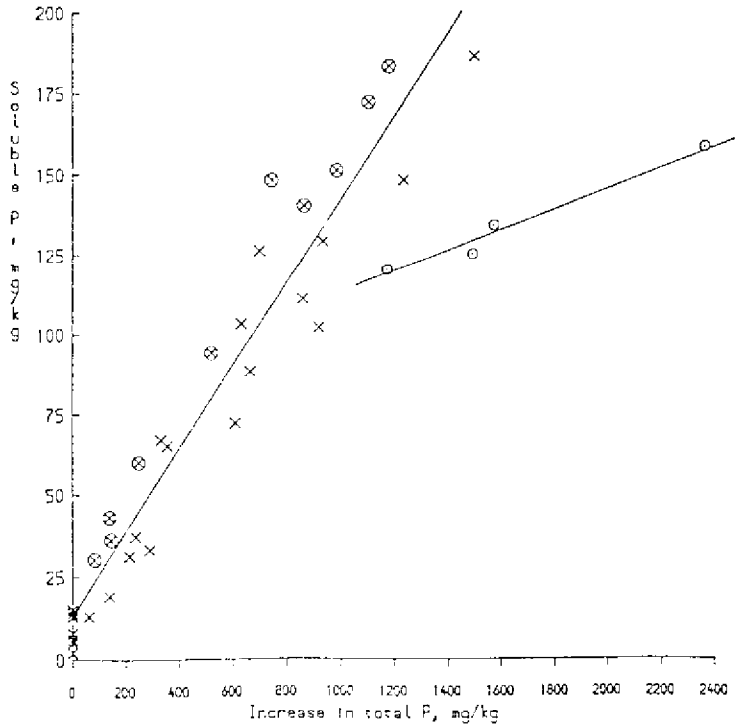

Figure 4. Relationship between $NaCHO_3$-soluble P and increase in total P in long-term experiments receiving P regularly. Light textured soils, ⊗; medium textured soils, X; light textured soils receiving sewage sludge, O (see text).

Soils which received sewage sludge were not used in the above analysis but have been added to Figure 4 to show that less than 4% of the extra total P has remained soluble (see earlier discussion for possible reasons).

Four of the soils in Figure 4 received FYM or vegetable compost in the Market Garden experiment (Johnston 1975). They were sampled in 1960, 18 years after the experiment started and the data fit the relationship well. In 1967 the soils were re-sampled and Table 2 shows that whilst total P had increased appreciably there had been little further change in soluble P. This suggests that sites holding P soluble in this reagent had become saturated. It is not known to what extent this "saturation" is an important feature in many soils but it does suggest that there could be an upper limited above which P manuring would not be justified.

Table 2. Change in both total and NaHCO3-soluble P with time in a sandy loam soil receiving large amounts of farmyard manure and vegetable compost

Treatment	Total P mg/kg		$NaHCO_3$-soluble P mg/kg	
	1960	1967	1960	1967
FYM rate 1	865	1031	140	149
rate 2	1180	1491	183	182
Compost rate 1	985	1044	151	146
rate 2	1105	1324	172	173

Rates 1 and 2 were 37.5 and 75 t/ha fresh material each year

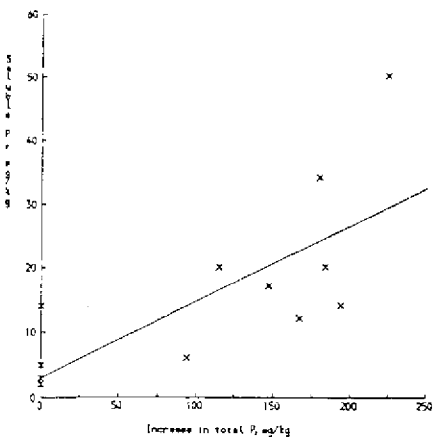

Figure 5. Relationship between NaHCO3-soluble P and increase in total P in long-term experiments where P was applied intermittently.

When P was added either at infrequent intervals or some years before the measurements were made, there is much more scatter in the data (Figure 5); the percentage variance accounted for was only 47%. The gradient of the fitted line gives an average of 12% of the extra P remaining soluble, not appreciably different from the value given by Figure 4. However, in some cases the values are much smaller than this which may reflect the effect of soil type, age of residues and cropping patterns.

Organic phosphorus

The determination of total organic P in soil is notoriously difficult and accurate estimation of changes in organic P, especially over short periods, are likely to be subject to even more error (Chater and Mattingly 1980, cite a number of references). However, it is important to get some estimate of this fraction of total soil P and the way it changes as farming systems change and this has been done at Rothamsted and Saxmundham (Chater and Mattingly 1980) and at Woburn (Mattingly et al. 1975). These authors used ignition and extraction methods and reported results as averages of both.

Changes in organic P were always related to changes in total N and C, but, like Black (1968), Chater and Mattingly (1980) found no evidence for a fixed ratio of gains and losses. changes due to modification of mainly arable farming systems were often small over many years and changes in soil pH often had appreciable effects.

In one experiment lasting 110 years, two Norfolk 4-course rotations, turnips, barley, fallow or clover, winter wheat, were compared together with a test without and with NPK fertilizers. Where the soil was fallowed once in four years the increase in organic P was about 15% of the extra total P, with the clover rotation the extra organic P was about 30% of the increase in total P. Under a 12-year grass ley which followed these rotations, the increase in organic P was small (6 mg P kg^{-1}) although the ratios of the increases ΔN: Δ org P, 158: 10: 0.5 were very similar to those for pasture published by Barrow (1961).

Where FYM was applied, Chater and Mattingly (1980) found that when 35 t/ha was applied each year for 26 years only about 30% of the organic P in the FYM could be found as extra organic P in soil. When 100 t ha^{-1} was applied during two years 81% of the added organic P remained as extra organic P in soil the following year but 6 years later only 12% was still present as organic P.

Johnston (1981) showed that after 18 years of applying superphosphate, sewage sludge and FYM, there were large differences in the total P in the surface 0-23 cm depth of soil and small differences in the 30-46 cm horizon (Table 3). There was much more organic P in surface soils treated with sludge but there was no significant difference between the variously treated soils when organic P was expressed as a percentage of total P. There was also little difference in percentage organic P between surface and subsoils.

For soils under arable cultivation Chater and Mattingly (1980) calculated that the net rate of mineralization of organic P ranged from 0.5 to 8.5 kg P/ha each year. The values were least (0.5 - 1.4 kg P) on old arable soils which had received no organic manures and greatest (7.6 - 8.5 kg P) on soils recently ploughed out from permanent pasture or containing residues from recent large amounts (100 t ha^{-1}) FYM. Even the largest amounts of P mineralized would supply only about half the P removed in a cereal crop

yielding 4.5 to 5.0 t ha^{-1} grain. The amounts of P turning over in grassland soils may be much greater. Brookes et al. (1984) found that the flux of P through the soil microbial biomass was as large as 23 kg P ha^{-1} each year for the grassland soils they examined. This was about the same quantity of P which was removed in the harvested hay crop.

Table 3. Amounts of organic and total P, mg kg^{-1}, in soils in 1960 treated with superphosphate, sewage sludge and FYM

Depth cm	Treatment[a] 1942-60	Organic P	Total P	$\frac{\text{Organic P}}{\text{Total P}} \times 100$
0-23	Superphosphate	146	1120	13
	Sewage sludge	350	3000	12
	FYM	182	1780	10
30-46	Superphosphate	104	850	12
	Sewage sludge	126	850	15
	FYM	100	960	10

[a] Sewage sludge and FYM applied at 75 t/ha fresh material each year

Transfer of phosphorus between readily-soluble and less-soluble forms

Table 4. Relationship between P balance and decline in $NaHCO_3$-soluble P in an experiment on a sandy clay loam, Saxmundham 1969-82

$NaHCO_3$-soluble P mg/kg 1969	3	7	21	28	39	44	54	67
P removed in crops kg/ha 1969-82	94	153	217	237	253	256	263	263
Decrease in soluble P kg/ha 1969-82	8	12	27	50	65	78	87	120
Change in soluble P as a % of crop uptake	8	8	12	21	26	30	33	46

Figure 1 shows the transfer of phosphorus not only between readily-soluble and water (or soil solution) soluble fractions but also between readily-soluble and less-soluble forms. Transfer from readily-soluble to less-soluble forms is implied in the data in Figures 3 to 5 and is generally accepted. There is less information on the reverse process. Johnston and Poulton (1977) gave some data from a long-term experiment at Rothamsted where different levels of soil-P accumulated between 1856 and 1901 from applications of superphosphate and FYM. During this period the increase in soluble P (in kg/ha) ranged between 14 and 17% of the extra P remaining in the soil. After 1901 crops were grown without further additions of P. The decline in soluble P during 1903-58 and 1959-74 accounted for only 38% and 21% respectively of the P removed in the harvested crops. Similar evidence for the support or

buffering of soluble P by less-soluble reserves is in Table 4 which shows data during 1969-1982 from an experiment on a sandy clay loam with a wide range of amounts of soluble P. On soils with least soluble P nearly all the P removed in the crop came from the non-soluble reserves. On four soils with larger amounts of soluble P yields were very similar and P offtakes almost identical but even then not more than 50% of this offtake was accounted by a decline in soluble P.

Modelling the decline of soluble P in soil. The plots from which the data in Table 4 are taken were sampled in alternate years and soluble P determined (Figure 6A). Visual inspection of this data suggested that each individual decay curve was a segment of a more comprehensive exponential-type decay curve and suitable horizontal shifts brought all the individual curves into coincidence (Figure 6B). From the combined curve it was calculated that the half-life of soluble P in this soil was nine years.

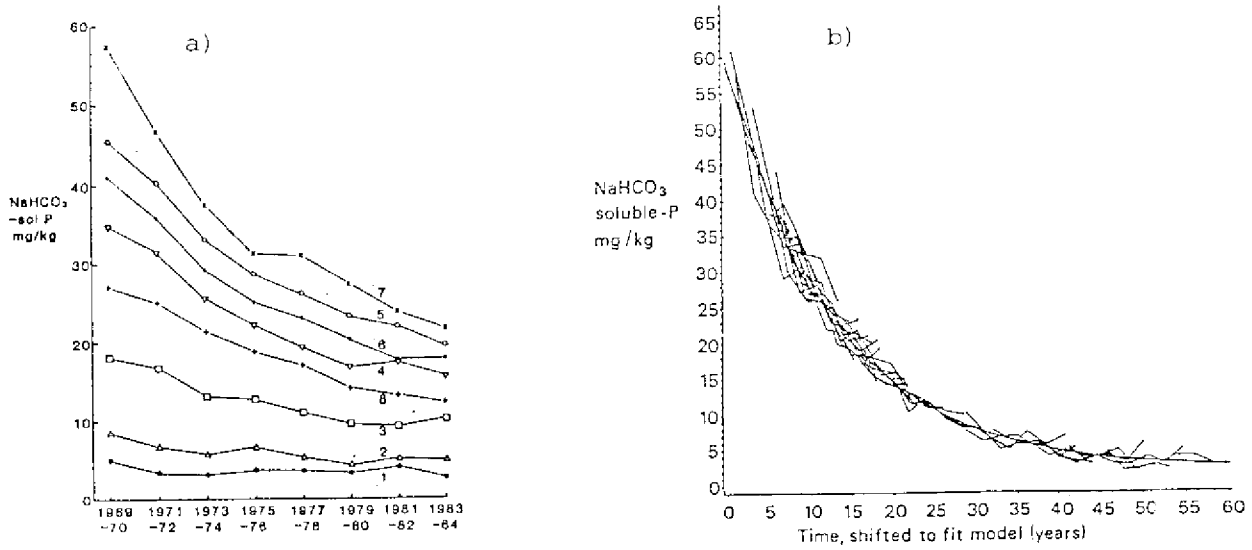

Figure 6. Decline in NaHCO3-soluble P in soil given no P, a) Soils from individual plots, b) Computer print-out showing all data for individual plots shifted horizontally to bring curves into coincidence.

Crop response to soluble P in soil

Most agricultural experiments have tended to test the response of crops to additions of freshly applied P fertilizer. Statistical analysis of a series of experiments in England and Wales (reviewed by Johnston et al. 1985), which measured the response by a range of arable crops to fresh P showed that by far the largest proportion of the variance in this response could be ascribed to differences in soluble P in soil. Subsequently a series of experiments was started at Rothamsted, Woburn and Saxmundham to relate the yield of a range of arable crops to soluble P in soil. Results on a sandy loam at Woburn were given by Johnston et al. (1976). The data in Figure 7 (taken from Johnston et al. 1985) are for the sandy clay loam at Saxmundham. The asymptotic regression of yield on soluble P accounted, on average for 84% and 73% of the within-year variance in the fields of potato tubers and sugar from sugar beet respectively. Clearly there is a relationship between yield and soluble P in soil. Yields of both potatoes (Figure 7b) varied by a factor of two between groups of years but the point of inflection in the response

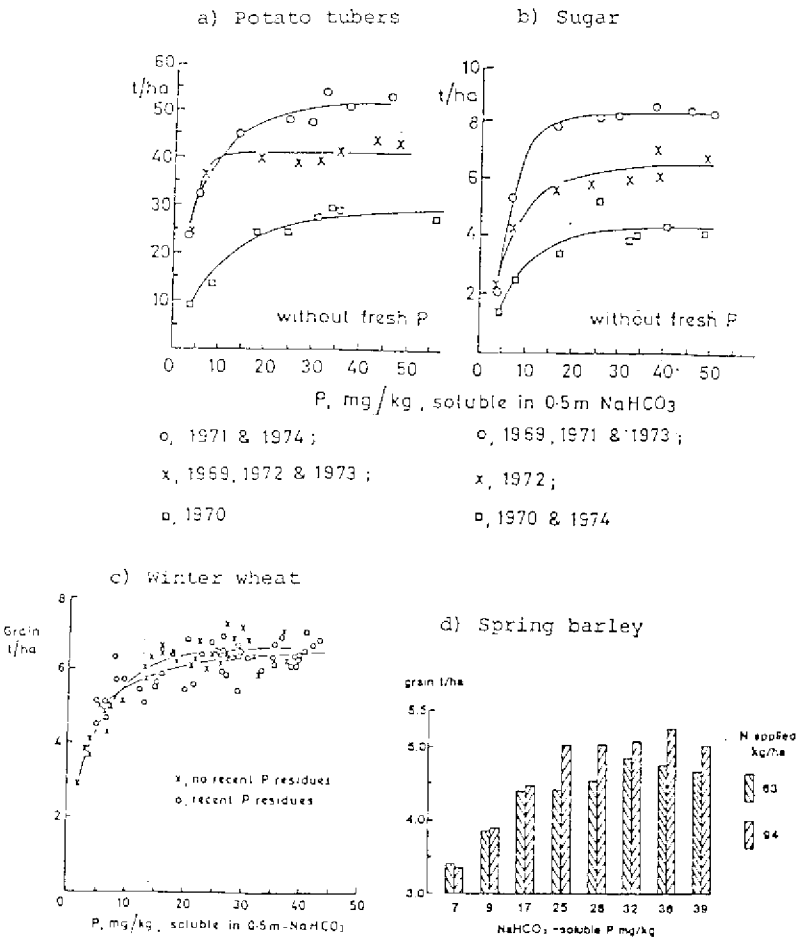

Figure 7. Asymptotic regression of crop yield on $NaHCO_3$-soluble P averaged over years with similar response for potatoes (Figures 7a); sugar (Figure 7b); winter wheat (one year only) testing P residues of different ages (Figure 7c); and the response by spring barley to two amounts of fertilizer N (Figure 7d).

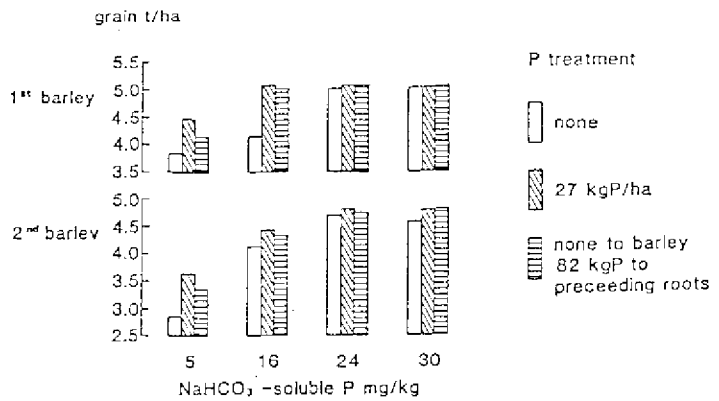

Figure 8. Response by spring barley to annual and triennial applications of P at different levels of soil P.

curve was similar. A factor other than soluble P was controlling yield and the authors suggested that this was summer rainfall. For winter wheat (Figure 7c) there was no significant difference in the response to 'old' or 'new' residues whilst spring barley did not respond to N below a certain level of soluble P (Figure 7d).

This lack of response to extra soluble P in soil lead to experiments testing rotational P manuring designed to maintain levels of soluble P in soil. Figure 8 shows that at very low levels of soluble P yields were increased more by annual P manuring than by the same total amount of P given once in three years (triennial manuring). With more soluble P in soil there was no response to either annual or triennial P dressings both of which maintained soluble P levels.

This suggests that rotational P manuring is a possibility which allows farmers some flexibility in managing their manuring programmes. Whilst it will be necessary to maintain a soil P level suitable for the most sensitive crop in the rotation, this can in part, be arranged by applying fresh P fertilizer just before the sensitive crop is grown. For example, most of the fields on Rothamsted Farm follow a seven-course rotation but P is applied only twice in that rotation (Johnston et al. 1981). The total amount of P given is equal to the estimated offtake in all crops grown in the seven years. Seventy percent is applied before potatoes grown in the fifth year, part in autumn to be ploughed in, part in spring before planting. The remaining 30% is applied in the autumn of the second year before spring barley is grown in the third year. This approach to P manuring can be tested by soil sampling to check that there is no large increase or decrease in soluble P in the soil. On Rothamsted Farm this sampling is done in the spring of the year before potatoes are grown because that is likely to be the time when soils will have least soluble P. Recent checks have shown that most of the Rothamsted fields are being maintained at acceptable levels of soluble P using this manuring policy.

Summary

On soils with pHs ranging from 6 to 7.5 in water and textures ranging from sandy loam to silty clay loam the experimental results presented here suggest that P cycling in intensively managed arable soils can be quantified by an approach which seeks to determine balance sheets. There has been little significant loss of P by leaching especially when P has been applied as superphosphate. Changes in soluble P reflect changes in total soil P content. The latter accurately reflects the balance between P applied and that removed in the crop for both positive and negative values providing leaching and erosion did not remove P. Relating crop yield to soluble P in soil suggests that, irrespective of level of yield, there is a soluble P value above which yield does not increase appreciably. This value is different for different arable crops and tends to be larger for spring- rather than winter-sown crops. When the soils are above these "limiting values" P manuring can be on a rotational basis. When crops are grown in rotation, the aim will be to maintain soils at a satisfactory level for the crop most sensitive to P and fresh P can be applied just before that crop is grown.

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PHOSPHORUS FERTILIZERS-
CHANGES IN INORGANIC AND ORGANIC SOIL PHOSPHORUS FRACTIONS AFTER LONG-TERM SOIL FERTILITY EXPERIMENTS

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Introduction

Theories about the reaction of phosphate with soil have been described by several authors, e.g. Larsen (1967) and Barrow (1983). The problems involving P movement by diffusion and its uptake by plant roots have been reviewed by Nye & Tinker (1977) and Barber (1984). Despite a better understanding of the behaviour of P in soils, it is still difficult to predict the effectiveness of P applications and to estimate the value of P already present in soil.

The availability and ageing of fertilizer P varies with the type of P source and soil. Addition of water-soluble P usually gives a higher yield response in the year of application than slow-acting sources which, however, age more slowly (Larsen, 1967). Barekzai & Mengel (1985) followed the ageing of water-soluble P in different soils in a pot trial during six months. They found that the reduction in phosphate availability was highest in an acid brown earth and lowest in a rendzina. Therefore, for many acid and high P-fixing soils a slow-acting P-source is a better alternative than water-soluble P (Sanchez & Uehara, 1980). On the other hand, for soils that are less acid and that have a lower P-fixing capacity repeated applications of water-soluble P are often agronomically and economically justified.

The long-term effect of the added P in a weathered soil is usually a build-up of the inorganic P pool and a minor effect on the size of the organic P pool (Smeck 1985, Gunnarsson 1987, Sharpley 1986). Previous application of P can increase the amount of easily soluble P for many years (Johnston et al. 1976, 1986, Halvorson & Black 1985).

Changes in soil use and farming system may also influence the availability of soil P. Mineralization of organic P due to cultivation has been shown by Tiessen & Stewart (1983) and O'Halloran et al. (1987). A task which needs more investigation is the possibility of keeping the P in more easily soluble form through a favourable cropping system. A tendency for an increased amount of easily soluble P in a crop rotation for cattle production than in a crop rotation without livestock has been shown by Jansson (1983).

There are three physical chemical criteria for soil P characterization: equilibrium, kinetic and fractionation methods (Olsen & Khasawneh, 1980). In addition to fractionation methods concentrating on the inorganic P (Chang & Jackson 1957) or on the organic P (Anderson 1961, Bowman & Cole 1978) there is a more recent method which attempts to cover both aspects (Hedley et al. 1982). This method has been used for many American soils (Tiessen et al. 1984) and also in Spain (Trasar et al. 1986).

This paper deals with the P situation in the soils of two field sites which both have been subjected to different P fertilization and crop rotations in long-term soil fertility studies. Soil samples from these fields and a

growth chamber experiment with a new application of P fertilizer were used to characterize the P situation in the soils with regard to the recovery and availability of earlier and fresh P additions.

Materials and Methods

In 1957 a series of long-term soil fertility experiments was started in Skåne, the southernmost province of Sweden. Results from two of these six field sites will be discussed in this paper. Both sites have been cultivated for at least 100 years. One of the sites, Örja, is considered to be of high fertility and has not had cattle since 1912 and the other field, Orup, has a low fertility and had cattle until 1957. The location and meteorological data are presented in Table 1 and soil characteristics in Table 2. The clay fraction of both these soils consists of about 40 % mica, 20 % vermiculite and 40 % kaolinite. For a more detailed description, see Ivarsson & Bjarnason (1988).

Table 1. Location of the experimental fields and meteorological data (normal annual values 1951-1980) from the most representative meteorological station

Site	Lat. N	Long. E	Altitude (m)	Precipitation (mm)	Temperature °C
High F	55°53'	12°52'	10	730	7.9
Low F	55°49'	13°30'	75	865	6.9

Table 2. Soil characteristics (1957) for the fields

Site	Clay %	Sand %	Org C	Org N	pH[1]	CEC	B.S.[2]	P-AL[3]	K-AL[3]
			----$mg \cdot g^{-1}$---			$ceq \cdot kg^{-1}$	%	--$mg \cdot Kg^{-1}$--	
High F	16	51	13	1.3	7.2	20.2	100	59	80
Low F	12	54	26	2.2	6.2	13.2	67	24	38

1. in H_2O
2. Base saturation
3. P in ammonium lactate acetate extracts

The treatment design of the experiments includes all 32 combinations of two crop rotations, four PK levels and four intensities of N fertilization (Table 3). The second highest intensity of N fertilization was chosen for this investigation. Mean yields for the various crops are shown in Table 4 (Bjarnason & Seeger 1988).

Table 3. The treatment design

Crop rotations:	1. Cattle production	2. Without livestock
Year	Crop	
1957, 1961, 1965, 1969 1973, 1977, 1981, 1985:	Barley	
1958, 1962, 1966, 1970 1974, 1978, 1982, 1986:	Grass/Clover	Oilseed crop
1959, 1963, 1967, 1971, 1975, 1979, 1983, 1987:	Winter wheat	
1960, 1964, 1968, 1972, 1976, 1980, 1984, 1988:	Sugar beet	

PK levels

A. No PK addition
B. Replacement of PK removed by harvesting
C. Replacement + 60 kg P and 160 kg K.ha-1 and rotation (approx. double replacement)
D. Replacement + 120 kg P and 320 kg K.ha-1 and rotation (approx. treble replacement)

N levels ($kg \cdot ha^{-1}$)

	Barley	Grass/clover Oilseed crop	Winter wheat	Sugar beet
0:	0	0	0	0
1:	30	50	50	70
2:	60	100	100	140
3:	90	150	150	210

In rotation 1 straw and beet tops are removed, manure (20 tonnes ha-1) is applied to the sugar beet crop. In rotation 2 the crop residues are worked into the soil, no manure.

Table 4. Mean yields ($kg \cdot ha^{-1}$) 1964 -1983 for the various crops. Grain and oilseed yields are quoted on the basis of 15 % moisture, hay, and sugar beet on a dry matter basis

Field	Barley	Ley	Oilseed Crop	Winter wheat	Sugar beat
High F	3957	4588	1897	4996	9306
Low F	3183	5003	1236	3581	5805

For a growth chamber experiment soil samples were taken after 27 years of field experiments from both crop rotations and PK levels A and D. The 8 soil samples were dried at 40°C and ground to <2.0 mm. Subsamples of 200 g of soil were mixed with 200 g of sand, KNO_3 and fresh P fertilizers (0, 7, and 14 g corresponding to 0, 87.5 or 175 P $kg \cdot ha^{-1}$, the sand excluded). The soil/sand mixtures were put into shallow pots replicated three times and perennial ryegrass (Lolium perenne) was grown for 26 days, starting 18 days after fertilization.

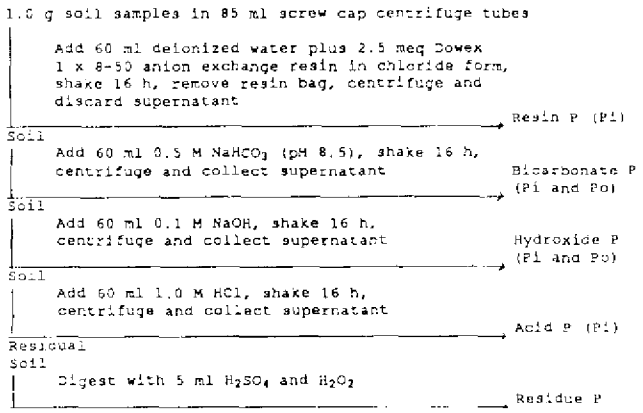

Figure 1. Sequential extraction procedure for soil P.

For chemical fractionation the soil sampled in the field was dried at 40°C and ground to <0.5 mm. The soil samples from the growth chamber experiment were not dried before extraction. In both cases 1.0 g of soil was extracted sequentially according to the procedure in Fig. 1, which is a modification of the one described by Hedley et al. (1982). The inorganic P content in the acidified (0.9 M H_2SO_4) or digested (conc. H_2SO_4 + H_2O_2) extracts was determined by the molybdate-ascorbic acid procedure of Murphy & Riley, modified by Watanabe & Olsen (1965). Thus, the content of organic P was obtained by difference between the digested and acidified extract.

According to Tiessen et al. (1984), the different P fractions can be described in the following way. Resin and bicarbonate extractable inorganic P are labile forms of P, adsorbed on surfaces of more crystalline P compounds, sesquioxides or carbonates. Hydroxide extractable inorganic P is associated with amorphous and some crystalline Al and Fe phosphates. Acid extractable P is largely Ca bound P. Bicarbonate extractable organic P is easily mineralizable and contributes to plant uptake. Organic P extracted with hydroxide is a more stable form. Finally, the residual fraction consists of occluded inorganic and organic P of minor importance for plant uptake, but also particulate organic material that may become available upon decomposition.

The fractionation experiment was analysed statistically according to a three-way classification with the interaction field*rotation*PK-level as the error term. The growth chamber experiment was analysed as a split-plot trial (Brook & Arnold, 1985) according to following model:

$$Y_{ijkl} = \mu + a_i + block_j + e_{ij} + \beta_k + a\beta_{ik} + d_{ijkl}$$

i=1-8 soils, j=1, k=1-3 fresh P additions, l=1-3

All statistical results were obtained using SAS programmes (SAS Institute Inc., 1985)

Field data were also used in a simulation model (Parton et al.1988). Simulations of the plant production, the nutrient uptake and the changes in the soil during 27 years were compared to real data (Sanford, this conference).

Results

The effects of P fertilization on the contents of total P in the topsoil are shown in Figure 2. At the start of the experiments the low-fertility site had an average P-content of 640 ppm in the topsoil and the high-fertility site had 450 ppm. The discrepancy between the 1957 values and the values for treatment B (replacement) can be explained by soil sampling and analytical errors.

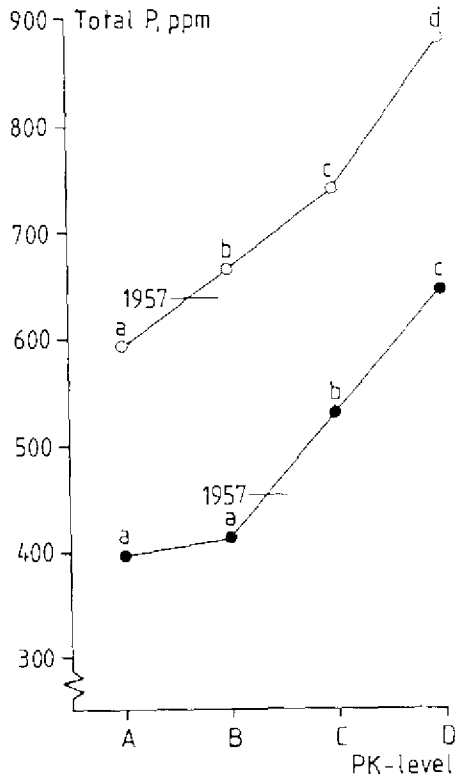

Figure 2. Total P in soil (the sum of the fractions obtained by the Hedley procedure) for the low-fertility site (unfilled circles) and the high-fertility site (filled circles). The mean values in 1957 and the mean values for each PK level 27 years later are shown. Different letters above the curve identify values differing at the 0.05 level of probability within each site.

P fertilization effects on the size of separate P fractions are shown in Figure 3. After 27 years of intensive P fertilization the increase in resin-extractable P was similar for the two sites, but at different levels. The high-fertility site had a somewhat higher effect of P fertilization on resin P

and lower on bicarbonate-Pi. The higher contents of total P at the low-fertility site (Figure 2) were due to higher contents of organic P, NaOH-P_i, and HCl-P. P fertilization increased NaOH-P_i more at the low-fertility site, and HCl-P only at the high-fertility site. The residual P was about 100 ppm for both sites and no differences due to treatment were found.

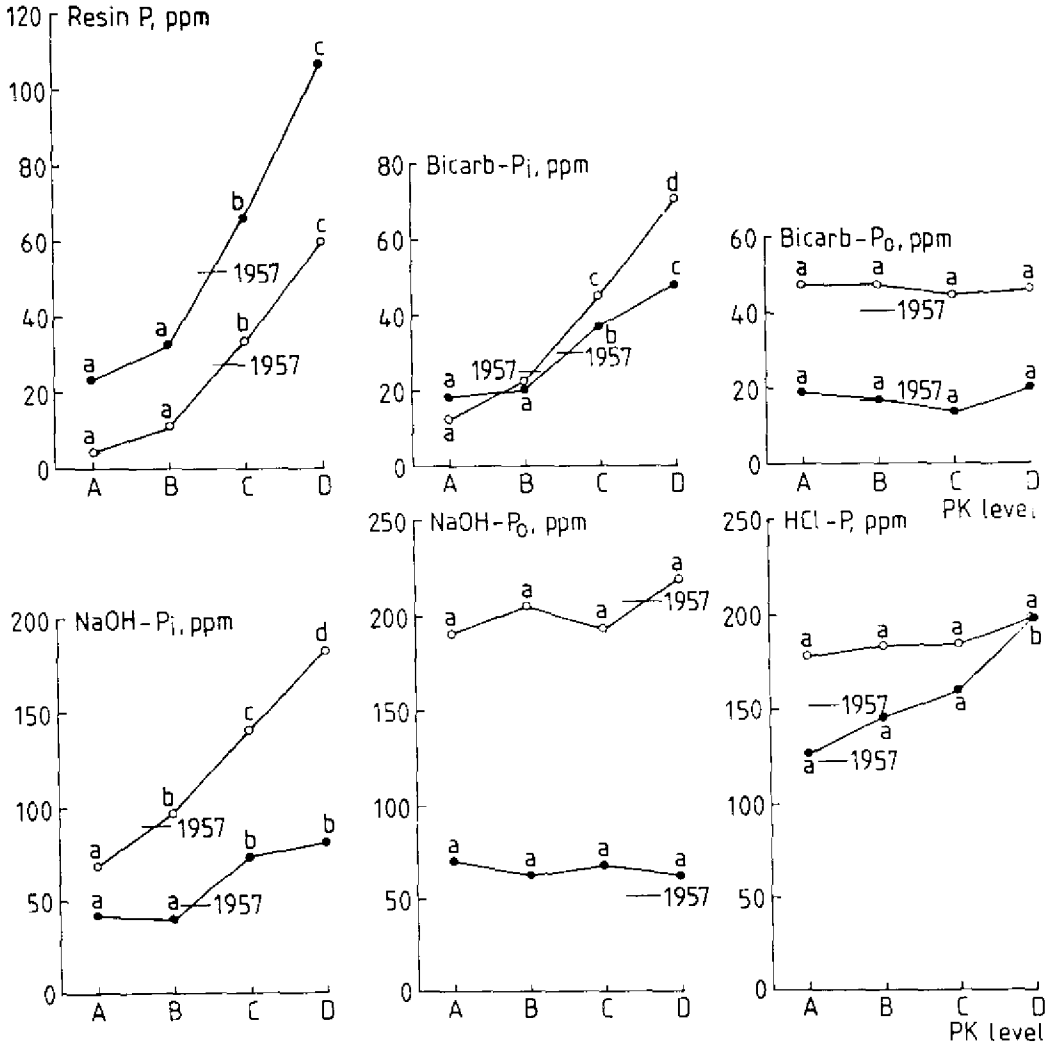

Figure 3. P fractions at different P fertilization levels for the low-fertility site (unfilled circles) and the high-fertility site (filled circles). The mean values in 1957 and the mean values for each PK level 27 years later over both crop rotations are shown. Different letters above the curve identify values differing at the 0.05 level of probability within each site.

The crop rotation for milk production had a higher content of resin P, inorganic bicarbonate P and acid P in the high-fertility soil (Figure 4). These were the only significant differences between the crop rotations.

Results from the growth chamber experiment showed that freshly added P increased the resin P 18 days after fertilization for all the chosen soils except one (Figure 5). The increase was largest in soil from crop rotation 1 and PK level D and larger on the high-fertility site.

The P-yields of perennial ryegrass also increased due to fresh P fertilizer (Figure 5). The largest increase was seen for the soil with 27 years of no P. The low-fertility site had both the highest and the lowest P-yields at all three levels of fresh P.

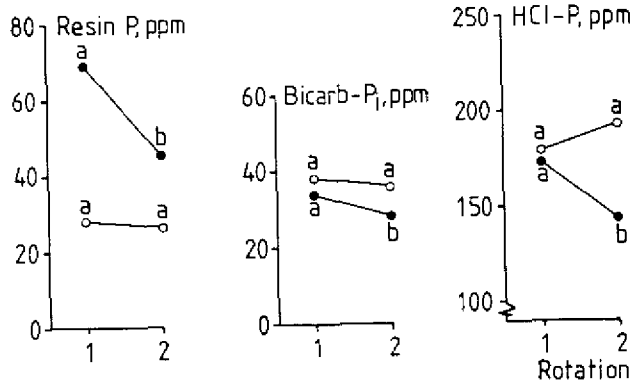

Figure 4. Resin P, bicarbonate Pi, and acid P for the low-fertility site (unfilled circles) and the high-fertility site (filled circles) at different crop rotations (1. milk production 2. without livestock). Different letters above the curve identify values differing at the 0.05 level of probability within each site.

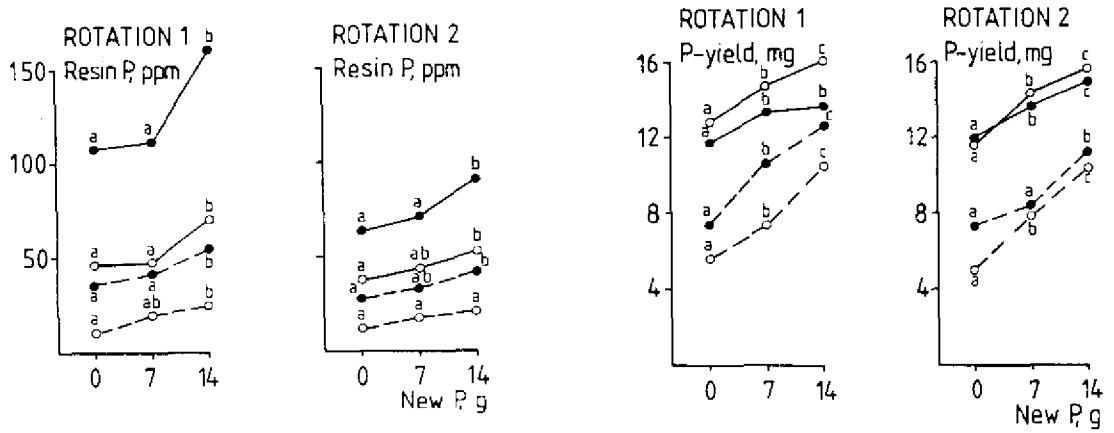

Figure 5. Resin P and P-yield of perennial ryegrass for the low-fertility site (unfilled circles) and the high-fertility site (filled circles) at the lowest (---) and highest (——) PK level 18 days after wetting of soil and addition of fresh P. Different letters above the curve identify values differing at the 0.05 level of probability within each soil.

Discussion

The differences between the two sites shown in Figures 2 and 3 are in accordance with results from the other four sites in the series of long-term soil fertility experiments in southern Sweden. The three low-fertility sites have higher contents of total P than the three high-fertility sites, mostly due to higher contents of organic matter and organic P (Gunnarsson, 1987). In this investigation the low-fertility soil also has a somewhat higher content

of Fe- and Al-phosphates (NaOH-Pi fraction) and Ca-phosphates (acid P), and definitely a lower ability to keep the P in an easily soluble resin P form due to its stronger P fixation power than the high-fertility soil.

Compared with the situation in 1957, the supply of P in fertilizer on the principle of replacement has not been sufficient to keep the resin P at a constant level (Figure 3). Earlier studies of the long-term soil fertility experiments have shown that about a two-fold replacement of P kept the ammonium lactate acetate (AL)-extractable P close to constant (Jansson 1977).

The formation of Fe- and Al-phosphates (NaOH-Pi) after fertilization, especially in the low-fertility soil, is also illustrated in Figure 3. On the other hand, for the high-fertility soil there was an increase of HCl-P that can be explained by its high pH value (Table 2).

Considerable changes of the organic P content during the 27 years of experiment can not be expected since both soils have been cultivated for at least 100 years. However, this investigation does not show the flow of P through the pool of organic matter. That flow may be of importance for keeping the P in a soluble form (Hedley et al. 1982).

A positive response to the crop rotation with ley, removal of crop residues, and addition of manure was only found in the high-fertility soil, where labile P and acid P were increased (Figure 4). Thus in this soil the importance of good management practices for keeping the P in a more easily soluble form was shown. A reason for this can be a larger flow of P through the pool of organic matter.

Can 27 years of unfavourable fertilizer history be compensated by a single application of P? Figure 5 shows that the answer is usually no. Only in one case, at the high-fertility site and treatment 1A, was the P-yield obtained with fresh P equal to 27 years of intensive P fertilization. Furthermore, a comparison between PK levels A and D shows a larger P-yield response in the low-fertility soil than in the high-fertility soil and the reverse as regards the increase of easily soluble resin P (Figure 5).

The P added to soil by fertilization will generally increase the dry matter yield and its P-content, particularly in straw, ley and root crops. Therefore, after intensive fertilization more P will be taken away from the field but a large part of the added P will accumulate in the soil.

As shown, some of this accumulated P will remain as labile P and increase the soil fertility. Apart from by means of fertilization, labile P can also be increased by a favourable crop rotation and a favourable soil. A soil with a fast formation of stable P pools can often be characterized as a low-fertility soil, since its content of labile P is low despite an often high content of total P.

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BALANCE OF PHOSPHORUS IN AN AGRO-ECOSYSTEM UNDER NORFOLK CROP-ROTATION

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Introduction

The current objective in agricultural development of the GDR is to achieve high productivity and crop yields. For this purpose, large amounts of chemical fertilizers and biologically active substances are introduced into the environment. However, such activities potentially threaten the stability of the natural ecosystem balance.

We have studied the effects of this agricultural practice on a few well-selected representative case studies of agro-ecosystems, with the objective of developing concepts of the mechanisms underlying ecosystem function and stability. Total budgets of the most important nutrient elements have been established for several case studies over several years, in order to assess the tendencies for change in these agro-ecosystems. The data obtained serve as a basis for the modelling of processes like the phosphorus (P) cycle, or for analysing the behaviour with time of environmental parameters and agricultural yields.

Site of investigation

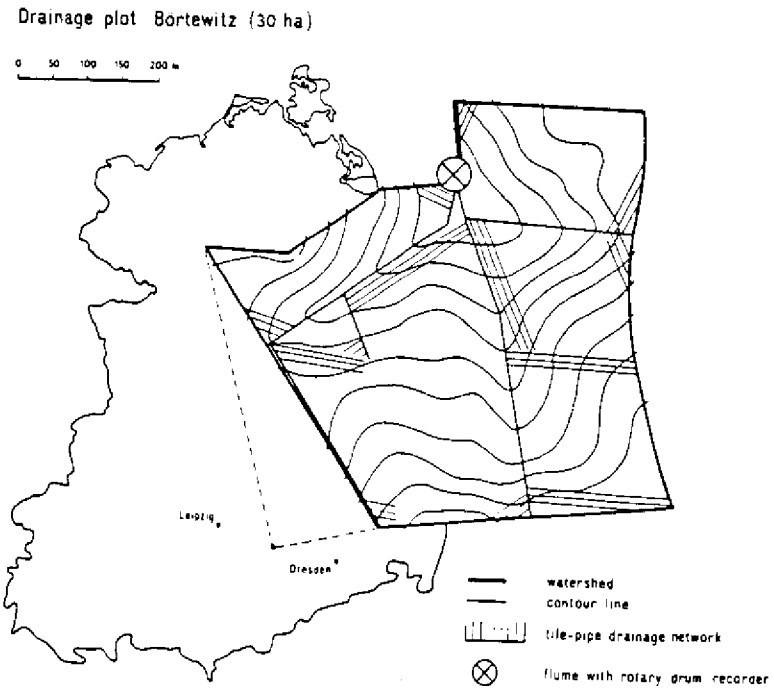

Figure 1. Map of the experimental area

The test plot of Börtewitz is situated in the northern part of the Loess Region of Central Saxony (Figure 1) and consists of a 30 ha field, which belongs to an agricultural co-operative. Its limits coincide with a small hydrological catchment area with relatively gentle slopes, situated between 210 and 220 m above sea level. Surface runoff and erosion are negligible in the catchment except during snow melt. The soil parent material of Young-Würmian-loess is very homogeneous. The thickness of loess is 4 to 10 m above the geological substratum of kaolinized porphyry. In the top layer the soil consists of 14% clay, 84% silt and 2% sand, which change to 21% clay, 74% silt and 2% sand at a depth of 120 cm. Below 80 cm, the soil density is increasing (hydraulic conductivity < 10^{-8} $m \cdot s^{-1}$, D > 1.6 $g \cdot cm^{-3}$). Soils consist of Orthic Luvisols on the upper slopes and Gleyic Phaeozems in the small valley, with Gleyic Luvisols as dominant soils on the mid-slopes. Mid-slope positions are frequently eroded, with a loss of a A- and E-horizons. Eroded materials accumulate in the valley bottoms to form Gleyic Greyzems and Gleyic Phaeozems. Weather conditions at a meteorological station about 12.5 km from the test plot are as follows: the long-term annual precipitation is between 610 and 650 $mm \cdot y^{-1}$. Mean annual temperature is 8.0 - 8.5°C. Over the last 12 years, precipitation ranged between 411 and 791 $mm \cdot y^{-1}$, with mean annual temperatures between 7.6 and 10.1°C. The plot itself is managed by the co-operative with a typical Norfolk rotation (Table 1).

Table 1. Rotation, precipitation and temperature of the study area of Börtewitz from 1977 - 1987.

	77/78	78-79	79-80	80-81	81-82	82-83	83-84	84-85	85-86	86-87
	sb†	ww	wb	sb	ww	wb	rc	sb	ww	wb
	BL - -	CE - -	CE	BL - -	CE - -	CE	BL	BL - -	CE - -	CE
pptn††	660	618	680	730	559	667	584	556	612	791
Temp	8.5	7.7	8.0	9.0	8.1	10.1	8.3	8.1	8.8	7.6

† sb - sugar beet, ww - winter wheat, wb - winter barley
rc - red clover, BL - broad leaves, CE - cereals
†† precipitation and temperature for October-September

Method

Nutrient flow in the agro-ecosystem was analysed by comparing inputs by fertilization or atmospheric deposition and outputs by harvest or leaching. Sorption and desorption processes occurring in the soil will modify the input/output balance in a way that is only partially understood, and therefore limit the validity of this approach. In addition, the fertilizer inputs applied by the co-operative can often be determined only by information from the agricultural enterprise, without confirmation by direct measurement. Atmospheric deposition is measured in a 200 cm^2 rain gauge with 2 - 3 samples of rain water per month. The export of nutrients by plants is determined by test harvests at 15 points representing the different soil conditions of the plot. According Donev & Markov (1986) fields with a more uniform nutrient status (CV 27 - 29%) require 10 - 15 sampling points as an optimum. Less uniform fields require between 15 - 25 sampling points for the evaluation of available P or K. We used the change of available nutrient content in the surface soil, in order to improve the nutrient budget calculated. The

determination of changes in nutrient storage of a soil was carried out at the same points as the test harvest. The soil was sectioned according to genetic horizons (3 - 6 for 1 m depth), and plant available nutrients were determined. A tile pipe drainage system was used to measure leaching (GERDS, 1987). The following parameters were measured:

1) drainage discharge: measured continuously by a Thompson weir with a rotary drum recorder; water samples taken every fortnight, macro-nutrients in drainage water and precipitation were analysed (Na, K, Ca, Mg, NH_4, NO_2, Cl, SO_4, HCO_3, PO_4)

2) soil samples: the samples were taken immediately after the yearly harvest and analysed (NH_4, NO_3, N_t, humus, pH, total acidity, PO_4, K, Ca, Mg, Na, Cl, SO_4, Zn, Cu, Mn, B, Mo, Fe).

3) plant samples: divided into compartments and analysed (N, NO_3, P, K, Ca, Mg, Na, Cl, SO_4, Zn, Cu, Mn).

Soil P was extracted by the double-lactate method (P_{DL}) of Egner & Riehm (1955; TGL 25418/07). Plant samples were digested and P determined by the ammonium-molybdate-vanadate method (TGL 21875/12). All analyses were carried out by the Agrochemical Investigation and Consulting Service of the GDR.

Results

During the entire investigation period, from 1978 - 1987, fertilizers were applied in autumn, according to recommendations of the Agrochemical Investigation and Consulting Service. Large amounts of P, together with manure were applied as storage fertilization before broad leaves were sown (Table 2). This practice of storage fertilization with a long-term rate of utilization of only about 55 - 65% (Müller et al. 1977) precluded calculation of annual P balances.

Table 2. Phosphorus fertilisation ($kg \cdot ha^{-1} \cdot y^{-1}$) from 1977 - 1987

	78/79 ww	79/80 wb	80/81 sb	81/82 ww	82/83 wb	83/84 rc	84/85 sb	85/86 ww	86/87 wb
FYM	--	--	48	--	--	--	36	--	--
SP	--	50	50	--	30	40	--	--	--

FYM - P in farmyard manure
SP - P in Superphosphate

The P_{DL} method is used by the Agrochemical Investigation and Consulting Service because of its relatively good correlation with plant uptake (Marks 1977). Although the actual amounts of P extracted are not corresponding to the total P available to plants over the whole year. Labile P values are also known to vary with time, depending on soil moisture and the thermal index of the sampling month (Kemp et al. 1985).

Plant P contents were found to be within published ranges (Nehring et al. 1981). The standard value for red clover for the first cut, is 3.4 $mg \cdot g^{-1}$ and

for second and third cuts 2.9 $mg \cdot g^{-1}$. The values measured in red clover during 1983/84 in Börtewitz correspond to these values. Standard concentrations for the tubers of sugar beets are between 1.2 and 1.4 $mg \cdot g^{-1}$, and for leaves between 2.5 and 2.7 $mg \cdot g^{-1}$ (Beiss 1978). Between 1981 and 1985, sugar beets reached values from 1.6 - 1.8 $mg \cdot g^{-1}$ in tubers, and 3.5 $mg \cdot g^{-1}$ (1981) and 2.8 $mg \cdot g^{-1}$ (1985) in harvested leaves. In 1987, similarly high values were also found in the straw of winter barley, which contained 1.9 $mg \cdot g^{-1}$ of P as compared to the standard value of 0.8 $mg \cdot g^{-1}$. Winter wheat straw reached levels of 0.8 $mg \cdot g^{-1}$. The standard values for winter wheat grain and winter barley are 3.8 and 4.0 $mg \cdot g^{-1}$ respectively. These values were only reached in 1979 (ww). The value for winter wheat grain of 2.2 $mg \cdot g^{-1}$ remained below the standard (Table 3).

In practice, P contents ranging between 1 and 5 mg.g-1 in plants have little effect on yields. Only the P uptake during an early development phase is of significance for the yield (Römer 1985, Munk 1981). Corn, for instance, takes up 1 - 2 kg.P.ha-1 daily during this time, although the root system is still undeveloped, and roots only have access to P with a radius of 1 - 2 mm around their hair roots. Mengel (1985) gives the following sequence of importance for parameters of P uptake: root length > P concentration in the bulk soil solution > root radius > P buffer power > diffusion coefficient. This emphasizes the importance of root length. In addition, thin roots proved much more efficient in P exploitation than thick ones (Peterson & Barger 1981 cit. by Mengel 1985). In compacted soils (like at Börtewitz) thinner roots predominate. This explains in part why the P contents measured showed no significant patterns of variation and are independent from the amount of fertilizer applied. Köhnlein (1976) obtained similar results. Thus, in practice the amounts of P fertilizer applied are often much higher than plant exports (Timmerman 1983).

A comparison of P contents in the same plant species with precipitation reveals that the highest values in the straw and grain of winter barley (1987) and the relatively high values in sugar beets (1981) occur with the greatest precipitation in these nine years. (Table 1 and 3). It is known that in dry years the P consumption of plants is lower than in moist years (Timmermann & Winkelmann 1979).

Table 3. Plant parameters from 1977 - 1987

Year Cult.	78/79 ww	79/80 wb	80/81 sb	81/82 ww	82/83 wb	83/84 rc	84/85 sb	85/86 ww	86/87 wb
Y/1	4.4	5.6	33.0	6.3	5.6		34.3	61.5	6.1
Y/2	2.2	2.7	46.0	3.0	3.0	65.2	40.6	2.5	2.7
P/1	2.2	3.9	1.8	4.0	3.4	3.4	1.6	3.2	4.0
P/2	0.8	0.8	3.5	0.6	0.7	2.9	2.8	0.8	1.9
EXP	12	24	38	27	21	34	30	23	30

Y/1 - yield of grain or tubers, $t \cdot ha^{-1}$
Y/2 - yield of straw or leaves, $t \cdot ha^{-1}$
P/1 - P content in grain or tubers, 1st cut of clover, $mg \cdot g^{-1}$
P/2 - P content in straw or leaves, 2nd and 3rd cut, $mg \cdot g^{-1}$
EXP - total P export, $kg \cdot ha^{-1}$

The average P export of about 20 $kg \cdot ha^{-1}$ for winter wheat, 25 $kg \cdot ha^{-1}$ for winter barley and 34 $kg \cdot ha^{-1}$ for sugar beets and red clover is lower than stated in literature. Hirmer (1984) gives an average export of 4.4 - 4.9 $kg \cdot ha^{-1}$ in 1 t corn (grain & straw), Amberger (1980) 4 $kg \cdot ha^{-1}$ and for sugar beets an export of 7 $kg \cdot ha^{-1}$ in 10 t tubers and leaves.

At the Börtewitz plot the P export in 1 t grain and straw was only 2.4 $kg \cdot ha^{-1}$ for winter wheat and 2.9 $kg \cdot ha^{-1}$ for winter barley, the export with 10 t sugar beets (tubers & leaves) was 4.4 $kg \cdot ha^{-1}$.

The P export through leaching is negligible. Only during some heavy summer rains, traces of P could be observed in the drainage water. The reason for this is the fast infiltration of surface water through macropores, i.e. through shrinking fissures, worm holes etc. Normally, there are no traces of P in the drainage water, because of the high P absorption capacity of this loess soil. The pH values for the soil varied between 6.5 in the top horizon, and 5.4 in the 100 - 120 cm layer.

Table 4. Available soil P_{DL} ($mg \cdot Kg^{-1}$) between 1977 - 1987

Year Cult.	78/79 ww	79/80 wb	80/81 sb	81/82 ww	82/83 wb	83/84 rc	84/85 sb	85/86 ww	86/87 wb
depth (cm)									
0-20	82.7	102.0	57.8	79.5	79.3	--	67.7	82.1	71.0
20-40	54.2	56.7	31.9	47.9	54.0	--	57.6	56.9	50.1
40-60	16.3	16.4	17.8	18.6	28.4	--	30.4	21.2	20.7
60-80	13.8	16.2	26.7	16.1	24.1	--	18.6	15.3	14.5
80-100	15.6	15.5	40.2	15.7	22.9	--	12.8	17.3	14.0
100-120	16.3	16.9	61.3	20.7	24.0	--	14.1	20.2	15.1

Available P levels of the soil (Table 4) varied between optimum and best (Amberger 1980), with highest contents in the top 20 cm and a rapid decrease between 40 and 100 cm depth. The P contents in the deepest layer, however, are still high enough for good yields (Richter, et al. 1977). Below 100 cm there was slight increase in available P levels, and we observed considerable variation in the P values of lower soil layers between different years. Leaching of P in such quantities is unlikely (Kretzschmar 1964, Scheffer & Schachtscabel 1976, Bramm 1981). Cooke and Williams found values of P movement of 0.1 - 0.1 $cm \cdot y^{-1}$ (*in* Ohlendorf 1976). On the other hand, the period of 1980-1981 had the highest precipitation and drainage discharge observed during the experiment (Table 1). Similarly high precipitations in 1986-1987 did not result in similar discharges, probably due to the low rainfall and higher evaporation of the preceding years. A heavy rainstorm in August of 1983 (180 mm in 5 days) might be responsible for the homogeneous distribution of available P below 40 cm in samples taken in September of 1983. Mishra and Khanna (1979) report a close dependence of P transfer on water movement in this soil. Nevertheless, movement and turnover of P within the soil cannot be fully described with the present analyses, because of the transfer of P between different P fractions in the soil environment. The dependence of available P on different soil chemical parameters is exemplified in table 5, which shows a significant correlation of available P with soil pH only for the 60 - 80 cm layer. Above and below, other determinant factors are overriding this relationship.

Table 5. Correlation of Phosphorus and pH value

Depth (cm)	P ($kg \cdot ha^{-1}$) Mean	SD	pH Mean	SD	Corr. Coeff.
0-20	227	37.0	6.2	.35	.16
20-40	150	26.9	6.2	.31	-.20
40-60	61	20.0	6.1	.30	-.65
60-80	56	15.7	5.9	.29	-.69*
80-100	62	29.5	5.8	.28	-.46
100-120	77	51.3	5.7	.27	-.29

Table 6. P balances ($kg \cdot ha^{-1}$) of the study area of Börtewitz from 1977 - 1987

Year Cult.	78/79 ww	79/80 wb	80/81 sb	81/82 ww	82/83 wb	83/84 rc	84/85 sb	85/86 ww	86/87 wb
Input		50	98		30	40	36		
Output	12	24	38	27	21	34	30	23	30
Netb.	-12	+26	+60	-27	+9	+6	+6	-23	-30
P_{DL} †	+78	+72	-88	+15	+109	...	-100	+36	-84

† P_{DL} - annual change of P_{DL} content in 120 cm of soil

Comparing the annual balance of inputs and outputs of P with the net changes in available P (Table 6) shows average changes in available P of 73 $kg \cdot h^{-1} \cdot y^{-1}$, fertilizer inputs of 28.2 $kg \cdot h^{-1} \cdot y^{-1}$ and plant outputs of 26.5 $kg \cdot ha^{-1} \cdot y^{-1}$. The unbalanced large variation in available P shows that the DL extractable P fraction is highly dynamic and can be easily replenished by other soil P fractions. A reason for this may be the extensive P fertilization in the mid-seventies, when P applications averaged 100 $kg \cdot h^{-1} \cdot y^{-1}$. Such application levels pose the danger of over-fertilization, which may lead to P leaching once the soil's absorption capacity is exhausted. Clearly, active P reserves in the experimental plot far exceed the annual input/output balance. First signs of danger caused by common over-fertilization have also become apparent in a negative correlation between P fertilization and yield of winter wheat in the district of Leipzig over the last 10 years. There is a trend now to reduced P fertilization, and today the average application is about 50 $kg \cdot h^{-1} \cdot y^{-1}$. The net balance over the entire nine-year investigation period of P is:

input	254 $kg \cdot ha^{-1} \cdot y^{-1}$
output	239 $kg \cdot ha^{-1} \cdot y^{-1}$
balance	+15 $kg \cdot ha^{-1} \cdot y^{-1}$.

During the same period, available P has shown large fluctuations, but the nine-year net increase amounts to only 39 $kg \cdot ha^{-1}$. Yields on the plots were higher than in the years previous to the observation period, during which very heavy P fertilization was practiced. This indicates that a sufficient quantity of P is mobilized from the soil reserves to satisfy crop demands, and current fertilizer practice nearly balances crop exports.

In summary, investigations of the P cycle under field conditions, need to consider the P balance over several years, rather than of one year only. The dynamics of P within the soil preclude an accurate determination of the soil storage component of P, and thus do not permit an accurate P balance over the entire agro-ecosystem. Therefore, agricultural practices which pose a potential danger of over fertilization, require long-term investigations in the form of a monitoring system. The agro-ecosystem at Börtewitz does not represent an apparent danger to downstream ecosystems due to over fertilization, and at the same time, current fertilization levels adequately maintain yields.

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PHOSPHORUS BALANCE IN NON-CHERNOZEM ZONE OF RUSSIAN FEDERATION

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Experience from recent years of intensive agricultural use of non-chernozem soils indicates that improved crop yields are obtained when phosphorus (P) fertilization is practiced above the quantities immediately required by crop plants (Postnikov 1983). This practice though raises the problem of physical-chemical and biological P fixation in the soils (Griffit et al. 1977, Kudeyrov et al. 1984, Brookes et al. 1986). The fertilizer use efficiency is usually only 10-15%, both during the first and subsequent years after application (Postnikov 1980, VASHNIL 1988, Hollo 1984, Cooke 1984). Economic application of P requires the monitoring of available P reserves in the upper soil layer in order to determine limits beyond which there is no negative P balance due to crop export.

Table 1. Distribution of arable lands on different soil groups of the non-chernozem zone of the Russian Federation

Soil group	soil group	arable land	arable
	------thousand ha------		%
Dernovo-podzolic soil (including gley-like soils)	23538	17141	57.5
Vegetable soils (including flood-plain and carbonate soils) (calcareous)	4331	1173	3.8
Gray-forest soils (including gley-like)	7601	6761	22.1
Chernozem soils	4525	4153	13.9
Gully-narrow complex	1499	51	0.2
Totals	48920	30986	100

We (Postnikov 1983, Postnikov 1980) and other authors (Cooke 1984, Johnston et al. 1986, Nosko 1982, Derzhavin and Popova 1988) demonstrated predictable yield increases in dependence on levels of available P in the soil, and we suggest that both P and potassium fertilizers should be applied on the basis of 'productive balance' (Postnikov 1980). Soils with low available nutrient levels should receive supplemental fertilization, while those with adequate levels of P should be fertilized according to fertilizer

balance calculations. This concept is supported by other researchers (Hollo 1984, Milcheva 1985, Debretzeni 1984). The present contribution reports on the results of 15 years investigations in the All-Russian Institute for Scientific Research and Research Planning of Agricultural Chemical Use, and its associated research stations.

During the 15 years, 3 series of detailed agro-chemical investigations have been conducted on agricultural land in the non-chernozem zone of the Russian Federation. The content of available P (in 0.2 HCl extract) was determined annually on about 5 million hectares. At the same time, P removal through yield was determined, and the annual P balance was completed with information on mineral and organic fertilizer use.

In the non-chernozem zone of the Russian Federation, there are 48.9 million ha of agricultural lands, 31 million ha of which are arable. About 60% of the area are dernovo-podzolic soils (Table 1) and more than 80% of the soils are heavy textured. In 1987 each hectare of planted land received on average 61 kg of nitrogen, 19 kg of P and 43 kg of potassium (Table 2).

Table 2. Average fertilizer application to different crops in the non-chernozem zone (1987)

	Total area	grain crops	technical crops*	potato	fodder crop
Total	123	118	181	232	115
Nitrogen	61	54	55	67	68
Phosphorus	19	22	36	42	12
Potassium	43	42	90	123	35

* sugar beet, flax, hemp, tobacco, oliferous and other crops

Table 3. Organic and mineral fertilizer use between 1971 and 1985

Years	Total	With mineral fertilizers	With organic fertilizers
1971-1975 total amount	66	44	22
" average annually	13	9	4
1976-1980 total amount	96	72	24
" average annually	19	14	5
1981-1985 total amount	107	81	26
" average annually	22	16	6
1971-1985 total amount	270	198	72
" average annually	18	13	5

Table 4. Annual phosphorus balance for agricultural lands of the non-chernozem zone

Balance items	1966-1970	1971-1975	1976-1980	1981-1985	1986
Receipts total:	9.7	13.8	19.9	22.1	23.0
from mineral fertilizers	5.6	8.8	14.4	16.3	16.8
from organic fertilizers	3.5	4.4	4.8	5.2	5.6
from others	0.6	0.6	0.7	0.6	0.6
Expenditure total:	7.6	10.1	13.2	12.5	13.6
removal by yields	4.1	4.8	4.9	5.3	6.2
others	3.5	5.3	8.3	7.2	7.4
Balance	2.1	3.7	6.7	9.6	9.4

With these mineral fertilizers, approximately 30 million tons of organic fertilizers were also introduced. At the beginning of this period, low average agricultural yields in the region removed approximately 4.8 $kg \cdot ha^{-1} \cdot y^{-1}$ which increased to 6.2 $kg \cdot ha^{-1} \cdot y^{-1}$ (Table 4). During the 15 years a total of 270 $kg \cdot ha^{-1}$ of P have been introduced as fertilizer, and 75 $kg \cdot ha^{-1}$ were removed in yields, giving an overall positive balance (Table 4). However, it should be recognized that this overall positive balance is due to the relatively low yields of crops during the period, and this would change if the full production potential was realized. The average content of available phosphorus in the soils of the central district of the non-chernozem zone, as well as the total P balance was considerably greater (with 23 $mg \cdot kg^{-1}$ in 1971, and 45 $mg \cdot kg^{-1}$ in 1986) than in the rest of the non-chernozem zone (Figure 1, Table 4) .

Since the soils have a low natural content of P, it was planned to considerably exceed the quantity of P fertilizer required for crop production in order to increase the P level in the soils. We calculated the balance using the actual application of P to the soil, along with its removal by scheduled (but not actual) yields. In order to provide an optimum nutrient regime for most agricultural crops, and an economically viable fertilization with the aim to establish production of crops requiring increased fertility such as vegetables, potato, fodder- and red beets, it is recommended to increase the available P content to 87-109 $mg \cdot kg^{-1}$ of soil. Such levels of available P will make it possible to produce an average of 30 tonnes of potato, 50-60 tonnes of cabbage or 25-30 tonnes of beets per hectare, provided that adequate irrigation, nitrogen, potassium and micro elements are supplied. For plots with a less efficient use, it is foreseen to increase phosphate levels in the near future to 66-79 $mg \cdot kg^{-1}$ (0.2 HCl extract). For soils with low P content, the quantities of P fertilizers are to exceed 2-2.5 times the yield removal by plants, thus increasing the available P in the soil. A productive balance of 200-250% on average is to be achieved, with average P contents of 150% of present levels. When a labile P content of 109 $mg \cdot kg^{-1}$ is reached, applied fertilizers are to provide only the expenditure of P through crops.

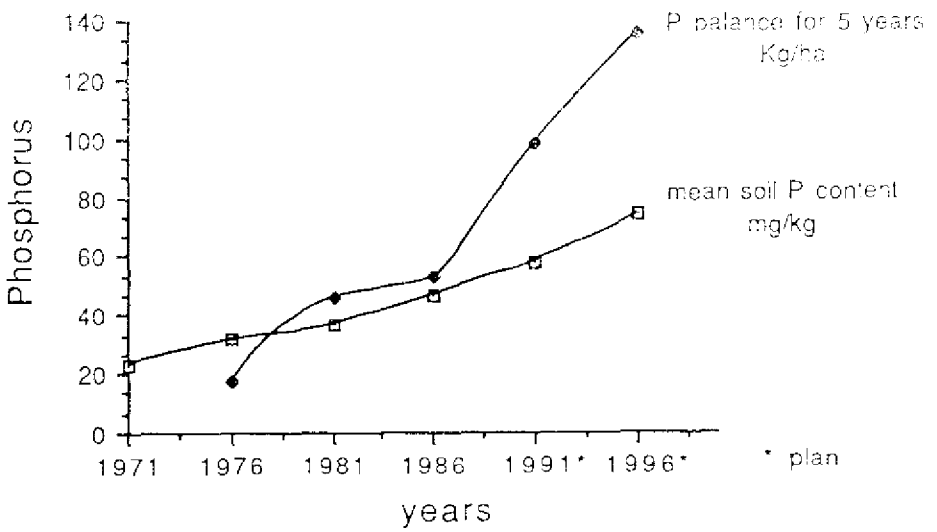

Figure 1. Changes in available phosphorus content and total phosphorus balance for the central district of the non-chernozem zone.

At the present time, on the 1st of January 1987, the labile P content in the non-chernozem zone of the Russian Federation has already reached its scheduled level on 6% of arable land. On an area of 4.6 million ha (1[illegible].1%) its content is between 66 and 109 $mg \cdot kg^{-1}$, on a further 5.1 million ha (1[illegible].7%) it is between 44 and 66 $mg \cdot kg^{-1}$, and on 19.1 million ha (62.2%) it is less than 44 mg.kg-1 of soil. A calculation of the potential demand for P fertilizers to cover the expenditure within scheduled yields, as well as further increase the soil P content, was carried out using the following formula:

$$D = \frac{B}{K} + \frac{(C1 - C2)\ H\ 0.1}{T}$$

where

D = Quantity of fertilizer P required to obtain a programmed yield and plant increase available nutrient content in the soil in $kg.ha^{-1}$.

B = nutrient removal by programmed yield in $kg.ha^{-1}$.

K = coefficient of productive action for mineral and organic fertilizers for the planning period in %.

C1 = desired amount of nutrient in the soil in $mg \cdot kg^{-1}$.

C2 = actual nutrient content in the soil in $mg \cdot kg^{-1}$.

H = nutrient application required to increase the P content in the soil by 4.4 $mg \cdot kg^{-1}$ of soil in $kg \cdot ha^{-1}$.

T = the time over which it is planned to reach the optimum nutrient content of the soil in years.

In order to actually implement the proposal of the investigators annual P resources are to be increased to 1.22 million tonnes, or to 39 $kg \cdot ha^{-1}$.

The introduction of the notion of "productive fertilizer action" gives a more objective idea regarding the processes taking place in the system soil - fertilizer - yield, which were formulated in the triangle of academician D.M. Pzynishnikov. The common notion "coefficient of fertilizer efficiency" reflects only the correlation between the plant and the fertilizers. Considering the low efficiency of P use by plants, many

investigators came to the conclusion that world P resources have been used uneconomically (Griffit 1977, Kudeyrov et al. 1984, Cooke 1984, Debrezeni 1984). The same opinion was also formed in the USSR (Postnikov 1984, VASHNIL 1988, Postnikov 1980, Nosko 1982, Derzhavin and Popova 1988), but investigations carried out over many years in VNIPTHIM showed that plants during a crop rotation with a 10 year period may productively use between 60-70% of P introduced together with other mineral and organic fertilizers (Table 5). The investigations carried out on the basis of the balance method predict changes in labile P content with reassuring accuracy (Table 6).

Table 5. Productive fertilizer action, and phosphorus expenditure in $kg \cdot ha^{-1}$ over and above the removal of P by crops to raise 0.2 N HCl extractable soil P content by 4.4 $mg \cdot kg^{-1}$ during the period 1981-1985.

Regions	Proportion of introduced P recovered in yields or as available soil P, in % of total introduced	P fertilizer required to increase labile P content of the soil by 4.4 $mg \cdot kg^{-1}$	
		calculated	actual
Brynskaya	79	35	39
Vladimirskaya	74	34	50
Ivanovsraya	72	38	40
Kalininsraya	98	33	31
Kaluzskaya	85	37	36
Kostromskaya	98	36	24
Moskovskaya	78	40	40
Orlovskaya	39	43	53
Ryzanskaya	87	42	43
Smolenskaya	77	37	48
Tylskaya	100	41	22
Yroslavskaya	76	35	55
Central region	84	35	37
Non-chernozem zone	69	36	69

The considerable extension of arable agricultural projects makes the problem of prognosis of nutrient element contents very urgent. The above work on P was carried out for the central district of the non-chernozem zone of the Russian Federation. The bases for all calculations is the information on balance of this element, along with the quantities of P fertilizers required over and above the requirements by crop yields, to increase the available P content by 4.4 $mg \cdot kg^{-1}$ of soil. The P balance was calculated based on scheduled deliveries of mineral fertilizers, the plan of organic fertilizer application, and the production of agricultural products. Actual changes in available P content of the soils turned out to be close to the predicted ones (Table 6). The amounts of P required in order to raise soil P levels by 4.4 $mg \cdot kg^{-1}$ were between 22 and 55 $kg \cdot ha^{-1}$ depending on soil type and texture (Table 5).

The balance of P use by crops and increases in available P content of the soil observed in the area indicate that there is little danger to water basins from P pollution, when between 39 and 57 $kg \cdot ha^{-1}$ are actually introduced. For instance, the average rate of P removal from agricultural lands within the Ladoga lake basin equals 1.4% or between 0.4 and 0.5 $kg \cdot ha^{-1}$ at a P application rate of 33-66 $kg \cdot ha^{-1}$ (Jonat et al. 1984). In the Oka river

basin (Moscow region) 0.7 - 1.0 $kg \cdot ha^{-1}$ of P are actually lost due to surface flow, with an annual level of P fertilizer application between 44 and 52 $kg \cdot ha^{-1}$ (Kudeyrov et al. 1984). Movement of P into reservoirs is primarily in the inorganic form, and the most important components are easily soluble mineral fertilizer residues. With the above-mentioned level of fertilization (44-52 $kg.ha^{-1}$) a positive P balance of 13-25 $kg \cdot ha^{-1}$ is reached. The average P content in small rivers of the basin is between 0.33 and 0.41 $mg \cdot l^{-1}$ (Kudeyrov et al. 1984). Investigations on the P content of small contributaries of the Upper Volga river (Kudeyrov et al. 1984) indicated variable P contents of 0.02 up to 0.39 $mg \cdot l^{-1}$. Sometimes there was no P detected. The classification of the CMEA countries for permissible P contents in surface waters for municipal water supply, food industry and fish farming allow the following maximum concentrations: class I < 0.5 $mg \cdot l^{-1}$, class II < 1 $mg \cdot l^{-1}$ (Peehahchi et al. 1977). The measured P contents in small rivers of agricultural basins are therefore considerably below the maximum permissible levels. In the absence of fertilizer application, as for instance in the forest reserve of the Oka river basin, general P content is about 0.04 $mg \cdot l^{-1}$. When P fertilizer was applied at a level of 44-52 $kg \cdot ha^{-1}$, P leaching into drainage waters was also small, at levels of 0.17-0.33 $mg \cdot l^{-1}$ (Kudeyrov et al. 1984).

Table 6. Predicted and actual phosphorus content in arable lands of the central region of the non-chernozem zone.

Regions	P production balance amount for 1981-1985 $kg \cdot ha^{-1}$		Average labile P content $mg \cdot kg^{-1}$ of soil		
				on 1.01.1986	
	plan	actual	on 1.01.1981	prognosis	actual
Brynskaya	122	86	48	64	58
Vladimirskaya	101	104	38	53	47
Ivanovsraya	118	107	25	40	37
Kaliniskaya	114	88	37	52	49
Kaluzskaya	85	76	35	47	44
Kostromskaya	126	93	24	49	41
Moskovsraya	228	180	56	83	76
Orlovskaya	60	58	33	40	38
Ryzanskaya	70	65	33	41	39
Smolenskaya	105	90	33	47	41
Tylskaya	73	69	32	41	45
Yroslavskaya	104	77	36	49	42

P leaching does not depend on the rate of fertilizer application, but is determined by the forms of P, by soil texture, the pH of underground waters and soil solution, and the soil organic matter content. Investigations have shown that drainage flow from fertilized fields, especially when polyphosphates were applied, contained stable complexes of polyphosphates, with metals and soil organic matter which have high mobility (Kudeyrov et al. 1984, Kudeyarova and Kvaratskheliys 1984). Besides polyphosphatic fertilizers, soil polyphosphates are formed biologically as a result of the metabolism of many types of microrganisms (Kudeyrov et al. 1984, Illarionova,

1978). Such polyphosphates are microbially formed, particularly when both orthophosphate and organic substances (carbohydrate) are abundant. Polyphosphates become important in the P cycle, particularly in acid soils of very low calcium content, where they easily leach into underground waters (Kudeyrov et al. 1984). In our experience, fertilizer P is mainly in the ortho form, and polyphosphate fertilizers are used only rarely. This limits the pollution potential to drainage waters from P fertilization. On the other hand, polyphosphates may be introduced into water bodies with detergents (Griffit et al. 1977).

An additional issue with the use of P fertilizers is the accumulation of toxic micro elements, especially cadmium, in both soil and plants as a result of long term P fertilizer application (Jones et al. 1987). According to Sharpley and Menzel (1987), accumulation of Cd in plants becomes a problem when recommended fertilizer rates are applied for more than 50 years. With our present P application rates, based on calculation of productive balance, we exclude the danger of significant Cd applications in the near future.

Summary

The recommended evaluation of fertilizer efficiency uses both the P uptake in crop yields, and the contribution of P towards soil fertility. The proportion of added P recovered directly or indirectly in yields was on average about 69%. The amounts of fertilizers required to raise labile P content in the soil by 4.4 $mg \cdot kg^{-1}$ varied between 22 and 55 $kg \cdot ha^{-1}$. At these application levels there was little danger of small watershed and river pollution due to losses of applied fertilizers.

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PHOSPHORUS IN AGROECOSYSTEMS

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Phosphate ions are considered to be of low mobility, strongly fixed in soil, and non-toxic to people and animals. Moderate fertilizer P applications to slightly or moderately tilled soil, are almost unleachable. And yet, significant amounts of P reach water bodies, due to water erosion and runoff (VASKHNIL 1986, Kuznetsov 1981), although the amounts of P are less than those of nitrogen or potassium.

The greatest risk of leaching or runoff of P or other nutrients, occurs with the practice of fall-plowing. While the risk is least under perennial grasses (Table 1) P removal from a grassland is mostly in dissolved form, while suspensions of particulates predominate on fall-plowed land. In the latter case, the proportion of organic P increases markedly (Table 2). Contour plowing can reduce P runoff dramatically. In an experiment with winter rye, to which 90 kg of P were applied, phosphorus losses from from contour plowed land were less than those from an unfertilized site that had been plowed down slope (Table 2).

Table 1. Nutrient losses due to erosion (sward-podzolic soils)

		Nutrient losses ($kg \cdot ha^{-1} \cdot y^{-1}$)					
		Total from soils and fertilizers			From fertilizers		
Location	Crops	N	P	K	N	P	K
Lithuania Research Institute of Agriculture	Winter and spring grains	35.1	1.2	6.6	4.8	0.4	0.4
Experimental Station Dukshtas	Perennial grasses	4.9	0.5	5.5	0.5	0.4	1.8
Smolensk Division of VIUA	Fall-plowing, snow melt (slope 5-5.5°)	12.8	2.5	41.8	3.2	0.3	2.9

The introduction of intensive cropping, with increasing use of mineral fertilizers and other agrochemicals, promote environmental damage, if conservation requirements are overlooked and the importance of soil and ecological conditions for fertilizer use is underestimated. Two key factors are parent material and land form (Lipkina 1979, Lipkina et al. 1985). Soils formed from different parent material, even though they belong to the same soil type, and may have similar values of pH, humus, labile P and K for the topsoil, may differ markedly in effective P fertility, P mobility and the ratio of available P to other nutrients. This may greatly change fertilizer efficiency, even under conditions of similar labile P levels and fertilization rates. Barley yields obtained from an unfertilized loessial loam (Novoselskoe

experimental farm, VIUA) were between 120 and 215 $kg \cdot ha^{-1}$ higher than those obtained from unfertilized soils formed from acid loamy moraine. Liming will sharply increase the fertility of soils on moraine, but not of loessial loams. The application of $N_{60}K_{60}$ without P, to moraine soils with low P fertility, seems to be ineffective, while yield increases are obtained on loessial loams. On acid moraine soils, barley yield increased progressively with increasing P applications, from 0 - 180 $kg \cdot ha^{-1}$, with a basal dressing of $N_{60}K_{60}$. On loessial loam, yields level off at P rates of 60 $kg \cdot ha^{-1}$, unless N and K rates are simultaneously increased (Lipkina 1983). These data imply that overall soil conditions need to be known to optimize P fertilizer use. Differences in native fertility levels are also dependent upon weather conditions.

Table 2. Phosphorus in surface run-off from fields plowed along and across slope

Management	total P Kg	total P %	mineral P In solutions %	mineral P In suspensions %	organic P In solutions %	organic P In suspensions %
Fall-plowed land						
Along slope	62.7	100	6	4	10	80
Across slope	11.5	100	6	14	12	68
Winter Rye						
Along slope	22.6	100	54.4	14.1	23.7	7.8
Across slope	23.4	100	54	11	18	17

Table 3. Phosphate status of light sward-podzolic soils, Meshchera lowlands

Land Use	Horizon and depth cm	Particle Size, mm 0.001 %	Particle Size, mm 0.01 %	pH_{KCl}	P (Kirsanov) mg/kg soil	P (.03N K_2SO_4) $mg \cdot l^{-1}$
Forest	A1 0-10	2.4	9.0	4.08	5	0.01
	B 30-40	1.8	4.6	4.50	5	0.01
	B 70-80	2.6	4.1	4.55	100	0.02
	BC(C)130-140	2.6	3.9	4.45	99	0.03
Field	Ap 0-25	1.1	9.3	5.16	107	6.9
	A2 39-49	1.1	8.5	4.94	253	5.4
	B1 88-92	1.8	4.0	5.27	187	6.3
	BC(C)130-140	10.4	12.0	4.51	37	0.16

The P fertilizer use efficiency is known to be only 5-20%, and experiments conducted by VIUA have shown that residual P migrates down through

the soil profile. The rate and depth of this migration depend on soil texture, mineralogy and slope. On light soils, P losses from the soil profile can be clearly observed (Table 3) (Lipkina 1979). P movement is similarly noticeable in loamy soils (Lipkina et al. 1985). Table 4 shows that labile P accumulated at 1.5 m in the soil profile. For its utilizations, deep rooting crops may be recommended (Ivanov et al. 1969, 1971, 1975, 1976, Kobzarenko 1983, Shidlovskiy and Melozerova 1978).

Table 4. Phosphate status of sward-podzolic soils, region of Kaluga

Horizon and depth, cm		Particle size,% 0.01mm	0.001mm	pH_{KCl} 1965*	1980**	P (Kirsanov) $mg \cdot kg^{-1}$ 1965	1980	P (.03N K_2SO_4) $mg \cdot l^{-1}$ 1965	1980
Ap	0-20	23.7	6.6	4.2	5.8	5	48	0.04	.07
A1	20-25	-	-	4.2	-	7	-	0.01	-
A2	25-30	38.7	6.5	4.2	4.6	41	77	0.01	0.03
B3	110-120	-	-	4.1	4.5	107	114	0.07	0.05
C	135-145	39.0	22.5	4.1	4.5	107	116	0.01	0.04

* 1965- idle land **1980- cultivated field for 15 years

Phosphorus pollution can be important in areas where wind erosion occurs. According to VIAU data (Shidlovskiy, Melozerova 1978) obtained for the territory of the Armavir wind corridor (near Krasnodar) 2.5 cm of calcareous chernozem topsoil are annually removed as a result of slight wind erosion. This amounts to a loss of 300 $t \cdot ha^{-1} \cdot y^{-1}$ of soil, equivalent to 175 $kg \cdot ha^{-1}$ of total P and 3 kg of labile P. Moderate to severe erosion levels can remove 3-5 times as much P (Table 5). Dust-born nutrients are a source of environmental pollution, particularly when they reach water bodies.

Table 5. Losses of P due to wind erosion

Intensity of wind erosion	Thickness of Erodible layer cm	Soil loss $T \cdot ha^{-1}$	Losses of P per year total, $T \cdot ha^{-1}$	labile, $kg \cdot ha^{-1}$
Low	2.5	300	0.2	3.6
Medium	7.5	900	0.7	11
High	12.5	1500	1.1	18

Practices for erosion control are generally available, and include field management such as minimum tillage, protective strips of long-stem plants, etc. Highly erodible sandy soils (in the USSR, they occur adjacent to the Pripyat Woodlands of Poland) lose less P than the black soils, however given their low P supply this still seems to be an important problem.

The interactions of land form and parent material further complicate the biological and geological cycles of nutrients. VIUA investigations showed significant effects of relief on the nutrient status and on ratios of major to minor nutrients under intensive cropping. Soils in lower and mid-slope positions, are often nutrient richer than those at shoulder and top-slope positions of a watershed (Table 6). The differences in nutrient contents and ratios along the slopes are responsible for significant yield differences. Consequently, rates of NPK and micronutrient application should be adjusted according to slope position. The studies indicated that the P to Zn ratio is critical, not only in chernozemic, but also in sod-podzolic soils. On the basis of a four factor regression model, we established the effect of the Mn to Fe ratio on barley yields at high P levels. The equation is:

$$Y = -99.6 + 207.2\,(Mn/Fe)^{0.5} + 35.9 \cdot A - 46.4\,Mn/Fe - 78.7 \cdot (A \cdot Mn/Fe)^{0.5}$$

(R=0.64) for a loessial loam. In another case of an acid moraine loam soil, with a P content between 7 and 10 $mg \cdot kg^{-1}$ along the catena, a positive relationship between barley yields, the P to Zn and the Mn to Fe ratio has been established:

$$Y = 7.4 + 33.2\,A - 0.04\,(P_2O_5/Zn) + 55.5\,(Mn/Fe) + 0.94\,(A \cdot P_2O_5/Zn)^{0.5} - 86.8\,(A \cdot Mn/Fe)^{0.5}$$

(R=0.77). This indicates that a full understanding of all nutrient interactions of a specific soil is required for optimum P fertilization.

Table 6. Average nutrient ratios for arable layer of loamy sward-podzolic soils (Viua Experimental Farm, Novoselskoe, Lipkina G.S.).

Relief elements	P, mg/kg (Kirsanov)	N:P:K	P/Zn	P/Mn	P/Fe
1. Watershed	170	1:2:1	14	1.2	0.4
2. Slope medium (≈2.5°)	160	1:3:3	10	0.5	0.4
3. Slope bottom (≈5°)	100	1:4:15	18	0.5	0.5

A side effect of heavy P fertilizer applications are the disadvantageous accumulations of trace elements present in fertilizers: stable strontium, radioactive uranium and radium, and fluorine. Rock phosphates always contain fluorine in amounts between 0.5 and 5%. With every ton of P, about 160 kg of fluorine enter the fields. This highly reactive element may disturb the ecological stability by, for instance, interfering with enzymes and catalysts of plants and animals that require Fe or Mn co-factors. Prediction or elimination of such effects require a detailed ecological analysis. New forms of P fertilizers, on the basis of polyphosphoric acids, have not yet been completely evaluated for their possible effects. However, available data indicate that linear polyphosphates undergo complexation with a number of soil constituents. Primary targets of agriculture should not only be increased crop yields, but also a strict compliance with the requirements for environmental protection, even though the main sources of phosphorus in waterways are industrial and domestic wastes, including detergents which contain about 3-5% percent of P. Agriculture accounts for only 10-15% of the overall pollution in waterways.

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PHOSPHORUS CYCLING IN AGRICULTURAL LANDSCAPES OF THE EUROPEAN USSR

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Intensification of modern agriculture on the basis of soil amelioration, and the use of chemicals and modern technology in agricultural crop production, has resulted in an intensification of P cycling within the soil-fertilizer-plant system, and in a deterioration of the ecological state of the land (Kovda 1985, Dobrovolskij et al. 1985). Therefore, it is necessary to closely monitor the ecological state and develop methods to forecast possible ecological changes in agricultural landscapes.

The landscapes of the European USSR can be subdivided into automorphic ones (atmospheric supply), transit (slope landscape) and subordinated (dependent on neighbouring landscapes) depending on the biogeochemical nutrient cycles which supply them. Subordinated landscapes, for instance, include river valleys dependent on landscapes on higher location. In addition to nutrient supply, moisture supply is used to further subdivide landscapes into automorphic, semi-hydromorphic and hydromorphic landscapes. Rather than concentrating on soil fertility alone, we prefer to consider the fertility of an entire landscape or biosphere (in our case the noosphere). The noosphere (Vernadskij 1985) should have a fertility state adequate for maximum biological production, but should also be ecologically balanced, i.e. not deteriorating. An increase in the overall fertility of the total biosphere is impossible without fertility increases in its structural units: soil-bioclimatic zones, provinces, districts etc. up to every simple biogeocenosis (Anonymous 1983).

Agricultural landscapes are of anthropogenic origin and may be arable lands, grasslands, pastures, orchards or vineyards; but at the same time these agricultural areas are located on previous natural landscapes of tundra, forest, forest-steppe and steppe zones, with different hydrological conditions and biogeochemical cycles of nutrients. Both natural and anthropogenic developments take place in parallel in these agricultural landscapes.

One method for assessing the state of the agricultural landscape is a nutrient balance analysis. This method can usefully be applied to P and provides an assessment of the soil P regime and a forecast of its change. Calculation of the regional P balance within the territories of administration units (farm, district, region, territory, republic, economic region and country) is the most often applied method in the USSR (Pannikov and Mineev 1977, Peterburgskij and Nikitishen 1983, Postnikov 1983).

On the basis of studies of P cycling and balance in long-term experiments on different soils of the European USSR, scientists of the V.V. Dokuchaev Soil Institute recommend that the active P balance should be calculated including inputs from fertilizers, seeds and atmospheric precipitation. Biological components of the active P balance included supply with stubble and root residues. The passive balance should include P removal in agricultural production and losses due to leaching and erosion (Dokuchaev Institute 1987). Soil P before and after agricultural production is not included in the balance for practical reasons.

The ratio of inputs to exports calculated as a percentage of inputs is called the balance intensity. This balance intensity exceeded 100% in the west central and northern regions of the European USSR in the years 1976-1980. The eastern and southern regions had a negative balance with a balance intensity of 60-73%. Overall, a significant increase of mobile P was noted in the arable soils of the region (Shishev et al. 1987) due to a sharp increase in mineral and organic P fertilizer application (Table 1).

In recent years, the rates of increase in mobile P levels in non-chernozemic Russia have been stable (Shafran 1987). In addition to the calculation of regional P balances, an agro-chemical survey of fields is carried out every five years to assess the mobile P content. Results of this survey are used to evaluate the level of P supply for plant nutrition. In the European USSR, mobile P is determined by three methods: after Kirsanov, Chirikov and Machigin (Ginsberg 1975).
Kirsanov's method (0.2 N HCl, soil to acid ratio = 1:5, shake 1 minute, leave 15 minutes, then analyse photocolorimetrically) is used to determine mobile P in sod-podzolic and podzolic soils.
Chirikov's method (0.5 N, CH_3, COOH, soil to solution = 1:25, two hours of shaking, then immediate photocolorimetric analysis) is used for grey forest soils and non-carbonate chernozem.
Machigin's method (1% solution of $(NH_4)_2CO_3$, soil to solution = 1:20, shake 20 minutes, leave 20 hours, then photocolorimetric analysis) is used for carbonate soils (chernozem, kastanozem).

Table 1. Some characteristics of the P cycle in arable land of the European part of the USSR (annual means 1976-1980)

Republic, economical region	Input of P $kg \cdot ha^{-1}$	ratio of mineral to organic fertilizer P	Balance intensity, %
USSR	12	2.9	88
North-west	25	3.2	82
Central	20	3.4	100
Volgo-Vjatka	16	4.3	103
Central-Chernozemic	12	3.6	73
Volga-region	7	2.9	60
North-Caucasus	12	3.0	66
Latvian SSR	28	2.2	113
Estonian SSR	31	9.9	111
Lithuanian SSR	23	2.2	140
Byelorussian SSR	31	1.7	141
Ukraine	18	1.9	87
Moldavian SSR	22	4.7	83

An important component of the P cycle in agricultural landscape is residual P from mineral fertilization. Phosphorus applied regularly with crop rotations was found to be stored in the rooting zone in forms that are plant available (Ostanin et al. 1983). Mobile P supply in the soil increased by 1.5-2 times with regular P applications. At the same time, the share of soil P in plant nutrition naturally decreased, but did not fall below 58% in experiments with maize, and 64% with oats.

The complete compensation of P withdrawal from the soil by means of mineral fertilization ensures the optimum level of available P content in the

soil without any yield or fertility decrease; and that actually means a 100% utilization of applied fertilizers. With moderate rates of fertilizer P application, P is not significantly leached from soils of medium or fine loamy texture. The mean annual P losses resulting from erosion are 2.2 kg·ha^{-1} for sod-podzolic and 1.7-2.2 kg·ha^{-1} for chernozemic soils of the European USSR.

In experiments carried out by the Ukrainian agrochemical and pedological institute the optimization of P levels in soils was found to be one of the basic factors to increase fertility of chernozems and podzolized forest soils in the Ukraine. An increase in available (Chirikov) P content from 16-31 to 70-78 mg·kg^{-1} of soil resulted in an increased cereal production of 80-140 kg of cereal per 0.44 mg of P. Residual P from fertilizers remained more mobile in natural P for periods of 12 years or longer, and maintained and increased solution concentration of P in the soil (Nosko, 1984). Long-term field experiments on a typical chernozem carried out by the Dokuchaev Institute on soils with fine loamy texture in the Middle-Russian upland, revealed increases in Chirikov P content from 40 to 60 mg·kg^{-1} resulting from mineral and organic fertilizer P application at a rate of 262 kg·ha^{-1} over two crop rotations. This resulted in mean yield increases of: winter wheat grain - 290 kg over 6 years, winter rye - 95 kg over 5 years, peas - 100 kg over 7 years, sugar beet - 1,850 kg·ha^{-1} over 6 years. The creation of a favourable soil phosphorus regime for plant production due to the supplementation of the P cycle of agricultural landscapes is one of the basic conditions for stable high level agricultural productivity and the effective use of mineral fertilizer.

Table 2. Recommended levels of available phosphorus (P) content in soils of European part of the USSR (mg·kg^{-1})

Soil	Method of estimation	Levels of fertility		
		low	mean	high
Sod-podzolic				
clay loam and clay	Kirsanov	23-44	45-65	66-87
loam and sandy loam	Kirsanov	18-35	36-52	53-66
loamy sand and sand	Kirsanov	9-22	23-35	36-52
Sod-carbonate				
grey forest	Kirsanov	35-65	66-131	132-213
clay loam and clay	Kirsanov	23-44	45-65	66-87
Chernozem				
Podzolic, degraded, typical	Chirikov	18-35	36-70	71-87
ordinary	Chirikov	9-22	23-44	45-71
south	Machigin	5-7	8-13	14-21
Black chestnut and chestnut	Machigin	4-7	8-15	16-21

The basic trend in agricultural developments in the European USSR at present, and in the future, should be the aim to obtain available P contents in the plough layer (to 25 cm) adequate for a medium to high soil fertility level (Table 2). However, the complexity of the P cycle and the high P levels required in agriculture, require special care in the application of ecologically safe levels of P fertilizers. Fertilizer P application results in such negative phenomena as: P losses due to erosion (water and wind), fertilizer runoff from the soil surface, P leaching and its ultimate transport to surface waters, causing P pollution with resulting eutrophication. High single rates of P fertilizer application over and above crop demand can result in increased P content in the crop and an imbalance of the nutrient ratios in the crop.

Determination of regional balances is not exact, and especially large distortions occur through the extrapolation of local data to regions. For this reason, the landscape principle has been introduced into the study of P cycling and balances. This principle will increase the reliability of experimental data and improve the understanding of the internal processes of any ecosystem and therefore provide the knowledge required to avoid many negative phenomena associated with high rates of P fertilization.

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PHOSPHORUS MIGRATION IN LAKE LANDSCAPES OF LITHUANIA

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This article presents data obtained between 1975 and 1987, on the distribution and cycling of inorganic phosphorus in hilly lake landscapes of Lithuania. Post-glacial hilly lake landscapes are characterized by a complex, spacial arrangement of elementary landscape units and areas of different land use. On flat hilltops, where erosive and accumulative processes have insignificant effects on the predominant sod-podzolic soils, autonomous eluvial landscapes predominate. These areas occupy between 8 and 23% of the landscape. Hillsides, which cover between 39 and 42% of the investigated area, experience both import and export of soil material due to erosion. At foot slope positions and in the narrow interhills, erosive soil accumulation predominates. These areas occupy approximately 17 - 37% of the land surface, while water-logged interhill areas cover between 16 and 18% of the territory (4).

The distribution and cycling of phosphorus in these landscapes is determined by water movement as well as the erosive and accumulative processes occurring in the different landscape units. Studies on the budget of water and dissolved elements in soils, have therefore been complemented by considerations of their position in the catenary sequence. In particular, three areas have been distinguished: the agricultural landscape on the upper slopes, the forest belt on lower slope positions, and the water bodies in the valley positions.

Labile soil phosphorus was determined by the method of Egner-Riehm (1) which uses 0.04 N calcium lactate, at a pH of 3.5 - 3.7, and a soil to solution ratio of 1:50. The method is a standard soil test method throughout the USSR. Phosphorus discharge to the ground water was calculated from the composition of 571 ground water samples, and estimates of ground water flow were based on level changes in 42 bore holes at different positions in the landscape (2). Surface runoff was studied in 8 runoff plots and microbasins located at different slope positions, and under different management. Phosphorus discharge from drain tiles in four agricultural sectors was also determined (3). The present discussion will concentrate on inorganic P cycling in an agricultural area of about 50 ha. Total P levels are relatively similar in different positions of the landscape, while labile P levels are more variable and may vary by a factor of 10 - 50 times in different horizons of the same profile (Table 1).

Phosphorus input with mineral fertilizers varies depending on crops from 18 - 67 kg ha^{-1} yr^{-1}. Inputs with precipitation amount to only 0.1 - 0.5 kg ha^{-1} yr^{-1}, 90% of which come with rain, which has considerably higher P concentrations than snow (Table 2). Most of this P input is in available forms.

The cycling of soluble phosphorus varies in the different landscape units. On hilltops, vertical cycling and intensive biological assimilation of phosphorus takes place because moisture and temperature

regimes favour plant production, and the effects of erosion are minimal. Very little phosphorus is leached into the ground water from these landscape positions (PO_4 ions constitute only 0.1 equivalent percent of the total dissolved anions). In years with exceptional spring runoff a small proportion of phosphorus (less than 0.01 kg ha^{-1}) is transported by surface runoff from the hilltops.

Table 1. Amounts of phosphorus in soils and rocks (mg kg^{-1})

Landscape, soil	Total P	Mobile P
Parent material	500-650	53-67
Hilltops		
Plough layer of sod-podzolic soil	500-600	13-40
Iluvial layer of sod-podzolic soil	200-500	2-31
Shoulder & mid slopes		
Eroded plough layer	500-650	4-36
Toe slopes		
Deluvial layer	450-650	0.1-22
Burried soil humous layer	600-750	4-22
Burried soil illuvial layer	500-700	0.1-53
Valleys		
Topsoil layer	-	9-80
Peat layer	-	2.6-53

Table 2. P concentration (mg l^{-1}) in precipitation, surface runoff, and drainage water.

Water type	Minimum	Maximum	Mean	C_v
Precipitation:				
rain	0.00	0.97	0.18	0.35
snow	0.00	0.09	0.03	0.35
Surface runoff	0.00	0.61	0.20	1.00
Drainage	0.00	0.40	0.07	0.32

Shoulder and mid-slope positions are characterized by exposures of parent material, due to erosion, and relatively small biological accumulations of phosphorus. In landscapes with small hill sizes, midslope positions accumulate larger quantities of snow with a higher

phosphorus load, due to blowing of snow and exposed soil in the late winter months. This windblown material may have PO_4 concentrations 8.5 times higher than in fresh snow (Table 3). It is estimated that between 0.3 and 0.6 kg ha^{-1} of available phosphorus are carried away from mid-slope positions, due to erosion from cultivated areas. Surface runoff accounts for up to 0.1 kg ha^{-1}, since total PO_4 concentrations in runoff are not large (Table 2) and account for only 0.6% equivalent of all anions in surface runoff. Larger amounts of PO_4 are found in accumulated runoff and valley bottom positions. Eroded fine silt and clay particles may contain 4 - 6 times higher concentrations of P than the uneroded soils. These fine materials accumulate at foot and bottom slope positions, where much of the phosphorus enters the abundant vegetation. This explains the relatively low concentrations of P in ground water in those landscape units. The highest P concentrations are found in ground water of the the waterlogged valley positions, where P may amount to 3.8% equivalent of total dissolved anions.

Table 3. Mean P concentrations (mg l^{-1}) in soil-ground water (minimum and maximum in brackets)

Elementary landscape	Season: Winter	Spring	Summer	Autumn	Mean annual
	Lake landscape with small-size hills				
Hilltops	0.16 (0.02-0.39)	0.19 (0.00-0.39)	0.28 (0.00-0.64)	0.11 (0.01-0.28)	0.22
Shoulder & mid	0.14 (0.03-0.55)	0.22 (0.00-1.19)	0.34 (0.00-2.28)	0.08 (0.02-0.40)	0.22
Toe slopes	0.39 (0.02-2.47)	0.13 (0.03-0.30)	0.17 (0.00-0.92)	0.10 (0.01-0.28)	0.19
Valley bottoms	0.39 (0.02-1.09)	0.44 (0.00-1.19)	0.64 (0.00-2.57)	1.07 (0.06-5.67)	0.63
	Lake landscape with large-size hills				
Hilltops	0.16 (0.06-0.25)	0.14 (0.03-0.31)	0.32 (0.04-0.76)	0.07 (0.03-0.12)	0.17
Shoulder & Mid	0.27 (0.00-0.92)	0.09 (0.00-0.18)	0.29 (0.00-1.34)	0.21 (0.04-0.68)	0.21
Toe slopes	0.14 (0.00-0.47)	0.10 (0.02-0.36)	0.34 (0.00-1.28)	0.21 (0.00-0.87)	0.20
Valley bottoms	0.19 (0.01-1.09)	0.12 (0.00-0.45)	0.30 (0.00-1.38)	0.27 (0.00-0.81)	0.22

Phosphorus concentrations in all landscape units vary widely, partly due to variable inputs of fertilizers, but generally only 0.1 -

0.6 kg ha^{-1} of P are removed from the landscape by percolating water, while only half that much is carried by runoff. Biological cycling of phosphorus at lower slope positions reduces total exports to the hydrological cycle. The general pattern is that phosphorus losses from hilltops equal total inputs with precipitation, while in shoulder and mid-slope positions phosphorus runoff is twice as large as the inputs from the atmosphere, and in lower positions of the catena a net phosphorus accumulation takes place.

Several agricultural areas at bottom slope positions near lakes were investigated in detail (Table 4). The sites had received between 100 and 270 kg ha^{-1} of granulate superphosphate, corresponding to between 9 and 24 kg of P ha^{-1}. Only 2 - 4 % of the total incoming phosphorus comes from precipitation. A major portion of the applied phosphorus is subsequently removed with the harvest, and only 2 - 6% are lost due to leaching and runoff. All sites showed a positive P balance of between 1.9 and 11.8 kg ha^{-1}, while available P levels did not appear to increase significantly beyond their original range of 6 - 17 mg kg^{-1}. On sandy loam with a average yield of 2.5 - 3.0 t ha^{-1}, and a mean P input of 24 kg ha^{-1} y^{-1}, 48% of the input remain in the soil. At this balance, 230 mg kg^{-1} of available phosphorus have been found in the plough layer, while available phosphorus has also increased to 99 mg kg^{-1} in the B horizon. In deeper horizons, it amounts to 7 - 46 mg kg^{-1}. In heavily fertilized soils, a maximum of available phosphorus amounting to 200 mg kg^{-1} has been found immediately above the parent material. This layer appears to act as an alkaline barrier for the downward migration of phosphorus in the profile. During periods of intensive leaching or elevated water table, phosphorus from such a saturated layer may move into the ground water or to open water bodies.

Table 4. Inorganic phosphorus (P) balance of agrolandscapes at toe-slopes

Balance components	Sandy loam		Clay loam		Clay	
	kg ha^{-1}	%	kg ha^{-1}	%	kg ha^{-1}	%
Input						
with precipitation	0.4	2	0.4	3	0.4	4
with fertilizers	24.3	98	13.5	97	9.0	96
sum	24.7	100	13.9	100	9.4	100
Loss						
with surface runoff	0.1	0.4	0.1	1	0.1	1
with ground water runoff	0.5	2	0.7	5	0.1	1
with harvest	12.3	50	11.2	80	6.9	73
sum	12.9	52	12.0	86	7.1	75
Balance	+11.8	48	+1.9	14	+2.3	25

Forest belts on lake margins perform an important ecological role in significantly reducing P loads from runoff and ground water flows

before they reach the lake system. The role of forest belts as a barrier to phosphorus migration, is confirmed by measurements of dissolved phosphorus in the litoral zone of a lake. The least amounts (0.01 - 0.06 mg l^{-1}) were detected in lakes of wooded basins. Similar amounts (0.04 - 0.05 mg l^{-1}) were found in lakes of basins with 30 - 40% forest, or where lakes were surrounded by forest shelter belts. Lakes in sparsely wooded basins contained maximum phosphorus concentrations of 0.49 mg l^{-1}, with mean values 6 - 7 times above the means found for wooded basins.

The average increase of available phosphorus in Lithuania's cultivated topsoils, is 8 - 10% per year. With an intensive development of agriculture, an increasing tendency will persist in the future, and an understanding of P cycling and the factors limiting P pollution to inland waters is therefore essential.

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DISTRIBUTION OF PHOSPHORUS IN MEADOW AND CULTIVATED FIELD ECOSYSTEMS

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1. Introduction

Long-term studies on agroecosystem functioning carried out by the Department of Agrobiology and Forestry, Polish Academy of Sciences, in Poznan, provided data for the evaluation of energy flow and nutrient cycling processes in agricultural landscapes. One of the results of these studies is the total biomass evaluation for a whole range of biota present in agroecosystems, typical for the landscape studied (Ryszkowski 1985). Using this information as well as estimates of phosphorus contents in organisms and abiotic components of the agroecosystems the pattern of phosphorus distribution in a wheat field and adjacent meadow was evaluated.

2. Description of the area

The area of study is situated in mid-west Poland, about 40 km southwest of Poznan at the Turew Research Station of the Department of Agrobiology and Forestry, Polish Academy of Sciences. The terrain consists of ground moraines and is slightly undulating with slopes of less than 4%. Elevation differences between lower and higher parts of the area do not exceed several meters. There is a 4 m wide drainage canal running across the study area starting from a lake of 108 ha situated about 6 km away. Drain tiles distributed over the area, carry subsurface water from land to the canal.

The climate, by Polish standards, is rather warm with the average annual temperature 8°C. Mean temperature for July is 18°C and for January -2.4°C. The average annual precipitation for the period 1881-1985 is 527 mm (Ryszkowski and Kedziora 1987), almost 85% of which is used for evapotranspiration. Mean annual runoff of water is equal to 80 $l \cdot m^{-2}$ (Stachy 1965). West winds with annual average speed of 2.5 $m \cdot s^{-1}$ prevail. There is no serious wind erosion in the area of study; although, during dry springs with very strong winds dust storms happen once in several years.

The research was carried out in a typical section of an agricultural watershed consisting of cultivated fields separated from the canal by a strip of meadow 80 - 90 m wide. The soil is a light sandy mollic udipsamment. Soil pH in H_2O ranges from 6.7 (field) to 7.7 (meadow) and in KCL from 5.6 (field) to 7.1 (meadow). The pH of water in the canal and lake varies between 7.4 and 8.1. Organic carbon contents range from 5.3 $mg \cdot g^{-1}$ (field) to 19.5 $mg \cdot g^{-1}$ (meadow).

Generally, the cropping pattern of arable fields consists of 50% cereals (rye, wheat, barley and oats), about 25% row crops (beet, potato and rapeseed), 10% perennial fodder crops and 15% others. Shelterbelts are characteristic components of the Turew landscape. They were planted in the

1820s and were used as enclosures for cattle pasturing as well as for wood production, and to change the microclimatic conditions of adjoining fields.

3. Methods

Primary production of plants was evaluated by the method of summation of biomass increases including mortality of above-ground parts of plants between sampling dates (Ryszkowski 1984).

The biomass of animals living in the area was evaluated by various methods pertinent to a given taxonomic group (Wasilewska 1974, 1979, Nabialczyk-Karg 1980, Karg 1980a, 1980b, Paprocki 1985, Ryl 1980, 1984, Ryszkowski 1982, 1985, Karg and Ryszkowski 1985, Karg and Ryszkowski in press), and bacterial biomass was estimated by direct count and volume estimation of cells (Kaszubiak and Kaczmarek 1985). Fungal biomass is usually estimated as being 3 - 4 times higher than bacterial biomass occurring in forest and grassland ecosystems (Shields et al. 1973). A value of 3:1 for the ratio of fungal to bacterial biomass (Kaszubiak, in press) was used in this paper. Phosphorus concentration in soil microorganisms varies greatly. For instance Chauhan et al. 1981 state that C:P ratio in microorganisms may change from 20:1 to 60:1. Hedley and Stewart (1982) also observed variations in concentration which ranges from 1.7 to 8.6 $mg \cdot g^{-1}$ in bacteria, and in fungi from 2.2 to 14 $mg \cdot g^{-1}$. Martin and Holding (1978) claim that phosphorus concentration in bacteria is 10.7 $mg \cdot g^{-1}$ and this value was used in the paper. Phosphorus concentration in fungi was calculated on the basis of values given by Hedley and Stewart (1982) and Hayman (1975) who estimate P concentration in fungi and Actinomycetales as 5-10 $mg \cdot g^{-1}$. The value of 7.8 $mg \cdot g^{-1}$ as the mean concentration of P in fungi was used in the paper. The same value of P concentration as in bacteria (10.7 $mg \cdot g^{-1}$) was assumed for soil Protozoa. P concentration in Nematoda was accepted as 5 $mg \cdot g^{-1}$ (Anderson et al., 1981) , in Enchytraeidae 11.2 $mg \cdot g^{-1}$ (Coulson and Whittaker 1978) the same value was assumed for Lumbricidae, and 15 $mg \cdot g^{-1}$ for Acarinae (Mochnacka-Lawacz 1978).

The total P concentrations in insects, plants and soil samples was estimated after digestion by a mixture of sulphuric and nitric acid. P concentration in plants was calculated on the basis of our own as well as data of other authors (Perkins et al. 1978, Heal and Smith 1978). The following mean P concentration values were estimated: for above-ground parts of plants in meadow 1.87 $mg \cdot g^{-1}$; wheat straw 1.75 $mg \cdot g^{-1}$; wheat grain 4.7 $mg \cdot g^{-1}$; for roots in both ecosystems P concentration was 0.52 $mg \cdot g^{-1}$ and for litter 0.85 $mg \cdot g^{-1}$.

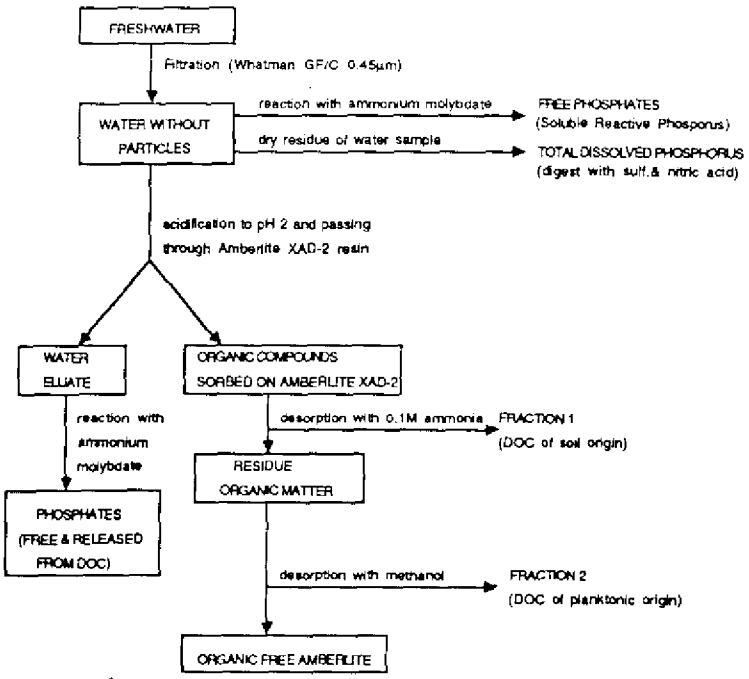
Plant available P in soil was determined by extraction with 0.04N calcium lactate (pH 3.6) and P was determined in the extract colorimetrically with ammonium molybdate.

Free phosphates (Soluble Reactive Phosphorus) were determined in fresh water after filtration through Whatman GF/C glass filter paper (0.45 µm) by colourimetric analysis using ammonium molybdate. Total Dissolved Phosphorus was analysed in dry residue of water samples after digestion by a mixture of sulphuric and nitric acid. Afterwards, the same water sample was acidified to pH 2 with concentrated hydrochloric acid and passed through a glass column packed with the Amberlite XAD-2 resin. The concentration of released phosphates was determined again. The differences between these two estimates shows the amount of PO_4 - P bound to dissolved organic carbon. Separation of dissolved organic compounds was carried out with column chromatography on

Amberlite XAD-2 resin using ammonia solution followed by methanol as desorbents which produced two fractions (figure 1).

Physicochemical properties of these substances were compared by elemental analysis and IR, UV and VIS absorption spectra. It was shown that the substances desorbed with ammonia solution have aromatic structures and are of humus origin (Szpakowska et al. 1986). The compounds, desorbed from Amberlite XAD-2 resin with methanol, consist of polysaccharides and polyamides and are of planktonic origin (Zyczynska-Baloniak and Szpakowska in press).

Figure 1. Flow diagram of phosphorus fractionation



4. Results and discussion

4.1 Input and output of phosphorus in meadow and cultivated field agroecosystems. The concentration of total P in the field soil was 900 $mg \cdot kg^{-1}$ and in the meadow soil 1200 $mg \cdot kg^{-1}$. The concentration of plant available P was 45 $mg \cdot kg^{-1}$ (field) and 63 $mg \cdot kg^{-1}$ (meadow) (Table 1). Soil bulk density was 1.65 $g \cdot cm^{-3}$ (wheat field) and 1.36 $g \cdot cm^{-3}$ (meadow).

Phosphorus fertilization, on the area under discussion, amounts to 3.9 $g \cdot m^{-2} \cdot y^{-1}$. Annual fluctuations in quantity of applied P fertilizers during the study period were small. The same amount of P was applied to both field and meadow. Manure (containing about 0.4% P) is applied only to some crops such as sugar beet, rape and potatoes. On average the input of P with manure was equal to 0.8 $g \cdot m^{-2} \cdot y^{-1}$. Liquid manure is not used in the area. Bartoszewicz's analyses (personal information) showed that annual input of P from precipitation is equal to 6.6 $mg \cdot m^{-2}$ PO_4-P which constitutes only 0.13% of the P input from fertilizers in the cultivated field.

Annual primary production, in the wheat field by the main crop including the catch crop (after-crops or fore-crops if raised additionally to main crops during the same year) was 1420 $g \cdot m^{-2}$ dry matter (DM), in which yield (straw

and grain) constituted 70% or 985 $g \cdot m^{-2}$ (Ryszkowski in press). Average P concentrations were 4.7 $mg \cdot g^{-1}$ in grain and 1.75 $mg \cdot g^{-1}$ in straw. The amount of P removed in the crop (400 $g \cdot m^{-2}$ grain and 585 $g \cdot m^{-2}$ straw) was 2.9 $g \cdot m^{-2}$.

Table 1. Distribution of phosphorus in components of a wheat field and a meadow ecosystem (to 30 cm soil depth)

Component	Wheat Dry matter ($mg \cdot m^{-2}$)	Wheat Phosphorus ($mg \cdot m^{-2}$)	Meadow Dry matter ($mg \cdot m^{-2}$)	Meadow Phosphorus ($mg \cdot m^{-2}$)
1. Mean Standing Mass ($mg \cdot m^{-2}$)				
Above ground (total)	265014.0	467.36	158647.0	299.53
Plants	264660.0	463.15	158400.0	296.21
Animals (total)	354.0	4.21	247.0	3.32
Saprovores	9.0	0.09	9.0	.10
Herbivores	283.0	3.20	183.0	2.34
Predators + parasit.	46.0	0.70	39.0	0.66
Other	16.0	0.22	16.0	0.22
Below ground (total)	794689.0	5939.74	2788137.0	16354.96
Plants (roots)	104580.0	54.38	937500.0	487.50
Animals (total)	2109.0	20.16	10637.0	181.46
Saprovores	1256.0	13.09	8170.0	162.39
Herbivores	383.0	2.03	1784.0	11.86
Predators + parasit.	030.0	0.33	155.0	1.56
Other	440.0	4.71	528.0	05.65
Bacteria	172000.0	1840.40	460000.0	4922.00
Fungi	516000.0	4024.80	1380000.0	10764.00
Litter	36290.0	30.85	127030.0	107.97
Soil (total P)	49431200.0	439634.80	406160000.0	473914.00
Available P	-	22275.00	-	25704.00
Grand total	49540799.0	446072.75	409233810.0	490676.46
2. Primary Production ($mg \cdot m^{-2} \cdot y^{-1}$)				
Plants	142000.0	336200.00	1336000.0	1810.00

Primary production of the meadow reached 1336 $g \cdot m^{-2}$ (DM) in which the removed yield (hay) amounted to 40% i.e. 531 $g \cdot m^{-2}$ (Ryszkowski in press). Phosphorus concentration in hay was 1.78 $mg \cdot g^{-1}$ which results in an export of 1 $g \cdot m^{-2}$ P by man. The annual uptake of P by plants was estimated using values of primary production and estimates of P concentration in plant tissue. Uptake of P by plants in meadow was 1.81 $g \cdot m^{-2} \cdot y^{-1}$, while in the wheat field it amounted to 3.36 $g \cdot m^{-2} \cdot y^{-1}$. Thus, because of the high P concentration in grain, the wheat agroecosystem used almost twice as much P in primary production as the meadow ecosystem.

In addition to the P in harvested yield some amount of P was removed with water runoff and leaching from the study area. Ground water for PO_4 analysis was sampled in drainage pipes. Ground water level under the field was at 2.4 - 3.7 m and under the meadow at 0.45 - 1.1 m. The direction of ground water flow was from the field across the meadow to the canal. The PO_4-P concentration in ground water on the field's edge amounted, on the average, to 0.19 $mg \cdot l^{-1}$. A more than twofold decrease in the concentration was observed when subsurface water flow carrying PO_4-P passed under the 80-90m wide meadow, and PO_4-P concentration declined to 0.07 $mg \cdot l^{-1}$ (Bartoszewicz and Ryszkowski in press). If the runoff of water in the study landscape amounts to 80 $l \cdot m^{-2} \cdot y^{-1}$, then, it could be calculated that 5.6 $mg \cdot m^{-2} \cdot y^{-1}$ of total PO_4-P is lost every year from the watershed. Free phosphates constitute from 15% to 45% of total P migrating in water (chapter 4.3). Thus, between 12.3 and 36.8 $mg \cdot P \cdot m^{-2} \cdot y^{-1}$ is lost from the landscape due to water movement. If the cultivated field were not separated from the canal by a meadow, losses of free phosphates might amount to a much larger 15 $mg \cdot m^{-2} \cdot y^{-1}$ (0.19 $mg \cdot P \cdot l^{-1}$ times 80 l at the edge of field). Correcting this last value for the amount of P bound to organic compounds, losses of total P from the field not separated from the canal by a meadow are 33.7 to 101.3 $mg \cdot m^{-2} \cdot y^{-1}$, depending which correction factor (15% or 45%) is assumed. Taking into account all known inputs and outputs of P the following balance sheet can be approximated:

A. In the cultivated field

Inputs ($g \cdot m^{-2} \cdot y^{-1}$)			Outputs ($g \cdot m^{-2} \cdot y^{-1}$)	
Fertilizers:	mineral	3.900	Removed with yield	2.900
	manure	0.800		
Precipitation		0.006	Leached: from 0.033 to 0.101	
Total		4.706		up to 3.001

B. In the meadow

Inputs ($g \cdot m^{-2} \cdot y^{-1}$)			Outputs ($g \cdot m^{-2} \cdot y^{-1}$)	
Fertilizers:	mineral	3.900	Removed with yield	1.0
Precipitation		0.006	Leached: from 0.012 to 0.037	
Total		3.906		up to 1.037

It seems that the agroecosystems under study and especially the meadow accumulate phosphorus, although the losses of P due to wind erosion both in field and meadow as well as losses due to early spring floods in the meadow are unknown. This conclusion is supported by the observation of Boratynski (1981) indicating that total P concentration in the majority of Polish soils increased during the recent period of intensive application of mineral fertilizers.

4.2 Distribution of phosphorus in the biota of meadow and cultivated ecosystems. The total amount of P in meadow was estimated to be equal to 490.7 $g \cdot m^{-2}$ (Table 1). Out of this total only 3.4% (16.6 $g \cdot P \cdot m^{-2}$) is contained in living parts of the ecosystem while 473.9 $g \cdot P \cdot m^{-2}$ consists mostly of inorganic plant available and stable P in the top 30 cm soil layer (Table 1). Vegetation contains about 0.8 $g \cdot m^{-2}$ P, animals (mainly soil invertebrates) about 0.18 $g \cdot m^{-2}$ and soil microorganisms (fungi and bacteria) about 15.7 $g \cdot m^{-2}$. Generally as much as 98% of P contained in the living part of the ecosystem is found in soil organisms (about 16.3 $g \cdot m^{-2}$) and only about 0.3 $g \cdot m^{-2}$ in above ground organisms (Table 1).

Table 2. Phosphorus concentration in insects

Group	Average phosphorus concentration (%)	Number of taxons	Development stage
Coleoptera	0.72	29a	
Diptera	0.95	13b	
Hymenoptera	0.86	9c	
Heteroptera	0.91	7d	adults
Homoptera	0.65	4e	
Lepidoptera	0.96	4f	
Others	0.71	2g	
Adults	0.79*	74	
Larvae	1.19*	28	-
Saprovores	1.08*	19	adults
Herbivores	0.80*	58	and
Predators	0.99*	25	larvae

* statistically significant differences ($P<0.01$) between the groups.
a. Diochrysa fastuosa (Scop.), Haltica quercetorum (Foudr.), Lema cyanella (L.), L. melanopus (L.), Gastroidea viridula (Deg.), Melasoma populi L., Leptinotarsa decemlineata Say., Cionus scrophulariae (L.), Strophosomus sp., Phyllobius sp., Polydrosus sp., Aphodius fimetarius (L.), Aphodius sp., Melolontha melolontha (L.), Serica brunnea (L.), Geotrupes sp., Coccinella septempunctata L., Halyzia sedecimguttata (L.), Melanotus sp., Dolopius sp., Leptura maculicornis Deg. Strangalia melanura L., Carabus coriaceus L., Harpalus sp., Meligethes aeneus (F.), Cantharis sp., Silpha sp., Staphylinidae.
b. Andrenosoma atra F., Dasypogon teutonus L., Machimus sp., Scatophaga stercoraria L., Lucilla sp., Empis tessellata F., Opomyzidae, Chironomidae, Culicidae, Dolichopodidae, Tabanidae, Muscidae, Tipulidae.
c. Tenthrendo maculata Geoff., Cephus pygmaeus (L.), Dolerus sp., Vespula germanica (F.), Lasius niger (L.), Formica rufa L., Camponotus sp., Ichneumonidae, Pteromalidae.
d. Graphosoma lineatum (L.), Aelia acuminata (L.), Eurygaster sp., Coreus marginatus (L.), Trigonotylus sp., Capsodes sp., Miridae.
e. Aphrophora alni (Fall.), Delphacidae, Iassidae, Aphidodea.
f. Spilosoma menthastri Esp., Plusia chrysitis (L.), Crambus sp., Boarmia sp.
g. Chrysopa sp., Thysanoptera.

In the field under wheat cultivation, the total amount of P to a depth of 30 cm was only 9.1% lower than in meadow (Table 1). Only 6.4 $g \cdot m^{-2}$ was contained in the living part of the ecosystem, that is less than half of that in meadow. Levels of plant available P were similar in the field and meadow. Standing crop of plants contained about 0.5 $g \cdot P \cdot m^{-2}$ that is less than half of the meadow, animals contained as little as 0.02 $g \cdot P \cdot m^{-2}$ (only a tenth of the meadow). Soil microorganisms contained a third as much the P as in meadow but still accounted for the major part of biomass P.

Concentration of P in various taxonomic and trophic groups of insects as well as their various development stages (larvae, adults)was studied in detail. All together 102 taxons of insects characteristic to the landscape studied were analysed. The lowest P concentration was found in adult Ichneumonidae (2.2 $mg \cdot g^{-1}$) and the highest in larvae of Rhagionidae (46.6 $mg \cdot g^{-1}$). Thus, the range of variation in P concentration in insects is over twentyfold. Phosphorus concentration in adult insect bodies belonging to higher taxonomic groups is similar across orders of insects with a range from 6.5 $mg \cdot g^{-1}$ (Homoptera) to 9.5 $mg \cdot g^{-1}$ (Diptera) (Table 2).

Statistically highly significant differences in P concentration were found between adult and larval forms. Larvae of some species (e.g. Scatophaga atercoraria., Diptera, or Rhagionidae, Diptra), show exceptionally high P concentrations of above 45 $mg \cdot g^{-1}$. For adult insects, an average concentration of P of 7.9 $mg \cdot g^{-1}$ obtained while in larvae as much as 11.9 $mg \cdot g^{-1}$ P was found (Table 2). Similarly high concentrations were noticed in insect eggs. Thus, egg and larval stages of insects have higher concentrations of P than adults.

Analysing various trophic groups of insects it was found that saprovores show higher P concentration than herbivores while predators show intermediate values (Table 2). Food of the three distinct trophic groups is very different in P contents. Dead plant remnants, which make the main food of the majority of saprovores contain the least P while the highest amount of P can be found in prey of predatory species. So the species which are richest in P are the ones living on food which contains very low concentration of P and vice versa. This phenomenon is probably an effect of various adaptations in the metabolism of different trophic groups. Nevertheless, one can indicate that saprovorous insects function in an ecosystem as efficient P concentrators.

There are differences in P distribution in the animals from field and meadow. As was already mentioned above, a large part of soil biomass P is contained in the soil fauna (83% for wheat cultivation and 98% for meadow, Table 3). Much greater amounts of P were found in animals living in the meadow soil (0.181 $g \cdot m^{-2}$) than in animals under the cultivated field (0.020 $g \cdot m^{-2}$, Table 3). This difference is caused not only by a lower standing crop of soil fauna in the cultivated field (2.11 $g \cdot m^{-2}$ DM) than in the meadow (10.64 $g \cdot m^{-2}$ DM) but also by lower concentrations of P in soil animals of the cultivated field. Agriculture impoverished soil fauna (Ryszkowski 1985), and most strongly eliminated groups like larvae of insects and earthworms that have high P concentrations. Thus, average P concentrations in soil animals are lower in cultivated fields than in meadows (9 and 17 $mg \cdot g^{-1}$ respectively). Biomass of saprovores makes up the biggest component of all animals living in the cultivated field and the meadow (Table 3). The concentration of P in saprovores is higher than in other trophic groups of animals. Due to these two reasons P in saprovores accounts for 54.1% of total animal P in the cultivated field, and 87.9% of total P in the meadow.

Table 3. Distribution of phosphorus in animal biomass of a wheat field and a meadow ecosystem

Group	Wheat field Biomass $mgDM \cdot m^{-2}$	Wheat field Phosphorus $mg \cdot m^{-2}$	Meadow Biomass $mgDM \cdot m^{-2}$	Meadow Phosphorus $mg \cdot m^{-2}$	Source of data[a/] (for biomass estimations)
Above ground fauna (Total)	354.35	4.216	247.40	3.325	
Insecta (adult, total)	123.85	0.993	57.40	0.491	
Diptera	10.92	0.107	16.78	0.149	
Coleoptera	5.17	0.029	1.04	0.009	
Heteroptera	2.12	0.014	0.96	0.006	J. Karg
Homoptera	99.79	0.801	8.24	0.053	
Hymenoptera	0.84	0.007	0.85	0.005	
Orthoptera	0.00	0.000	27.29	0.254	
Thysanoptera	4.60	0.032	1.80	0.013	D. Szeflinska
Other	0.41	0.003	0.44	0.002	J. Karg
Insecta (larvae, total)	44.24	0.429	2.64	0.028	
Coleoptera	7.39	0.077	-	-	
Hymenoptera	26.40	0.243	-	-	J. Karg
Lepidoptera	3.90	0.060	-	-	
Other	6.55	0.049	-	-	
Araneae	3.40	0.037	4.50	0.049	P. Wegorek
Amphibia	9.00	0.173	9.00	0.173	L. Berger
Aves	17.30	0.455	17.30	0.455	J. Truszkowski
Mammalia	156.56	2.129	156.56	2.129	Ryszkowski 1982
Below ground fauna (Total)	2109.14	20.163	10636.78	181.461	
Protozoa	440.00	47.10	528.00	5.650	Paprocki 1985
Nematoda	557.39	2.797	816.58	4.083	T. Witkowski
Lumbricidae	940.00	10.528	3840.00	43.008	Ryl 1984
Enchytraeidae	50.90	0.570	198.60	2.224	Ryl 1980
Acarina	11.25	0.169	305.00	4.575	Sell 1985
Collembola	47.40	0.360	65.60	0.499	Czarnecki 1979
Winged insects (mainly larvae)	62.20	1.029	4883.00	121.422	Nabialczyk-Karg 1985 J. Karg
Grand total	2463.49	24.379	10884.18	184.786	

a/ Personal communication where year is not given.

Due to the greater abundance of crop pests in cultivated fields than in meadows, the herbivores living in the wheat field contained 21.5% of total animal P in comparison to 7.7% found in herbivores of the meadow ecosystem.

Thus, in P cycling saprovores and herbivores play an important role in the cultivated field ecosystem, while in the meadow saprovores predominate.

The most important role in P cycling among the entire range of organisms is played by microbes (Table 3). The standing biomass P of bacteria and fungi in the wheat field was 5.9 $g \cdot m^{-2}$, which is more than the P uptake associated with annual primary production (3.4 $g \cdot P \cdot m^{-2}$). In meadow an eightfold higher amount of P was contained in standing biomass of bacteria and fungi (15.7 $g \cdot P \cdot m^{-2}$) than in annual primary production (1.8 $g \cdot P \cdot m^{-2}$). The P in bacterial and fungal biomass is equivalent to 26% of plant available P in the cultivated field and 61% in meadow. These results show the central role of the microbial population in P cycling.

4.3 Movement of phosphorus with water. Cultivated fields are characterized by very leaky nutrient cycles (Ryszkowski 1975). Many compounds, used in agricultural production, are leached, blown by wind or volatilized into the air from agroecosystems.

Investigations have shown that water in the lake and canal situated in the landscape studied contained both dissolved organic compounds (DOC) as well as free phosphates (soluble reactive phosphorus) (Figure 2 and 3). It is well known that organic compounds such as humic substances which are rich in functional groups are strong organic ligands and bind considerable amounts of ions. Many ions bound to organic compounds have a higher solubility product than their inorganic forms, and thus could be more mobile in a water environment. Separation of DOC into two fractions of soil and planktonic origin indicate that about 50% of dissolved organic compounds in the water of the lake and canal was leached from soil of surrounding terrestrial ecosystems, mainly from the cultivated field (Table 4).

Table 4. Variation of dissolved organic carbon (DOC) and bound and free forms of phosphorus over a year

Compounds	Lake Water Min.	Max.	Mean	%	Canal Water Min.	Max.	Mean	%
DOC Soil origin ($mg \cdot l^{-1}$)	10.0	45.0	24.9	48	13.0	57.0	25.6	53
DOC Planktonic orig. "	1.3	95.0	27.3	52	2.7	71.7	22.4	47
SUM DOC "	-	-	52.2	100	-	-	48.0	100
PO_4-P - Free ($\mu g \cdot l^{-1}$)	3.3	39.2	7.6	15	3.3	124.8	58.8	45
PO_4-P - Bound "	3.3	45.9	17.6	35	3.3	94.8	35.5	28
Other P-Forms "	-	-	25.2	50	-	-	35.2	27
Total dissolved P "	14.1	87.6	50.4	100	49.4	228.4	129.5	100

The seasonal variation of both fractions of DOC was pronounced (Figure 2 and 3). Variations of total dissolved P and free phosphate concentrations during the course of year were also pronounced in both water bodies. The highest concentration of total dissolved P was detected in autumn and winter months reaching 228 $\mu g \cdot l^{-1}$ in the canal and 88 $\mu g \cdot l^{-1}$ in the lake (Table 4,

Figure 2. Seasonal variations of dissolved organic compounds (DOC) and various forms of phosphorus in canal water

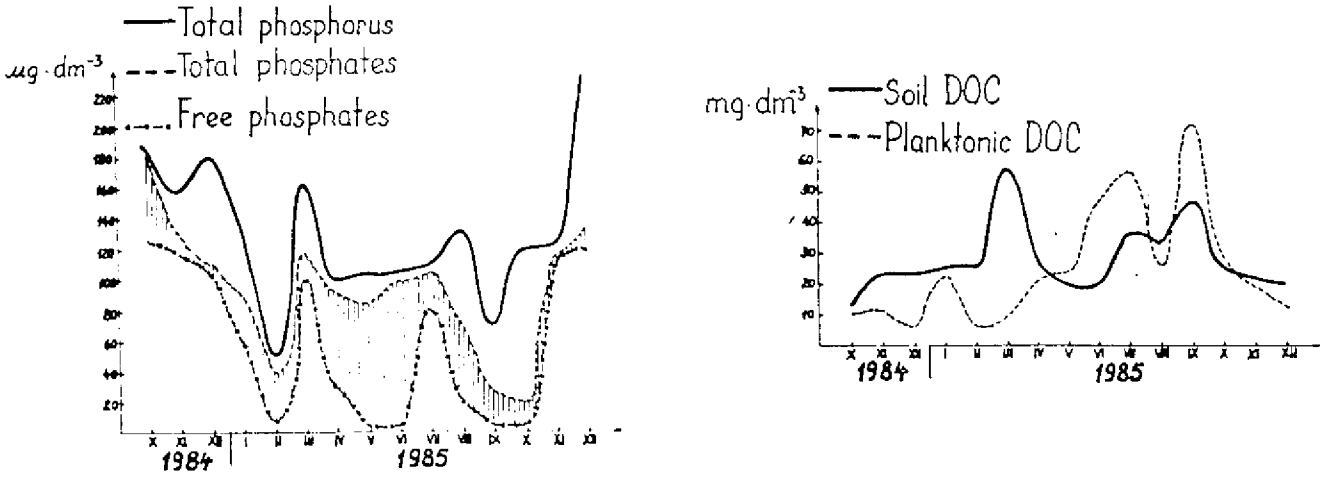


Figure 3. Seasonal variations of dissolved organic compounds (DOC) and various forms of phosphorus in lake water

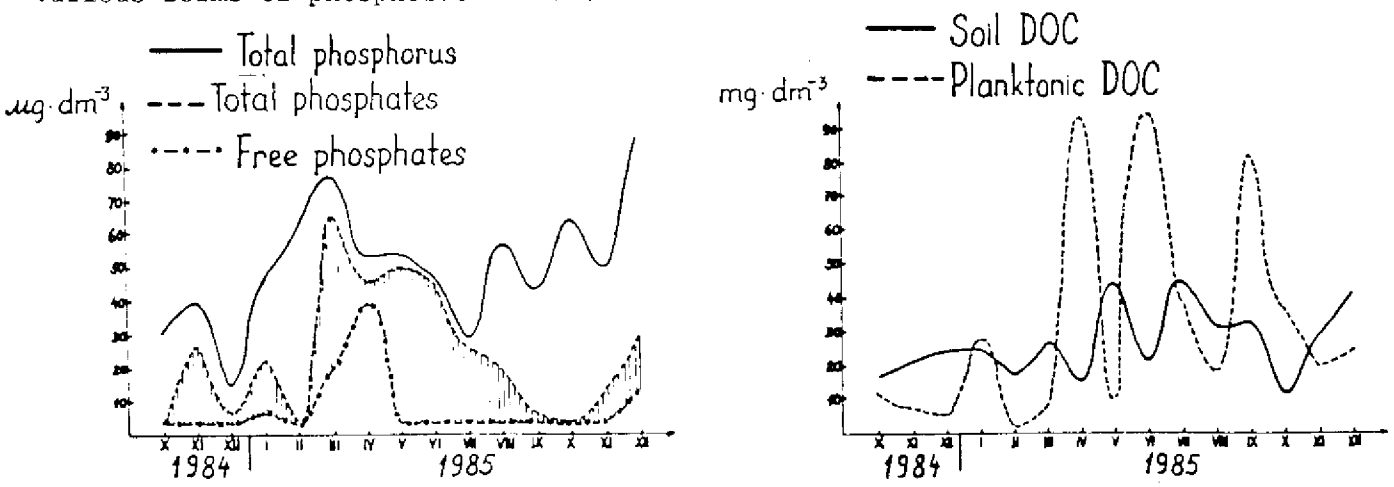


Figure 4. Relationship between total amount of phosphorus and dissolved organic compounds

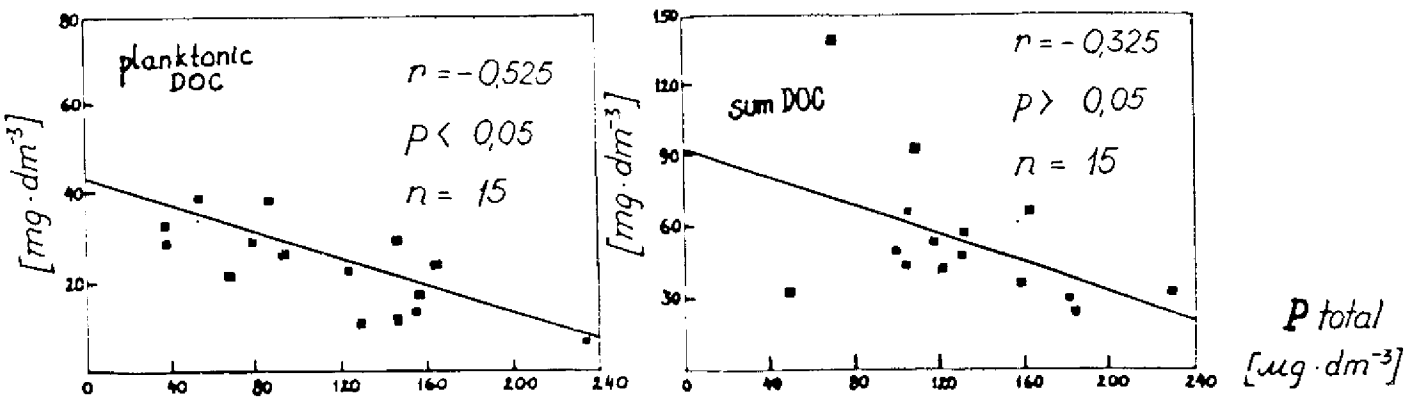


Figure 2 and 3). Concentrations of P bound to DOC also showed variations in time (Figure 2 and 3). In summer months, both in the lake and canal water, a considerable decrease of the concentration of phosphates bound to DOC as well as free phosphates was observed. It seems that this decline could be caused by liberation of phosphate bound to DOC under the influence of ultraviolet rays and then by rapid uptake of free phosphates by algae. It was found that relative solar insolation in summer months was 46% higher (Kedziora personal information). Desorption of phosphates from organic compounds caused by photoreduction was shown by Francko and Heath (1982) and Cotner and Heath (1988). It was estimated that on the average 28% and 35% of PO_4-P is bound to DOC in canal and lake water respectively. These two mean values of PO_4-P bound to DOC were used to approximate the total amount of dissolved P leached from the field and meadow. (see the balance sheet of P in chapter 4.1).

Because substantial amounts of phosphates migrate in water as PO_4-P bound to DOC, one could suspect a correlation between concentration of total dissolved P and total DOC but none was found (Figure 4), probably because of intensive photoreduction processes of PO_4-P bound to DOC during summer months and intensive uptake of free phosphates by abundant algae. A statistically significant negative correlation was found between total dissolved P and concentration of DOC of planktonic origin (Figure 4). If planktonic DOC is taken as index of algae abundance, then lower concentration of total P in water is correlated with greater density of algae which prove the assumption that algae control P concentration in water ecosystems as was pointed out by many hydrobiologists. Thus, in a situation characterized by low density or even lack of algae, the water transport of P could be accomplished mainly by migration of dissolved forms of P. This situation is typical for subsurface flow of water. Our preliminary studies have shown that concentrations of DOC varied from 6.3 to 34.4 $mg \cdot l^{-1}$ in ground water of the watershed studied. This indicates that not only free phosphates are transported but also DOC bound P. Therefore a correction was made to the P balance sheet in the cultivated field and meadow ecosystems.

5. Conclusion. Both the cultivated field and the meadow accumulated P at the rate 1.6 - 2.8 $g \cdot P \cdot m^{-2} \cdot y^{-1}$. If P accumulation is estimated in terms of mass of the top 30 cm soil layer then the annual accumulation is between 0.0003% and 0.0006% which can not be detected by methods of P determination. Thus, there is no possibility during the period of a few years to check the results of the P balance in the field. Recent publications indicating low or no effect of P fertilizers on yield (e.g. Reddy 1983, Gosek et al. 1984) could indirectly support the assumed P accumulation in some agroecosystems. One point more should be stressed. Because of input of dissolved P forms with subsurface water flow into meadows usually situated in lower terrain, the grassland ecosystems could accumulate more P than cultivated fields situated in upper parts of the watershed.

Phosphate concentrations in ground water flowing from the field into the meadow showed substantial decreases. Root systems of meadow grasses reaching a shallow ground water table may affect the chemistry of ground water which explains the decrease of P concentration when water passes under the 90 m wide meadow. In addition, ion sorption by the meadow soil could also influence the chemistry of percolating water. Both these effects would change the P output of a watershed depending on whether cultivated fields adjoin directly to canals or streams or whether they are separated by a meadow. Thus the chemistry of water runoff depends on the spatial arrangement of plant cover in the watershed.

Analysing the P cycling in the two ecosystems under question the following characteristics could be stressed (Table 5). Wheat takes up twice as much P as do meadow grasses. This is mainly the effect of high P storing capacities in grain.

Table 5. Characteristics of phosphorus cycling in a wheat field and a meadow ecosystem

Coefficient	Wheat	Meadow
$\frac{\text{Primary production P}}{\text{Plant available P}} \cdot 100$	15.1	7.0
$\frac{\text{Primary production P}}{\text{Microbes + animals P}} \cdot 100$ a/	7.8	5.1
$\frac{\text{Organisms P}}{\text{P in Runoff}} \cdot 100$	4.2	29.7

a/ without yield

The ratio of P stored in plant residues left in the ecosystem after harvest to the P contained in standing biomass of heterotrophs (microbes + animals) is similar in both ecosystems. This indicates the existence of a constant relationship between input of P contained in plant debris and level of P contained in heterotroph biomass of both ecosystems.

In the meadow the greater amount of P is contained in the total range of organisms (plants + heterotrophs) in relationship to P removed in water runoff than is observed in the cultivated field (Table 5). This indicates the closer P cycling within the meadow than in cultivated field.

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TRANSPORT AND TRANSFORMATION OF PHOSPHORUS COMPOUNDS IN WATERSHEDS OF BALTIC LAKES

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Introduction

The belt of Baltic lakelands situated in the northern region of Central and Eastern Europe forms a significant part of European lake resources (Figure 1). The Baltic lakes occur in a post-glacial landscape formed by the last glaciation of about 13000 - 16000 years ago, which is highly heterogeneous in respect to land use and land form patterns. Hilly-moraine areas of highly variable slopes co-occur with outwash plains. The geological substrate that is associated with these land forms varies from clay to sandy boulder clay, gravel and occasionally peat. Soils are rich in lime and moderately rich in available phosphorus (P). The variable relief and parent material are responsible for great variations in surface runoff and vertical infiltration of precipitation, and therefore affect nutrient distribution. There are many marshy areas covering as much as 25% of this type of landscape in Poland. The dominant land use in the lakeland regions is agriculture (mainly arable) followed by forestry consisting of pine and pine-spruce woods as well as wet alder woods. Both land use systems are interspersed in the landscape and they may alternate in many areas, producing a patchwork of different vegetation in different successional stages. The average resident population density is moderate, but the human impact greatly increases during the warm season due to tourism. Climatic conditions are relatively cold and windy, with wet summers.

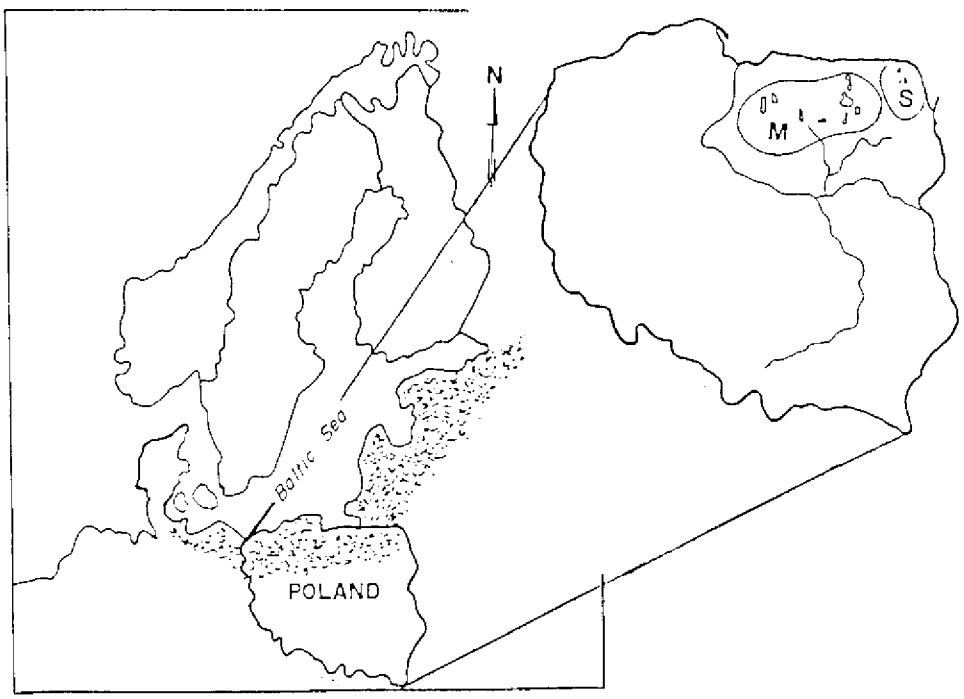

Figure 1. Localisation of the Baltic lake region in Europe, and of the Masurian (M) and Suwalki lake lands in Poland

Lakes are very numerous, and in some subregions of Poland make up about 20% of the area (Kondracki 1980). They are classed as the former Thienemann's baltic lakes i.e. temperate, lowland, harmonic lakes of the mesoeutrophic series but presently undergoing accelerated eutrophication (Hillbricht-Ilkowska 1985a). Gliwicz and Kowalczewski (1981) gave impressive evidence for the eutrophication of twelve relatively large and deep Great Masurian Lakes (Figure 2). In all lakes, including the deepest one, the oxygen deficit in the hypolimnion has increased since the late fifties. At the same time, transparency of the water decreased in the majority of the lakes. The accelerated eutrophication is mainly due to point sources of P input from urban and tourist wastes, which are believed to be controllable. However, the question arises what the role of uncontrollable non-point sources of P input is. Specifically, what is the input rate of P with runoff from watersheds and with wet and dry aerial deposition? What is the seasonality and the bioavailability of P from these latter sources? What is its relation to the physiogeographic and climatic conditions in the region? And finally, what is the relation of the non-point P load to the permissible and/or dangerous value for further eutrophication?

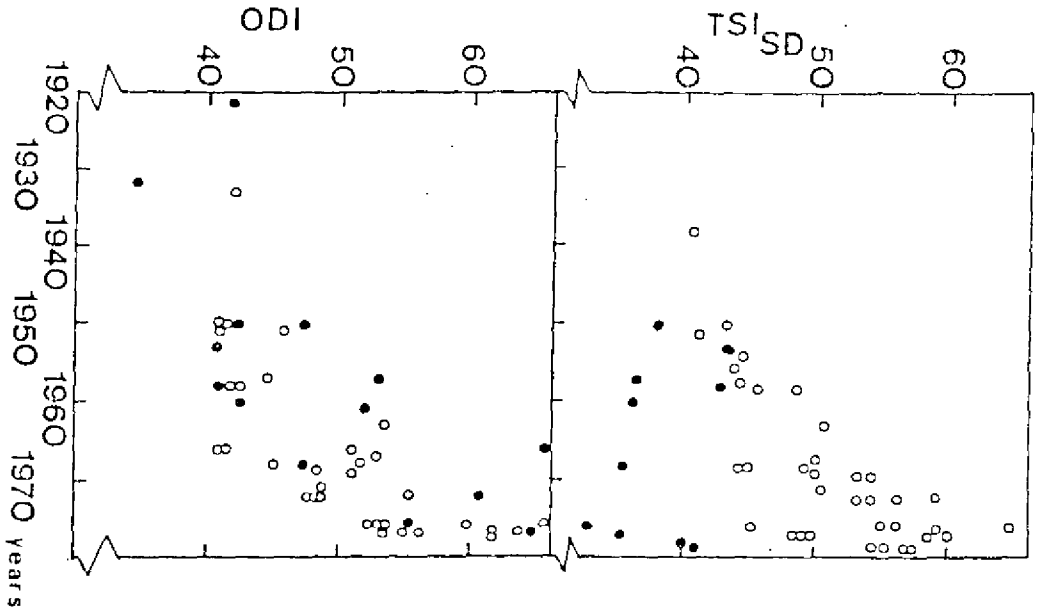

Figure 2. Yearly changes in trophic state index by Secchi Disk readings (TSI_{SD}) and oxygen deficit index (ODI) in the hypolimnion of Great Masurian Lakes (solid points: deep lakes, cirkles: all other lakes) (Gliwicz and Kowalczewski, 1981)

Results of studies carried out on selected areas in the Masurian Lakeland may be typical for the situation of the environment throughout the Baltic Lakelands (Figure 1). These results were obtained from the watersheds of five lakes connected with river Jorka in the Masurian Lakeland with an area of 63 Km^2 (Hillbricht-Ilkowska, Lawacz 1983a, Daszkiewicz 1983, Goszczynska 1985, Hillbricht-Ilkowska et al. 1981, 1983b) and the Suwalki Lakeland with the watersheds of the rivers Hancza, Szeszupa and Szelmentka, with a total area of 80 Km^2, including 25 lakes (Hillbricht-Ilkowska 1985b, 1987, 1988a). Both lakelands differ with respect to relief and climate. Generally, the Suwalki Lakeland has a more differentiated pattern of landforms, with higher hills and steeper slopes, and a more severe continental climate, as well as weaker human

impact. The relief and climate in the Suwalki Lakeland create the conditions for intensive erosion.

The Export Rate of Total P from Different Watersheds and its Relation to Selected Habitat Factors

A comparison of the annual export of Total P (TP) from selected Masurian watersheds of mosaic land use, with those reported for lowland homogeneous watersheds (Table 1) shows that even polluted Masurian watersheds have low or very low export levels. Generally, the values obtained for moraine landscapes are in the lower range of those for pasture or arable lands, and are comparable with values reported for homogeneous forested areas. Similarly, low values of annual TP export are obtained for the Pomeranian Baltic coast region with the same type of landscape, but with fewer lakes and under exclusively arable land use (Table 1).

Table 1. The annual TP export rates ($kg \cdot ha^{-1}$) from areas of different land use and relief

Landscape (Lakeland)	Land use	TP export ($kg \cdot ha^{-1} \cdot y^{-1}$)	
Flat, homogenous lowland[1]	forest	0.04-0.2	(0.9)
	meadow and pastures	0.05-0.17	(10.0)
	arable land	0.06-2.9	(54.0)
	bare soil	0.6-2.9	(54.0)
	urban runoff	1.0-5.3	
Hilly-moraine, heterogenous			
(Masurian)	peat, wet meadows[2] scarse alder wood	≤ 0.01	
	cultivated meadows[2] pastures, arable land, scarse wood fragments	0.01-0.06	
	farmland, pastures[3] polluted (manure), runoff	0.2-0.97	
(Pomeranian)	arable land, pastures[4]	0.1-0.3	

[1]selected from Kajak 1979, see also Hillbricht-Ilkowska 1984, in brackets - extreme values.
[2]Hillbricht-Ilkowska, Goszczynska, Planter 1981, Lawacz et al. 1985.
[3]Daszkiewicz 1983.
[4]Wilamski, Sliwa 1978, Taylor 1987, rounded values.

In the mosaic heterogeneous landscapes of the Baltic lake regions, the probable background level of annual TP export from relatively intact, unpolluted areas, is normally not higher than 0.1 $kg \cdot ha^{-1}$ and from moderately

polluted, fertilized arable land, it is no higher than 0.2 - 0.3 $kg \cdot ha^{-1}$. These values are about an order of magnitude less those obtained from flat, homogeneous areas situated in other landscapes (Table 1).

Slope gradients, which affect the intensity of erosion, seem to be the major factor influencing the base export rates of TP in hilly moraine landscapes. This could explain the slightly higher summer values obtained in Suwalki, as compared to the Masurian region (Table 2) and the higher values obtained in areas with steeper slopes, but similar land use within the Masurian Lakeland (Table 3). No relationship was found between the prevalence of land use (forest or arable in %) and the TP export rates in both study regions (Hillbricht-Ilkowska 1985b), since such a percentage does not reflect the spacial pattern of land use in a moraine landscape (cf. Ryszkowski et al this volume).

Table 2. Monthly (for summer) TP export rate and its bioavailability from unpolluted watersheds in Suwalki and Masurian lakelands of comparable land use* (according to Hillbricht-Ilkowska 1987, modified)

Lakeland:	No. of water-sheds studied	area km^2	slope %	TP export rate ($kg \cdot month^{-1} \cdot ha^{-1}$)	TP concentration ($mg \cdot l^{-1}$)	% P dis-solved in TP load
Suwalki	26	0.1-17.3	17-110	0.001-0.06	0.05-0.360	18-89
Masurian	7	0.3-2.3	4-15	0.001-0.007	0.02-0.100	50-95

* arable land (about 50%), meadows, pastures, scarce wood fragments.

Table 3. Range of annual TP export rates ($kg \cdot ha^{-1}$) from several Masurian lake watersheds of different land use and slope (from Hillbricht-Ilkowska, Goszczynska, Planter 1981)

No. of watersheds studied	area km^2	slope %	land use	TP export $kg \cdot ha^{-1} \cdot y^{-1}$
2	0.2-0.5	3	peat, wet meadows, scarse alder and birch wood plots	0.007-0.008
3	0.5-2.3	5	cultivated meadows pastures, arable fields	0.01-0.02
2	0.5-0.8	8-15	(as above)	0.3-0.6

The shape of the relationship between water discharge Q of a watershed and the TP concentration and/or the TP load is important for the prediction of

TP inputs into lakes, and for evaluating the relative importance of point versus non-point sources of P in a watershed. These relationships were analyzed for small watersheds with low average discharge rate (Q up to 100 $l \cdot s^{-1}$) such as the streams supplying selected Masurian lakes (Hillbricht-Ilkowska et al. 1981, Daszkiewicz 1983, Lawacz et al. 1985) as well as for the bigger watersheds drained by Pomeranian rivers (Q up to 1000 $l \cdot s^{-1}$) (Taylor 1987). In general, there is no relation between concentration of TP in stream water and its flow in unpolluted small or large watersheds in a moraine landscape. The concentration of TP is unpredictably variable, sometimes being higher after heavy storms, due to erosion. However, there is a relationship between flow Q and the load of TP. The correlation between mean monthly values for polluted and unpolluted Masurian watersheds (Figure 3) of very low (up to 20 $l \cdot s^{-1}$) and low (up to 100·l·s) discharge rate are:

$$\text{TP load (kg)} = 0.045 + 0.052\ Q\ (l \cdot s^{-1}), \qquad (r^2 = 0.71,\ P < 0.05)$$

for unpolluted streams (Figure 3) and

$$\text{TP load (kg)} = 5.58 + 0.87\ Q\ (l \cdot s^{-1}), \qquad (r^2 = 0.74,\ P < 0.05)$$

for polluted streams (Figure 3).

A similar relationship was found by Lawacz et al. (1985) for river Jorka with a flow up to 400 $l \cdot s^{-1}$ flowing through several lakes:

$$\text{TP load (kg)} = 0.14\ Q\ (l \cdot s^{-1}) - 0.87, \qquad (r = 0.93,\ N = 120)$$

The regression between Q and TP load was also given for the bigger Pomeranian watershed of river Reda by Taylor (1987) for three successive hydrological years. The correlation between TP concentration and flow Q were found only for polluted small watersheds i.e. areas with intensive farming and pasture management on Masurian Lakeland (Figure 3):

$$\text{TP}\ (mg \cdot l^{-1}) = 102.9 + 2.75\ Q\ (l \cdot s^{-1}), \qquad (r^2 = 0.67,\ P < 0.05)$$

The increase of flow from 10 to 100 $l \cdot s^{-1}$ may affect the TP concentration, and therefore TP load, through more intensive P runoff with increased flow rates from areas of agriculture and pasture use.

A portion of available P transported in streams, may be sorbed to suspended soil particles which, depending on the flow rate, could be deposited on the bed of the stream before entering a lake (Lawacz et al.1985). This process is apparent from the ratio of dissolved versus particulate P, in short versus longer streams or in successive sections of two streams studied in the Masurian Lakeland (Figure 4). Streams, therefore, are not only the main carrier of P in the lake watershed, but are also a place for P transformations that affect subsequent eutrophication effects. The density of the network of streams in the lake watershed (the so-called density gradient) and stream flow patterns seem to be the main factors, together with land use and slope, which regulate the non-point input of available P into lakes.

Atmospheric Transport of P in Lake Environments

Phosphorus occurring in air or transported with air movements, is either dissolved in water drops, or bound to dust particles. Studies carried out in the Masurian Lakeland, revealed that the annual deposition rates of TP with

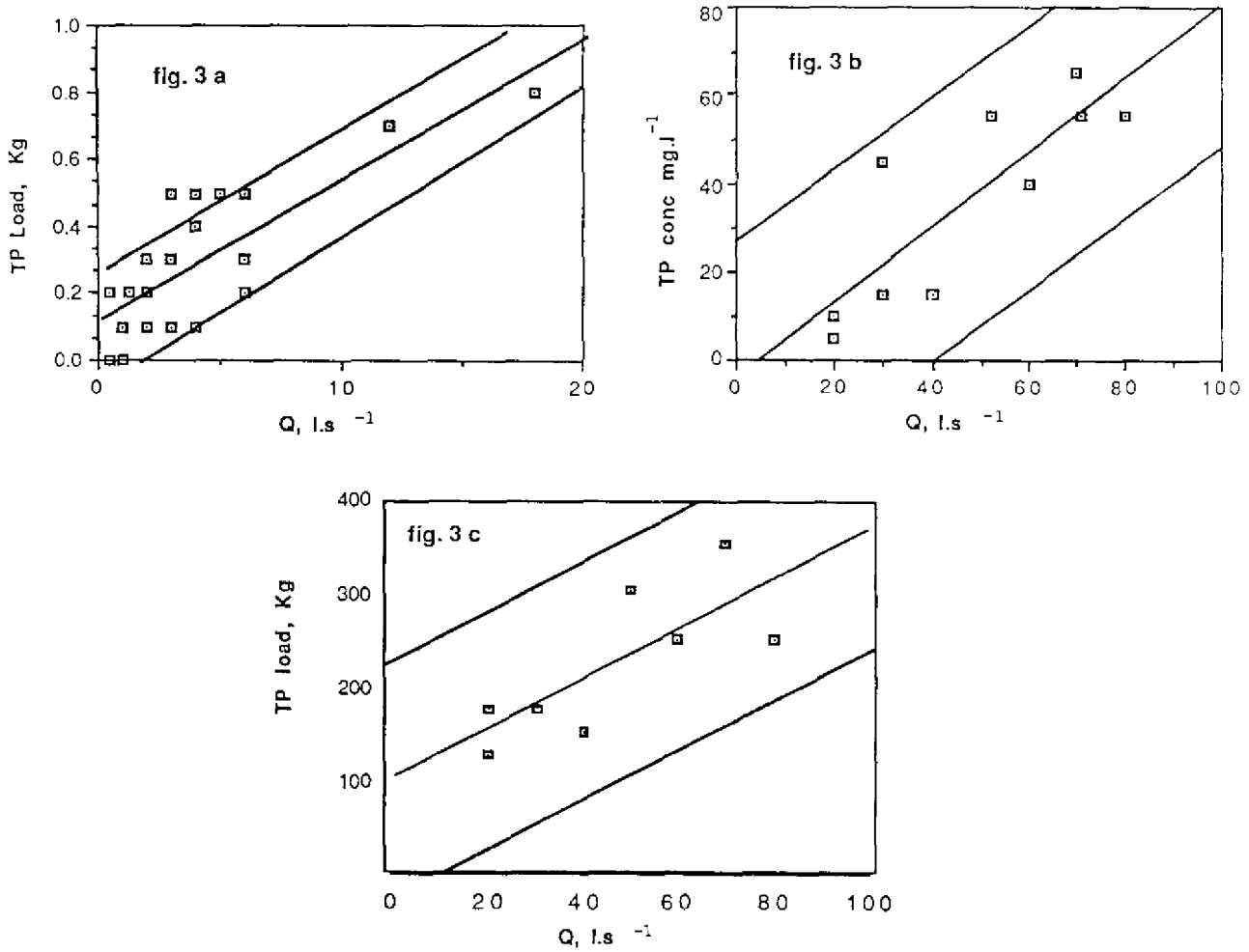

Figure 3. Relationships between the monthly average values of discharge (Q) and TP concentrations or loads in unpolluted small straems (a), in streams polluted by farming or pasturing (b,c) which supply the lakes in the r. Jorka watershed (Masurian lake land) (modified from Lawacz et al. 1985)

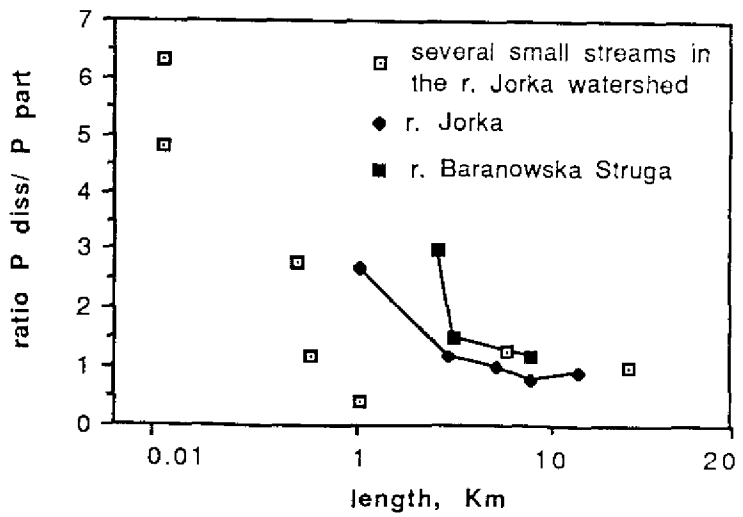

Figure 4. Changes in the ratio of dissolved : Particulate P in the annual TP load along the lenth of several streams in the Masurian lake lands(based on: Hillbricht-Ilkowska et al. 1981, Lawacz et al.1985)

dust (dry deposition) are two to three times higher than with wet precipitation (Goszczynska 1983, 1985, Hillbricht-Ilkowska et al. 1981) The TP concentration in the dust is moderately variable (range 0.9 - 2.0 $mg \cdot g^{-1}$, mean 1.3 ± 0.4 $mg \cdot g^{-1}$) between seasons and from year to year (Goszczynska 1983). The rather constant ratio of P to N and organic C in the dust (around 100:10:1) suggests that aerial P is mainly contained in organic particles eroded from the topsoil by wind, and carried over considerable distance. Dust loads are increased under conditions of bare, unfrozen soil with easterly or southeasterly winds, and decreased under frozen or wet conditions with westerly or southwesterly winds that normally bring rains (Table 4).

Table 4. Relationship between the amount of airborne dust (y, in $g \cdot m^{-2} \cdot y^{-1}$) and the meteorological factors (x) (Goszczynska 1983)

Meteorological factor	Relationship	positive/negative
1. Number of days with ground exposed to wind erosion	r = 0.58, N = 24 y = 0.20x +1.87, p > 0.01	+
2. Number of days with ground not exposed to wind erosion	r = -0.58, N = 24 y = 4.31-0.15x, p > 0.01	-
3. Precipitation		
rain (mm)	r = 0.38, N = 18 (not significant)	
snow (mm)	r = 0.20, N = 6 (not significant)	
number of days with snow cover	r = 0.63, N = 10 y = 2.12-0.035x, p = 0.05	-
number of days with rain > 1.0 mm	r = 0.46, N = 18 y = 5.93-0.25x, p = 0.05	-
4. Coefficient of erosion - number of days ground is exposed to wind erosion multiplied by the number of cases with wind speed > 7 m (s)	r = 0.46, N - 24 0.02 > p > 0.05 y = 0.011x + 2.085	+
5. Direction of wind		
SE	r = 0.50, N = 18 y = 0.16x + 2.57, p > 0.05	+
SW	r = 0.48, N = 18 y = 6.16-0.14x, p > 0.05	-
W	r = 0.67, N = 18 y = 6.64-0.14x, p > 0.01	-
E	r = 0.46, N = 18 y = 0.16x + 3.4, p > 0.05	+

Goszczynska (1985) found a correlation between the amount of dust deposited (D in $g \cdot m^{-2} \cdot y^{-1}$) and the amount of TP deposited on watersheds or lake surfaces, for the Masurian Lakeland (Figure 5):

$$TP = 0.0016D - 0.0065 \quad (r = 0.90,\ N = 30,\ p < 0.05).$$

For the range of dust fall from 10 to 60 $gm \cdot m^{-2} \cdot y^{-1}$, it gives an annual TP input between 0.02 and 0.08 $g \cdot m^{-2} \cdot y^{-1}$, with an average for the region of about 0.04 $g \cdot m^{-2} \cdot y^{-1}$.

The amount of TP input from rain, as found by Goszczynska (1983) for the same region, is about 0.017 $g \cdot m^{-2} \cdot y^{-1}$. The data on TP concentration and load in rainfall for other non urban European regions, given by Goszczynska (1983) shows that levels for the Masurian Lakeland are low (0.017 vs. 0.01 - 0.088 $g \cdot m^{-2} \cdot y^{-1}$). The TP concentration in rain water seems to be unpredictably variable, but the TP load (in $g \cdot m^{-2} \cdot y^{-1}$) could be roughly predicted from the amount of rain (R in mm), according to the formula:

$$TP = 0.00076R - 0.0183 \quad (r = 0.74,\ N = 33,\ p = 0.001)$$

for the range of R of 400 - 1000 mm (Figure 5).

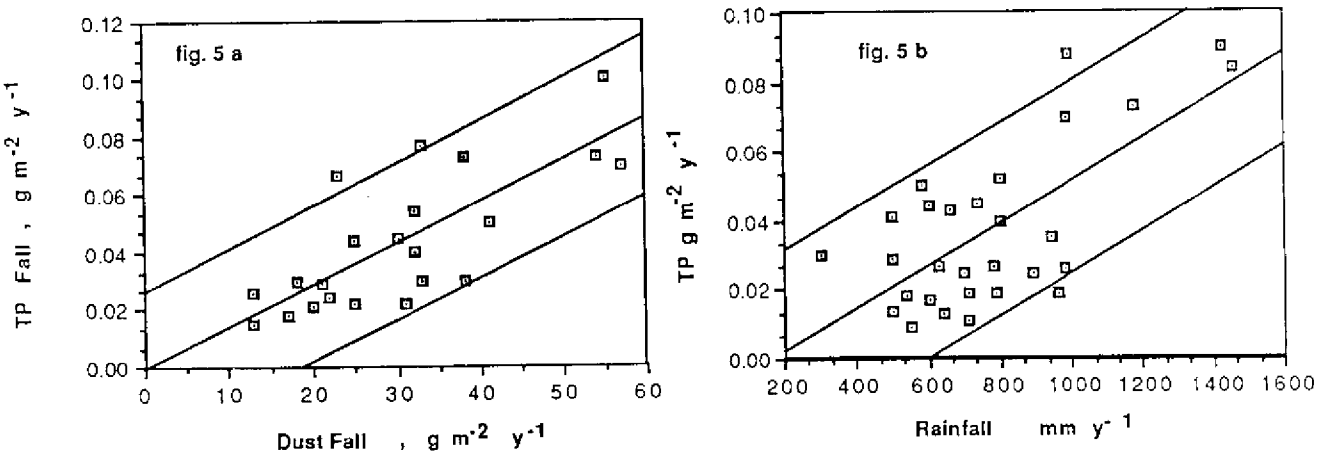

Figure 5. Relationship between the annual amounts of dust (a) and rainfall (b) and the TP load (after Goszczynska 1983, 1985), correlations are given in the text

The Bioavailability of P and Seasonality of its Input from Different Sources

The amount of P bound to light organic particles of soil origin from aerial inputs is quite high in the lakeland environment, due to predominant agricultural activities and a generally windy climate. Goszczynska (1985) has shown that dissolution of P from dust particles during the sedimentation in a water column is quite rapid (Table 5). Phosphate is readily dissolved if initial phosphate concentrations in the water are low, and dissolution may be as much as 10 - 20% of the original P contained in the dust. Uneroded soil particles release much less P (Table 5).

Only dissolved inorganic phosphate can be directly metabolized by planktonic organisms in the lake ecosystem. The relative proportions of P bound to seston particles, and dissolved P are therefore of great importance. Unavailable forms of P accumulate in areas strongly affected by erosion, since more P is bound to eroded clay and soil particles. This is likely the case in the Suwalki lake watersheds, which have slopes of up to 110%, and are characterized by low proportions of dissolved P, in comparison with Masurian lake watersheds, with slopes up to 15% (Table 2).

Table 5. Leaching of P-PO4 from dust and soil into the lake water (after Goszczynska 1985)

Initial concentration of $P-PO_4$ in lake water $mg \cdot l^{-1}$	Losses of P (per cent of the content in dust and soil) after leaching from: dust	soil
0.3-0.4	(+)2-3	(-)5
0.01-0.02	(+)10-20	(+)1-2

(+) positive losses (-) negative losses = sorption

The availability of P also depends on site-specific geochemical conditions. In half of the twenty-six small watersheds examined in the Suwalki region, conductivity of stream waters was found to be high (600 - 1000 $\mu S \cdot cm^{-1}$) (Table 6). This phenomenon, typical for the river Szelmentka watershed, suggests that underground deep waters are dominant in supplying the streams and lakes of this river. There are no significant differences between the export rates and concentrations of TP in the normal and hard water streams of comparable slope conditions and land use within their watersheds (Table 6). In waters of high conductivity though, more P occurs as dissolved phosphate and less is bound to particles, indicating that the hard waters have had less contact with erodable land surfaces.

Table 6. The bioavailability of TP in the watershed waters (surface runoff) of lakes of different conductivity in Suwalki Lakeland, Poland (after Hillbricht-Ilkowska 1988b)

Watershed of river:	No. of small watersheds studied	Area of studied watersheds km^2	Conductivity $uS \cdot cm^{-1}$	TP export rate (summer) $kg \cdot month^{-1} \cdot ha^{-1}$	% P in seston	% P in TP load as: dissolved	$P-PO_4$
1. Hancza and	14	0.14-11.4	280-450	0.012	0.54	55	28
Szeszupa				n.s.	s.	s.	s.
2. Szelmentka	12	0.1-17.3	600-1000	0.017	0.18	75	55

n.s., s. - means that the difference between the average values for the waters of high (600-1000 $uS \cdot cm^{-1}$) and normal (280-450 $uS \cdot cm^{-1}$) conductivity is non significant or significant (at $p < 0.05$ or < 0.01) respectively.

The seasonal patterns of P inputs from watershed and precipitation have been analysed for several Masurian lakes (Figure 6, Hillbricht-Ilkowska et al. 1983b). About half of the total yearly input of P in unpolluted watersheds of this region, is coming during the flood period between March and May. However, due to a large proportion of eroded particulate P, its availability is lower than of the P load reaching waters later in the year (Figure 6). The inputs from organically polluted portions of watersheds (farms and pastures), is prolonged until the middle of August, being connected with the animal breeding season and the summer peak of precipitation (Figure 6). This P source is similarly characterized by a low availability compared to P loads in unpolluted watersheds. It appears that much of this organic P is transported in particulate form.

The peak season for dry deposition of TP is May and June, during which most of the fields are bare and susceptible to erosion. Much of the P deposited with dust particles readily sediments to the lake bottom, together with an injection of dust material which accumulated over winter in the snow and ice cover. This heavy input of dust enters the lake system during the short melting period, usually two weeks in April, and brings with it significant amounts of TP in rather concentrated form (Goszczynska, 1987). Therefore, dust should be recognized as a significant source of P in the lakelands during spring and early summer (Figure 6).

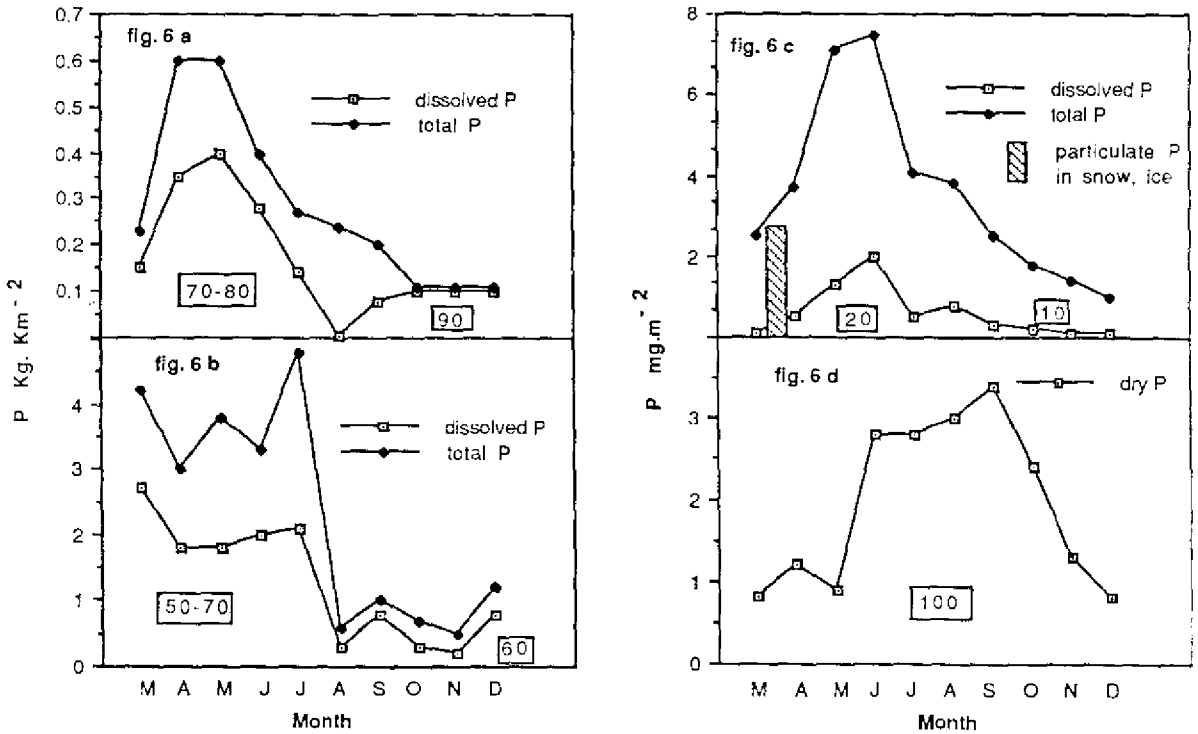

Figure 6. Seasonal changes in total and dissolved P in unpolluted (a) and polluted (b) small watersheds, and total and dissolved P inputs from wet (c) and dry (d) deposition. Framed numbers are percentages of P in dissolved form (after Hillbricht-Ilkowska et al. 1983b). note: different y-axes scales

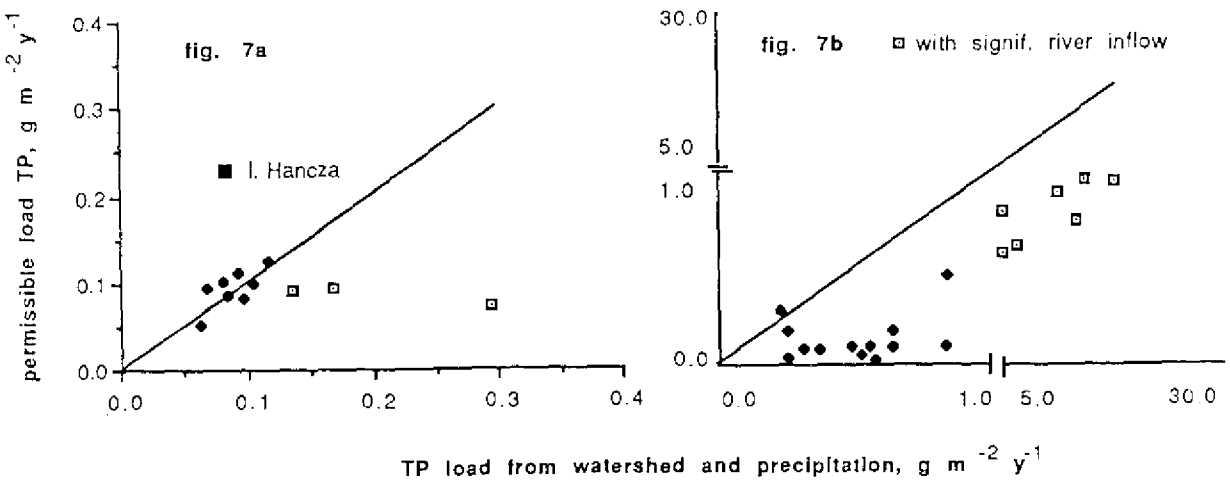

Figure 7. Permissible TP loads (Vollenweider, 1968) versus estimated diffuse TP inputs (from run-off and aerial deposition) for mesotrophic Suwalki (a) and eutrophic Masurian (b) lakes. Lake Hancza is the deepest (108.5m) mesotrophic lake.

Wet deposition of P follows the rainfall patterns and peaks in midsummer. Figure 6 illustrates the strong seasonality of TP inputs from the watershed (surface runoff), with dust accumulated over winter and surface runoff dominating in April and May, runoff from farming operations predominating in May and June and wet deposition of highly soluble phosphate dominating later in the summer.

Phosphorus Inputs from Non-point Sources and Permissible Load

Wuhrmann (1984) has pointed out that the TP loads from non-point sources like surface runoff and atmospheric deposition are sufficient in many lakes to maintain eutrophication and that the elimination of point sources like sewage, would only slow, but not stop further trophic changes. The actual TP loading calculated as the sum of inputs from surface runoff and stream inflows into lakes, as well as atmospheric deposition were compared with permissible load values, according to Vollenweider's (1968) criteria i.e. based on mean depth of the lake and residence time of lake waters.

The permissible load limits TP concentrations in the spring to approximately 20 $\mu g \cdot l^{-1}$ i.e. below the level which enhances algal blooming. Double that P concentration is called the dangerous value and would likely provoke intensive development of phytoplankton. The comparison between the permissible loads according to Vollenweider, and calculated TP inputs, was made separately for 11 mesotrophic Suwalki lakes, and for 20 mostly eutrophic Masurian lakes, located in the Masurian Landscape Park (Figure 7). The ranges of water transparency (SD readings) for the summer months was 3 - 8.5 m for the Suwalki lakes and 2.0 - 4.0 m for the Masurian lakes. The ranges of areas are 3.6 - 356 ha and 35.9 - 841 ha and the ranges of mean depth are 5.6 - 16 m and 0.6 - 12.7 m for the Suwalki and Masurian lakes respectively. These values exclude Lake Sniardwy (10970 ha) in the Masurian and the mesotrophic lake Hancza (109 m) in the Suwalki regions. Lakes affected strongly by stream or river inflows i.e. those with low water residence time, are distinguished in both data pools (Figure 7).

It is clear from figure 7 that the TP loads for both series of lakes from non-point sources is higher or at least equal to the permissible value. The unique exception is Lake Hancza, in which the non-point load is about four times lower than the permissible load. This explains why this deep lake has remained mesotrophic over the entire period of observations, with SD readings during summer of 8.5 m, oxygen concentrations in the bottom layer not lower than 5 - 8 $mg \cdot l^{-1}$, and an oxygen maximum in the metalimnion (Hillbricht-Ilkowska 1988a). While in most Suwalki lakes non-point TP loading is equal to the permissible load, in all but one of the Masurian lakes, the TP load is two to six times above the permissible value. This means that TP inputs from non-point sources alone exceed the dangerous level in all meso-eutrophic or eutrophic Masurian lakes. The worst situations occur in lakes which receive the greater part of their annual load from stream or river inflows, or from other upstream lakes. Although such lakes have a greater trophic capacity, due to the high flow-through regimes, they receive TP loads from non-point sources far above the dangerous value. It must be stressed that calculated TP loads do not take into account loads from point sources like farm, sewage, tourist centres and urban areas, and in some Masurian lakes like Lake Mikolajskie, this TP input exceeds the non-point load by about 1.5 times (Hillbricht-Ilkowska 1988b).

The above situation of mesotrophic and eutrophic lakes of Northern Poland can be considered typical for all Baltic lakes in hilly-moraine postglacial

landscapes. In all such lakes, TP loads from non-point uncontrollable sources could sustain further eutrophication irrespective of loads from point sources.

Conclusions

Analysis of the inputs of total and soluble P into the aquatic system of the typical Baltic lakelands situated in the postglacial landscape of Northern Poland, indicated relatively low TP loads, relative to flat homogeneous lowland areas. The very heterogeneous nature of hilly moraine landscapes, with its mosaic of arable land, forest fragments, marshy areas and frequent bogs and pools, as well as a dense network of streams, appears to favour P accumulation in stream beds and marshy and terrestrial sites on lake margins, and therefore has a high internal P sorption, even if half of the land is used for agriculture or pasture. However, these lake regions, particularly the Suwalki lakes, are strongly affected by erosion, which is probably the main factor controlling the P loads. This was confirmed by Stasiak and Tatur (1985) in a history of the lakes of river Jorka, in which the intensive deforestation in the watershed coincided with the accumulation of eroded materials in the bottom deposits, and was followed by an increased eutrophication of the lakes.

If soluble P is transported together with eroded particulate material, its direct bioavailability is decreased through absorption and sedimentation processes. Peak TP loads during March to May therefore only have about 50 to 70% bioavailability, as compared to the lower loads of TP with 90% bioavailability later in the year. On the whole, P inputs from rain and dust are significant, and their role has usually been underestimated. Even moderate or low annual export rates of TP from the watershed, when converted into TP loads of inland waters and combined with TP loads deposited from the air, give values at least equal, but often higher than the permissible value according to Vollenweider's (1976) criteria. This means that in the European Baltic belt of lakes the TP input from non-point, uncontrollable sources could sustain the further eutrophication irrespective of the existence of controllable point sources of P like waste waters of various origin.

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PHOSPHORUS FERTILIZERS IN EUROPE

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Introduction

The first phosphate fertilizer - ground bones - was widely used in Europe during the early part of the 19th century. Treatment of bones with sulfuric acid began about 1830. Dilute acid was used and the product was a slurry which was distributed in wooden casks. Potash salts and sulfate of ammonia or nitrate of soda were sometimes added, thus producing the first liquid mixed chemical fertilizers.

In about 1840 treatment of phosphate rock with sulfuric acid was found to yield an efficient fertilizer, which was called superphosphate. The first successful commercial superphosphate production was started by Lawes in England in 1842. The production of concentrated or triple superphosphate first started in Germany in 1870, but the acid was mostly used for other purposes than fertilizers. Triple superphosphate did not become a common fertilizer before the 1950s.

Although ammonium phosphate had long been known to be an effective fertilizer, it did not become popular until the 1960s. Ammonium phosphate is now the leading form of phosphate fertilizer in the world. Manufacturing of nitrophosphate fertilizers was started in Europe in the 1930s. They have had an increasing popularity in Europe and several plants have been built in other continents (IFDC 1979).

Table 1. Production of raw phosphate in Europe in 1000 tonnes P

Country	Year 1986
Finland	79
Sweden	30
USSR	4300
Total	4409

Sources of phosphate rock

Early sources of phosphate rock for the European fertilizer industry were small deposits in several European countries. Most of these deposits are no longer mined because of their low grade or because they have been exhausted. Except for Finland, Sweden and the USSR (Table 1) (Brit. Sulfur Corp 1987) the

production of raw phosphate takes place outside Europe. All European countries except the USSR and Finland must import nearly all their rock phosphate (Table 2). Present supplies are mainly from the United States and Morocco besides Russia, with smaller outputs from the Near East, several African countries, Brazil and some islands in the Pacific. New large deposits were discovered in the late 70s (IFDC 1979). Probably as much as 85% of the world's production of phosphate rock is used for the manufacturing of fertilizers.

Table 2. Production of fertilizer P as compared to production of rock phosphate in 1985-86, in 1000 tonnes

	Rock phosphate	Fertilizer P	Balance
Western Europe	127	2120	-1993
Eastern Europe	4300	4816	516

European production and consumption of P

The world's production and consumption of P increased steadily until the end of World War II. From then on it has risen sharply and is now more than 8 times the amount consumed in 1946 (Figure 1). The European consumption was 55% of the world's consumption in 1967, now it is about 47%.

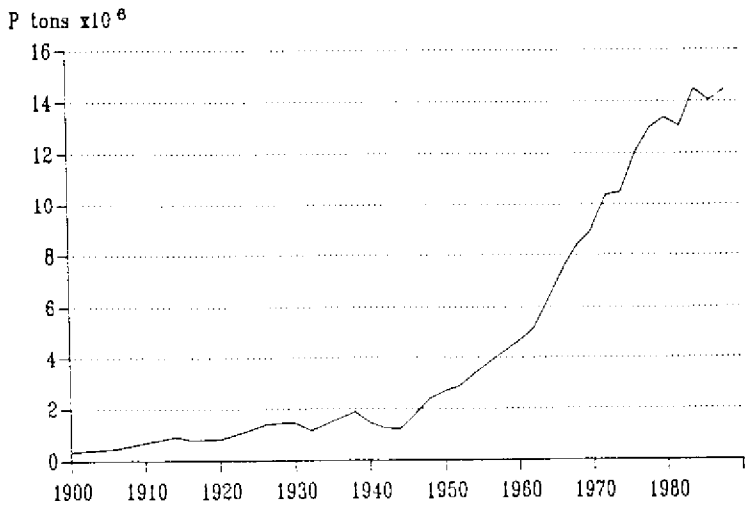

Figure 1. World consumption of P from 1900 to 1986.

In Western Europe the consumption rose until - and reached a peak in 1973-74. The consumption was then slightly more than 2.6 million tons of P. From 1973 on the consumption pattern has varied, but it has had a downward trend, and in 1985-86 it was at its 1967-68 level with less than 2.2 million tons P (Figure 2). The use of P on each hectare of arable land and permanent crops (Table 3) in Western Europe has reached a satisfactory level of about 24 $kg \cdot ha^{-1}$ as compared to a world average of only 10 $kg \cdot ha^{-1}$ (Table 3). This

partly explains why consumption has leveled off and reflects farmers responses to policy changes, regulating price support and production control measures. The use of P is expected to be stagnant or to decline slightly over the next 10 years. There has also been a decrease in production in Western Europe in recent years, due to poor domestic and export market conditions. This has resulted in idle plants or closures and/or lower utilization of production capacities.

Table 3. Consumption of P per hectare of arable land and permanent crops in kg.

	1984-85	1985-86
Western Europe	24.7	23.9
Eastern Europe	15.0	16.4
World	10.0	9.8

In Eastern Europe and the USSR, P consumption has increased steadily, and shows no signs of leveling off (Figure 3). Consumption per hectare is still less than 18 $kg \cdot ha^{-1}$. Phosphate consumption is expected to increase in the near future, especially in the USSR, but this will depend upon the effect of lower fertilizer prices and efforts made to improve quality of fertilizers and reduce losses (FAO 1987). Consumption forecasts indicate an increase of 1.2% per year in Eastern Europe and an increase of close to 3% per year for the world (Figure 4) (FAO 1985, FAO 1987, IFA/ISMA 1987).

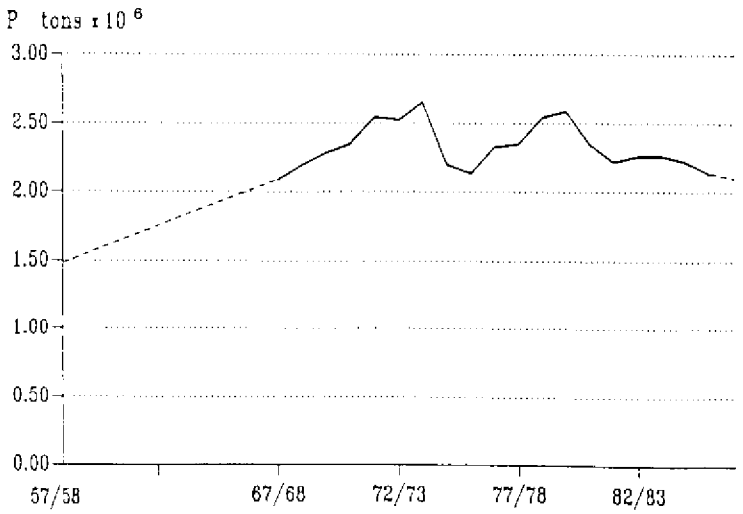

Figure 2. Western European Consumption of P from 1957 to 1985.

Table 4 shows the figures for production, import, export and consumption in Europe in 1985-86. The difference between Production + Import and Consumption + Export is about 500,000 tonnes, or more than 5%. This represents losses at different levels of production, handling and transport.

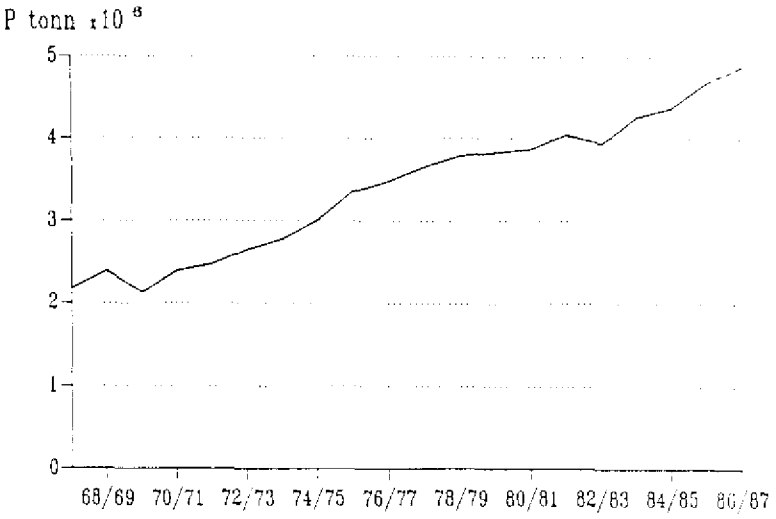

Figure 3. Eastern European consumption of P from 1967 to 1985.

Table 4. Balances of P production and consumption in Europe 1985-86, in 1000 tonnes

	Production	Import	Export	Consumption
Western Europe	2120	954	696	2152
Eastern Europe	4816	434	352	4687
Total	6936	1388	1048	6839

Different phosphate fertilizers

A wide variety of phosphate fertilizers are produced, most commonly by dissolving phosphate rock in different strong acids.

Mechanical treatment of rock P. After removal of dust, organic matter and $CaCO_3$, the remainder of the phosphate rock can be ground very finely and used as a fertilizer with varying success. They contain between 10 and 15% P. Rock phosphates are water and citric acid insoluble. There are indications that reactive rocks may be useful sources for at least part of the P requirement of many crops grown on acid soil (IFDC 1979), but the reactivity varies greatly with different sources.

Reactions of rock P with sulfuric acid. By adding sulfuric acid to phosphate rock, a mixture of monocalcium phosphate and calcium sulphate is obtained. This is the well known superphosphate, or single superphosphate (SSP): $3Ca(H_2PO_4)_2 + 7CaSO_4$. SSP has been the principal phosphate fertilizer for over a century and supplied over 60% of the world's demand as late as 1955. Since then it ha gradually decreased in importance and is now supplying somewhere between 10 and 15% of world fertilizer demand.

Phosphoric acid is also produced by treating phosphate rock with sulfuric acid. It can be utilized directly in liquid fertilizers. Under-acidulated superphosphate is obtained by the partial reaction of sulfuric or phosphoric acid on phosphate rock and/or by a mixture of superphosphate and rock phosphate containing mainly: monocalcium phosphate, tricalcium phosphate and calcium sulphate. The total P content is 10% of which at least 40% should be water soluble.

Reactions of rock P with phosphoric acid. Reacting phosphoric acid with rock phosphate results in triple superphosphate, TSP, which is composed of more or less pure monocalcium phosphate; $10Ca(H_2PO_4)_2$. The content varies from 17 to 21% and is fully water-soluble. Since 1965 TSP has supplied approximately 15 to 20% of the worlds fertilizer phosphate. Unlike SSP, TSP has a higher content of phosphate than the rock it is made from, thus its production is best carried out near the source of the rock in large plants with shipment of the product to local mixing plants or to farmers. The reaction between phosphoric acid and ammonia produces monoammonium phosphate; $NH_4H_2PO_4$, and diammonium phosphate; $(NH_4)_2HPO_4$. The N-content varies between 11 and 21% and that of P between 20 and 27%.

Reactions of rock P with nitric acid. The reaction of rock phosphate with nitric acid produces a mixture of monocalcium phosphate and calcium nitrate. Calcium nitrate makes monocalcium phosphate unstable and the product is hygroscopic. Various processes have been developed to eliminate the calcium nitrate. Nitrogen is then restored by adding ammonia at some point. A fertilizer is obtained in which phosphate is partly in water-soluble monocalcium form, the rest being citrate soluble dicalcium phosphate in proportions depending on the process used. There are several other processes for making phosphate fertilizers, but they are all of local and minor importance (Figure 4).

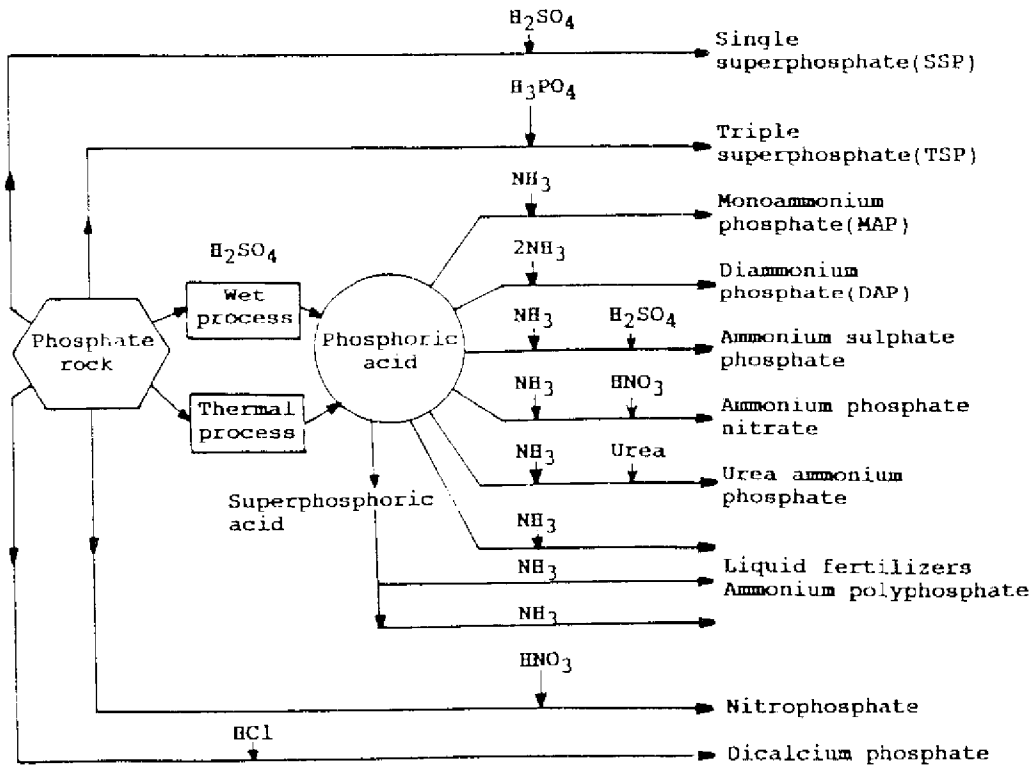

Figure 4. Different processes for making phosphate fertilizers.

Fertilizers made from iron ore (Basic slag). Limestone is mixed with molten iron ore rich in phosphorus, and oxygen is blown into the mixture. The slag floating on the top is cooled and ground. It contains phosphorus in the form of tetracalcium phosphate; $Ca_4P_2O_9$ and calcium silico-phosphate; $Ca_5SiP_2O_{12}$. The strength is 7 to 10% of which 15 to 20% is soluble in 2% citric acid.

In the late seventies and early eighties phosphoric acid was the source of about 90% of the new phosphate fertilizer production. In the period 1976-81 phosphoric acid supply increased from 6.9 to 9.6 million tons of P while supply from other sources only increased slightly from 5.5 to 5.7 million tons. Of the other sources nitrophosphate has gained while SSP and basic slag have lost in importance (ISMA 1986).

Other phosphorus "sources" than processed fertilizers. Organic sources of phosphorus such as plant residues, manure and sewage sludge are means of recycling phosphorus and should be utilized as efficiently as possible on the individual farm to improve P cycling efficiency on a global scale.

Properties of P fertilizers

Chemically processed phosphate fertilizers are water and citric acid soluble and usually more concentrated than other forms of phosphate fertilizers. When combined with other nutrients the total concentration of nutrients can become quite high which is important for the reduction of transportation costs.

Fertilizers with a high water solubility have proven to be an efficient means of supplying phosphates to most crops under almost all growing conditions except acid soils. As it is important that some soluble phosphorus be readily available to young plants to assist them with the rapid development of good root systems, phosphate fertilizers with a water soluble fraction of about 75% is desirable, especially for crops with a short growing season. Potatoes may, for instance, respond to a water solubility of up to 100%. On acid soils and/or for permanent crops or crops with a long growing season, the requirement for water solubility is not as high (Ellis 1985).

Phosphate fertilizers made by treatment of phosphate rock with sulfuric acid and phosphoric acid will have a water solubility of over 90%. Fertilizers made by treating phosphate rock with nitric acid will have a solubility varying from 35 to 85% depending upon the method used.

Other factors influencing phosphate availability

A factor that may influence the efficiency of phosphates is the balance of nutrients found in the composition of complex fertilizers. Depending on the mixture of fertilizers used, the availability of phosphates may vary. This is a research area that has not been explored to any significant degree, and should be given some priority in the future (Larsen 1986, Terman et al. 1964).

Biological and enzymatic processes as well as genetic manipulation may prove valuable in the future in order to utilize soil phosphorus reserves to a

larger degree than at present. Inoculation with mycorrhiza has, for instance, shown some promising results.

Much work has been done in order to evaluate the best methods for placement of phosphate fertilizers in different soils and for different crops. The knowledge in this area is substantial, but possibly the average farmer, for different reasons, does not have or does not use the knowledge properly.

Conclusions

1. Western European farmers apply adequate quantities of phosphate fertilizers.

2. Eastern European farmers, especially USSR farmers, may increase their yields by increasing their phosphate fertilization

3. Europe is highly deficient in phosphate rock, but production of fertilizers is close to being sufficient at present demand.

4. Europe as a whole will show an increasing demand for phosphate fertilizers in the near future.

5. Better utilization of soil phosphate reserves may decrease the demand for phosphate fertilizers in the future, and will come from genetic manipulation, mycorrhiza inoculation and better agricultural practices rather than from improved phosphate fertilizers.

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ANTHROPOGENIC SOURCES OF PHOSPHORUS: DETERGENTS

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Composition and function of detergents

In order to understand the function and significance of different components of detergents, a brief look at detergents and how they deal with 'dirt' will be helpful.

Dirt has been defined as 'matter in the wrong place'. This implies that virtually any matter can be dirt and may have to be removed from laundry. Detergents contain a mixture of ingredients that together can deal with most kinds of dirt (Table 1).

Table 1. Key ingredients in modern detergents and what they remove

Detergent ingredient	Dirt constituent
Surfactant	fat, oil
Builder	clay
Bleach	color
Enzyme	protein

Surface active agents (surfactants) remove oils and fats by wetting out the substrate and then displacing liquid dirt or dislodging solid dirt.

Builders remove other solid dirt, in particular dirt that is bound to the substrate by calcium or magnesium bridges. For the builder to complex the Ca and Mg the complex-constant between the builder species present in the washing liquor and Ca/Mg must be of the order of 10^{-5} to 10^{-6} for effective stain removal to occur.

Bleaches oxidize colored material, such as fruit, stains. The most commonly used bleach in Europe is sodium perborate. This bleach only effectively generates oxygen in the wash at the temperatures above 80°. With a trend towards lower washing temperatures, 'bleach activators' are being used. These are organic materials, such as tetra acetyl ethylene diamine, that form organic peroxides in solution with perborate at relatively low temperatures. The organic peroxides then act as low temperature bleaches.

The most commonly used enzymes are proteases. They remove protinaceous material such as blood.

Real dirt generally is a mixture of materials. For example, chocolate milk contains fat, proteins and colored matter. Thus, the above ingredients usually all provide part of the action necessary to clean fabrics. The

cleaning action is further supported by minor ingredients in detergents, that keep dirt in suspension, provide and maintain the optimum pH and act as electrolytes.

Sodium tri phosphate

Detergents use different phosphates as builders; the most generally used material is sodium triphosphate (STP) $Na_5P_3O_{10}$. Other phosphates used to a minor extent are sodium orthophospate Na_3PO_4, tetra sodium pyrophosphate $Na_4P_2O_7$ and sodium hexametaphosphate $(NaPO_3)_6$.

STP is the most commonly used builder because it works well and fulfills a number of the other functions that otherwise would need the addition of several minor ingredients. Another reason for the preference of detergent manufacturers for the use of STP is that the material is toxicologically entirely safe. This is an important attribute for the manufacturer who carries the ultimate responsibility for the safety of his products.

STP is one of the condensed phosphates, salts of the acids obtained by eliminating water from orthophosphoric acid H_3PO_4. It is produced specifically for use in detergents. The amount used is approximately 5% (Gilbert and De Jong 1973, Griffith 1973) of the total phosphate rock consumed. Most of the rock is used for the production of fertilizer (McClellan and Hignett 1973). Table 1 gives a break-down for the 1980 estimated world consumption (Kirk-Othmer 1982).

Table 2. Use of phosphate rock (in % of total)

Fertilizers	90
Detergents	4.5
Animal feeds	3.4
Food and beverages	0.7
Metal treatment	0.6
Water treatment	0.3
Others	0.7

Historical

STP came into general use shortly after synthetic surfactants had been introduced. The traditional surfactant had been soap, a material of which part is first used to sequester the calcium and magnesium present in the washing liquor, the dirt and the fabrics. Once the hardness has been sequestered, i.e. when the solution starts to form suds, additional soap will be available to act as a surfactant. Synthetic surfactants, however, do not sequester hardness.

Synthetic surfactants were developed already towards the end of the last century, but their use remained essentially restricted to industrial processes. The research accelerated between the two World Wars, particularly in Great Britain and in Germany; the United States followed somewhat later. Synthetic detergents for consumer use were marketed in Europe and in the U.S.A. during W.W. II, but their performance suffered from the absence of a

'builder'. This changed when in 1947 a built detergent for consumer use was marketed in the U.S.A.

Similar built detergents were marketed in Europe in the 50's. Their market penetration was directly proportional to the increase in washing machine ownership, in particular front loading drum machines. The soap based detergents disappeared from the market when the consumer demand ceased. This conversion took place in the late 50's and the early 60's. The conversion in West-Europe was last in the U.K. where soap-based products had fallen from approximately 600,000 tons in 1950 to less than 225,000 tons in 1970. At present, soap based detergents have virtually disappeared from the market in West-Europe.

Modern developments

The introduction of STP took place at a time of a rapidly increasing use of detergents and its environmental effects were increased due to changing living habits. The most important changes are discussed in this section.

The population of Europe grew at rates, shown in Table 3. The effect of this growth is that the population of Europe including the USSR, has increased from 610 million in 1953 to 766 million in 1984, that is by 25%.

Table 3. Annual growth of the population in Europe (percent per year)

	1950-55	1980-85
Eastern Europe	1.0	0.6
Northern Europe	0.4	0.1
Southern Europe	0.8	0.6
Western Europe	0.8	0.1
USSR	1.7	1.0

During this period, the standard of living also increased, with the expected beneficial effects on the quality of life. For example, the life expectancy at birth increased in Europe (excluding USSR) from 69.7 years in 1960-65 to 73.2 years in 1980-85. Part of the reason was a sharp drop in the infant mortality rate: from 37 per 1000 live births to 16 for the same two periods.

The food availability increased by approximately 7.5% over a period of 15 years with a correspondingly higher phosphate intake and excretion. Pre-W.W. II studies report on average 1.6 g P $pers^{-1}.day^{-1}$, while post W.W. II studies indicate approximately 1.9 g P $per^{-1}.day^{-1}$. Olsthoorn (1984) estimates that the total increase in phosphate metabolized is around 30%, part of which is due to a change (rather than an increase only) in the food consumed.

The effects of these changes became more noticeable because concurrent urbanization concentrated the population and its waste. Urbanization also meant a shift from septic tanks and land disposal to communal sewering. Table 4 shows the degree of urbanization in different parts of Europe.

Table 4. Urbanization in Europe (percent of population)

Eastern Europe	59
Northern Europe	85
Southern Europe	63
Western Europe	78
USSR	63

The average degree of urbanization in Europe in 1985 was 74%; this is up from 56% in 1950. Similarly, the USSR increased from 39% in 1950 to the level shown.

Detergent phosphate consumption

A more wealthy and urbanized population now consumes on average 10 kg detergent per person per year. The STP level in these detergents varies over a wide range (Table 5).

Table 5. STP level in West-European detergents (expressed as % P)

Austria	3.8 - 6.9
Belgium	3.8 - 7.4
France	5.2 - 8.4
Germany (West)	5.0 - 7.4
Italy	1.8 - 2.5
Netherlands	4.3 - 5.4
Spain	4.0 - 11.9
Sweden	3.3 - 6.4
United Kingdom	5.0 - 5.2

These figures are given because they are readily determined and, hence, are often presented. In fact, such figures are insufficient because they are only one of the factors determining the annual amount of phosphate used by the consumer which depends on:

- the level of phosphate in the product,
- the density of the product,
- the volume of product used for a washing machine load and,
- the number of loads washed.

In countries without phosphate restrictions (see later) the total detergent phosphate consumption per person is approximately 2 g P per day. In countries with partial restrictions, this amount is around 1.3 g (Netherlands) and in countries with a ban (Switzerland), it obviously is nil.

The reductions in P use have been achieved through the introduction of phosphate substitutes. A large amount of effort has been invested by the chemical industry in the development of such materials, but with rather disappointing results. STP is toxicologically so safe for man and the environment and simultaneously so effective in removing dirt, that no

substitute has been found that possesses all the favourable properties of STP. A material without safety concerns is zeolite A, a sodium aluminum silicate. However, it needs the addition of other compounds to maintain the hygienic qualities of the laundry. The progress in formulating zeolite based detergents has been sufficient that several detergent manufacturers are now voluntarily marketing such products. Ironically, there now also are public authorities, in particular those responsible for drinking water, who advocate to maintain the current levels of STP in granular detergents, because they are unhappy about the use of new chemicals.

A fairly recent development is the introduction of heavy-duty liquid detergents. These products are partially built with fatty acids, and partly achieve the necessary cleaning by an increased use of surfactants. These products already have taken over one third of the market in the U.S.A. The market share in Europe is currently less than half the U.S.A. level, but is still increasing. It is expected that the growth in West-Europe will remain behind that of the U.S.A., because sodium perborate is not (yet) stable in liquid detergents. This is not a problem in the U.S.A., where chlorine bleaches are generally used, but is an obstacle to growth in West-Europe. Still, their introductions has resulted in a proportional drop in the consumption of STP.

Phosphates and sewage

Detergents are after use discharged to municipal sewage. The STP partly hydrolyses in the washing machine and continues to hydrolyse in the sewer and in the sewage treatment plant. The half-life in sewage is approximately 15 hours (Devey and Harkness 1973), and shorter at higher temperatures, such as exist in the washing machine. It is safe to assume that most of the STP then will be hydrolysed before it reaches the aquatic environment.

Phosphates are removed from sewage to an extent that depends on the nature of the sewage treatment process used. This topic is addressed on a separate contribution (Kelderman) and will not be discussed further here.

Regulatory measures

The difficulties in controlling eutrophication made regulators consider limiting the use of detergent phosphates. This was opposed by the detergent manufacturers who pointed out that there was no good substitute for STP on the market and that a detergent phosphate ban does not constitute an effective solution. The result of the combination of the severity of the eutrophication problem, the progress in installing sewage treatment facilities and the detergent debate, resulted in different positions in the West-European countries (Table 6 on page 7):

- A detergent phosphate ban exists in Switzerland only. It was instituted well after sewage phosphorus removal had been installed and was dealing effectively with metabolic as well as with detergent phosphate.

- Detergent phosphate restrictions exist in several countries, either voluntarily or by law. These restrictions limit phosphate in detergents typically to 1.3 g P $pers^{-1}.day^{-1}$.

  Nil-P detergents have been developed by most manufacturers and are marketed in countries with general eutrophication problems. The market

share of these products ranges from a high of over 50% in West Germany to 30% in Austria and 20% in The Netherlands. These share levels are still increasing and it is too early to say where they will level out.

- No restrictions in those countries where eutrophication problems are less wide spread, not predominantly due to municipal sewage and/or effectively corrected by regional measures.

Table 6. Restrictions on P content of detergents in Europe

Country	Limit (% P)	Since	Status
Austria	5	1985	legal
Belgium	-	-	-
Denmark	-	-	-
Finland	7	1980	voluntary
France	-	-	-
Germany	5	1984	legal
Italy	2	1988	legal
Netherlands	5	1983	voluntary
Norway	3	1986	legal
Portugal	-	-	-
Spain	-	-	-
Sweden	7.5	1970	voluntary
Switzerland	0	1986	legal
United Kingdom	-	-	-

Potential benefits of regulation

A rational approach to the use of detergent phosphates obviously requires assessing benefits and disadvantages. It is important to quantify the contribution of detergent phosphorus to the loading of endangered waters. The contribution on a national scale has been calculated for several countries. The amount in the U.K. was estimated at 11% (Bowman 1973), in The Netherlands it was roughly the same (Olsthoorn 1984) and is now down to 7%; the amount in Germany was 17% in 1987 and continues to decrease; in France it is estimated to be around 10% (Rhône-Poulenc 1988).

The magnitude of the potential reduction in phosphorus loading from a P-ban is insufficient to solve any case of eutrophication. However, the situation in a given watershed may be different from the national average. This has encouraged several countries to deal with eutrophication on a case specific basis. For example, the U.K. has not taken nationwide measures, but deals with specific lakes, in particular Lough Neagh and the Norfolk Broads. This approach is now becoming more generally accepted and results in a more effective use of the available means.

It is this author's impression that balance is gradually being achieved. The detergent manufacturers have made a major effort to minimize the use of phosphate. When it became clear that the chemical industry could not develop a substitute material that combines all the favourable attributes of phosphates, the detergent industry combined the chemicals and technologies available to formulate low or nil-P products. The authorities became better equipped to formulate effective eutrophication abatement programs; these

programs showed that the role of detergents was as important one as had been assumed in the late 60's. Simultaneously, the toxicological safety of phosphates was increasingly appreciated.

These two developments suggest that in countries with effective government action and a cooperative attitude of the detergent industry, the use of phosphate-based detergents is likely to continue.

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PHOSPHATE IN SEWAGE AND SEWAGE TREATMENT

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Introduction

The importance of phosphates in promoting algal growth in surface waters has been recognized for several years. Moreover, it is widely accepted that the effluent discharged from sewage treatment plants is one of the major sources of phosphate emissions. In response to this, dephosphating processes were introduced in the Netherlands some years ago. However, not more than 21 sewage treatment plants were involved in the initial programme. This is equivalent to only 6 percent of the total treatment capacity of 22 million population equivalents (p.e). Comparing with other European countries there is more dephosphating in Western Germany, Sweden and Switzerland. In Western Germany there is about 9% dephosphating of the total 100 million p.e. In Switzerland nearly half of the total amount of municipal waste waters are dephosphated. In Denmark in 1987 a programme was started to reduce nutrient discharges. In the beginning of the nineties the nutrient removal at treatment plants will take place on about 30% of the Danish discharge of waste water.

Recent policy changes will necessitate that not only more sewage treatment plants will have to be equipped with dephosphating facilities, but that the effluent will have to meet even stricter quality standards. The need to comply with these measures is closely connected with initiatives such as the Rhine Action Programme (1 October 1987). In this treaty, the governments of the Rhine Riparian States have agreed to reduce some priority pollutants by 50% of 1985 levels before the year 1995. One of the priority pollutants is phosphate. In addition, on 24 - 25 November 1987 a similar programme has been introduced for the North Sea in which comparable reductions of phosphate need to be achieved over the same period.

However, most experts agree that it will be extremely difficult to meet these standards with current techniques and that new, improved methods will therefore have to be introduced.

Sources of phosphates

There are many sources of phosphate discharges to surface waters, among others:

* municipal waste water;
* industrial emissions (e.g.phosphate-fertilizer industry);
* deposition;
* agriculture.

Much of the phosphate will reach surface waters by municipal and industrial waste water discharge, and even after biological treatment of the waste water there remains a large P load.

In the Netherlands there is also a big input from rivers that cross the borders with (Table 1) the biggest load to Dutch surface water contributed by

the river Rhine. The contribution from Dutch agriculture is mainly through runoff. In 1983, it was only a small contribution to the whole problem since most of the phosphate is adsorbed to soil particles. In the coming years the importance of agriculture P load will increase greatly because of leaching. Deposition gives only a small contribution to phosphate load of surface water.

Table 1. Phosphate-P load of the Dutch Surface waters in 1983 (in millions of kg) (1)

Municipal discharges	11.4
Industrial discharges	2.9
Phosphate-fertilizer industry	12.0
Agricultural run off	3.5
Other sources e.g. deposition	0.7
Subtotal sources	30.5
Input Rhine	42.0
Input Meuse	5.0
Input Scheldt	4.6
Input other rivers	3.0
Subtotal crossing rivers	54.6
General total	85.1

In 1986 a report was prepared by the Commission of the European Communities on the phosphate load for the whole of Europe (2). According to this report the load by domestic waste water was 280 million $kg \cdot y^{-1}$ phosphate-P. A very rough estimation of the total surface water load gives 760 million $kg \cdot y^{-1}$.

Phosphate in sewage

Domestic waste water contains 2.7 - 3.4 g phosphate-P per inhabitant per day (2,3). About 1.4 g phosphate-P originates from excrements; somewhat more than half from urine, the rest from faeces. These phosphates are mainly in the form of ortho-phosphates. Detergents used for washing of textiles and kitchen utensils are responsible for 1.3 g phosphate-P, mainly as poly- and tripoly-phosphates. Besides ortho-phosphates, poly- and tripoly-phosphates there are also small amounts of pyro-phosphates and natural organic phosphates (3) in sewage.

In the sewerage domestic waste water will be mixed with industrial waste water and rain-water. Rain-water can contain (inorganic) phosphates from deposition and run off. Research has shown that for the Dutch situation deposition is about 0.15 $kg \cdot ha^{-1} \cdot y^{-1}$ Phosphate-P and run off about 2 $kg \cdot ha^{-1} \cdot y^{-1}$.

In the Netherlands about 92 % of the domestic waste water is collected in sewers (4), 5% is released to the soil and 3% goes to surface water after passage of septic tank systems. Of the total amount of the municipal waste water 81% (that is 88% of the collected sewage) is treated in waste water treatment plants. The rest is discharged to surface water without any treatment (Figure 1).

Approximately 30 - 40% of the phosphates present in waste water are removed in conventional biological sewage treatment plants. In Figure 1 the maximum of phosphate removal (40%) is used. These phosphates are collected in

the sewage sludge, the remainder stays in the water phase. This results in a total annual discharge into the surface waters of 8.8 million kg after treatment.

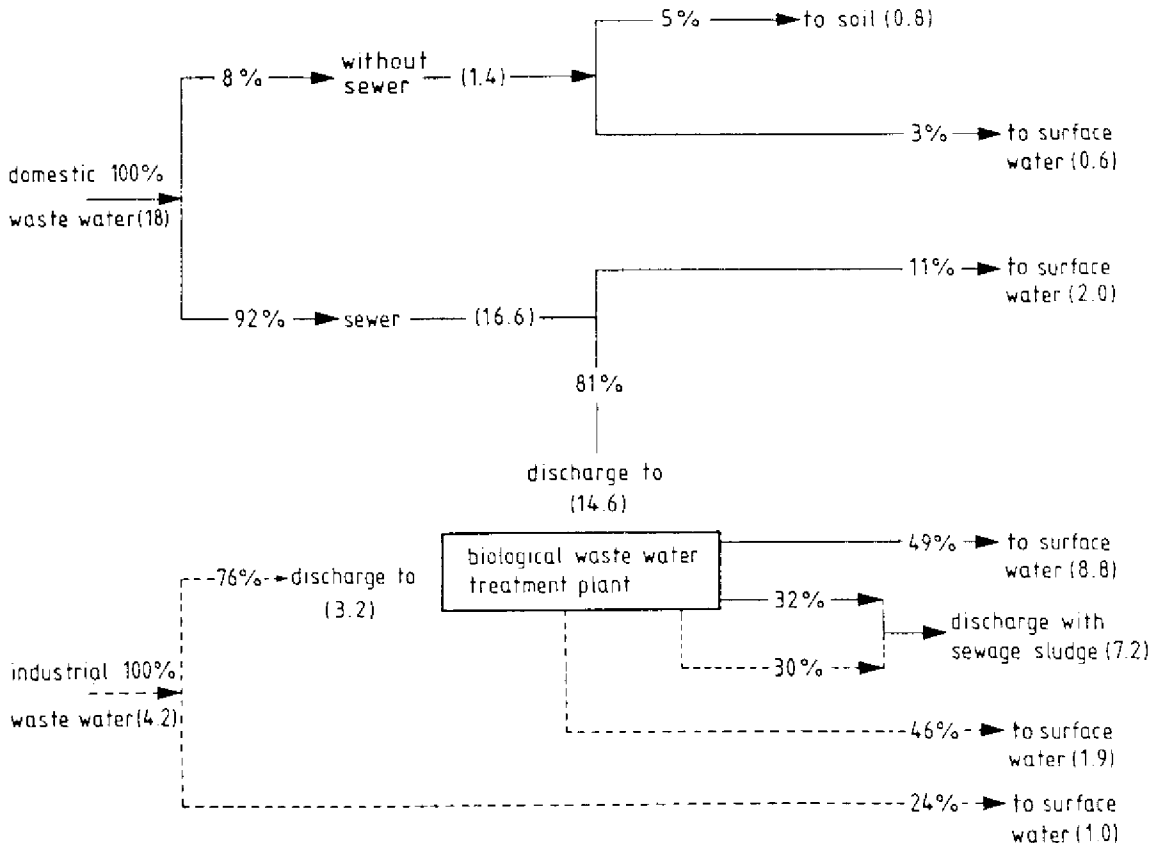

Figure 1. Pathways of Phosphate-P (in millions of kg) in sewage in the Netherlands

The structure of the discharged phosphates

The availability of the phosphates to algae is a main point in studies of eutrophication. It is therefore important to know what kind of phosphates are discharged. Of the phosphates in raw sewage about 75% are ortho-phosphate and about 25% other phosphates (partly organic, partly inorganic bound). The composition of domestic waste water that is not treated is similar. When waste water is treated in biological treatment plants, 90-95 % of the phosphate in the effluent will be ortho-phosphate. The other part is bound to very small suspended solids which are expected to be as mobile as ortho-phosphates.

Dephosphating processes will have an influence on the ratio of the ortho-phosphate to the rest of the phosphates. In the dephosphated effluent there is about 50% ortho-phosphate and 50% bound phosphates such as small calcium-phosphate particles with very high availability and mobility. Therefore, after treatment of the waste water, all the discharged phosphate will be readily available for algal growth. Only in the case of a direct sewage discharge to surface water a part of the phosphate (about 10-20 percent) is initially unavailable because it is bound to coarser particles that settle near the point of discharge.

Dephosphating techniques for waste water

The pressure to remove not only oxygen-consuming compounds but also phosphates has increased considerably over recent years. This has resulted in the development of several promising dephosphating techniques.

One factor which is of particular importance in determining the suitability of dephosphating processes is the quality standard prescribed for the effluent. Quality requirements are clearly a function of the receiving water under consideration. Until now, dephosphating standards of 1-2 $mg \cdot l^{-1}$ total phosphate-P have been adopted for most surface waters, where applicable. The introduction of this limit was not simply an arbitrary choice, but a reflection of what could actually be achieved with existing physico-chemical techniques. Recent studies of eutrophication in surface waters have led to a greater understanding of the importance of this phenomenon. As a result, it is now thought that phosphate levels of 1-2 $mg \cdot l^{-1}$ total phosphate P are too high for more stagnant surface waters and that levels of 0.5 $mg \cdot l^{-1}$ would be more appropriate. This has significant implications for the type of dephosphating processes to be considered.

Another important factor that must be assessed when selecting suitable processes is the residual products that are formed. These substances are produced when the phosphates contained in the water phase are converted to solid matter, and in current dephosphating techniques are regarded as waste materials. Although the proportion of waste that originates from such processes on an annual basis is, at present, relatively small. Wider application of conventional dephosphating techniques would lead to considerable increases in the amount of waste material that is produced. Such developments would obviously be unpopular, especially in view of the controversy that surrounds the existing waste mountain. In the Netherlands, the situation is further complicated by the current review of the disposal of sewage sludge and farm manures on farmland. It appears that the use of sewage sludge for agricultural purposes will be prohibited in the near future and that phosphate-rich waste (e.g. granular phosphate) would probably fall under this prohibition. At present, the bulk of the waste material produced with conventional physico-chemical techniques is disposed of by dumping. However, in order to comply with more responsible environmental policies, increasing emphasis will have to be placed on dephosphating methods that produce less solid waste or which produce compounds that can be recycled or reprocessed into useful products.

Physico-chemical dephosphating. Of all the techniques currently available for removing phosphates from waste water, physico-chemical dephosphating has undoubtedly been applied on the widest scale (5). This process relies on chemical additives which react with the phosphates in the water phase to produce an insoluble phosphate-salt. There are two basic types of physico-chemical dephosphating methods.

The first is simultaneous dephosphating. This involves dosing of chemicals to the waste water during the biological treatment process. Compounds commonly used for this purpose are ferrous or ferric chloride, various aluminium salts or waste materials from the aluminium and iron processing industries. When ferrous chloride is added, the iron is first oxidized by the oxygen of the treatment plant and subsequently forms ferric phosphate salts. A disadvantage of simultaneous dephosphating is the large increase in the amount of sludge that is produced in the treatment plant. The

phosphate salts that have been removed are, of necessity, mixed with the produced sewage sludge of the total plant.

A second method employed for physico-chemical dephosphating is that of post-treatment. This involves treating the biologically purified effluent in a further processing stage. The chemicals used are generally the same as those applied during simultaneous dephosphating. However, since an additional source of oxygen is not available, ferrous chloride cannot be used. One advantage of the post-treatment option over simultaneous dephosphating is that the phosphate sludge is kept separate from the rest of the sewage sludge. This factor is particularly important for the potential recycling of the phosphates.

On the whole, simultaneous phosphating is more commonly applied than a post-treatment stage because of the lower costs involved. Experience has shown that, on average, phosphate levels of 1-2 $mg \cdot l^{-1}$ total phosphate-P are achievable with this technique.

However, one shortcoming of physico-chemical dephosphating is that the waste materials which are produced cannot be reused at present. Moreover, some of the additives used increase the salinity of surface waters. An additional problem that could be important with simultaneous dephosphating is the negative effect that this could have on nitrification (5).

On balance though, physico-chemical dephosphating is particularly liked because of its relative simplicity. Changeovers to this technique can be accomplished without the need for complex modifications to the plant, which is a considerable advantage.

Biological dephosphating. Biological dephosphating techniques are based on the principle that, given the right conditions, certain bacteria are able to remove phosphates from water (6). These bacteria, for instance the Acinetobacter genus, are able to accumulate more phosphate than is required to maintain the cell structure thereby reducing the phosphate content in the water phase. Acinetobacter organisms need volatile fatty acids to grow, which means that an anaerobic zone must always be provided within the sewage treatment plant. Phosphates are removed from the waste water during the subsequent aerobic phase. In this process, inorganic phosphates are converted to energy-rich polyphosphates, which accumulate in the cells of the bacteria. If the bacteria are moved to an anaerobic environment, the stored energy is released as the phosphates are returned to the water phase. A proportion of the phosphates are used to produce new cells and the rest undergoes a chemical conversion process with the calcium and sodium ions present in the water phase. As a result, insoluble phosphate salts are formed. In a normal aerobic activated sludge unit some 30 - 40% of phosphates can be removed from the waste water.

The acceptability of biological dephosphating processes is very much dependent on the use to which the phosphate-rich sludge is put. This sludge must be prevented from entering into an anaerobic phase, otherwise the stored phosphates will be released. Since it can be assumed that anaerobic conditions will occur in almost every treatment stage, apart from direct disposal for agricultural purposes, it is clear that additional measures will be necessary to address these problems. In the Netherlands this matter will assume even greater importance in the future if, as expected, the amount of sludge that is permitted to be disposed of on farmland is drastically reduced.

The latest application of relevance in this field is the pho-strip process. By keeping the phosphate-rich sludge under anaerobic conditions in a tank, the phosphates can be released in a controlled way. The phosphates that have been removed from the sludge are extracted in a phosphate-rich upper course. This upper course has a much smaller volume than the original influent and can subsequently be treated with chemicals. The major advantage of this method is that the phosphate salts formed contain less contaminants and are therefore more suitable for reuse. Practical tests have shown that it is feasible to reduce phosphate levels in the entire effluent to 3 $mg \cdot l^{-1}$ total phosphate-P if a few minor modifications are made to the treatment plant. This is, of course, always conditional on the sludge being kept under aerobic conditions, which means that the sludge has to be disposed of in its wet form without having undergone sludge fermentation or thickening.

Reductions in phosphate contents of this order (3 $mg \cdot l^{-1}$) can therefore readily be achieved in countries where the majority of the sludge is disposed of in a wet form. A more intensive treatment is needed if lower phosphate levels are required in the effluent. In such cases, pho-stripping could offer a potential solution. However, it remains to be seen whether this method can be applied successfully in full-scale plant. Nevertheless, a process operating on the pho-stripping principle is currently being marketed in America. It is claimed that phosphate levels of less than 1 $mg \cdot l^{-1}$ total phosphate-P can be achieved with this technique.

Biological dephosphating has already proved itself outside Europe, particularly in Canada and South-Africa. However, in Europe, only a relatively small number of treatment plants have been equipped with such facilities. This is partly a reflection of the fact that few if any requirements exist in Europe with regard to phosphate levels.

A further way of meeting lower phosphate requirements is to combine biological dephosphating with a pysico-chemical post-treatment stage. The principal advantage with this approach is that less chemicals are required than with conventional physico-chemical treatment.

Another point that should be considered in this context is that biological dephosphating and anaerobic pretreatment are not compatible, as both methods are essentially aimed at the same substrate. If nitrogen removal is also required, this can present even more problems. Recent research has shown that biological dephosphating can lead to decreases in the level of nitrification, particularly in winter.

Fluid-bed pellet reactor. A new method of dephosphating is the so called fluid-bed pellet reactor(7,8). This process does not result in sludge but in pellets of calcium or sodium phosphate which can be used in phosphorus industry thus bringing the phosphate into a cycle.

The principle of the fluid-bed reactor is as follows. A part of the reactor is filled with a base for the pellets, such as sand. The effluent of the waste water treatment plant is brought into the fluid-bed in up-flow direction. With the addition of calcium or sometimes sodium ions the process-conditions are adjusted to form phosphate pellets with the calcium ions and the sand as a nucleus. When the pellets are big enough they are removed from the system. This technology is capable of bringing total-phosphate content in the effluent down to about 1 $mg \cdot l^{-1}$. Normally, the effluent of the fluid-bed reactor contains residual phosphate in suspended form. Another step is necessary to reduce the final effluent content to 0.5 $mg \cdot l^{-1}$ total P. This

step is a sand-anthracite filter. The first fluid-bed granular reactors to operate on a full scale will shortly be introduced in Denmark and the Netherlands. The experience gained in running these plants is expected to yield valuable information concerning the maintenance and costs of such units. These demonstration projects will also show whether the phosphate pellets that are produced, can be reprocessed in large quantities. The re-use of the phosphate is the crucial factor for the successful implementation of the fluid-bed as a dephosphating technology.

Magnetic separation. Magnetic separation (9) was originally thought to be suitable only for removing certain metallic elements from waste water. However, it soon became clear that non-magnetic materials could also be separated in a similar way. For removing non-magnetic materials it is necessary to add magnetite, a magnetic ferric oxide. The magnetite becomes adsorbed onto certain particles present in the water phase, which allows them to be removed under the influence of a magnetic field. Under these circumstances it is possible to remove even phosphate.

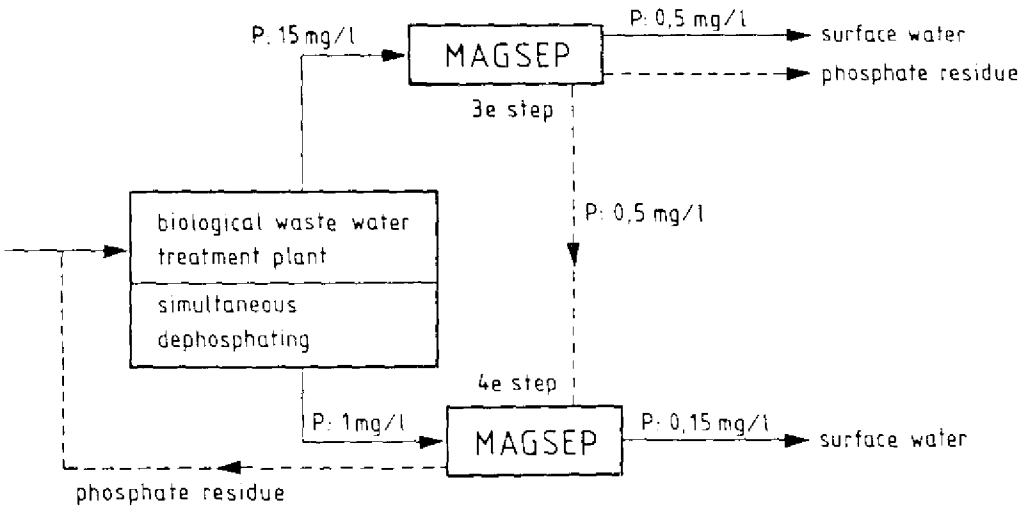

Figure 2. Magnetic separation as a dephosphating technique

Preliminary dephosphating tests have already been performed with this technique. The first set of trials (Figure 2) was carried out at a sewage treatment plant where dephosphating techniques are not normally applied. Magnetite was added to the effluent, which was subsequently passed through a magnetic field. In this way, calcium phosphate (with the magnetite) was separated from the waste water, which reduced the phosphate level from 15 $mg \cdot l^{-1}$ to 0.5 $mg \cdot l^{-1}$ total phosphate-P.

Initial indications of these tests are that the calcium phosphate is extracted in a relatively pure form. After a drying stage, a comparatively high dry matter content can be obtained, although it remains to be seen whether this product can be recycled in the phosphate processing industry. As with the fluid-bed reactor, implementation of this technique depends on the re-use possibilities.

A second set of trials was conducted with effluent that had already undergone dephosphating. The majority of the magnetite that was added to the effluent became attached to the suspended matter that is present in the effluent. Previous research has shown that most of the residual phosphate is

contained in this fraction, which implies that the separation process is essentially a matter of retaining the suspended matter. The residual fraction is subsequently returned to the influent of the plant. For sake of economics it is possible to recuperate the magnetite from this residual fraction. Nevertheless, for a good operation of the plant recuperation is not necessary. In this trial it became clear that it was possible to reduce the content of phosphate in the effluent from an already relatively low starting level of 0.7-1 $mg \cdot l^{-1}$ to 0.2 total P. Sometimes values of 0.15 $mg \cdot l^{-1}$ total P and even lower were measured. At the moment few techniques available can reach such low contents. Combining physico-chemical techniques with magnetic separation can therefore be seen as yielding extremely favourable results. However, the considerations on recyclability of waste products made in the preceding chapters also apply to this method.

Cultivated reeds or plants. There are some places in Europe (UK, Western Germany) where reeds are used for waste water treatment, the so called root zone method (10). The method relies on the degradation of organic materials by microorganisms within the aerobic zone around plant roots, which is accompanied by P removal. At root zone facilities in Western Germany the removal of phosphate was 99%. The effluent values decreased from 25-30 $mg \cdot l^{-1}$ total P to less than 0.1 $mg \cdot l^{-1}$. The removal is mainly a physico-chemical process. The phosphates stay in the soil because of complexation with cations and filtration of bigger particles. As a result the soil will be enriched with the phosphate, and after 20 - 30 years it is necessary to remove the soil.

In the Netherlands a facility of about 1700 p.e. has been built according the zone filtration principle (11). At this site 75% of the total phosphates are removed, although the structure of the soil is not optimal. In addition research is carried out on biological removal from already biologically treated waste water using macrophytes (reeds) in ponds. In this case phosphate uptake should support reed growth and the reed field would remove the suspended solids by filtration. At the end of the season the phosphates are removed from the facility by harvesting the reed. Although the principle appears correct, the results were disappointing. The reed growth was not stable enough because of the composition of the (purified) waste water. The load of organic material seemed to be too high. Another disadvantage was that a reed field with the aim of filtration, has to be very large.

Sand filtration. Sand filtration should not be regarded as a dephosphating technique in its own right, as it is always applied in combination with other methods. The effectiveness of this technique in reducing the amount of phosphate in waste water has already been demonstrated in many practical applications, particularly in Switzerland. It has been shown that levels in the order of 0.2 $mg \cdot l^{-1}$ total phosphate-P can be achieved. Furthermore, sand filtration can be considered as an extremely useful way of protecting the quality of surface waters. However, a disadvantage of this method is that it fails to address the problem of the waste materials that are left behind.

Costs

In table 2 and 3 the costs of a few dephosphating techniques are given. The figures are not absolute but can be compared with each other. It is not yet possible to make a comparable calculation of costs for biological dephosphating, sand filtration and the root zone method.

It is clear from table 2 that the differences in costs are mainly associated with the sludge disposal. The caculations for magnetic separation are based on an useful disposal of sludge. If this is not feasible, the future perspectives for this technique will be less favourable.

Table 3 indicates that simultaneous dephosphating becomes more expensive if a limit of 0.5 $mg \cdot l^{-1}$ total P in the effluent of sewage treatment plants is required.

Table 2. Calculation of costs for dephosphating in Dutch guilders per population equivalent per year.

(50,000 p.e., effluent concentration $1 \cdot mg \cdot l^{-1}$ total phosphate-P)

	Fluid bed	Simultaneous	Magnetic separation
Capital costs	4.55	1.75	4.00
Maintenance	0.85	0.35	0.80
Chemicals	2.70	3.25	2.82
Sludge disposal	0.00	4.40	0.60
Energy	0.60	0.20	0.36
Operation	1.25	1.25	0.60
Total	9.95	11.20	9.18

Table 3. Comparison of costs at different effluent concentrations (total phosphate-$P \cdot l^{-1}$) and capacity of the treatment plant. Costs in Dutch guilders per population equivalent.

	Fluid bed	Simultaneous	Magnetic separation
50,000 p.e.			
-1.0 mg/l	9.95	11.20	9.18
-0.5 mg/l	11.25	16.55	11.94
-0.2 mg/l			18.83
100,000 p.e.			
-1.0 mg/l	9.45	10.80	8.37
-0.5 mg/l	10.75	15.85	11.13
-0.2 mg/l			17.55

Future perspectives

At present, several techniques are available to reduce the total phosphate levels in municipal waste water to 0.2 $mg \cdot l^{-1}$ [12,13]. However, no solution has yet been found for the by-products that are produced. These products are often unusable in their present forms. A major factor to consider when reducing excessive phosphate contents in surface water is that the dephosphating technologies used should not harm other parts of the environment. Future attention will therefore not only have to be focused on the recycling of residual products, but also needs to be directed to the use of chemicals that are less detrimental to the environment. The enormous quantities of salt that would be discharged into fresh surface waters if dephosphating is introduced on a large scale, would give rise to grave concern.

Conclusions

All sewage contains a certain amount of phosphate. When the phosphate originates from sources other than food, a reduction seems to be possible. Nevertheless, it appears that the total load of phosphate can be reduced by only about 30-40%. The consequence is that dephosphating techniques remain necessary.

Almost all of the discharged phosphates to surface water are in the form of ortho-phosphates, the remainder being attached to small particles. This makes almost all the phosphate available to promote algae growth.

Dephosphating techniques are now available that can reduce total phosphate levels in the effluent from sewage treatment plants to 0.2 $mg \cdot l^{-1}$. However, the problems associated with the disposal of sewage sludge will remain a key factor in deciding which methods should be adopted. If stricter requirements are introduced for the disposal of sludge, this will stimulate the use of technologies which allow waste products to be recycled.

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CYCLES, FORMS AND AVAILABILITY OF PHOSPHORUS IN FRESH WATER

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The concentration of phosphorus in streams and rivers in Central Europe is now usually of the order of 100 $\mu g \cdot l^{-1}$ (House and Casely, this volume; Popovsky 1981). The aim of the present paper is to review the sources of this phosphorus, its pathways in aquatic systems, particularly in reservoirs and lakes and then to discuss briefly its forms and their availability for aquatic organisms. While TP includes both dissolved (TDP) and particulate (TPP) determined after digestion by perchloric acid, pesulphate or UV radiation, reactive P (Pr) is the fraction which reacts with molybdate and after reduction yields molybdenum blue; it may be both dissolved (diss. Pr), or particulate (part. Pr) and need not include only inorganic P or orthophosphate (Strickland, Parsons 1968, LeLoir, Cardini 1957).

Phosphorus transport in aquatic systems is also useful for monitoring of processes going on in other systems, e.g. impact of agricultural procedures, urbanization etc., particularly since P occurs only in negligible amounts in gaseous forms.

Sources of Phosphorus

The sources of P in streams and rivers may be classified into 1) runoff from land, both dissolved and particulate, 2) runoff from animal farms, where feces and urine are not processed into manure, 3) sewage from human population, particularly urban, 4) industrial and other pollution, 5) aerial input.

1) Runoff from land. This was mostly studied in defined experimental watersheds (area frequently in the order of 10 ha) by recording, multiplying and integrating concentrations and flow rates. An important component of these budgets is weathering of minerals and subsoils. In unfertilized basins without human settlements and farm animals, weathering is the most important source of P, but unfortunately this is not appreciated in many studies on more developed catchments. Losses of TP were found to be linearly and directly proportional to percentage of farmland in a watershed (Ryding 1983, Kauppi 1984a). Brink and van der Meulen (1987) found for a rural area that losses of P increase with increasing "erosion" which again is correlated with livestock and inhabitant density. For US data from the sixties see Verduin (1971). Willrich and Smith (1970) are useful as a first reference for older data, though some earlier loss rates might be overestimated. Procházková et al (1983) observed for several years a basin, free of human settlements and livestock, where transport of soil particles was largely prevented by grassy balks at the lower end of the fields and TP losses ranged between 0.031 and 0.180 $kg \cdot ha^{-1} \cdot y^{-1}$.

Brink (1982, 1986) suggests that 2% or less of applied fertilizers are leached in Sweden (ca 0.6 kg $P \cdot ha^{-1} \cdot y^{-1}$), but even this may cause quite severe

eutrophication problems in aquatic systems. At a specific discharge rate of ca $2000 m^3 \cdot ha^{-1} \cdot y^{-1}$ (= $6.3\ l \cdot km^{-2} \cdot s^{-1}$) which may be typical for some parts of the temperate zone, this would result in an average concentration of 300 µg $P \cdot l^{-1}$. About one sixth of this amount (0.1 kg $P \cdot ha^{-1} \cdot y^{-1}$) would be a maximum tolerable level if mass accumulation of phytoplankton is to be avoided - not considering other P sources (Dillon and Rigler 1974). Losses of dissolved P are reported to be increased by application of manure (Brink 1986), and Willbrich and Smith (1970) reported for the Lake Mendota watershed, that manured land is the biggest contributor of P with a loss of 1.1 kg $P \cdot ha^{-1} \cdot y^{-1}$. So far little attention was evidently paid to the relationship between maturity of solid or liquid manure (e.g. Saviozzi et al. 1988) and P losses. Unmatured manure may offset redox equilibria in soils and enhance losses of P to ground and surface waters. Root respiration and possibly P-uptake might also be affected.

Losses of particulate P from farmland are even more important than losses of the dissolved forms. This is particularly applicable to continental areas and northern latitudes, where a high percentage of runoff occurs during spring snow-melt, when water flows over frozen ground and takes the surface layer of soil particles to streams (Kopland-Diks et al. 1985, Brink 1986).

Bulatkin (1986) in his review (p. 32-49) has summarized some data on erosion in the European part of the USSR. About 13 to 20% of the eroded particles were flushed down to streams and rivers; a recorded peak value was 2.53 g (d.w.) $\cdot l^{-1}$. In agricultural areas the losses of particulate material are of the order of 1 $t \cdot ha^{-1} \cdot y^{-1}$, but a 7-year detailed study in the Lubozhina River basin gave a variation 1.11 to 19.5 with a mean of 7.8 $t \cdot ha^{-1} \cdot y^{-1}$. Phosphorus concentrations in particles ranges between 0.13 - 0.19% (d.w.), losses of particulate P are mostly in the order of 2 $kg \cdot ha^{-1} \cdot y^{-1}$. Viner (1988) found smaller particles in a New Zealand river to be richer in P than bigger particles; phosphorus and iron content were proportional and most of P was available to algae.

Martin et al. (1970) refer to established "tolerance" limits of soil loss 7.5 - 10 $t \cdot ha^{-1} \cdot y^{-1}$. For Luisiana Bengtson et al. (1986) reported annual losses of 4.9 $t \cdot ha^{-1} \cdot y^{-1}$ in non-drained plots. Phosphorus losses were 8 kg $P \cdot ha^{-1} \cdot y^{-1}$. Drainage decreased the losses by ca 30%. Schmidt and Eckert (1986) refer to an average loss by "sheet and rill erosion" of 10.5 $t \cdot ha^{-1} \cdot y^{-1}$ for the U.S. Brink (1986) estimated particulate P losses of up to 117 kg $P \cdot ha^{-1} \cdot y^{-1}$, with precipitation, heavy clay soils, slope of the field and application of manure as factors increasing erosion losses of P. Kopland-Diks et al. (1985) suggest a roughly straight relationship between soil loss and P export in a log-log plot - up to 20 kg $P \cdot ha^{-1}$ at a soil loss of 50 $t \cdot ha^{-1}$. Kauppi (1984a) found, in sparsely populated Finnish basins, that losses of P were related to percentage of agricultural land in the watershed ($r=0.75$), other relationships to sewage, livestock and percentage of fine particulate soils were less close ($r \approx 0.5$). The correlation to discharge was poorly significant. Brink (1986) and Kopland-Diks et al. (1985) suggest vegetation cover as an important protecting factor against P losses, the latter authors found spring thaw loss of 1.5 g $P \cdot ha^{-1} \cdot mm^{-1}$ runoff in a winter wheat field, but as much as 23 g $P \cdot ha^{-1} \cdot mm^{-1}$ runoff in a similar fallow-field. For free pasture farms in Poland, Hillbricht-Ilkowska et al.(1983) reported TP export rate of 0.230 $kg \cdot ha^{-1} \cdot y^{-1}$.

The effect of soil cover is even more evident in forests. In the first and classical study on small watersheds - the Hubbard Brook Ecosystem (Likens

et al. 1977) the estimate of P export rate from a northern hardwood forest is probably underestimated (Pr only), but it is evident that the cycling rates within the system are multiples of the both input and output rates. Keller (1983) in his review gives TP export rates for 9 forested watersheds with less than 10% agricultural area. The rates are all less than 0.5, with a mean of 0.122 kg $TP \cdot ha^{-1} \cdot y^{-1}$. Inhabitants and animals are not specified. Most of the export is probably in particulate form and Keller suggests careful logging and road construction, minimizing surface runoff after cutting and maintaining full vegetation cover to minimize P losses. Procházková et al. (1983) give 0.017 - 0.150 kg $TP \cdot ha^{-1} \cdot y^{-1}$ as export rates from a completely forested basin without inhabitants and animals (except free living game). Also Knight et al. (1985) suggest that P losses from undisturbed forested watersheds are less than 0.05 kg $TP \cdot ha^{-1} \cdot y^{-1}$.

2) **Runoff from animal farms** with livestock kept indoors is usually estimated using "cow equivalents", one lactating cow is assumed to produce ca 10 g $P \cdot day^{-1}$ (Maynard 1947, Brink and van der Meulen 1987, Duchon and Hampl 1959). High concentration of animal production results in transportation, composting and deposition problems with both solid and liquid manure. Bowman (1979) suggests that about 13% of animal excreta are not used as manure in the UK, but in his discussion the estimate was considered as too optimistic.

3) **Sewage from human population, particularly urban.** Its magnitude is generally also estimated using population equivalents, its physiological value was about 1.5 g $P \cdot day^{-1}$ per individual, but where P detergents are used, the population equivalent is about 2.5 - 2.7 g $P \cdot day^{-1}$ (Vollenweider 1975, Collingwood 1979). Some 20 - 40% of P may be retained in a regular activated sludge process, but the majority goes to effluents. In England and Wales about 41,000 tonnes of P were reaching sewage works annually 10 years ago, about 15,000 tonnes were retained in sludge and the rest was disposed to rivers (Collingwood 1979). This author and Starkenburg and Rijs (this volume) discuss the problem and the dephosphating techniques in detail. It is evident that urban sewers are a major route of P input into waters, its control is both a problem of economy and disposal or reuse of resulting P concentrates. Use of sludge and other products of sewage processing may be complicated by heavy metals released to sewers by small industries.

The importance of sewage is further increased when not only cities but also villages are attached to sewer systems. With less concentrated country populations without sewerage, some P is retained in the basin and does not reach the watercourses. Kauppi (1984b) found by regression analysis of her data from a sparsely distributed rural population an equivalent of 0.12 kg $P \cdot y^{-1}$, which is ca 12% of the human equivalent for a population attached to a sewage system.

4) **Industrial phosphorus pollution** will likely be fairly specific from case to case. Fertilizer and foodstuff industries are the most likely contributors, for Netherlands case see Starkenburg and Rijs (this volume).

5) **Aerial input.** In the practical absence of gaseous P compounds in nature and particularly in biochemical cycles, the only important route of aerial transport of P are windblown soil, fertilizers and possibly other P-containing

particles and their dry and wet deposition. Most of this transport is included in collected bulk precipitation, except for particles blown very low above ground. Bulk precipitation data mostly suggest a minor role of aerial P transport in the budgets of basins, the data mostly range between 0.055 and 0.34 kg $P \cdot ha^{-1} \cdot y^{-1}$ (Procházková et al. 1983, Goszczynska 1987, Broberg and Persson 1984). In Bowman's (1979) balance sheet for the UK, aerial input of P constitutes 1.5% of all inputs, the rest being cargo imports to the British Isles from overseas. Aerial P inputs do not represent so much real inputs, but rather redistribution within bigger systems. On a geological time scale wind blown soils are important features, which have been moved over the surface of Earth long before mankind and its technology appeared. Broberg and Persson (1984) consider the input of 0.1 kg $P \cdot ha^{-1} \cdot y^{-1}$ directly on the oligotrophic lake Gordsjön surface as a very important contribution.

Cycles of P in Aquatic Systems

Phosphorus, which arrives in a stream or river is immediately cycled by both abiotic mechanisms and the biota. Particles are moved down the stream, may sediment and are flushed out again during the next flood event. Dissolved P may be taken up by epiphytic organisms on the stones and released again by their grazers, e.g. some insect larvae. Macrophytes and mud-water P exchange also participate in the cycle. The cycles will here be discussed for lakes or reservoirs, a discussion of rivers is given by House and Casely (this volume).

Heavier particles entering a stagnant water body sediment at the inflow together with the P they contain. Other P materials, including fine soil particles, dead algae, fractions of animal excreta and abiotic particles formed within the water body settle in lower sections of lakes. Between about 20 - 80% of inflowing P may sedimentate in a lake or reservoir, the percentage was reported to be proportional to inflowing TP concentration (Procházková and Blazka 1984) and retention time (for references see Ahlgren 1980). The upper section of the concentration relationship is poorly known, in Hartebeespoort Dam, one of the most eutrophic water bodies studied, only 65% of inflowing P is retained (Twinch 1986), in this case the anoxic hypolimnion may be responsible for the low retention.

In the temperate zone, after spring thaw, there is usually a spring peak of phytoplankton utilizing the high winter concentrations of phosphate from both the sediments and the inflows. This peak is essentially not controlled by grazing zooplankton, except perhaps towards its end (Sommer et al. 1986). The grazers which have a slower growth rate compared to algae and bacteria, later control the biomass of primary producers, but the grazers are again under the control of their predators, both fish and invertebrates (Hrbácek, 1962; Brandl and Fernando 1978). In terms of P cycling this means that at the height of the warm season and in its second half, P taken up by algae (growth rate of the order of 1 per day) is consumed by the grazers and within a few hours is largely excreted or defecated and becomes again available for algae and bacteria (Peters and Lean 1973, Ganf and Blazka 1974). A smaller part is incorporated in the grazers and later in their predators.

A fraction of algae dies for some reason (e.g. disease, parasites, loss of buoyancy, etc.) and the cells settle down to the bottom. Part of their P eventually reaches the sediments, but the rest is released to the water column by cell lysis and bacterial action. This results in a decreasing of TP and Pr within the euphotic zone of reservoirs and lakes during the warm season. Hypolimnetic concentration may remain high during the whole year. The concentration in the euphotic layer is however an equilibrium point between

uptake and release of P by biota (Peters and Rigler 1973, Ganf and Blazka 1974, Lehman 1980, Blazka and al. 1982).

Table 1. Components of the summer epilimnetic phosphorus cycle for a lake, where fish predators control planktophagous fish.

Total P	15 $\mu g \cdot l^{-1}$
Reactive P (Pr)	2-3 $\mu g \cdot l^{-1}$
Pr release rate by 100 individuals of Daphnia galeata per litre	4-5 $\mu g \cdot l^{-1} \cdot day^{-1}$
Pr uptake rate by algae 10 μg chlorophyll $\cdot l^{-1}$	4-5 $\mu g \cdot l^{-1} \cdot day^{-1}$

Cycling of P by grazers might be about 2 times faster (on relative scale-ratio in biomass) than that of carbon and nitrogen (Blazka et al. 1982). Predators contribute to the P cycle by excreting and defecating that part of prey P which they do not utilize in their own bodies.

During autumn, the biomass of algae decreases sharply in temperate lakes and the biotic cycle continues during winter at a much reduced rate. In tropical lakes. there is no or little annual light or temperature variation and the daily cycle may be more prominent than the annual one (Greenwood 1976). Mean (of five daily measurements) excretion rates of zooplankton varied less than two-fold (Ganf and Blazka 1974).

One of the most discussed limnological problems is the release of P from sediments to the water column. It is now widely accepted that sediments are on a year-round basis P traps (Premazzi and Provini 1980). On a larger scale P may be released during homiothermy (no stratification) during floods and other events which perturb the sediments - exceptional events in a deep lake, which is stratified in summer and in winter. For a shallow lake however, where wind action permits just a short term (a few days) stratification, the transport of P from sediments to the epilimnion is much more frequent and intensive. These lakes are therefore (just one of a few reasons) more prone to eutrophy. Sedimentation of P is provided in well oxygenated waters at slightly acidic pH. Hydrous ferric oxides are precipitated and sorb phosphate, phosphate esters and polymers (di- and polyphosphates). This complex keeps the sorbed phosphates in a stable position with the sediment, it may however be released by at least two mechanisms: one is the microbially mediated reduction of Fe^{3+} to Fe^{2+}, the complex is solubilized and its components may diffuse freely in the interstitial water and to the hypolimnion. Some (up to 1/3) may be released for simple stoichiometric reasons (due to the valency change), but the rest is likely to be in the form of stable but soluble ferrous complexes (Einselle 1936, Mortimer 1941, 1942, Premazzi and Provini 1985, Boström et al. 1982, Nürnberg 1988). Through this mechanism P arriving in a lake in mineral soil particles attached to Fe^{3+} may eventually be released to the water column. The process would however not work without an input of organic substrates for the bacteria. The second mechanism involves displacement of PO_4^{3-} by a ligand of higher affinity

(higher stability constant) e.g. OH^- (Stumm and Morgan 1981, Boström et al. 1982). Many papers discuss the release of P from sediments in the context of just one factor, most frequently sediment anoxia. Boström et al. (1982) feel that the evidence of the early reports (Einselle, 1936 and Mortimer, 1942) was perhaps too nice and has obscured the other mechanisms involved.

There is one important situation, when sediments will supply P to the water column most of the time. These are lakes which were eutrophic or hypereutrophic for some time, e.g. through input of treated or untreated sewage and the P input was recently returned to normal e.g. by sewage diversion or by implementation of dephosphatation in treatment. It may take a long time, frequently many years, before the lake gets back to the previous state (Premazzi and Provini, 1985), first signs of improvement may however appear considerably sooner. Lakes, which did not accumulate much sediment P return to a roughly normal condition in a few years, the famous case being Lake Washington, WA (Edmondson 1972).

Lean et al. (1986) studied the reverse process, transport of P from hypolimnion to the sediments and have found, that it is insignificant under anaerobic conditions. In aerated hypolimnion it increased to 4 mg $P \cdot m^{-1} \cdot day^{-1}$ and could be further increased fivefold by addition of 300 µg $Fe^{3+} \cdot l^{-1}$.

Forms of Phosphorus and their Availability

Four basic fractions are generally acknowledged (Strickland and Parsons 1968): reactive (frequently called inorganic) dissolved P, reactive (inorganic) particulate P, dissolved organic P and particulate organic P. They are separated by filtration, usually through 0.2 µm filters, and two analytical procedures - straightforward determination of reactive phosphate by one of the molybdenum blue techniques and determination of TP after mineralization by perchloric acid, persulphate or UV radiation (Armstrong et al. 1966). Organic P is considered to be the difference between TP and Pr.

Lean (1973) has incubated lake water including biota with ^{32}P-orthophosphate, and by Sephadex-gel chromatography of filtrates he was able to distinguish three fractions with ^{32}P-activity: one of large molecular size (200,000) - LMWP or colloidal P, a second, which did not appear quite regularly, of medium molecular size he called XP and a third, which behaved like non-processed orthophosphate. LMWT was accompanied by a peak of organic matter and this suggested that LMWP may be an organic P compound produced and excreted by the biota. Blazka (1979) was able to produce LMWP in an inorganic system, a mineral solution similar in ionic composition to soft lake waters. Fe^{3+} was essential for LMWP formation. LMWP was formed at pH 5.5 - 6.5, but not at pH > 7.5. The pH range corresponds to solubility diagrams of Fe-phosphates (Stumm and Morgan 1981).

Another aspect of P forms is their availability for algae and other microorganisms. Data on the seasonal time course of Pr in the epilimnion of lakes have since the thirties suggested a nearly complete uptake by algae; uptake of organic P was evidently more difficult (Golterman 1972). Culture techniques were proposed to estimate availability of P from different media (e.g. DePinto et al. 1981). Viner (1988) suggested that most of acid-extractable P from New Zealand river suspensions was available to algae in a culture test.

On the other hand Kuenzler and Ketchum (1962) have shown by an isotopic technique that a major part of ortophosphate in a culture medium is not available to marine diatoms, Rigler (1966) by a similar, but not identical technique has shown, that only ca 1% of Pr is available to freshwater phytoplankton.

These data strongly suggest some transformations between the fractions. In an attempt to estimate transformation rates Blazka (unpublished results) has made experiments with highly active natural nannoplankton assemblages and algal cultures lasting one or two hours. He estimated 32Pav by the radiotracer Rigler test (1966) at the beginning and the end of the experiments, and Pr and incorporation of ^{32}P-phosphate into particles (nannoplankton) during the course of the experiments. ^{32}Pav was between 0.01 and 0.1 µg $P \cdot l^{-1}$ at the beginning, and about half that value at the end of the experiments. During the incubation, up to 0.2 µg P $l^{-1} \cdot min^{-1}$ was incorporated. Analytical uptake data agreed approximately with the ^{32}P rate estimates, provided P_r concentrations were used as basis of ^{32}P-uptake data. Uptake approximately followed decreasing logarithmic curves. It is suggested that complex-formation of phosphate with iron and possibly with other ions make a plausible explanation of the observed phenomena. An attempt to saturate Fe_{tot} (ca 3 µmolar concentration) by an up to 20-fold excess of PO_4-P to decrease the discrepancy between ^{32}Pav and P_r was unsuccessful: at all PO_4-P additions 32Pav was 0.1 µg.l-1. This suggests a role of calcium and magnesium in the formation of complexes that are reactive, but unavailable in radioactive Rigler assays.

A frequently discussed subject in aqueous P cycling is release of phosphatases by biota at low Pr concentrations, which would enable hydrolysis of ortophosphoric acid esters and the uptake of released ortophosphate by aquatic microorganisms (Berman 1970, Hoppe 1983). In these studies their authors have used substrates enabling determination of phosphatase activity, but comparatively little effort was spent to learn more about phosphatase substrates occurring in waters. Some more recent reports suggest that only a minor fraction of organic P in water and sediments are hydrolyzed by phosphatses of aquatic biota (Boavida and Heath 1988, Hino 1988). In planning further experiments specificity of alkaline phosphatase should be respected: Degens (1976) considers alkaline phosphatase, pyrophosphatase and Ca-ATPase as one enzyme.

Conclusions

1) Main sources of high concentrations of P in aquatic systems are sewage, animal excreta and surface runoff of soil including soil particles, particularly from fertilized land.

2) Sedimentation of P in lakes and reservoirs is an effective trapping mechanism. Sediment P may reenter the water, particularly (but not only) under anoxic conditions caused by microbial respiration due to high organic matter inputs to the hypolimnion and sediments. Accumulated sediments may release P in reclaimed lakes for a number of years.

3) Phosphorus in water is cycled between the inorganic compounds and the biota with rates up to the order of 1 day^{-1}. This cycling is dependant both in structure and rates on the structure of the biocenoses.

4) Forms of P in fresh water include high molecular inorganic entities. Information on organic P fractions is so far only incomplete. Some transformation rates between the forms are of the order 1 min^{-1}.

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BIOTIC CONTROL OF PHOSPHORUS CYCLING IN FRESHWATER ECOSYSTEMS

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Phosphorus is the main chemical compound limiting production in non-eutrophic aquatic environments. The ratio of P concentrations in aquatic plants to that in water is on average as high as 80,000 and may reach 800,000 during periods of peak production and maximum demand. For other elements like Ca, Fe, Mg, S, K etc., the concentration ratio is usually less than 1,000. Total P (TP) concentrations in fresh waters can range widely from several thousand $\mu g \cdot l^{-1}$ to nearly zero (Kajak 1979a, Wetzel 1985). More than 90 % of the TP contained in the aquatic ecosystem (consisting of water with seston, bottom deposits, macrophytes, and fish) was contained in the top 10 cm of the bottom deposits (Kajak 1979a). The sediment has a very strong gradient of P concentration and the top 3 cm alone still contain about 80 % of all P in the ecosystem. This layer is in very active exchange with the overlying water, illustrating the importance of sedimentation in the P cycle. The following is a brief overview of the main aspects of the P cycle. The biological processes influencing the cycle in the pelagic environment are partitioned into three groups:

1. Those diminishing P amounts,
2. Those increasing P amounts,
3. Those changing the structure of the ecosystem P cycle.

An important level of comparison of P concentration are Vollenweiders permissible loads which are 0.07, 0.10 and 0.25 $g \cdot m^{-2} \cdot y^{-1}$ for lakes with average depth of 5, 10 and 50 m respecitvely. Dangerous loads leading to rapid eutrophication are approximately twice those levels.

Processes diminishing amounts of P in the limnetic zone

The retention of P in the littoral zone occurs mostly in macrophytes which account for about 1 to a few percent of TP of the ecosystem. Amounts in littoral bottom deposits and other littoral components probably double this figure (Kajak 1979, Ball et al. 1985, Wetzel 1985).

Sedimentation of bioseston and organic but abiotic seston depends on the character of the particles - their size, shape, density etc., and these features depend partly on environmental conditions but also on their biotic origin. Sedimentation of phytoplankton varies from below 0.1 to about 7 $m \cdot day^{-1}$. The elimination of P from the epilimnion by sedimentation usually increases with increasing trophic status (Wetzel 1985) ranging from about 20 to more than 90 % of the annual load of a water body.

Zooplankton and sestonophagous fish feeding on small seston particles transform them to bigger fecal particles which sediment several times faster (Uelchinger and Bloesch 1987, Hoskin and Courtney 1983, Kajak 1979b), resulting in decreased seston amounts in the water (Figure 1). Fecal pellets of Copepoda with higher specific weight sediment faster than feces of Cladocera. Other filter feeders (Dreissena polymorpha and some Chironomidae in lakes and Trichoptera, Simuliidae and others in streams) play a similar role, although they are usually less important than zooplankton. Sometimes

the removal of phytoplankton by zooplankton can exceed the growth rate of the phytoplankton (Horn 1981). In some lakes, Dreissena, despite its moderate population, removes 0.2 -0.3 g $P \cdot m^{-2}$ during the growing season, i.e. more than 4 times the permissible load (Stanczykowska 1984) thus efficiently clearing the water (Kajak 1979a, 1981). Although the density of fish biomass in water is often similar to that of zooplankton most seston is filtered by the zooplankton as the following calculation shows: zooplankton at 8 $mg \cdot l^{-1}$ and a daily food intake of 150% of body weight uses 84 $g \cdot m^{-2}$ of fresh seston per day corresponding to 13 $g \cdot m^{-2}$ of P per vegetation season of 150 days. Fish at 350 $kg \cdot ha^{-1}$ or 5 $mg \cdot l^{-1}$ with a daily food intake of 20 % of body weight only removes 1.5 $g \cdot m^{-2}$ of P per season. Zooplankton was thus able to remove 120 times the permissible load while silver carp only removed 10 times the permissible P load during one season.

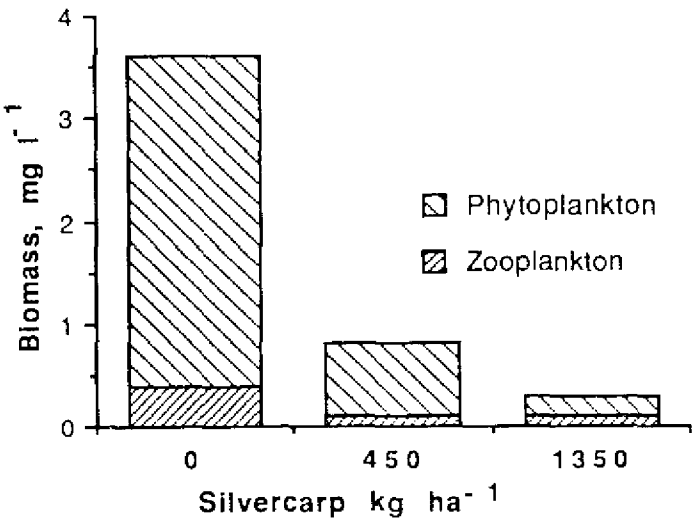

Figure 1: Reduction of plankton biomass by silver carp stock at 0, 450 and 1350 $kg \cdot ha^{-1}$ in limnocorrals of $6m^2$ and 1.5m depth in a eutrophic lake.

It must be remembered that the further fate of sedimented feces depends on water stratification, fish and other animal activity, etc.. Phosphorus is released from sedimenting tripton due to decomposition (Wetzel 1985). In addition there is a permanent exchange between particulate and dissolved organic matter (Wetzel 1985), and sedimenting tripton can act as a P sink by absorbing dissolved P or by being colonized by P rich bacteria. Dissolved organic P can be transformed by bacteria into refractory coloidal or particulate P which sediments thus decreasing the P concentration of surface waters (Stockli 1985, Yasumiho 1986). Sedimentation rates are also dependent on environmental and trophic conditions (Schoenberg and Carlson 1984) since the larger species of phytoplankton occuring in eutrophic waters are less available to zooplankton.

In stratified lakes P is also transported downwards by migrating Cladocera which feed in the epilimnion and later redigest and release phosphate in the hypolimnion (Wright and Shapiro 1984, Dimi et al. 1987). Under conditions of high primary production pH of the water is increased which favours the formation of calcite particles. These particles sediment rapidly at about 3 $m \cdot day^{-1}$ (Koschel et al. 1987). Calcite particles often form on the surfaces of algae and frequently occur in close connection with detritus. They absorb significant amounts of phosphate and may be responsible for the complete elimination of P from the epilimnion even at initially high P concentrations of 250 $\mu g \cdot l^{-1}$ (Murphy et al. 1983). The formation of a layer

of calcite on bottom deposits further influences P circulation in lakes (Benndorf et al. 1983). Phosphorus export from lake systems usually plays a minor role and may be due to emerging insects, amphibians or birds and mammals which feed in water and defecate on land.

Processes increasing P amounts or reducing P losses in the limnetic zone

Processes counteracting sedimentation are fragmentation and dissolution of particles, or the mineralization of organic P by bacteria or free enzymes. Phosphatase is released into the water by algae under conditions of low P availability (Broberg 1985, Currie et al. 1986, Chróst et al. 1984), or by bacteria independently of P concentration (Wetzel 1985). The dynamics of P depends on the DOM supply which in turn depends on bacteria and phytoplankton, and their control by predators, all of which depend on species composition, abundance and activity as well as environmental factors (Hamilton and Taylor 1987). Live phytoplankton can also release phosphate to water but the quantities involved are not well known (Reynolds 1984, Wetzel 1985). Viral bacterial of fungal diseases of phytoplankton stimulate autolysis and decomposition with resulting P release. The interactions of bacteria and their predators also appear to be important in bottom deposits (Bostrom et al. 1985, Gaertz et al 1987). The release of P from organic matter digested by zooplankton and other animals can be greater than P demands by phytoplankton and bacteria (Gulati 1984, Ejsmont-Karabin 1984). Generally the P amounts excreted per unit biomass of an animal is inversely proportional to its biomass (Ejsmont-Karabin 1983, Olsen 1986, Wetzel 1985) (Figure 2). Phosphate released by fish for example is negligible by comparison to that released by zooplankton (Sternik 1983, Nakashima and Leggett 1980). Nitrogen to P ratios in release products similarly depend on animal size (Figure 2). Species and size composition of zooplankton, therefore, has a strong influence on P cycling (Schoenberg and Carlson 1984). Some algae transport P from the meta- and hypo- to the epilimnion by vertical migrations (Klemer et al. 1985, Salonen et al. 1984). Phosphate turnover times in the limnetic zone can vary between 1 minute and 200 hours (Ejsmont-Karabin 1983, Riber 1984, Leonov 1986, Wetzel 1985). The processes underlying this turnover are extremely variable and need further quantification (Tarapchak and Nalevajko 1986 a,b).

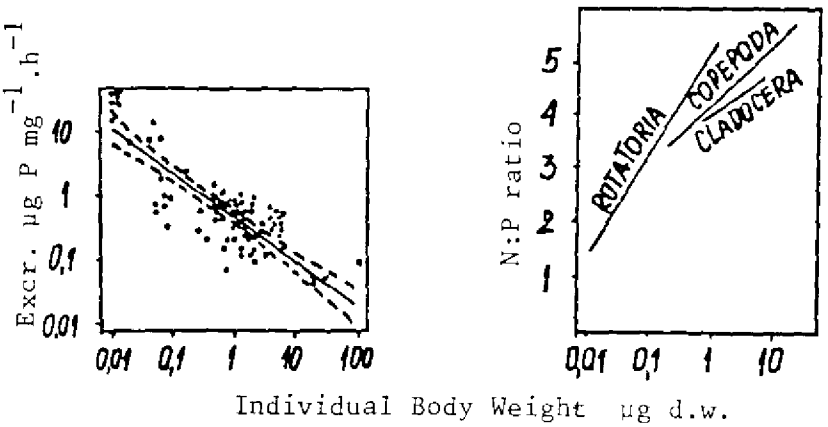

Figure 2: Dependence of PO4-P excretion and N:P ratio on individual body dry weight of zooplankton (after Ejsmont-Karabin 1984).

Phosphorus from bottom deposits is often released by macrophytes (Prentki et al. 1979, Kufel 1982, Shapiro et al. 1975) but only when the water itself is relatively P deficient. In P rich water, P is taken up directly from the water and accumulated in plant tissues or released to the bottom deposits (Wetzel 1985). In this way macrophytes have a eutrophying role in low P waters but a oligotrophying one in high P waters. Upon their death macrophytes release 20 - 50 % of their total P content to the water within several hours (Solski, cit. by Wetzel 1985). Some plants, especially submerged ones die and decompose during the growing season, but most of this process takes place in the autumn. Zoobenthos stimulates P transport from bottom deposits to the water by phosphate excretion. Chironomidae increase the rates of P transport by up to 20 times over the natural diffusion level (Fukahara et al. 1987) and phosphate release due to their activity can reach 10 - 50 $mg \cdot m^{-2} \cdot day^{-1}$ (Gallepp 1979, Wisniewski and Planter 1985, Gardner and Nalepa 1981, Tatrai 1987). This amounts to several $g \cdot m^{-2}$ per vegetation season which exceeds many times the permissible load (Kajak 1979a, Wetzel 1985). The passage of bottom sediments through Tubificidae undoubtedly stimulates decomposition and PO_4 release. According to Yoshiaki (1987), Tubificidae in shallow eutrophic lakes pass the surface 10 cm sediment layer 2 to 3 times per year through their intestines. The role of benthos is proportional to its population density which depends on oxygen conditions (Figure 3). Decomposition of organic matter and resulting PO_4 release normally increase after increased sedimentation of easily decomposable material such as algal blooms, fish feces, etc. In shallow zones, PO_4 produced in this process easily enters the water. Plants damaged during feeding of some native fish (mainly Scardinius erytrophthalmus, and Rutilus rutilus (Prejs 1984)), birds or invertebrates as well as the feces of these plant-eating animals undergo quick decomposition and provide a permanent P load during the growing season.

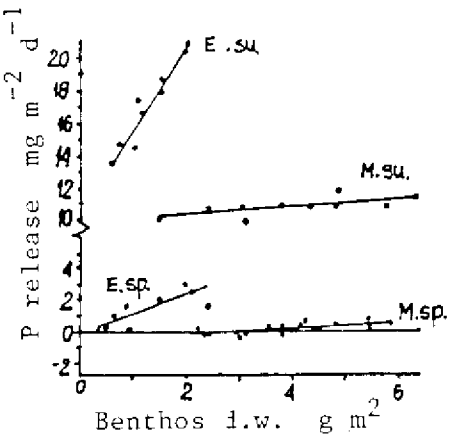

Figure 3. P release with increasing bethos density. E - eutrophic, M - mesotrophic lake, Su. - summer, Sp. - spring

Changes of the biocenotic structure of the aquatic ecosystem

The major internal cause of such changes are fishes. Grass carp (Ctenopharyngodon idella) can destroy macrophytes completely (Ewell and Fontaine 1982) so that the littoral zone loses its role of retention and transport of P with its normally well defined periodicity during the growing season. Elimination of macrophytes often leads, especially in shallow lakes,

to significant resuspension of bottom deposits, increased turbidity and decreased primary production. Common carp (Cyprinus carpio) plays a similar but less important role as the grass carp (Grivelli 1983). Crap also change size and species structure of zooplankton and other invertebrate fauna with consequent effects on P cycling (Kajak 1979a). Silver carp (Hypophtalmichthis molitrix) is a sestonophagous fish with high food intake and produces a great deal of feces which sink rapidly (Kajak 1981, Kuchlentz 1984, Leventer 1981). In deep stratified water bodies the P in the feces will remain in bottom deposits, thus reducing the P load. In shallow waters deposited feces stimulate decomposition and increase P load particularly if sediments are resuspended. Such resuspension is promoted by common carp during its bottom feeding. Fish, through their effects such as the elimination of zooplankton and bigger phytoplankton, can thus change the planctonic biocenosis and resulting P cycle completely (Opuszynski 1984, Schoenberg and Carlson 1987).

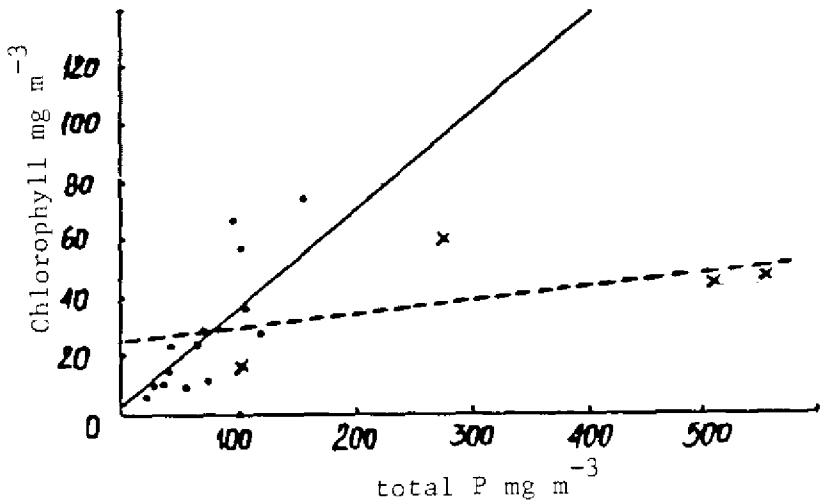

Figure 4 Relationship between chlorophyll and TP in lakes with (x) and without (·) abundant D. pulex. (After Shapiro et al. 1982).

In the practice of biomanipulation fish stock and species composition are adjusted in such a way that fish pressure on zooplankton is smaller, bigger zooplankters e.g. Daphnia become more abundant and deplete phytoplankton, thus preventing algal blooming (Figure 4). During this conversion unused P sinks to the bottom and its concentration in the water significantly decreases (Schoenberg and Carlson 1984, Kajak 1981, Dawidowicz 1985, Hrbacek et al. 1987, Leah 1980, Benndorf and Kneschke 1984, Pace 1984, Langeland et al. 1987). The complex mechanism of these processes have been discussed by Bartell et al. (1978), Wright and Shapiro (1984), Pace (1984), Dawidowicz (1985), Dawidowicz and Gliwicz (1980) and Prejs (1984). High populations of non-predatory fish and very small or young fish deplete the bigger forms of zooplankton. As a result small zooplankton species become dominant which are unable to control phytoplankton populations and which excrete more PO_4 than larger forms, overall resulting in higher P loads (Table 1). To avoid algal blooms such species must be controlled by introducing predatory fish or by the elimination of all fish by poisoning. Massive fish death as sometimes occurs through winter kill often results in sudden abundance of big Daphnia.

In summary most of the processes affecting the balance, concentrations and transformations of P in aquatic ecosystems are biologically controlled. The only exceptions are the sedimentation of allochtonic seston and P absorbed to it and the purely physical chemical adsorption of PO_4 to sedimenting

materials. The chemical release of PO_4 due to changes in O_2 or pH frequently is a result of biological processes. The complex interactions of these biological processes and the effects of varying environmental factors are often difficult to predict.

Table 1. Influence of fish / 900 $kg \cdot ha^{-1}$ on properties of water in a limnocorral, ineutrophic lake Trumman. (After Andersson et al. 1978). Data for September after 3 months exposure.

	Fish	
	absent	present
SD Visibility, m	1.9	0.2
pH	8.6	10.6
TP $\mu g \cdot l^{-1}$	62.0	400.0
chlorophyll $\mu g.l^{-1}$	20.0	440.0
Daphnia $ind.l^{-1}$	52.0	0.0

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TRANSPORT OF PHOSPHORUS IN RIVERS

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1. Introduction

Rivers are the main arteries of transport of phosphorus from agricultural, industrial and urban regions to freshwater lakes and the sea. The other forms of transport include glacial scour and continental dust fallout over the oceans. Although no specific information is available concerning phosphorus, it is estimated (Meybeck 1976) that the total load of rivers is around 90% of the supply of matter (dissolved plus particulate) to the oceans. Phosphorus is also known to be a pollutant responsible for the eutrophication of lakes and rivers and agreat deal of research has been directed to estimating the load of phosphorus associated with river inputs to lakes where eutrophication already exists or is seen to be a potential problem for the future. An increase in the load of phosphorus in a river catchment may not lead to a substantial change in the phosphorus concentration in the river water but signs of gradual eutrophication may become evident from chlorophyll a analyses of periphyton (Heinonen 1984) and gradual sliming of stones near the river banks. Excessive nutrients can also lead to problem growths of Cladophora in rivers (Bolas and Lund 1974).

There are many sources of phosphorus which may contribute to the total phosphorus load of a river. These include phosphorus from: (a) the leaching and weathering of igneous and sedimentary rocks such as calcium hydroxylapatite (HAP), fluorapatite, strengite, whitlochite and berlinite; (b) the decomposition of organic matter containing phosphorus compounds either weakly associated with the organic material or chemically bound to it; (c) effluents of domestic or industrial origin including of more recent importance the loads from fish farms; (d) diffuse inputs from agricultural land due to inorganic fertilizer use and organic manure applications; (e) atmospheric deposition and soil/river bank erosion during storm events.

The entry of phosphorus into a river may either be at apoint of discharge, eg sewage effluent input, or as land runoff (as distinct from direct wet and dry precipitation). Runoff maybe further classified as: (a) surface runoff which flows over the land surface and enters the river directly or via drainage ditches or storm sewers; (b) sub-surface runoff or that part of the precipitation which penetrates the upper soil horizons and flows into the stream above the groundwater table. This includes inputs from field tile drains; (c) runoff which percolates through to the groundwater table and enters the river as spring water or seepage.

Once phosphorus is in the river, it is usually classified according to the analytical procedure used in its determination rather than its more precise chemical formulation. The fractions most commonly referred to in the literature are as follows:

(a) Soluble Reactive Phosphorus (SRP). This is usually determined by filtering the water sample through a 0.45 µm filter and determination of phosphate by colourimetric analysis (e.g. Murphy and Riley 1962). A more accurate description of this fraction is "filtrable reactive phosphorus" because the arbitrary choice of 0.45 µm filter means that this fraction phosphorus associated with particles <0.45 µm in size. SRP is mainly PO_4^{3-} + HPO_4^{2-} + $H_2PO_4^-$ (inorganic phosphorus abbreviated, IP) but may include condensed phosphates and organic phosphorus which are hydrolysed or oxidised during the determination. Peters (1978) has shown that SRP may consistently overestimate IP.

(b) Total Phosphorus (TP). This includes all forms of phosphorus both dissolved and particulate matter in suspension. It is usually determined by acid digestion and oxidation using the persulfate digestion method (Mackereth et al. 1978). TP has also been determined by photo-oxidation using ultra-violet light (Rigler 1979) but found to give values of ≈20% lower than those determined using acid digestion procedures.

(c) Total Dissolved Phosphorus (TDP or simply solublephosphorus, SP). This is the fraction determined after filtration (usually 0.45 µm) and acid digestion. It includes both SRP and dissolved organic phosphorus (DOP).

(d) Particulate Phosphorus (PP). This is the difference between TP and TDP.

(e) Dissolved Organic Phosphorus (DOP). This may be defined as the TDP minus the acid-hydrolyzable phosphorus (mild acid hydrolysis to degrade condensed phosphates and may include easily hydrolysed organophosphorus compounds). If condensed phosphates are known to be absent then DOP = TDP-SRP.

The majority of catchment studies have limited the measurement of phosphorus to TP and SRP. However, it is important to consider the more precise speciation of phosphorus when considering heterogeneous reactions such as precipitation of solid phases, coprecipitation and sorption interactions with particulate material. The chemical speciation in rivers is generally variable depending on the type of catchment and the biological productivity.

Some studies have examined in detail the TDP fraction. Although organic phosphorus is largely uncharacterised, fractionation schemes have been suggested. For example, Stevens and Stewart (1982a) separated soluble phosphorus by precipitation with lanthanum, fractionation by acid and alkali treatment followed by gel filtration chromatography. The study concerned the six major rivers entering Lough Neagh, in which DOP amounted to 16% of TP (with 54% SRP) during the period from 1975-1979. Twenty-five percent of the DOP was recovered by acid extraction of the lanthanum precipitate and 40% of this had a molecular weight >10,000, 20% between 10,000 and 1500 and 40%<1500. A larger proportion of the DOP was obtained by alkali extraction (40%) of which 70% had a molecular weight >50,000 and was probably associated with humic materials. Seven percent of the acid-soluble organic phosphorus and 29% of the alkali soluble organic phosphorus appeared to be available for algal growth. Acid and alkali extraction of the particulate fractions (Stevens and Stewart 1982b) indicated that most of the organic phosphorus was associated

with a humic acid type of material which was alkali soluble. The majority of the acid extract was SRP.

The variation in the relative contribution of phosphorus fractions in a particular catchment is such that it is impossible to make any general conclusions about the occurrence of particular fractions in different rivers. When the SRP concentration is the major contribution to TP, eg originating from sewage effluent (Casey 1975), it is likely that SRP will show a negative correlation with river discharge (Casey and Clarke 1986). In other situations where surface runoff and erosion are important sources of PP (eg Crisp 1966), a positive correlation between TP and discharge may be expected. Large variations between the PP concentrations determined during low flow and high flow conditions are often evident. The river Redon entering Lake Geneva (Pilleboue and Dorioz 1986) had 5% PP, 85% SRP during low flow conditions ($<0.1\ m^3 \cdot s^{-1}$) and 78% PP and 15% SRP during high flow conditions ($>8\ m^3 \cdot s^{-1}$). Small Dartmoor streams in the UK also showed large variations in PP. On an annual basis about 75% of the phosphorus exported was in particulate form (Rigler, 1979).

2. Heterogeneous equilibria

The chemistry of phosphates in the environment is particularly complex and involves both biochemical and inorganic processes. McConnell (1979) has listed over 70 phosphate minerals likely to form under the influence of organisms in the environment of which a major part might be expected to occur in river waters and sediment. The most important reactions for freshwaters involve calcium, iron and aluminium phases as listed in Table 1.

Table 1. Solubility products of important phosphate minerals at 25°C

Mineral	Formulae	pK_{sp}+	Reference
Calcium hydroxylapatite	$Ca_5(PO_4)_3OH$	58.5	McDowell et al(1977)
Variscite	$AlPO_4.2H_2O$	18.2	Pagenkopf (1978)
Strengite	$FePO_4.2H_2O$	21.9	Pagenkopf (1978)
Vivianite	$Fe_3(PO_4)_2.8H_2O$	33.0	Snoeyink and Jenkins (1980)
Octacalcium	$Ca_4H(PO_4)_3.\ 2.5H_2O$	46.9	Moreno et al. (1960)

The formation of pure calcium hydroxylapatite (HAP) is expected to be a rare occurrence because of the possibility of substitution reactions to form carbonate apatites of general composition: $Ca_5(PO_4,CO_3)_3(OH,F)$. The concentration of carbonate ion may be of importance in determining not only the solid phase composition but also the kinetics of the nucleation and growth processes (Koutsoukos 1984). However, a consideration of the stability of phosphorus in freshwater with respect to HAP (and the more soluble calcium

phosphate minerals such as tri-calcium phosphate, octacalcium phosphate (OCP), and dicalcium phosphate dihydrate (DCPD)) will produce an estimate of whether the precipitation of calcium phosphates from river water is an important process. An example of this type of calculation for a synthetic hardwater with an inorganic phosphate (IP) concentration of 20 $\mu mol \cdot l^{-1}$ at 25°C is shown in Figure 1. The state of supersaturation of the water is quantified in terms of a saturation index (SI), defined as:

$$SI = \log_{10} (IAP/K_{sp}) \qquad (1)$$

where IAP is the ion activity product for the appropriate mineral phase. The solubility lines, SI = 0, are shown for calcite, HAP and OCP. Hardwaters with a calcium concentration between 1 and 2 $mmol \cdot l^{-1}$, phosphate concentration <20 $\mu mol \cdot l^{-1}$, pH = 8 and at ≈10°C are expected to be supersaturated with respect to HAP (and calcite) but not with respect to OCP. Nucleation of calcite is not likely to occur until SI >1.4 (House and Tutton 1982). In general, HAP is always found to be preceded by one or more precursors in a sequence that is in agreement with Ostwald rule of stages (van Kemenade and de Bruyn, 1987). Hence at pH = 8 and 25°C, the order of increasing stability is DCPD<OCP<HAP with HAP being the most stable phase in freshwaters at 1 atmosphere.

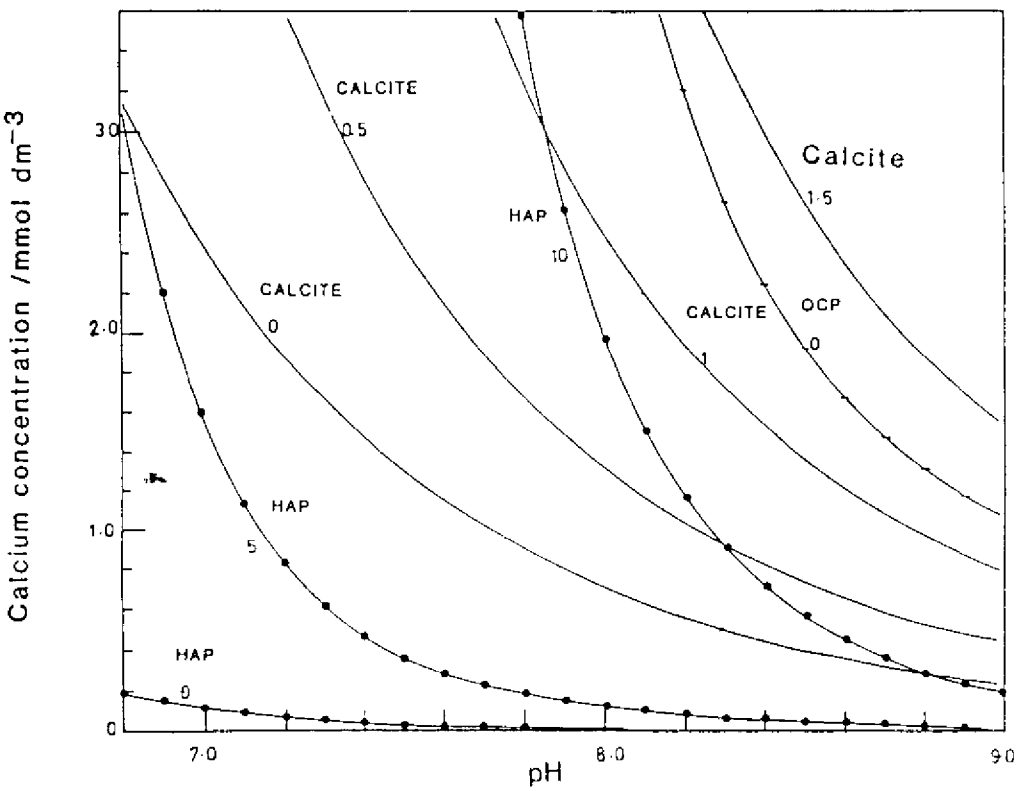

Figure 1. Coexistence diagram for the $Ca-CO_3-PO_4$ system at 25°C and 20 $\mu mol \cdot l^{-1}$ IP. The saturation indices (SI, equation (1)) are given for HAP, calcite and OCP. The isosats for SI = 0 correspond to the solubility lines for the appropriate mineral phase.

Present evidence suggests that in neutral to alkaline conditions, an amorphous calcium phosphate phase is the first step in the mineral formation followed by heterogeneous nucleation of OCP on the amorphous phase and subsequent epitaxial growth of HAP (Feenstra and de Bruyn 1979). Hence, according to Figure 1, the growth of a calcium phosphate mineral will only occur if the OCP solubility line is exceeded. It is also important to consider the effects of other ions in freshwater which may influence the precipitation of calcium phosphates (Zawacki et al. 1986) and explain differences in behaviour between waters of different composition waters. It is evident that HAP is unlikely to precipitate in most rivers unless the mineral is already present or the phosphorus concentration is particularly high. For example, Table 2 shows SI values for HAP calculated for a small hardwater stream receiving sewage discharge. It is clear that HAP is not expected to be formed under these conditions even with the high phosphate concentration in the sewage effluent and high values of SI achieved. Under these conditions the majority of inorganic phosphorus is present as HPO_4^{2-} but ion-pairs such as $CaHPO^0$ are also important (74% of SRP is present as HPO_4^{2-} and 21% as $CaHPO^0$ at the downstream site in Table 2). Calculations of IAP (equation (1)) for the Rhine and Rhone (Golterman and Meyer 1985) has shown that these rivers are saturated with respect to hydroxylapatite, although, as the authors indicate, the extent of supersaturation depends on the precise choice of the third dissociation constant for phosphoric acid used in the calculation. There is some debate whether HAP has any control on the concentration of ortho-phosphate in freshwaters (Golterman and Meyer 1985, Avnimelech 1980, House and Donaldson 1986), although it is likely that kinetic controls over competing heterogeneous reactions are of considerable importance.

Table 2. Supersaturation with respect to calcium hydroxylapatite of a small stream receiving sewage discharge (Drimpton stream, Devon, U.K.)

Site	Temperature °C	pH	Calcium concentration $mmol \cdot l^{-1}$	SRP $\mu mol \cdot l^{-1}$	SI (HAP)
Above discharge	10.1	7.68	1.70	4.2	5.6
At discharge	10.1	7.55	1.75	8.6	6.1
200 m downstream of discharge	10.1	7.55	1.78	18.3	7.1
Sewage effluent	10.1	7.52	2.44	191.7	10.3

Other phosphate minerals sometimes associated with the interaction of dissolved phosphate with suspended particles or sediments are variscite, strengite and vivianite (see Table 1). These minerals have been less studied than the calcium phosphates and so, although a great deal of information exists about the growth kinetics of various calcium phosphate phases, little information is currently available concerning the nucleation, growth and dissolution of aluminium and iron compounds. Stumm and Morgan (1970) have

calculated that strengite ($FePO_4.2H_2O$) is more soluble than variscite ($AlPO_4.2H_2O$) but this only reflects on the choice of the solubility product, K_{sp} (Table 1). Using the values of K_{sp} in Table 1, the solubility of iron phosphate is less than aluminium phosphate. This may be illustrated for a freshwater at 25°C, ionic strength 0.01 $mol \cdot l^{-1}$ activity coefficient, 3 ≈0.4 and pH = 4 and 6. At a relatively high total dissolved inorganic phosphate concentration of 20 $\mu mol \cdot l^{-1}$, the solubility line of variscite predicts an AI3+ concentration of ≈2 $mmol \cdot l^{-1}$ at pH = 4 which reduces to 0.2 $\mu mol \cdot l^{-1}$ at pH = 6. For strengite, the equilibrium concentration of Fe^{3+} under similar conditions is ≈0.4 $\mu mol \cdot l^{-1}$ at pH = 4 and ≈4 x 10-11 $mol \cdot l^{-1}$ at pH = 6. This simple calculation ignores the effect of ion-pair formation involving phosphorus and so the total aluminium and iron concentrations may be expected to be considerably higher. The formation of vivianite under reduced conditions is also possible although there is no evidence that its formation is an important sink for phosphorus in river sediments. Its occurrence has been reported in sewage effluent (Tomson and Vignona 1984) and in clays in the Great Lakes sediment (Nriagu and Dell 1974). It is also possible that the transformation from strengite to vivianite will occur as anaerobic conditions develop within a sediment. In oxidised conditions it is likely that the precipitation of an iron oxide phase will occur before the iron phosphate and lead to the subsequent coprecipitation of phosphorus.

3. Coprecipitation and sorption reactions

Although these reactions are heterogeneous in nature, they are considered separately because the solid phase or adsorption layer is generally variable in composition and cannot be defined in terms of a thermodynamic solubility product.

3.1 Adsorption and coprecipitation with calcite.

The coprecipitation of inorganic phosphorus with calcite has been reported in a number of publications (Rossknecht 1980; Murphy et al. 1983; Koschel et al. 1983). It is thought to be an important "self-cleaning mechanism" for some hardwater lakes and rivers particularly during periods of intense photosynthesis. Green et al. (1978) found that calcite was important in regulating the stream phosphorus concentration (SRP) although the phosphorus adsorbed onto calcite was found to be easily released. Phosphorus coprecipitation with calcite was also found to be an important mechanism describing the chemistry of experimental recirculating streams (House et al. 1986 and1988).

The mechanism for phosphate coprecipitation has been studied by House and Donaldson (1986) and the effect of phosphorus on the growth of calcite by House (1987). The results show that the coprecipitation can be described in terms of the adsorption of phosphorus onto the calcite surface, followed by its incorporation in the growing crystal. The amount of phosphorus incorporated does not depend on the adsorption kinetics but is affected by the solution pH, phosphorus speciation and temperature. The amount of phosphorus removed by coprecipitation, Δn_p, is described by the equation:

$$\Delta n_p(t) = N_A \, \delta\sigma g(t) \qquad (2)$$

where N_A is Avogadros constant, δ is the molecular area of $CaCO_3$ on the surface (20.101×10^{-20} $m^2 \cdot molec^{-1}$), σ is the maximum surface density of phosphorus on the surface ($\mu mol \cdot m^{-2}$) and g(t) is an integral describing the adsorption isotherm (House and Donaldson 1986) and the amount of calcium lost from the solution (Δn_{Ca}). Hence a knowledge of the temperature, solution composition and loss of calcium enables the loss of phosphorus to be calculated by equation (2) given a value for σ. This parameter has been evaluated experimentally at 10°C and 25°C for different river waters. The values at 10°C are shown in Table 3. The surface density of phosphorus, σ, depends on the surface density of other surface active chemicals in the solution including magnesium and iron (House et al. 1986). However, σ may be easily determined by the seeded growth method (House and Donaldson 1986) for any freshwater of interest. The magnitude of σ should then reflect whether the water contains chemicals that are competing with phosphorus for the calcite surface. It is also expected that the surface density of phosphorus will depend on the morphology of the calcite precipitated. The results using the recirculating experimental stream (Table 3) indicate that this is not likely to be an important consideration and from the results obtained so far, a value of $\sigma = 0.1$ $\mu mol \cdot m^{-2}$ appears reasonable for a range of hardwaters.

Table 3. Surface density of phosphorus coprecipitated with calcite at 10°C

Solution	Surface density $\mu mol \cdot m^{-2}$	Standard deviation $\mu mol \cdot m^{-2}$	Reference
Pure $Ca(HCO_3)_2$	0.162	0.02	House et al. 1986
Chalk acquifer Puddletown, Dorset	0.95	0.008	House et al. 1986
Experimental stream Puddletown, Dorset	0.077	0.006	House et al. 1986
R. Frome East Stoke, Dorset	0.055	0.010	House et al. 1986
R. Windrush Oxfordshire	0.075	-	unpublished

The phosphorus coprecipitated is distributed throughout the calcite and is only released upon dissolution. The ratio $\Delta n_{Ca}/\Delta n_P$ in the solid phase depends on the solution composition during precipitation but between 0.5-1.5 $\mu mol \cdot l^{-1}$ SRP, the ratio is expected to be ≈200-300 (House et al. 1986). At lower phosphate concentrations, the ratio increases sharply to values in excess of 1000 for SRP <0.1 $\mu mol \cdot l^{-1}$. These ratios are consistent with the analysis of calcitic sediments occurring in rivers (Green et al. 1978). The analysis of a calcitic sediment produced in an experimental stream gave a

value of $\Delta n_{Ca}/\Delta n_p$ of ≈730 (SRP ≈0.2 $\mu mol \cdot l^{-1}$) which compares with a value for soft-chalk of ≈920 (Worbarrow, Dorset) and 107 for naturally occurring large crystals of calcite (Osmington Bay, Dorset and New Mexico).

3.2 Adsorption and coprecipitation onto other sediment materials. Much of the research concerning phosphorus-sediment interactions has been done on lake sediments and is not directly applicable to fine sediments found in many river beds. In a recent review, Malati and Fox (1985) concluded that: "Further studies of phosphate eutrophication in rivers are needed, especially the kinetics of the interaction of phosphates and bed deposits".

River sediments may be important as both sinks and sources of dissolved phosphorus and in the transport of phosphorus either as suspended particulate or bed load. The sediments are usually extremely heterogeneous in nature with components from the local catchment and various anthropogenic sources.

Several approaches to understanding phosphorus-sediment interactions are available:

a) Sediment cores or surface sediment samples are taken from the river and used in laboratory experiments to determine the sorption/desorption behaviour. The oxidation state of the sediments should be maintained and bacterial activity minimized. The sorption behaviour is usually modelled using either a linear isotherm equation:

$$n_a = K_H(SRP) \qquad (3)$$

where n_a is the amount adsorbed ($\mu mol \cdot g^{-1}$) and K_H is the Henry's law adsorption constant, or the Langmuir equation:

$$n_a = n_m K_L(SRP)/[1 + K_L(SRP)] \qquad (4)$$

where n_m is the limiting amount adsorbed when the surface is saturated and K_L is the Langmuir constant which is related to the energy of adsorption. The Langmuir model assumes: (a) a homogeneous structured sediment with a single energy of interaction between inorganic phosphate and the different sediment materials, (b) that the interaction energy between the adsorbed species is negligible. It is also important to assess the reversibility of the adsorption isotherm and hence the capacity of a sediment to "fix" phosphate and to evaluate the kinetics of the sorption or desorption reaction.

Another approach, which is less useful for modelling the sediment-phosphorus interaction but does provide a relatively simple method of determining the response of a river sediment to changes in the dissolved phosphorus concentration, is the estimation of the equilibrium phosphate concentration or EPC. This is defined as the concentration at which no net adsorption or desorption takes place. It is determined by equilibrating the river sediment with different samples of river water which have been spiked with inorganic phosphate. A graph of the final phosphorus concentration against the adsorption/desorption amount allows the EPC to be estimated, i.e. when na = 0. Again, it is essential to evaluate the kinetics and also the effects of changing the adsorbent concentration. EPC for river sediments are

typically between 10-30 $\mu g \cdot l^{-1}$ ($\approx$0.3-1 $\mu mol \cdot l^{-1}$) although exceptionally high values (>100 $\mu g \cdot l^{-1}$) may be obtained near sewage outfalls or farm waste sources.

(b) Another approach is to analyse the sediments by XRD, electron microscopy, X-ray fluorescence and wet methods to identify the main mineral components and determine the total organic content. This information can be used to identify which of the sediment components are likely to have the greatest influence on the interaction and so permit more extensive study. This may be done using well characterised materials in synthetic solutions but with detailed comparisons between the natural water-sediment systems. In this way it is possible to accumulate information about the molecular processes which control phosphorus translocation and permit modelling applications to different sediment-water quality combinations. This can be a productive approach if the long-term goal is to model the movement of phosphorus in a river catchment. It is the approach which has been used to model phosphorus coprecipitation discussed in the last section and has also been used to study the processes occurring in sediments containing iron and aluminium oxides discussed below.

(c) A third option is to use a sequential extraction procedure similar to that discussed by Salomons and Forstner (1980) and Hieltjes and Lijklema (1980), e.g. treatment with dithionite-citrate to release phosphorus associated with iron phases. More recently a sequential fractionation scheme for separating calcium bound and iron oxide bound phosphates has been proposed by Golterman and Booman (1988). Suspended sediments in river water entering Lough Neagh have been fractionated by acid and alkali treatment (Stevens and Stewart 1982b). The extraction procedures of Hieltjes and Lijklema (1980) have been used by Swyngedouw et al. (1984) to fractionate the phosphorus associated with the sediment of a highly polluted shallow stream in Belgium. The sediment was in contact with a phosphorus concentration of $\approx$1.2 $mg \cdot l^{-1}$ ($\approx$40 $\mu mol \cdot l^{-1}$) and it was concluded that about 7% of the phosphorus was "weakly bound", 82% associated with iron and/or aluminium and 10% with calcium.

The extraction and fractionation methods should be regarded as an aid to the understanding of the association of phosphorus in river sediments. The treatment of the sediment to remove one phase and release phosphorus may also be accompanied by other reactions which effectively remove phosphorus compounds from solution and so produce erroneously low results, e.g. the action of hydrogen peroxide may release phosphorus into solution which may then react with calcitic minerals or iron oxides in the sediment.

Both iron and aluminium oxides have been implicated as important phases controlling the sediment-phosphate interaction (Stumm and Morgan 1970). It is unlikely that pure phases are precipitated from freshwater but mixed phases such as $(Al,Fe)(H_2PO_4)_n(OH)_{3-n}$ with phosphorus coprecipitated with mixed aluminium and iron oxides. The coprecipitation of phosphorus with iron oxides is determined by a change in the redox status of the sediment and it is unlikely to be as important a process in river sediments as it appears to be in lakes.

The adsorption of phosphate on freshly precipitated iron hydroxide has been measured between pH = 6 and 8 by Lijklema (1977). The initial adsorption

(equilibrium phosphate concentration <15 $\mu mol \cdot l^{-1}$) was found to be very strong. The value of K_H was estimated from the data of Young and Comstock (1986) for the partitioning of phosphorus between solid $Fe(OH)_3$ and a solution containing Fe/humic acid in a weight ratio of 2:1. The result shown in Table 4 is much higher than the values of K_H estimated for goethite, clay minerals, calcite and some river sediments.

Table 4. Comparison of the linear isotherm constant, K_H (or Henry's law contant) for different sediment materials (all in oxic conditions)

Mineral or river sediment	$K_H/l \cdot g^{-1}$	Reference
Iron oxide (goethite)	3.0	Hingston et al. 1974
Illite	0.25	Edzwald et al. 1976
Monmorillonite	0.10	Edzwald et al. 1976
Kaolinite	0.02	Edzwald et al. 1976
Calcite	0.01	de Kanel and Morse 1974
Calcite	0.04†	House and donaldson 1986
Amorphous hydrous iron oxide	175	Young and Comstock 1986
Suspended sediment:		
Tiffin River, high flow	0.31	Green et al. 1978
low flow	0.24	
Maumee River	0.16	
Auglaize River	0.24	
Alpenrhein	0.16	Stabel and Geiger 1985

† pH = 7.0, 25°C

An extensive review of the interaction between phosphates and clays is not appropriate here. Interest in clays originates from the observation of the positive correlation between sediment clay content and phosphorus adsorption capacity. The affinity of clays for phosphate is seen (Table 4) to lie between calcite (with a similar adsorption capacity to kaolinite) and goethite. The sorption of phosphate is generally pH dependent and not generally totally reversible. The kinetics of sorption is often divided into a relatively fast stage, i.e. within 2 hours, and a slower stage lasting between several hours to weeks, e.g. Stabel and Geiger (1985). For kaolinite, the sorption behaviour is very similar to that of α-alumina with a sorption maximum at pH $\approx$ 4. This is attributed to a surface charge reversal at this pH leading to a decrease in sorption with increasing pH. Similar charge reversals have been reported for montmorillonite and illite at respectively lower and higher pH values than kaolinite. An optimum pH for the adsorption of phosphate by illite has been reported (Edzwald et al. 1976) in contrast with the adsorption on montmorillonite which was found to increase with pH in the range of pH = 1 to 11 (Edzwald et al. 1976). The changes in adsorption behaviour are usually explained in terms of (a) changes in the surface charge with variations in pH, (b) changes in the speciation of phosphate with pH, (c) surface complex reactions between phosphate anions and clay surfaces, e.g. for alumina edges at pH $\approx$8

$$Al - OH + HPO_4^{2-} = AlO(HPO_4)^{3-} + H^+$$

In river sediments the situation is complicated by the presence of anionic compounds which compete with phosphate for the surface of minerals such as iron oxides and hydroxides. Young and Comstock (1986) found that humic acid affected phosphate adsorption onto iron hydroxide. Although humic acid was found to have very little affinity for phosphate, it is expected to complex with colloidal iron hydroxide and reduce the availability of adsorption sites. In certain situations however, the complexation between humic substances and phosphate plays an important role, e.g. humic bog water (Ohle, 1964). In general the effects of organic matter on the adsorption of phosphates is not understood because of the difficulties of characterising the organic colloids.

The examples of Henry's law constant, K_H, estimated from published data on the adsorption of IP on river sediments and shown in Table 4, illustrate the limited range of KH, with values much less than those for amorphous hydrous iron oxide. It is impossible to make any general conclusions about sediment sorption because of the wide range of minerals in river sediments. Both the composition of the sediment and aqueous phase determine the adsorption affinity and capacity for phosphate as well as the kinetics and reversibility of the uptake. Studies on natural sediments have enabled the effect of sorption processes on phosphorus transport to be assessed. For instance the studies of Stabel and Geiger (1985) on the Alpenrhein discharging into Lake Constance showed that the sorption interaction was relatively fast, with 70% sorption occurring in the first 24 hours. The sediment was found to be a mixture of quartz, calcite, dolomite, feldspars, chlorite and illite with a clay fraction (0.5-2 μm) of 17%, a silt fraction (2-63 μm) of 77% and the remainder sand (>63 μm). The sorption followed the Langmuir isotherm with a sorption capacity of ≈2.4 $\mu mol \cdot g^{-1}$. The sorption was found to be partially reversible with nearly 60% desorbed by repeated extraction. The remainder was assumed to be fixed by the sediment, either in the internal structure of the particles or as distinct solid phases formed in situ, e.g. by coprecipitation reactions.

4. Plant and algal uptake

The effects of algal and plant uptake on phosphorus concentrations in rivers is extremely complex. Casey and Clarke (1986) showed that even with sixteen years data, because of the large year to year variations both in load and biological activity, any model using the data would have extremely large residual variances. They showed that in the month of April nearly 50% of the soluble phosphorus load of the River Frome could be removed by biological activity. Reimann (1985) found a similar value during periods of rapid algal growth or during algal blooms.

The assimilation of phosphorus by algae in time t may be approximated by:

$$\Delta P_a = \int_0^t \mu M f S \, dt \qquad (5)$$

where ΔPa is the uptake of the phosphorus fraction available to algae per metre of stream, μ the specific growth rate of the river bed algae (h^{-1}), M

the algal population density (g chlorophyll a m^{-2}), S the wetted perimeter of the river cross-section (m) and f the ratio of the phosphorus content of the algae to that of chlorophyll a. If Pa ≈SRP then M and S may be measured and f determined by experiment (≈3.6, Aiba and Ohtake, 1977). The specific growth rate of the algae is more difficult to estimate because it depends on the water quality, light, temperature and grazing populations of invertebrates. However, estimates using dark and light bottles immersed in the river bed are possible with f evaluated from:

$$\mu = f_c \cdot (P - R) \qquad (6)$$

where P and R are related to the photosynthetic and respiration rates (expressed as mass of oxygen produced (or consumed) per mass of chlorophyll a in unit time). The constant f_c is the amount of chlorophyll a produced per mass of oxygen (f = 0.0023 g chlorophyll a g $oxygen^{-1}$, Aiba and Ohtake, 1977). In a polluted shallow stream (SRP ≈10 $\mu mol \cdot l^{-1}$), the data given by Aiba and Ohtake (1977), permit the calculation of the rate of assimilation of phosphorus by algae as ≈0.08 $g \cdot m^{-2} \cdot d^{-1}$ (which compares with an average of ≈0.16 $g \cdot m^{-2} \cdot d^{-1}$ for interaction of phosphorus with the sediment). In the study ≈15% of the phosphorus input to the stream was fixed by algae in the stream bed with sorption by suspended solids, hydrolysis of condensed phosphates making a negligible contribution to the mass balance.

The measurement of the production of field populations of algae is extremely difficult. Numerous measurements of photosynthesis using either oxygen or Carbon-14 methods have been made but the errors in extrapolation to algal production can be large. Marker and Casey (1982), using an experimental recirculating stream with controlled conditions, showed that even when diatom numbers were declining, uptake of silica suggested substantial continuing production. Newbold et al. (1981) , measuring nutrient spiralling in streams using phosphorus-32, found a spiralling length of 193 m in a small woodland stream. Algal uptake is likely to be significant in situations where dense populations of benthic organisms become established in shallow and open streams.

Information on the uptake by aquatic macrophytes is limited. Westlake (1968) suggested an annual utilisation of only 2-5% of the R. Frome phosphorus by *Ranunculus penicillatus* var. *calcareus*, the major plant in the river. Casey and Westlake (1974), working on a smaller stream with a low SRP (≈1 $\mu mol \cdot l^{-1}$) found phosphate removal in 1.6 km of stream was 12.5% of the total load. Norman (1967) working on a stretch of 1.5 km of a still smaller stream with a much higher SRP (≈40 $\mu mol \cdot l^{-1}$) found that ≈13% of the total load was removed. Ladle and Casey (1971) found that the comparison of phosphorus throughput in solution to be approximately 100 times that estimated uptake by aquatic plants during the main growing season. Because of the immense variability in the biomass density, range of species and local conditions, if macrophytes are expected to be a significant sink of phosphorus, their uptake may be estimated from the experimental determination of the plant biomass density and phosphorus content. Hill (1979) found an average accumulation of phosphorus in three species of macrophytes was 5.89 mg of phosphorus per g of dry plant material. However as shown by Casey and Downing (1976), the phosphorus content of plant leaves and roots increases to some extent as the phosphorus concentration in the water increases. This "luxury uptake" occurs

when phosphorus surplus to growth requirements are stored in the plant or algae.

The decay of dead plant and algal material is also a source of phosphorus although the forms released and the kinetics of release are likely to be extremely variable and are not well understood. Marker and Casey (1982) found release of phosphorus from diatom decay occurred over several weeks. Hill (1979) found that the breakdown of aquatic macrophytes may be a major source of available nutrients in aquatic ecosystems. In his study 100% of the phosphorus was lost from the macrophyte tissue within 50-64 days. These losses were in agreement with the findings of other published literature (Boyd 1970; Jewell 1971; Boylen et al. 1975; Knouver and Ayers 1977). Gabrielson et al. (1984) found no leakage of phosphorus into the water from undamaged actively growing *Elodea densa*. In a study of the Potomac river, Callander (1982) found that benthic regeneration in the estuary was sufficient to supply all the phosphorus requirements for net primary production in the lower tidal river and the transition zone of the river estuary.

In the larger lowland rivers, primary production is mainly planktonic. The extent of development of phytoplankton biomass depends on the climate conditions, chemistry and physical features of the rivers, mainly morphometry and hydrology. In many lowland rivers with a large catchment area intensively used for agriculture and with a high population density, the nutrient input is likely to far exceed the primary production requirements. In a recent study of the phytoplankton biomass and production in the R. Meuse, Descy et al. (1987) estimated that production ranged between 0.05 and 5.78 $gC \cdot m^{-2} \cdot d^{-1}$ with a mean daily production of 1.5 $gC \cdot m^{-2} \cdot d^{-1}$. This range is similar to that observed for other large European rivers, e.g. the Thames (Lack, 1971), the Rhine and Neckar (Backhaus and Kemball, 1978) or in some English rivers reviewed by Jones (1984). Seasonal variations in nutrients in the R. Meuse showed no depletion during 1983 and 1984. The uptake of phosphorus by phytoplankton may be estimated from the production data using the Redfield ratio of C:P of 42:1 by mass (Reynolds, 1984). For the 15 km stretch studied by Descy et al. (1987), with a mean river width of 100 m, production of 1.5 $gC \cdot m^{-2} \cdot d^{-1}$ and SRP of 0.128 $g \cdot m^{-3}$ the uptake of phosphorus is estimated as ≈9% of the throughput (assuming a low summer flow of 50 $m^3 \cdot s^{-1}$). This proportion is likely to increase with decreasing flow, phosphorus load and increasing productivity. Although this is only a rough estimate, it does indicate the importance of phytoplankton on phosphorus concentrations in larger rivers during the low flow of the summer months. The problem in obtaining better estimates is the variability of the C:P content of the algae, particularly its dependence on phosphorus availability and metabolic patterns. Fitzgerald (1969) demonstrated that the alkaline phosphatase activity of phosphorus-limited algae was as much as 25 times that of algae with sufficient phosphorus.

5. Models of phosphorus transport in rivers

The transport of phosphorus into rivers may be treated using a mass balance approach (Oglesby and Bouldin 1984) by dividing the watershed into n units. The area in each unit is assumed to have approximately the same surface runoff and concentration of phosphorus. These units may be related to different agricultural usage such as dairy farmland, woodland, arable or different types of industrial regions or urbanised areas. In this situation

the mass of phosphate input into a section of a river may be classified as a) surface runoff, R_1, (b) subsurface runoff, R_2, (c) groundwater runoff or input, R_3, (d) point sources, R_4. The mass of phosphorus in the surface runoff may be expressed in terms of a summation of the contribution from individual units within the matrix, i.e.

$$R_1 = \sum_{i=1}^{n} A_i S_i C_i \qquad (7)$$

where A_i is the area of the unit (ha), S_i is the runoff in a unit area ($l\ ha^{-1} \cdot d^{-1}$ and C_i is the concentration of phosphorus in the runoff. If $R_3 = 0$ then the subsurface runoff may be evaluated from the balance:

$$R_2 = C_G \sum_{i=1}^{n} (P_i - ET_i - S_i) A_i \qquad (8)$$

where P_i is the rainfall ($l \cdot ha^{-1} \cdot d^{-1}$), ET_i the evapotranspiration and C_G the concentration of phosphorus in equilibrium with the soil. The total input of phosphorus R_t into the river is then:

$$R_t = \sum_{i=1}^{n} (C_i - C_G)\ A_i S_i + C_G F \sum_{i=1}^{n} A_i + R_4 \qquad (9)$$

where F = constant = $P_i - ET_i$. With no manure or fertiliser additions $C_i = C_G$ for some units and equation (9) becomes:

$$R_t = \sum_{i=1}^{m} (C_i - C_G)\ A_i S_i + C_G F \sum_{i=1}^{n} A_i + R_4 \qquad (10)$$

for m units with $C_i \neq C_G$. (R_t may be expressed in units of $kg \cdot d^{-1}$.) A more accurate description would replace the sums in equation (10) by integrals to account for the variation of C_i and S_i with time.

The mass balance for a stretch of river may then be written in the general form:

$$0 = \int_0^t q_i c_i dt + R^t - \int_0^t q_o c_o dt + \sum_i f_i(t) \qquad (11)$$

where q_i and q_o are the inflow and outflow for the section and c_i, c_o the corresponding concentrations. The processes occurring in the section may be represented in terms of functions, $f_i(t)$. The processes may either consume phosphorus, e.g. sorption onto suspended solids or sediment, sedimentation, algal uptake or produce phosphorus, e.g. desorption, biological degradation, resuspension and can be applied to any of the phosphorus fractions as long as the interconversion between the various forms is included in $f_i(t)$. With information about discharges and flows into the river section it is possible to use equation (11) to evaluate $\Sigma f_i(t)$ and identify the major processes contributing to the sum. These processes are likely to vary with river size,

locality, e.g. sediment and suspended solids composition, biological productivity and season.

This mass balance approach has been utilized to understand processes involving phosphorus in an experimental recirculating stream (House et al., 1988). With the experimental stream in continuous flow conditions and a constant controlled inflow and outflow, equation (11) simplifies to:

$$-\sum_i f_i(t) = \int_0^t q_i(t)c_i(t)dt - \int_0^t q_o(t)c_o(t)dt - V[c_o(t)-c_o(o)] \qquad (12)$$

where V is the volume of the experimental stream and $c_o(o)$ is the concentration of phosphorus in the outflow at t=0. With the stream containing a productive community of aquatic macrophytes, algae and associated invertebrates, a series of 24 hour experiments were performed to evaluate $\sum f_i(t)$. At the time of the experiments the stream was dominated by a filamentous macro-algae (*Zygnema*). The dry biomass was estimated as 7.4 $g \cdot m^{-2}$ (standard deviation 2.7 $g \cdot m^{-2}$) with a total stream biomass of 583.5 g. The two major processes contributing to $\sum f_i(t)$ in equation (12) were phosphate coprecipitation with calcite and algal uptake. The stream had reached a steady-state condition with respect to SRP. The results of the analysis using equation (12), with the mass of phosphate coprecipitated calculated using equation (2), indicated that <6% of the phosphorus loss could be attributed to coprecipitation and the rest (≈0.22 $\mu mol \cdot h^{-1} \cdot g^{-1}$ (dry wt.) photosynthetic biomass) to uptake by plants and algae. The biological uptake was found to be constant over a 24 hour period.

Other processes which in general may contribute to the phosphorus balance, i.e. included in $\sum f_i$ are:

(a) sorption-desorption on suspended solids and sediment

(b) heterogeneous reactions and coprecipitation of phosphorus

(c) hydrolysis and microbial degradation of condensed phosphates and organic phosphorus including organo-phosphorus.

(d) uptake and release by organisms and plants in the sediment and bulk water. This includes uptake by micro-organisms such as yeast, bacteria, smaller metazoa and algae

(e) decomposition and release from dead plants and organisms in the sediment

Other mathematical models have been developed to simulate the concentration of phosphorus in rivers, e.g. the unsteady and one-dimensional differential equation described by Aiba and Ohtake (1977), but these are limited in application because of the approximation needed for a solution and the lack of reliable data on the important processes described above.

6. Catchment studies

The most effective studies of phosphorus in flowing waters have used a simple mass balance approach either on a whole catchment, e.g. terrestrial and freshwater components or just rivers. Reviews of watershed studies include those by Keup (1968), Vollenweider (1968), Ryden et al. (1973) and Dillon and Kirchner (1975). Keup (1968) concluded that the mass of phosphorus entering a

stream is affected by land use with streams in forested watersheds containing the least phosphorus and those in urban areas the greatest amounts caused by sewage effluent discharges. Ryden et al. (1973) examined in detail runoff from forested agricultural land used for animal rearing and urban catchments. Some of the data are summarised in Table 5 with additional information on European rivers selected from the literature shown in Table 6. In addition to those listed in Table 5, important sources are sewage effluents with TDP concentrations usually in the range of 100-450 $\mu mol \cdot l^{-1}$. Urban loads are usually calculated per head of population with daily estimates between 1.9-4.0 g of phosphorus per person entering rivers (Smith 1977; Pilleboue and Dorioz 1986).

In agreement with Keup (1968), the results in Table 5 show that forested catchments tend to be conservative and have the lowest loss of phosphorus to rivers. In most instances only minor variations in concentration occur throughout the year because of the small amount of surface runoff. The concentrations are similar to those found in subsurface runoff water (Ryden et al. 1973) from tile drains, e.g. ≈0.4-15.0 $\mu mol \cdot l^{-1}$ as SRP and unpolluted rivers, e.g. R. Brevon in France (Meybeck 1982) TDP ≈0.5 $\mu mol \cdot l^{-1}$ and R. Caragh in Eire (Dowling et al. 1981) highest mean SRP ≈0.4 $\mu mol \cdot l^{-1}$ between 1974 and 1976. Unexpectedly high losses from nutrient-poor tropical moist forests (0.46 $kg \cdot ha^{-1} \cdot y^{-1}$) have been measured by Lewis (1986).

Table 5. Summary of watershed review by Ryden et al. (1973)

Type	Phosphorus loss $kg \cdot ha^{-1} \cdot y^{-1}$ mean	range	Form of phosphorus	Range of concentration in water $\mu mol \cdot l^{-1}$
Forested	0.14	0.02-0.68	TP	0.2-2.3
Agricultural (mainly arable)	2.0	0.08-6.3	TP	-
Cereal field plots	≈21	0.1-67	TP	-
Urban (non-point)	2.4	0.92-3.4	TP/SRP	2.6-38

Kirchner (1975) has proposed an empirical relationship to predict the loss of phosphorus from forested catchments overlying igneous bedrock, i.e. loss of phosphorus ($kg \cdot ha^{-1} \cdot y^{-1}$) = 0.0114 + 0.0585 x DD, where DD is the drainage density (km^{-1}). The drainage density is the stream length (km) divided by the catchment area (km^2). For the eighteen catchments studied with drainage densities between 0.23 and 1.3 km^{-1}, the loss of phosphorus is predicted as ≈0.02-0.09 $kg \cdot ha^{-1} \cdot y^{-1}$ and is in the range shown for forested catchments in Table 5.

Table 6. Comparison of selected catchment outputs

River	Catchment Type	Catchment Area/ha	Output /kg·ha^{-1}·y^{-1}	Phosphorus determined	Population /people km^{-1}	Reference
Sike, U.K.	M	83	0.86	TP	V. low	Crisp (1966)
Lillan Sweden	F 57% A 42%	--	0.12	TP	8	Brink and Widell (1967)
Gt Ouse, U.K.	A	--	0.90	TDP	--	Owens and Wood (1968)
Various rivers	--	--	0.14-1.45	TP	--	Vollenweider (1968)
Various rivers (lower Alps)	A,F	--	0.23-0.59	TDP	<150	Gachter and Furrer (1972)
Various rivers, Lough Neagh	A 70-90%	3.9x105	0.08	TP	75	Smith (1977)
Hart Tor, U.K.	M	--	0.20	TP	--	Rigler (1979)
Po, other rivers, Italy	Mix	1.2x107	1.6	TP	207	Chiaudani et al. (1980)
Wye, U.K.	A 86% F 9%	4.3x105	0.21-0.44	SRP	47	Osborne (1981)
Meuse, Belgium	Mix	3.5x106	0.28	SRP	--	Descy and Empain (1984)
Gudena, Denmark	A 65% A 25%	2.6x105	0.02-0.90	TP	73	Heise (1984)
Mersey, U.K.	Mix	6.8x104	5.7	SRP	1200	Holland and Harding (1984)
Lot, France	Mix	11.8x106	0.08-0.24	SRP	31	de Camps et al. (1984)
Caragh, Eire	A	1.6x104	0.16	SRP	7	Heuff and Horkan (1984)
Girou, France	A 80%	4300	2.68	TP	≈0.2	Probst (1985)
	A 80%	4300	1.90	PP	≈0.2	Probst (1985)
Redon, France	A 70% F 30%	3300	1.4	TP	109	Pilleboue and Dorioz (1986)
Frome, U.K.	A	4.4x104	0.46	SRP	<200	Casey and Clarke (1986)
N. Svarta Sweden	A 46% F 38%	9.5x104	≈1	TP	≈8	Karlsson et al. (1988)
S. Svarta, Sweden	F 61%	1.9x105	<0.03	TP	≈8	Karlsson et al. (1988)

Key: M - Moorland; F - Forested; A - Agricultural; Mix - mixed urban, industrial and farming.

The effect of catchment size on the loss of phosphorus from forested watersheds has been examined in detail by Prairie and Kalff (1985). An examination of the data from 94 forested catchments (mainly in North America) revealed that the regression coefficient for the relationship between log(TP catchment export, $kg \cdot y^{-1}$) and log(catchment area, km^2), did not differ significantly from unity, log(TP export) = 0.914 + 0.986 x log(area), giving a TP output of $\approx 0.08\ kg \cdot ha^{-1} \cdot y^{-1}$ for catchments with areas between 0.4 and 69.3 km^2.

In any type of catchment without significant pollution, the main control over the transport of phosphorus is the contribution of surface runoff during storm events. For example, in the Rough Sike catchment (Crisp 1966) over 50% of the phosphorus export was due to peat erosion. There is often a good correlation between river discharge and the suspended solids concentration (usually in the range of ≈ 1-$1000\ mg \cdot l^{-1}$) with the rising limb of the storm producing the highest suspended solids concentration relative to the receding limb (Johnson et. al. 1976). A good correlation is also frequently observed between TP or PP and the concentration of total suspended matter (Chauvet 1981; Pilleboue and Dorioz 1986; Probst 1985). Phosphorus concentrations in suspended solids are normally in the range of 0.1-0.25% phosphorus (Johnson et al. 1976; Rigler 1979; Probst 1985). In the Girou river it was observed that as the total quantity of suspended solids increased, the particles became less concentrated in phosphorus (Probst 1985). The suspended matter was relatively more concentrated in phosphorus during low flow (0.21%) than during high flow (0.11%). This enrichment was attributed to the relative increase in suspended organic matter which is generally richer in phosphorus than inorganic material. This highlights the difficulties of measuring the total export of phosphorus from catchments when surface runoff contributes a major fraction.

The loss of phosphorus from agricultural catchments tends to be higher than forested watersheds except in conditions of base flow when the outputs are similar. The variability (see Tables 5 and 6) is dependent on the land use, soil structure, crops and the relative importance of surface and subsurface runoff. The surface runoff from various cereal plots shown in Table 5 is particularly variable. Although phosphorus is generally retained by most soils, subsurface runoff by field drains may contain relatively high concentration of SRP because of the diminished contact between the subsoil and percolating water. Even with prolonged contact, some sandy soils show little retention of phosphorus and the concentration in subsurface runoff can be comparable with surface runoff. The PP is generally a higher proportion of TP in agricultural watersheds compared with forested catchments (Prairie and Kalff 1986).

The application of fertilizers can produce enhanced phosphorus loads mainly from storm runoff. Generally, however, the phosphorus losses are considered to be small. In the R. Girou catchment, the annual input of fertilizer was estimated as 22 $kg \cdot ha^{-1}$ (as phosphorus) and the loss by surface runoff as 0.1 $kg \cdot ha^{-1}$ (Probst 1985). i.e. <1% loss. Pilleboue and Dorioz (1986) estimated that agriculture provided a significant contribution to the phosphorus outflow. This was $<0.8\ kg \cdot ha^{-1} \cdot y^{-1}$ or approximately 2.5% of the total fertilization although this load contributed ≈30% of the TP at the stream outflow to Lake Geneva. Owens and Wood (1968) have also estimated that ≈40% of the phosphorus load in the Gt. Ouse is from land drainage.

In contrast with forested catchments, the phosphorus load per unit area from agricultural catchments did decline with increasing catchment area (Prairie and Kalff, 1986). When the catchments were divided in terms of land usage, i.e. pasture, row crops, nonrow crops and mixed, it was discovered that the phosphorus export from row crops and pasture catchments were responsible for the decline, with other catchments behaving similarly to forested areas, e.g. mixed catchments (2-45 km^2) gave a catchment export of $\approx 0.6\ kg \cdot ha^{-1} \cdot y^{-1}$ independent of catchment size.

Manure applications to land may also be an important source of phosphorus in some agricultural areas. With the current trend towards more intensive livestock production and farm specialisation in Europe, the dangers of pollution are increasing. The most important sources of pollution in the U.K. are caused by manure storage (30%), silage effluent (28.5%), dirty water from yards (20%) and land runoff (7%). Reports of pollution incidents affecting rivers increased between 1979 and 1985, e.g. approximately 45% increase in prosecutions for 1984-1985 (WAA, 1986). Good husbandry requires that manure applications to land should be matched roughly to crop requirements for nutrients. Intensive pig and poultry units have difficulty meeting such standards. Legislation has been passed in The Netherlands to restrict manure application to land by setting a maximum phosphorus limit. It is intended that the application will reduce to 78 $kg \cdot ha^{-1} \cdot y^{-1}$ for crops and grass by 1999.

The form of phosphorus in fresh manure varies according to the feed. For poultry manure, organic phosphorus may be as high as 60% but for pig manure it is usually less than 40%. On storage, bacterial activity results in conversion to crystals of calcium phosphates. During a 3 year field trial (Unwin 1981) in which 1964 $kg \cdot ha^{-1}$ of phosphorus was applied to a sandy soil, no increase in the soil phosphorus was detected beyond a depth of 30 cm. The TP content of the leachate from the trial was estimated as $<0.03\ kg \cdot ha^{-1} \cdot y^{-1}$. The major concern is point sources of pollution by surface runoff directly into streams, drainage channels and rivers.

Fish farming is becoming an increasingly important source of pollution to rivers and inland waters in many countries in western Europe. The largest producers are W. Germany (32,000 t), Norway (317,500 t) and U.K. (10,000 t) (de Solb 1987). The majority of the W. German and U.K. fish farms are land-based whereas the Norwegian farms have net-caged fish in inland waters. Phosphorus (SRP) discharges from fish farms are determined by the concentration of phosphorus in the fish feed and by the availability of phosphorus to the fish. Fish food may contain between 0.3 and 5% phosphorus (by weight) although most modern proprietary feeds now contain $\approx 1\%$ phosphorus. The output of phosphorus (SRP) has been related to the concentration of phosphorus in the feed by an empirical relationship (Crampton 1987):

$$P_o = P_f \times f - 3.8$$

where P_o is the mass of phosphorus output per kg of fish growth, P_f is the concentration of phosphorus in the feed ($g \cdot kg^{-1}$ of feed) and f is a factor termed the feed conversion ratio. For a rainbow trout farm producing 24 t of fish per year the annual load of phosphorus (SRP) may be estimated as 1.4 kg (calculated assuming $f = 1.5$, $P_f = 14\ g \cdot kg^{-1}$) which is equivalent to about one

person's domestic sewage effluent. The average outflow of suspended solids from land-based fish farms (de Solb, 1987) was estimated as 1.35 t per tonne of fish produced. Assuming a phosphorus concentration in the particulate phase of ≈1%, this outflow corresponds to 324 $kg \cdot y^{-1}$ for 24 t of fish produced which is equivalent to the annual sewage effluent of ≈300 people. Further research is needed to evaluate the forms of phosphorus output, concentration in particles and the ultimate fate of the materials.

In general, in the nutrient richer rivers of southern European countries there is far more concern about the direct effects of the suspended solids and the impact on the downstream uses of the rivers. Only in the more northern oligotrophic waters, e.g. Sweden, Norway, Scotland, is there concern about eutrophication caused by nutrient inputs to rivers and inland waters.

Urban discharges of sewage effluents are probably the most important source of phosphorus in polluted rivers. There are many studies which show that sewage effluent dominates the phosphorus load in both small and large catchments. In the R. Frome catchment (Casey and Clarke 1986) 70% of the phosphorus came from sewage effluent, whereas in the R. Redon (Pilleboue and Dorioz 1986), more than 50% came from domestic inputs. In the R. Frome the percentage TDP relative to TP varied between ≈20 and 90% (see Figure 2) depending on the time of year and discharge at the time of sampling. During the summer months it is generally about 70-80% of TP. The SRP has a tendency to decrease with increasing mean weekly discharge (Casey and Clark 1986). However, there is a positive correlation between TP and discharge (see Figure 2) which reflects the increased amount of runoff and resuspension of the river sediment during storms. It is also obvious from these data that frequent sampling is necessary to obtain realistic phosphorus loads, particularly during storm events.

Casey and Farr (1982) showed that increases in phosphorus could result from increased discharge in the absence of allochthonous inputs during artificial spates. Harms et al. (1978) reported increased levels of SRP during natural spates that could not be accounted for by allochthonous inputs and they concluded that the release of sediment interstitial water, enriched with phosphorus was the most likely cause. However, this release did not occur in the majority of spates. Casey and Farr (1982) found that phosphorus release from sediments increased from >16 $\mu mol \cdot m^2 \cdot h^{-1}$ to >80 $\mu mol \cdot m^2 \cdot h^{-1}$ during an artificial spate. During this time, the suspended solids increased from ≈2 $mg \cdot l^{-1}$ to over 100 $mg \cdot l^{-1}$. Swyngedouw et al. (1984) found in laboratory studies in anaerobic conditions, the release of phosphorus of up to ≈160 $\mu mol \cdot l^{-1}$ from the sediment to the overlying water. In the interstitial water the SRP was ≈370 $\mu mol \cdot l^{-1}$. It appears that in polluted rivers, the release of SRP from river bed sediments during storms will be affected by the prior accumulation in the sediment and interstitial water.

In the Lough Neagh catchment (Smith 1977) about 62% of the SRP load originated from urban and rural sewage discharges. In the R. Giron catchment (Probst 1985) about 19%, 78% and 60% of the TDP, SRP and TP respectively came from point source pollution which was mainly domestic sewage. Nutrient loads have also been evaluated from the Emilia-Romagna area (north Adriatic sea) mainly associated with the river Po discharge. About 75.6% of the phosphorus load was attributed to point sources with 45.2% due mainly to human metabolism and 54.8% due to synthetic detergents (Chiaudani et al. 1980).

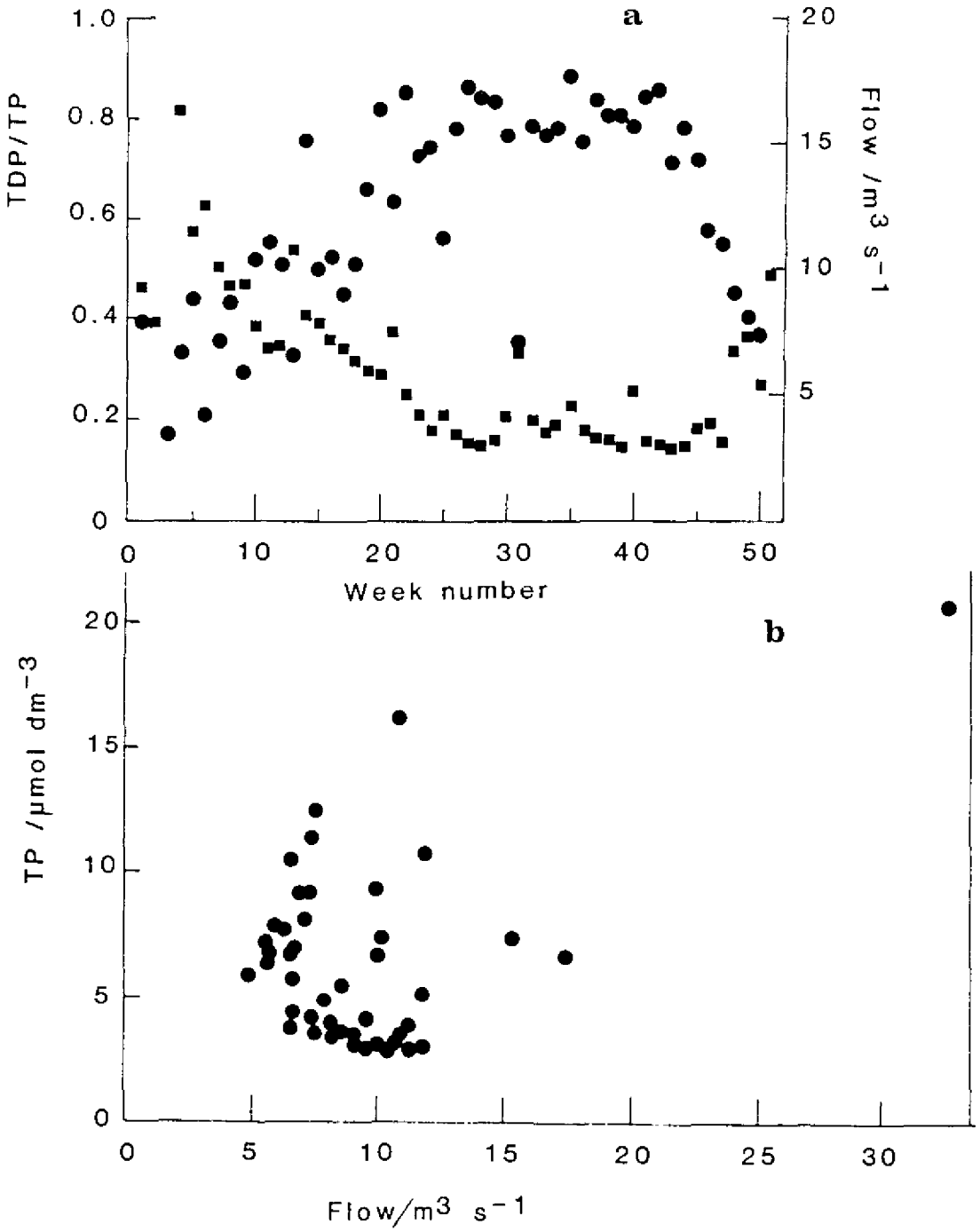

Figure 2. (a) Relationship between TDP/TP and river discharge at the time of sampling for the R. Frome (East Stoke, Dorset) during 1985. ■ ; discharge, •; TDP/TP,

(b) Correlation between TP and instantaneous discharge for the R. Frome (East Stoke, Dorset) during 1985.

In a study of twelve Welsh rivers, Brooker and Johnson (1984) found a significant correlation between the catchment load and population density of the catchment, i.e. catchment load ($kg \cdot ha^{-1} \cdot y^{-1}$) = 0.112 + 0.69 x D (number of people ha^{-1}) with the daily *per capita* contributions equivalent to 1.9 g. The phosphorus was measured as SRP and concentrations varied between ≈0.7 $\mu mol \cdot l^{-1}$ and about 24 $\mu mol \cdot l^{-1}$ (R. Taff) between 1974-1981. There were marked seasonal changes in the concentration of SRP in most of the rivers, with the highest concentration during the low summer flow and lowest concentrations during the winter. This behaviour again reflects the importance of sewage effluents in these catchments. The relationship between catchment load of SRP and population density is also supported by some of the data presented in Table 6, e.g. rivers Caragh and Mersey, although other data, e.g. R. Frome, indicate some disagreement.

Phosphorus loads for the larger rivers, e.g. the Mersey, Rhine and Meuse, are difficult to measure. Those listed in Table 6 are evaluated from measurements of the mean flow and concentration. The more intensive studies have been done on the smaller catchments, e.g. Redon and Gudena in France, where it is easier to separate different inputs to the river and construct mass balances of the form discussed in section 5.

7.Conclusion

This brief review has attempted to consolidate our present understanding of phosphorus in rivers. It has concentrated on the key processes involving phosphorus with a discussion of the magnitude of phosphorus exports from different river catchments. It is now intended to summarize the situation and suggest future developments.

1. Studies of different watersheds ranging from forested, agricultural and urban areas are advanced with a range of data now available from different regions. Diffuse inputs from forested catchments and point source inputs from sewage treatment are reasonably straight forward to quantify. Inputs to rivers from agricultural catchments are more uncertain and depend on the local soil, land management and agricultural practices. Future developments in intensive agriculture and fish farming need to be monitored to ensure that waste products are properly managed.

2. Mass balance studies of the transport of phosphorus are few with the most detailed work on the smaller catchments. Only broad estimates of loads are available for the larger lowland rivers. It should now be possible to process and model existing data obtained over several years to evaluate trends in the larger catchments.

3. The modelling of the transport of phosphorus in rivers, ultimately depends on our understanding of the chemical and biological processes occurring in the rivers, e.g. sediment-water interactions or algal uptake. Progress in recent years has been made in certain areas, e.g. (a) zphytoplankton production in large lowland rivers, (b) the nature of dissolved and particulate organic phosphorus in rivers, (c) the coprecipitation of inorganic phosphorus with calcite in hard waters, (d) the identification of minerals which are associated with sediment phosphorus, (e) fractionation

procedures. However, further progress is needed to understand specific processes which can now be identified as of importance in rivers, e.g.

(a) Sediment-water interactions. The general importance of precipitation reactions is still not known. The significant proportion of phosphorus considered to be fixed by river sediments suggests that these processes may be of considerable importance as a sink. A list of publications mention the affinity of phosphorus for iron and aluminium hydroxides but there is little direct evidence for the association in river sediments or suspended material.

(b) Resuspension and deposition of particulate phosphorus. These processes can be an important source or sink of phosphorus in a river. Little information appears to be available regarding the importance of these loads relative to the PP input from runoff and effluents.

(c) Modelling biological processes. Progress has been made on the modelling of inorganic processes such as sorption onto sediments. Further research is needed to develop general models to describe the assimilation of phosphorus by the biota and degradation of plant materials. These models could then be incorporated in the mass balance equation.

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PHYSICAL TRANSPORT OF PHOSPHORUS IN RIVERS

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Introduction

The geo-chemical cycle of Phosphorus (P) at the continent-ocean interface is important because of its controlling involvement in inorganic and biological processes in the major ecosystem components, hydrosphere, lithosphere and biosphere. The world's rivers are the major pathways for the transfer of P from continents to oceans. The study of the transport mechanisms of P in river water are important for the understanding of the role of riverine P in the global P cycle.

Phosphorus is the tenth most abundant element on earth, with an average concentration in the crust of 0.1%. Continental sediments average about 0.07% P, soils 0.08% P, igneous rock 0.1% and marine sediments 0.12% (Brink 1978). The terrestrial P cycle is important since P is often a limiting nutrient. Natural inputs of P to the land are due to precipitation. Meybeck (1982) has estimated the P content of rains collected at unpolluted stations as 5 $\mu g \cdot l^{-1}$ PO_4-P and 10 $\mu g \cdot l^{-1}$ TDP.

Humans have intervened in the P cycle by deforestation, which increases erosion; by the use of P fertilizers; and through the production of industrial wastes, sewage and detergents. This intervention is reflected in the increased concentration of P in rivers and lakes, where it has stimulated biological productivity, and led to eutrophication. The amounts of P transported by rivers, depend on natural processes in the drainage area (eg. climate, rock types), processes in the rivers such as sedimentation of particulate material, biological processes and human influence. The present discussion shall focus on river discharge from land as it relates to the overall P cycle.

Dissolved Phosphorus in River Waters

Sources of dissolved river P are the natural weathering and dissolution of P minerals, natural and agricultural release of P from organic forms, release from fertilizers, and soluble P from phosphate detergents and domestic or industrial wastes (Stumm 1973). The phosphate concentration in river water is regulated inorganically by the solubility of aluminium orthophosphate and apatites or by adsorption equilibria involving clay minerals and amorphous ferric hydroxide (Stumm and Morgan 1970). Dissolved P is naturally present in river water at low concentrations of around 10 $\mu g \cdot l^{-1}$ PO_4-P and 25 $\mu g \cdot l^{-1}$ TDP, which includes organic forms (Meybeck 1982). Most data are available on the concentrations of orthophosphate anions and it is generally agreed that this fraction is readily available to aquatic plants.

Stumm (1973) estimated that, based on the solubility of various inorganic P compounds, dissolved P levels in rivers should be 20 $\mu g \cdot l^{-1}$ PO_4. However,

all rivers from unpolluted regions have lower P concentrations, indicating that the theoretical solubility is not the deciding factor for regulating P levels. Biological processes are likely involved in the regulation, and about half of dissolved P and 40% of suspended P is in organic form.

Dissolved Phosphate Levels in Indian Rivers

Maximum values of dissolved P observed for various fresh waters in India are high (Table 1). The high values reflect addition from anthropogenic sources such as fertilizer, agricultural runoff and power plant emissions. The entire stretch of the Ganges is highly industrialized, and P levels at Calcutta are very high (0.55 ppm). In the Cauvery basin a number of paper industries and intensive agricultural activity contribute to enhanced P inputs into the estuarine region. Man's impact on the P cycle predicted by Garrels et al. (1971) is very much evident in a developing country such as India.

Table 1. P-fluxes in Indian and world rivers

River	Mean annual discharge $10^9 m^3 \cdot y^{-1}$	Dissolved inorganic phosphate ppm	Dissolved phosphate flux 10^{10} g $P \cdot y^{-1}$	Sediment load 10^6 $t \cdot y^{-1}$	P.Conc. in sediment $\mu g \cdot gm^{-1}$	Sediment P flux 10^{10} g $P \cdot y^{-1}$
Brahmaputra	510	0.12	2.00	597.23	995	57.03
Ganges	493	0.12	1.93	573.80	1360	78.04
Indus	207	0.15	1.01	-	-	-
Godavari	92	0.16	0.48	16.80	830	1.40
Krishna	30	0.07	0.07	10.56	774	0.82
Mahanadi	67	0.16	0.34	-	-	-
Narmada	41	0.10	0.13	-	-	-
Tapti	18	0.10	0.06	-	-	-
Cauvery	21	0.16	0.11	0.71	950	0.06
Indian Average	1700	0.12	6.60	1209.00	1100	133.08
Amazon	5518	0.012	2.16	900.00	1650	148.5
Danube	203	0.11	0.73	67.00	680	4.56
Mekong	577	0.02	0.38	345.00	2000	69.00
Niger	192	0.013	0.08	68.00	1600	10.88
Parana	203	0.07	0.46	112.00	1300	14.56
World Average	37400	0.06	80.00	17500.00	1150	2012.00

Influence of Discharge on Phosphorus Level in Rivers

Concentrations of different forms of P (total P, total dissolved P and PO_4-P) increased in the Girou river waters with increasing discharge rates (Figure 1) (Probst 1985). The discharge-concentration relationships calculated for the different P forms are always positive, confirming results obtained from many other rivers (Noval et al. 1975, Grobler et al. 1985). However, the lack of a similar relationship has also been observed in a few cases (Pilleboue et al. 1984).

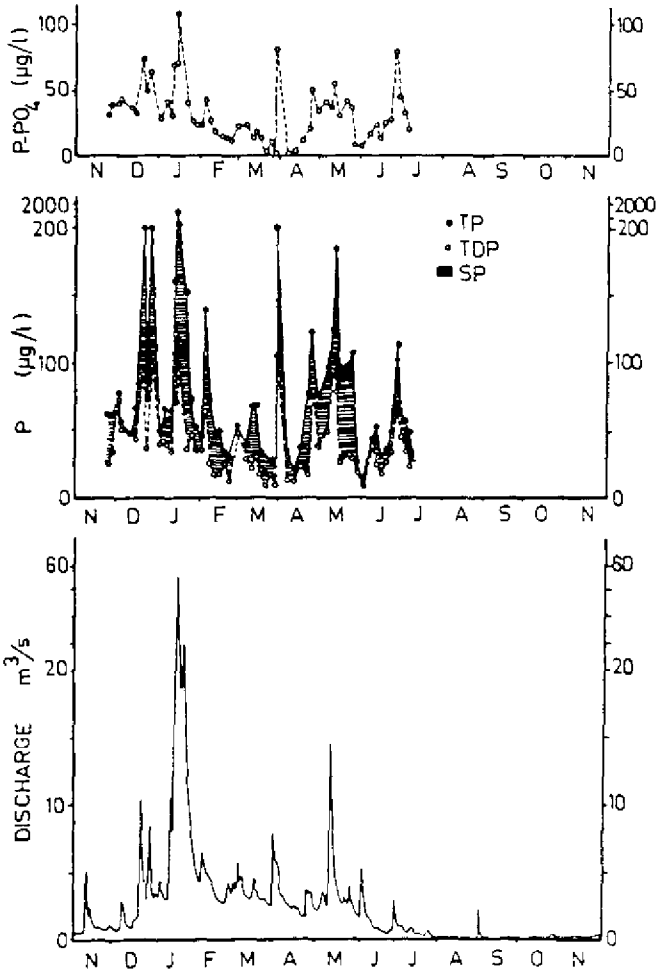

Figure 1 Comparisons between the fluctuations of phosphorus concentrations and the discharges in the Girou river.

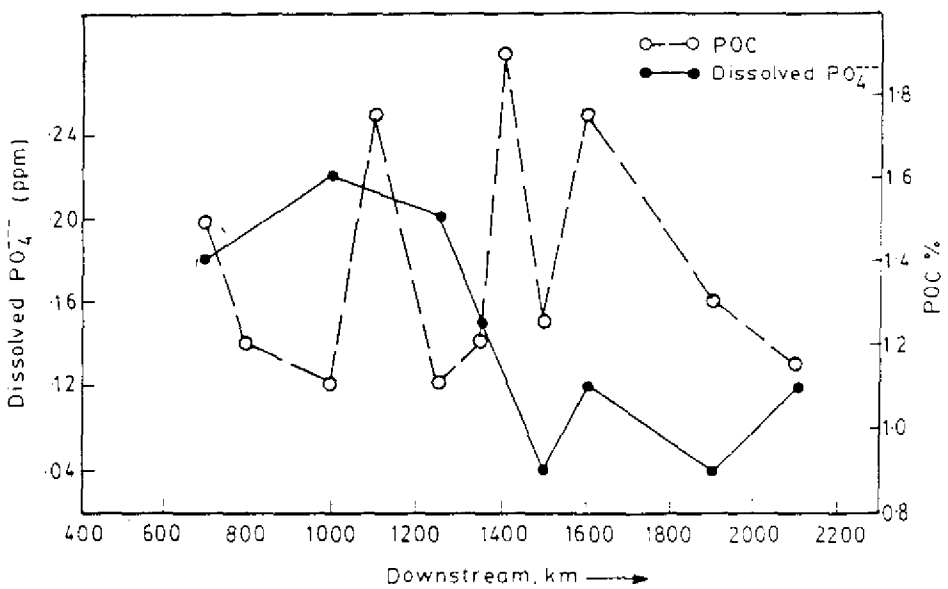

Figure 2 Relationship between dissolved phosphate and POC in Ganges river.

Relationships Between Dissolved P and Other Elements

The hydrogeochemical transformations of P are linked to those of biogenic elements such as carbon and nitrogen. For the aquatic environment, photosynthesis can be represented by the following equation:

$$106\ CO_2 + 16\ NO_3^{-1} + H_2PO_4^{2-} + 122\ H_2O + 18\ H^+ + (\text{trace elements, energy}) \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2$$

The above equation illustrates the importance of phosphate in the carbon-oxygen balance of waters. The average composition of plankton indicates that one P atom may, under suitable conditions, drive about 138 oxygen or 106 CO_2 molecules, and thus affect the redox potential and acidity of surface waters. As an illustration, the relationship between phosphate and planktonic organic carbon in the Ganges river is shown in Figure 2. Figure 3 relates the average nitrate and phosphate concentrations of major world rivers. Rivers from industrial regions have concentrations two orders of magnitude higher than those from pristine, tropical and arctic areas. Kempe (personal communication) noted that the molar ratios of N and P in polluted rivers are similar to those found in marine plankton. Thus, rivers can fertilize the estuaries and coastal seas. A strong positive relationship between calcium and phosphorus, and fluoride and phosphorus was found in the Cauvery river (one of the important peninsular rivers of India) suggesting that the transformation of these elements are linked (Figure 4).

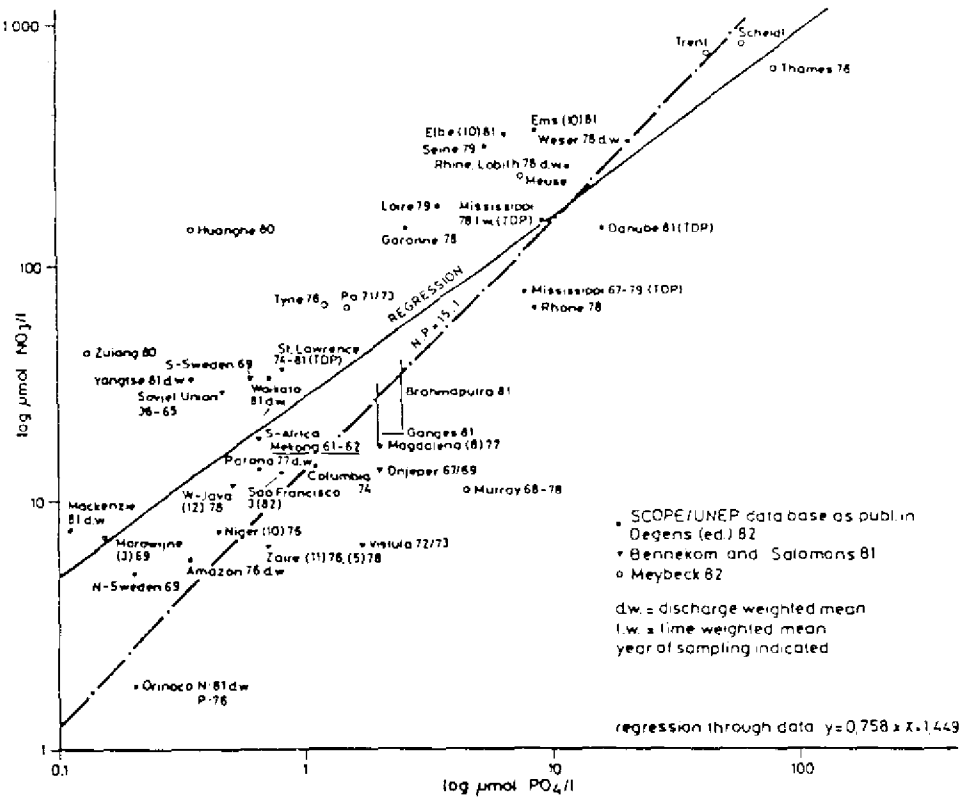

Figure 3 Plot of phosphate versus nitrate in world rivers.

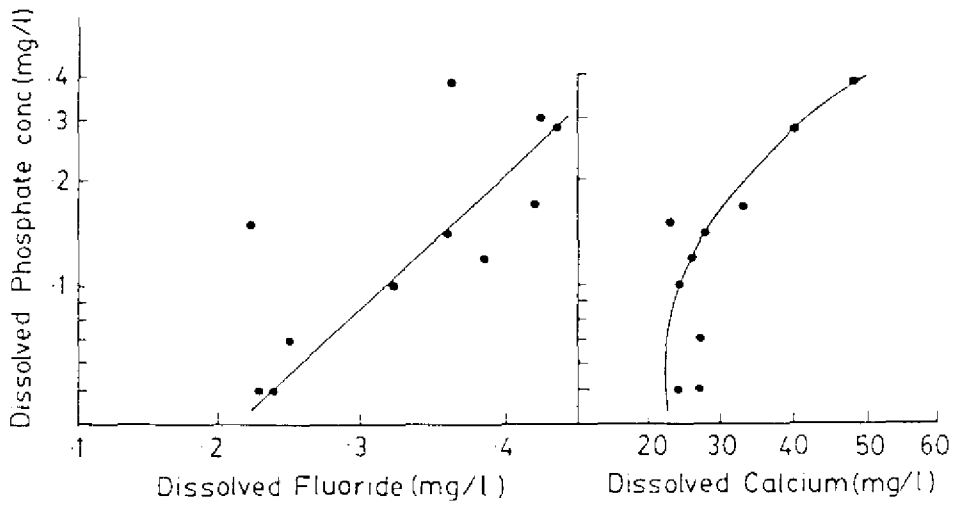

Figure 4 Phosphate, calcium and fluoride relationships in Cauvery water.

Relationships between Phosphorus and Fluoride

With the exception of rare occurrences of fluorite, dissolved fluoride levels in river waters are controlled by the dissolution of apatite, and are therefore linked to dissolved P levels. The relative concentrations of F and P in various parts of the environment are illustrated in Figure 5. Data point 1 is seawater (Turekian 1970), 2 and 3 are the averages of a number of fresh water bodies, point 4 is peridotite and points 5, 7, 8, 9 and 10 are values for various USGS rock standards (Flanagan 1977) while point 6 is the crustal average (Turekian 1972). Points 11, 12 and 13 are for various biological material such as humans, animal bones etc. There are two discontinuities indicated by dashed lines for which there have been no values reported so far. While P and F do not show a linear relationship, the plot indicates that the two elements are linked.

Influence of Clay Minerals on River Phosphate Concentration

The solid phase, both suspended particles and sediments, is of considerable importance in regulating dissolved P levels in water systems. Clay minerals adsorb dissolved P (Chen et al. 1973a; Edzwald 1975) and particulate matter was found to effectively remove P above a equilibrium concentration of 20 $\mu g \cdot l^{-1}$ from river systems (Hans-Henning et al. 1985). In the Cauvery river, dissolved P concentration increases with decreases in clay mineral percentage in suspended matter and vice versa. The concentration of P in the suspended matter also increases with clay content (Figure 6). The P sorption capacities of clays were found to be related to their free metal content (Edzwald 1975).

Particulate Phosphorus

Particulate P (organic and inorganic) represents 95% of P carried by rivers (Maybeck 1982) and average P concentrations in suspended material are around 1,150 $\mu g \cdot g^{-1}$. Part of the suspended particulate P is in the form of phosphate minerals, primarily apatite, and much of the remainder is due to human effects such as increased erosion from deforestation and agriculture,

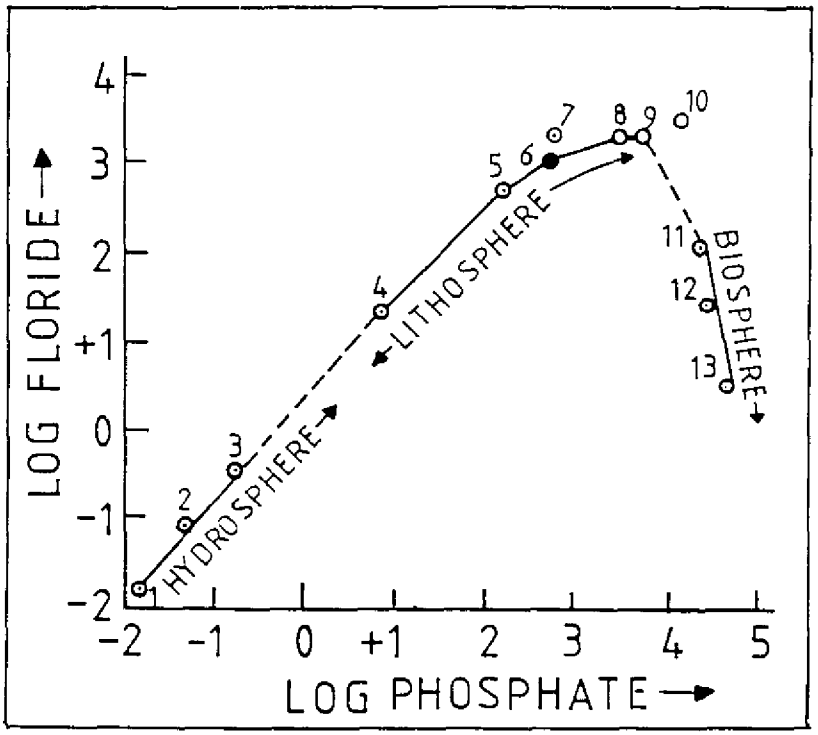

Figure 5 Relative concentrations of F and P in diverse segment of our environment.

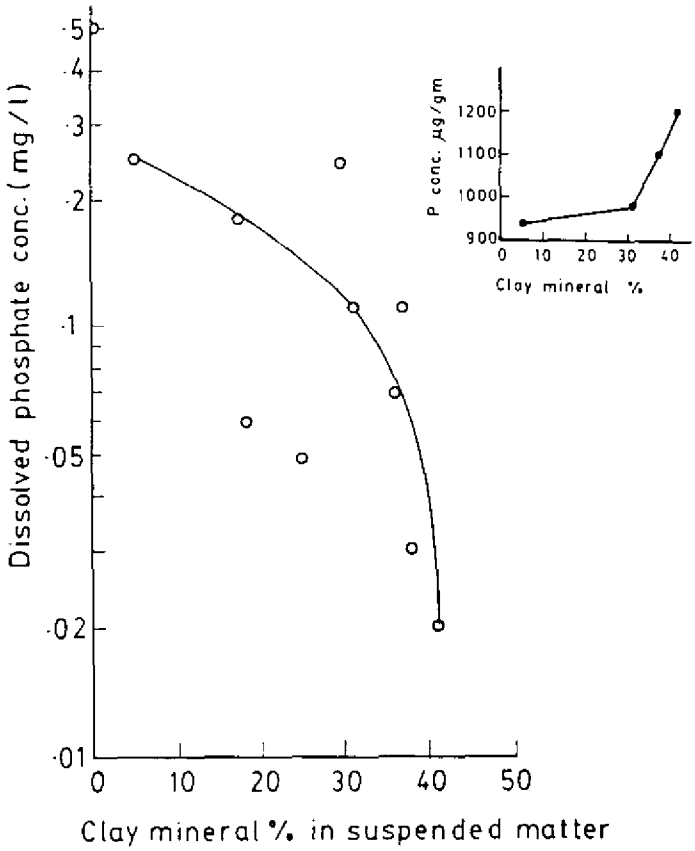

Figure 6 Relationship between clay mineral abundance and dissolved/ particulate phosphorus concentrations.

and increased organic inputs. Since P is relatively insoluble in water, much of the primary phosphate minerals remain in particulate form, and do not easily enter the biological cycle. In addition, insoluble Fe, Al and Ca phosphates and P adsorbed clay minerals remain preferentially in particulate form. Some Fe and Al phosphate as well as freshly adsorbed P are completely biologically available, but only 15% of the P in natural clay can enter the biological cycle (Golterman 1977). Overall only about 10% of the particulate P is reactive and enters biological cycling. P fractionation of river sediments may provide additional information about the potential availability and mobility of P.

Relationships between P and Other Elements in Sediments

The relationships between particulate P and Fe, Ca, Al and Si in the world's river systems (data from Martina nd Maybeck 1979) were examined by linear regression analysis (Figure 7). Al and Fe gave a good positive correlation with P, whereas Ca and Si were negatively correlated. The strong positive correlation of Fe and Al with P in suspension material suggests the presence of amorphous Fe or Al phosphates, or of cryptocrystalline forms of minerals such as strengite or vivianite.

Edzwald (1975) found a strong correlation between Fe and Al and P in lake sediments of the Ozarks. Similar correlations were reported by a number of authors (Upchurch et al. 1974, Schukla et al. 1971, Murty et al. 1972, Seralathan et al. 1979). A strong correlation of P with Fe compounds was reported for 14 Wisconsin lakes by Williams et al. (1971). A strong fixation of P to Fe is favoured by oxidation of Fe^{+2} to insoluble ferric species (Goldschmidt 1954). The basic reaction underlying P adsorption to clays can be summarized in terms of the following stoichiometric equation, proposed by Huang and Stumm (1972) for the specific adsorption of phosphate on hydrous aluminium hydroxide:

$$3Al\ (OH) + HPO_4^{2-} = ALPO_4^{3-} + \approx 8\ H^+$$

In polluted rivers with high dissolved P concentrations, suspended P is mainly in the form of iron and aluminium phosphates. (Brummer and Lichtfuss 1978). According to Garrels et al. (1973) fertilizer reaction products are aluminium and iron phosphates, which eventually may enter the suspended loads of rivers.

The correlation between carbon, nitrogen and P in riverine particulate matter (Figure 8) suggests the common involvement of these elements in biological activity. Although particulate organic P makes up nearly 40% of the total particulate P, the nature of the organic P compounds in rivers is not well understood.

Anthropogenic effects

Rivers receive P from point and non-point sources. Point pollution due to domestic and industrial discharges, and non-point pollutions due to fertilizer runoff and erosion, are important factors influencing the P transport in river basins. The importance of point sources was demonstrated for the upper Limpopo river drainage basin, where total P exports per unit runoff from geologically similar catchments were about 5 times higher in catchments dominated by point sources, than in those dominated by non-point emissions (Grobler 1985). Probst (1985) estimated the annual contributions of different P sources to the Girou river load as 7% from natural biogeochemical

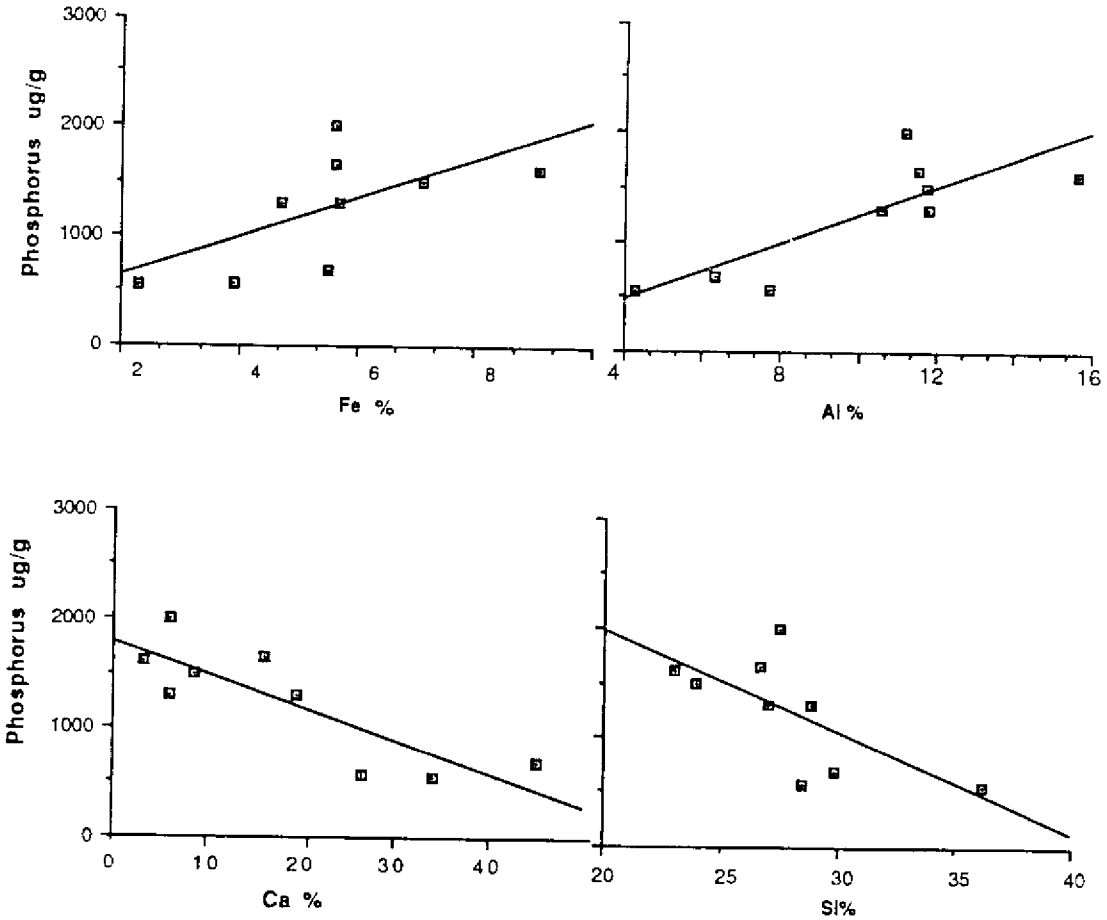

Figure 7 Correlation between phosphorus and other elements (Fe, Al, Ca, Si) in world river sediments.

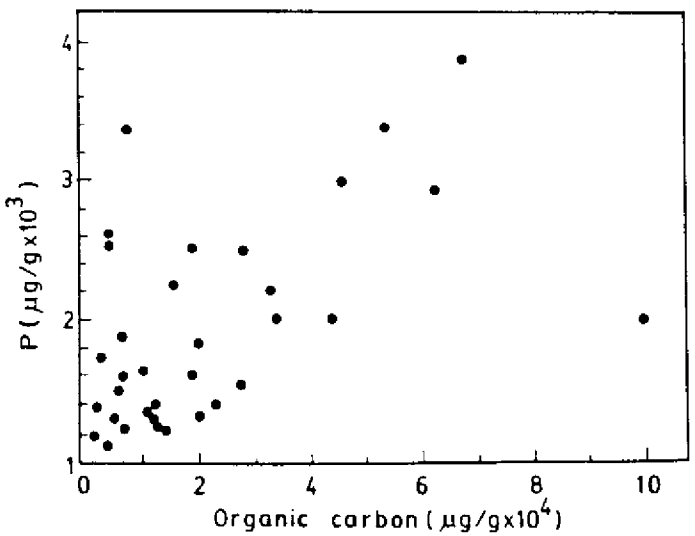

Figure 8 Scatter plot of phosphorus and organic carbon in the Yamuna river sediments.

processes, 32% from non-point pollutions and 60% from point sources. He also indicated that export rates of non-point pollution from land surfaces is less than 1% of P fertilizers applied, and that the remainder accumulates in the soil. Movement of point pollutants occurs during two phases: during low-flow periods dissolved P from point pollution is adsorbed and stored in river bed sediments; while the export of P occurs mostly during heavy runoff periods after resuspension of accumulated sediments.

Estuaries

Phosphorus loads from rivers are delivered to the oceans via estuaries, where extensive adsorption and desorption on suspended materials as well as biological mineralisation and immobilisation by estuarine organisms occur. Correll et al. (1975) suggested that suspended sediments may be a major source of dissolved P for the estuarine P cycle. Chase et al. (1980) observed substantial release of soluble P from natural suspended materials from the Amazon river over periods of many days, when such materials were kept in sea water. In the Zaire estuary with a salinity of 7 per mil, desorption of P from suspended material supported P concentrations twice as high as in the river itself (van Bennekom et al. 1978). Several studies of P behaviour in estuaries suggest that rapid desorption reactions from suspended matter buffers the reactive P concentrations at around 30 $\mu g \cdot l^{-1}$ over much of the salinity range. Dissolved reactive P data from the Ochlockonee river showing typical mid-estuary desorption input or buffering as well as Biological uptake is illustrated in Figure 9.

Phosphorus Inputs to Oceans

Over 90% of the total fluvial P inputs to the oceans are in particulate form (Tables 1 & 2). Froelich et al. (1982) estimate that the pre-agricultural river P flux due to weathering was about 10^{12} $g \cdot y^{-1}$. Human influence on the terrestrial P cycle has increased this value to about 24×10^{12} $g \cdot y^{-1}$. About half of the dissolved P is anthropogenic.

Table 2. Fluvial fluxes of phosphorus to oceans

	Total flux	Anthropogenic part
	$\times 10^{12}$ g $P \cdot y^{-1}$	
Dissolved PO_4-P	0.8	0.4
Dissolved organic P	1.2	0.6
Total dissolved P	2.0	1.0
Particulate organic P	8.0	?
Particulate inorganic P	12.0	?
Total particulate P	20	?
Total output	22	≥1.0
Reactive P flux	4	≥1.0

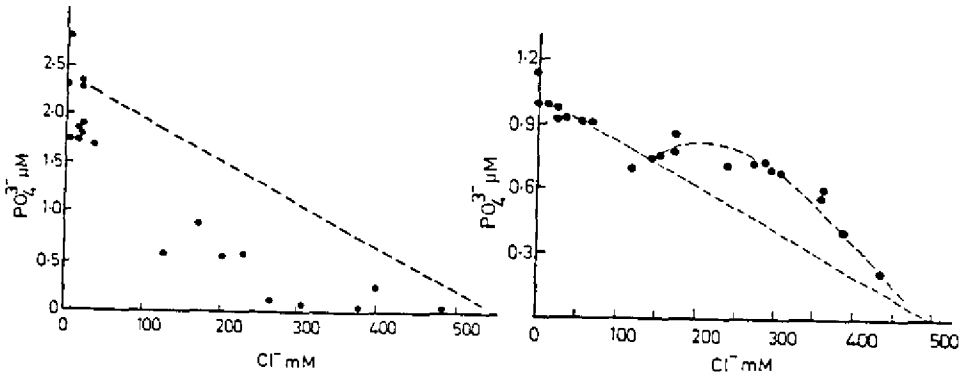

Figure 9 Dissolved reactive phosphorus and chlorinity plot in Ochlockonee river showing typical mid-estuary desorption input and typical biological removal.

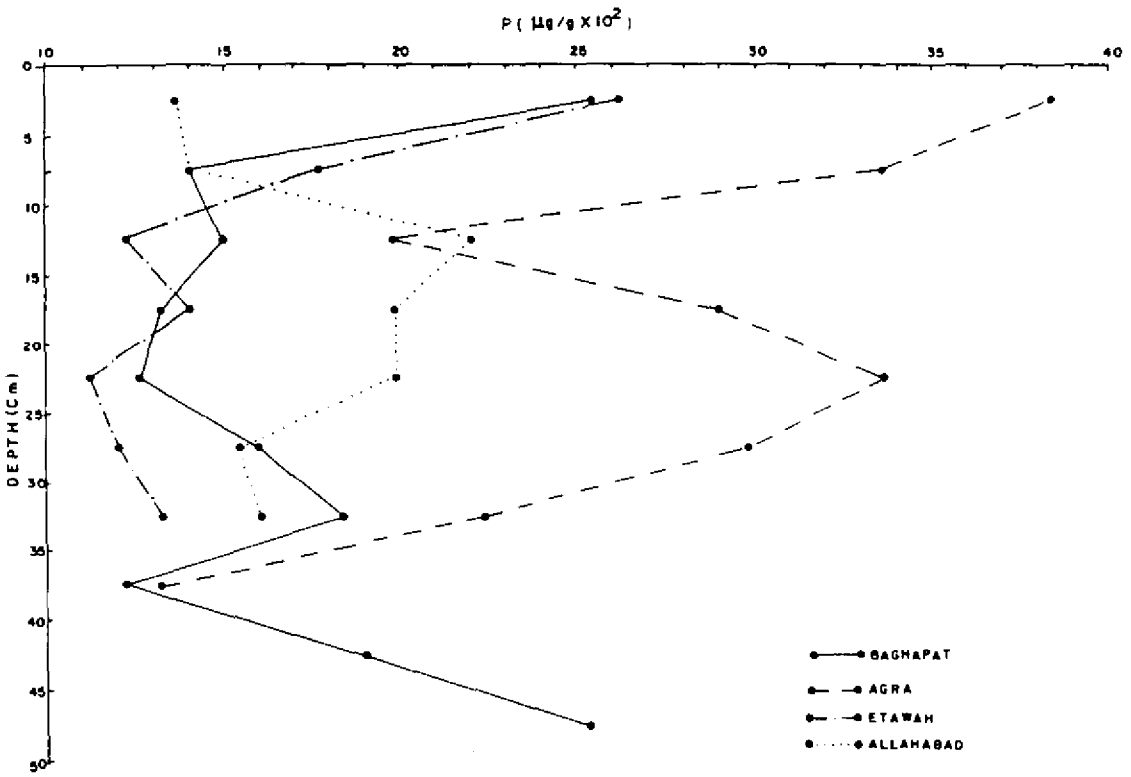

Figure 10 Depth variation of phosphorus in the Yamuna river core sediments.

The processes which are potentially important as P sinks in the ocean (Froelich et al. 1977), and the associated P fluxes (Froehlich et al. 1982) are:

1. Burial of P tied up in organic matter and fish debris ($4x10^{-9}$ moles $cm^{-2}\cdot y^{-1}$).
2. Sedimentation of biogenic calcium carbonate containing several hundred ppm of P ($4x10^{-9}$ moles $cm^{-2}\cdot y^{-1}$)
3. Burial of P in phosphorites ($<1x10^{-9}$ moles $cm^{-2}\cdot y^{-1}$)
4. Inorganic sorption and precipitation in hydrothermal processes ($1.1x10^{-9}$ moles $cm^{-2}\cdot y^{-1}$).

Organic P and calcium carbonate P make up about 40% each of the total identified removal, while phosphorite and hydrothermal burial comprise about 10% each. The sum of the burial fluxes equals about $10x10^{-9}$ $mol\cdot cm^{-2}\cdot y^{-1}$, at a reactive P concentration of about 1 µmol. The residence time of P in the oceans calculated from these figures is approximately 80,000 years. The burial rates estimated by Froelich et al. (1982) may not be constant due to fluctuations in the sediment deposition rates and variations in the amounts of sediment P which become reactive. Deposition rates in a given basin or marine environment vary with time, and also from river to river. Such variations are illustrated in the P concentrations of sediment columns as shown in the example from the Yamuna river (Figure 10). Table 3 summarizes the P and sediment deposition rates for both fresh water and marine environments of the Indian subcontinent.

Table 3. P and Sediment deposition rates in Indian rivers

River	Sediment deposition rate $cm.y^{-1}$	Sediment flux $gm\cdot cm^{-2}\cdot y^{-1}$	Conc of P $\mu g\cdot g^{-1}$	Deposition rates of P mg $P\cdot cm^{-2}\cdot y^{-1}$
Brahmaputra	0.184	0.1472	765	0.11
Krishna	1.1	0.968	825	0.8
Cauvery	0.09	0.072	950	0.07
Bay of Bengal	2.0	1.6	1100	1.8

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PHOSPHORUS LOAD FROM POLAND INTO THE BALTIC SEA

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Introduction

The 368,000 km^2 Baltic Sea is a mere 0.1% of the world's oceans but nevertheless unique in many ways. The Baltic Sea is semi-enclosed, constitutes the largest area of brackish water in the world, and it is close to the centres of air pollution in central Europe. Seven states have coastlines on the Baltic Sea. Each one of them is a highly developed industrial country and for each the sea is vital.

The Baltic Sea must cope with both municipal and industrial waste waters.An estimated 15% of the world's total industrial production originates in this area. Sixteen million people live on the coastline and produce a vast volume of communal waste waters. Agricultural effluent contains large amounts of the same substances as communal waste waters, i.e. organic matter, nitrogen and phosphorus. Together they cause substantial eutrophication. It has become evident that something must be done to reduce the pollution load.

The effects of eutrophication on coastal ecosystems have been well documented in many studies from all Baltic countries (Savchuk and Gutsabbath 1984, Sjaberg and Wilmot 1977, Larson et al. 1983). But the load discharged from the land into the Baltic by those countries is less known and poorly documented.

The aim of this paper is to present:

- Poland's share in the total phosphorus (TP) balance discharged into the Baltic Sea waters.
- Synthesis of Polish studies of P load discharged into the Baltic through rivers and from waste waters.
- State of Polish studies of the atmospheric share in the P balance of the Southern Baltic.

The Input Load of Phosphorus into Baltic Sea

The Baltic Sea is divided into nine sub areas. One or more riparian nations are responsible for the information given from each sub area. Thus, there are twenty different areas to be considered (Table 1).

Table 1. List of sub-areas and total phosphorus loads (Baltic Marine 1987)

Sub-area	Abbr. in Figure 1	Contracting party	P $t \cdot a^{-1}$
Baltic Proper, Bornholm	BAP-DAN	Denmark	300
Kattegat	KAT-DAN	Denmark	1,900
The Sound	SOU-DAN	Denmark	1,510
Belt Sea and Western Bays	WEB-DAN	Denmark	5,800
Archipelago Sea	ARC-FIN	Finland	614
Bothnian Bay	BOB-FIN	Finland	1,909
Bothnian Sea	BOS-FIN	Finland	1,048
Gulf of Finland	GUF-FIN	Finland	862
Baltic Proper	BAP-GDR	GDR	125
Western Baltic Bays	WEB-GDR	GDR	250
Western Baltic Bays	WEB-GER	GER	2,371
Baltic Proper	BAP-POL	Poland	19,100
Baltic Proper	BAP-SWE	Sweden	1,130
Bothnian Bay	BOB-SWE	Sweden	1,645
Bothnian Sea	BOX-SWE	Sweden	1,851
Kattegat	KAT-SWE	Sweden	1,195
The Sound	SOU-SWE	Sweden	1,030
Baltic Proper	BAP-SUN	USSR	829
Gulf of Finland	GUF-SUN	USSR	3,990
Gulf of Riga	GUR-SUN	USSR	1,060
		Total sum of P $t \cdot a^{-1}$	48,519

The P load is divided into three different load sources: municipal, industrial and river load. The division of the P load into just three sources is not binding, since the Contracting Parties are using different data collecting methods; and the particular sources are therefore not quite comparable. The values used in this compilation are delivered via official channels to the HELCOM Secretariat, no other sources have been used (Baltic Marine 1987). According to HELCOM data (Figure 1) the sum of TP load compilation is as follows:

- from municipalities 11,801 t a^{-1} TP
- through rivers 28,321 t a^{-1} TP
- from industry 8,397 t a^{-1} TP

total sum 48,519 t a^{-1} TP

The Input Load of Phosphorus from Poland

The TP load discharged from land within the borders of Poland is estimated to be 19,100 $t \cdot y^{-1}$. Of this 60.2% is discharged through rivers (11,500 $t \cdot y^{-1}$), 15.7% originates from municipal wastes (3,000 $t \cdot y^{-1}$), while 24.1% comes from industrial sources (4,600 $t \cdot y^{-1}$). Bearing in mind the population of the catchment area within the borders of Poland, the unit annual load is about 0.51 kg P per inhabitant per year (Trzosinska et al. 1988).

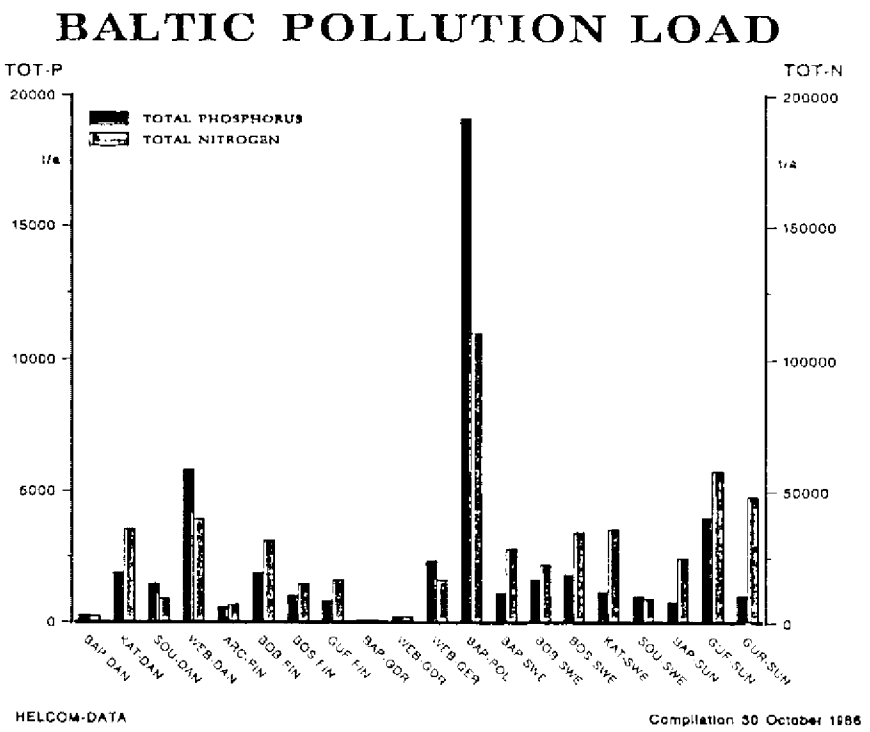

Figure 1. Regional distribution of total phosphorus and total nitrogen loads ($t \cdot y^{-1}$) discharged into Baltic Sea in 1986 (Baltic Marine...1987).

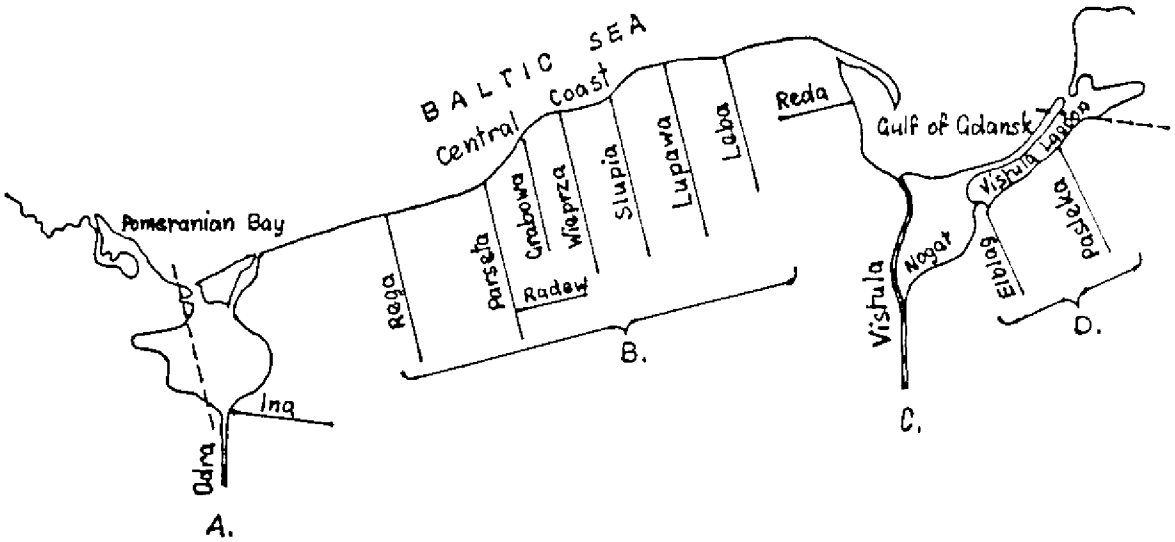

Figure 2. Polish coastal zone of the Baltic Sea. A - Odra: catchment area 118,600 km^2. B - Central Coast's rivers: catchment area 17,300 km^2. C - Vistula: catchment area 194,400 km^2. D - Vistula Lagoon: catchment area 6,500 km^2.

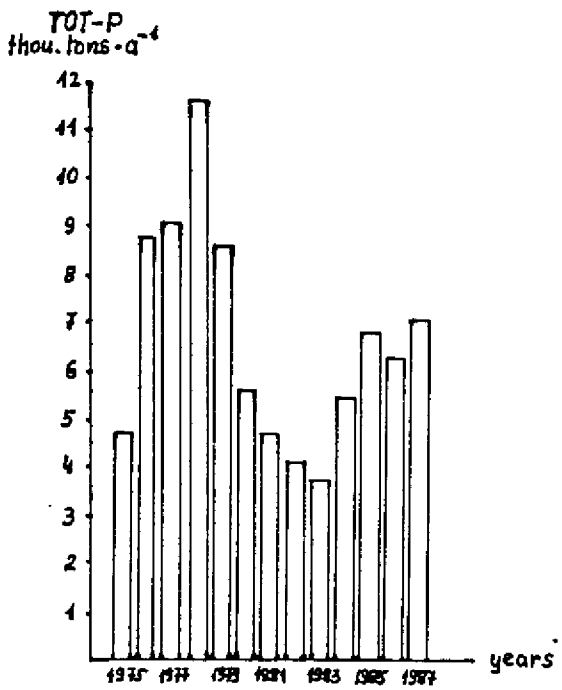

Figure 3. Annual phosphorus load (10^3 tons TP) carried into Baltic Sea through the Vistula in 1975 - 1987 (Rybinski and Niemirycz 1986).

In the years 1980-84 the annual TP loads carried by rivers into the Gulf of Gdansk amounted to 4,820 t, and those from direct municipal and industrial wastes to 3,430 t (Rybinski 1986a). Annual TP loads carried by rivers into the Pomeranian Bay amounted to 5,600 t, while those from direct municipal and industrial wastes to 3,550 t (Mutko et al. 1986). The Central Coast rivers carried an annual load of 500 t of TP, while direct municipal and industrial wastes delivered 390 t (Trzosinska et al. 1988). The rivers flowing from the Polish territory into the Vistula Lagoon carry 600 t of TP, while direct municipal and industrial sources bring 230 t (Rybinski 1986b). The input load of P into the Vistula Lagoon from the Nogat (0.41 $km^3 \cdot y^{-1}$ flow) amounts to 10% of TP carried into the Gulf of Gdansk through the Vistula.

In the estuarian catchment areas there is a considerable variation of P inputs (Table 3), particularly in the catchment areas of Central Coast and Vistula Lagoon rivers. With fairly short rivers, the towns and industries located in their estuaries increase the unit input loads of phosphorus.

Deposition of Airborne Phosphorus on the Coastal Zone of the Southern Baltic

Phosphorus compounds occurred in aerosols from the coastal zone of southern Baltic in a wide range of concentration (Table 4). In the warm half of year, from May to October (months when home heating is off) total P concentration ranged from 20 to 305 $ng \cdot m^{-3}$, phosphate accounted on average for 80% of TP. In winter, mean concentration of TP was 60% higher than in the summer months, and the proportion of phosphates was 68%. In aerosols from the coastal zone of the southern Baltic organic P compounds accounted for 20% of TP in the warm part of the year and increased to 32% in winter.

Table 2 presents P and PO_4-P loads brought into the Baltic by 14 Polish rivers shown in Figure 2. The highest quantities are carried by the Vistula and the Odra whose catchment areas take up 194,400 km^2 and 118,600 km^2, respectively. Some of these (38,500 km^2 = 12%) are outside the Polish territory. The total catchment area of Central Coast rivers amounts to 17,300 km^2, while rivers of the Vistula Lagoon have a catchment area of 6,500 km^2. The rivers of the Central Coast and Vistula Lagoon carry 10% of the Polish river P load into the Baltic. Inorganic P forms accounted from 38 to 48% - in various periods - of total P of all river inputs (Trzosinska et al. 1988).

Of the Polish rivers only the Vistula has been regularly and with appropriate frequency monitored for over 12 years. In the years 1975-84 the mean annual P load carried into the Baltic through the Vistula amounted to 6,700 t P (Rybinski and Niemirycz 1986). Fluctuation in TP loads of the Vistula between 1975-87 were considerable (Figure 3).

On the average, 44% of P comes from the territorial flow. Losses in mineral fertilizers are estimated roughly at 1.5% of applied P, with fertilization of 10 - 12 $kg \cdot P \cdot ha^{-1}$ (Trzosinska et al. 1988). Januszkiewicz et al. (1977) report that the annual TP load discharged from the Vistula catchment area reached 0.028 $t \cdot km^{-2} \cdot y^{-1}$. Rybinski (1986a) estimates TP discharges for the whole Polish catchment area of the Baltic at 0.058 $t \cdot km^{-2} \cdot y^{-1}$ and 0.10 $t \cdot km^{-2} \cdot y^{-1}$ for arable land alone.

Table 2. Phosphorus loads ($t \cdot y^{-1}$) discharged into the Baltic Sea by Polish rivers in 1983 (Pastuszak 1985, Rybinski et al. 1984, Niemirycz 1984, Trzosinska et al. 1988)

River	Total	PO_4-P
Odra	5540	2680
Ina	160	70
Rega	170	80
Parseta	120	60
Grabowa	30	10
Wieprza	200	60
Słupia	240	90
Lupawa	120	30
Leba	130	50
Reda	10	10
Vistula	3740	2800
Nogat	80	10
Elblag	320	50
Pasleka	140	60
Total	1100	6200

Table 3. Mean annual input of TP (Trzosinska et al. 1988)

Estuary	Inflow $l \cdot s^{-1} \cdot km^{-2}$	$t \cdot km^{-2}$
Pomeranian Bay	3.92	0.065
Central Coast	8.70	0.108
Gulf of Gdansk	5.92	0.039
Vistula Lagoon	5.56	0.115

Table 4. P compounds ($ng \cdot m^{-3}$) in aerosols in the coastal zone of the southern Baltic in 1981-85 (Falkowska and Korzeniewski 1988)

Component		n	x	SD	M_x	D_x	range
PO_4-P	w	20	120	90	70	40	10-300
	c	5	170	80	162		70-280
total P	w	20	150	120	90	50	20-390
	c	5	250	110	297		90-360

w - warm half-year
c - cold half-year
n - number of data
x - average
SD - standard deviation
M_x - median
D_x - modal value

Concentration of P compounds in rainfall collected close to the land is very variable (Table 5). Solid particles washed by rain from the atmosphere introduced 6 - 55 $\mu g \cdot P \cdot l^{-1}$, including 24 - 72% phosphates, into the coastal zone (Table 5). Atmospheric input of phosphorus compounds (Table 6) to the coastal zone can be characterised as follows:

- in the total annual input, dry deposition predominates over wet,
- organic P compounds account on average for 40% of totals
- on average, 4 kg of P are deposited annually on each square kilometer of the coastal zone of the southern Baltic.

Conclusions

In 1986 the P load from Polish territory was estimated at 19,100 t P, 60.2% is discharged through rivers, 15.7% originates from the municipal wastes, while 24.1% comes from the industrial wastes. The highest annual loads of P are carried by the Vistula into the Gulf of Gdansk and by the Odra into the Pomeranian Bay. Four kg of P are deposited annually on each square kilometer of the coastal zone of southern Baltic from the atmosphere.

Table 5. Concentration of P ($\mu g \cdot l^{-1}$) dissolved or as washed-out solid particles in rainfall of the coastal zone of the southern Baltic in 1981-1985 (Falkowska and Korzeniewski 1988)

Component	n	x	SD	± t SD√n	range
Dissolved P					
PO_4-P	5	40.2	44.9	± 55.8	0.6-112.3
TP	5	100.4	68.6	± 85.1	35.2-184.1
P in solid particles					
PO_4-P	5	12.4			4.7-20.5
total P	5	30.0			5.6-55.2

x ± t SDVn - confidence interval of mean at confidence level 0.95
t - critical value in t-test
Other denotations as in Table 4.

Table 6. Estimated annual flux of phosphorus compounds from atmosphere to the coastal zone of southern Baltic ($kg \cdot km^{-2}$) (Falkowska and Korzeniewski 1988)

Component	Deposition		Mean	Variability range
PO_4-P	Wet		0.023	0.000-0.065
		a	2.5	0.07-5.0
	Dry			
		p	0.007	0.002-0.012
	Total		2.530	0.072-5.077
total	Wet		0.058	0.020-0.107
		a	4.2	1.1-7.6
	Dry			
		p	0.018	0.003-0.032
	Total		4.276	1.123-7.739
Org-P	Wet		0.035	0.020-0.042
		a	1.7	1.03-2.6
	Dry			
		p	0.011	0.001-0.020
	Total		1.746	1.051-2.662

a - aerosol
p - solid particles washed from atmosphere by rain

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PHOSPHORUS CYCLES IN ESTUARIES AND COASTAL SEAS OF EUROPE

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Introduction

As the transition region between the fresh riverine and the open marine environment, estuaries and coastal seas play a marked role in the global phosphorus cycle. Recent studies for the European situation have demonstrated a general increase in the P contents of these waters, especially caused by anthropogenic discharges (Voipio, 1981; Postma, 1985). At present, doubling times of a few decades may be found for semi-enclosed areas like the Dutch and German Wadden Sea, the Baltic Sea and for localized areas of the Mediterranean. On a global basis, effects will only be limited to a narrow coastal region, due to the large buffering capacity of the world's seas and oceans.

This contribution aims at the present and future trends of phosphorus in estuaries and coastal seas of Europe. A continuous cycling between the various phosphorus forms takes place, both through biological and physico-chemical transformations. In this respect the role of the sediment acting either as a P source or sink deserves our special attention.

Phosphorus cycles in estuaries and coastal seas

Estuaries

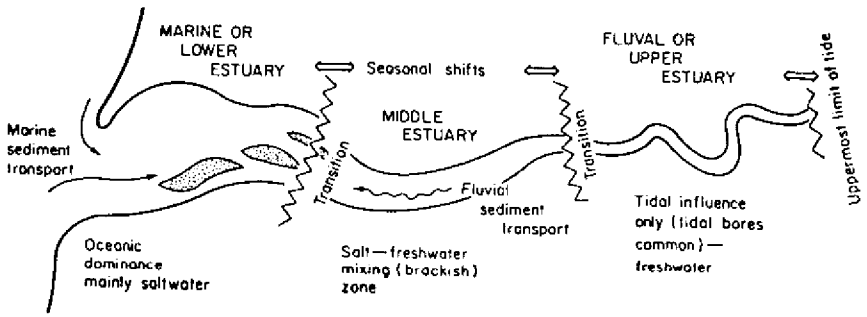

Figure 1. Idealized map of a typical estuary showing three divisions: lower, middle and upper; the boundaries are transition zones that shift according to season, weather and tides. From: Fairbridge (1980). Reprinted by permission of John Wiley and Sons, Ltd.

An estuary, according to the definition of Fairbridge (1980) is "an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, usually being divisible into three sectors: (a) a marine or lower estuary, in free connection with the open sea; (b) a middle estuary, subject to strong salt and fresh water mixing; and (c) an upper or fluvial estuary, characterized by fresh water but subject to daily tidal actions"; see Fig. 1.

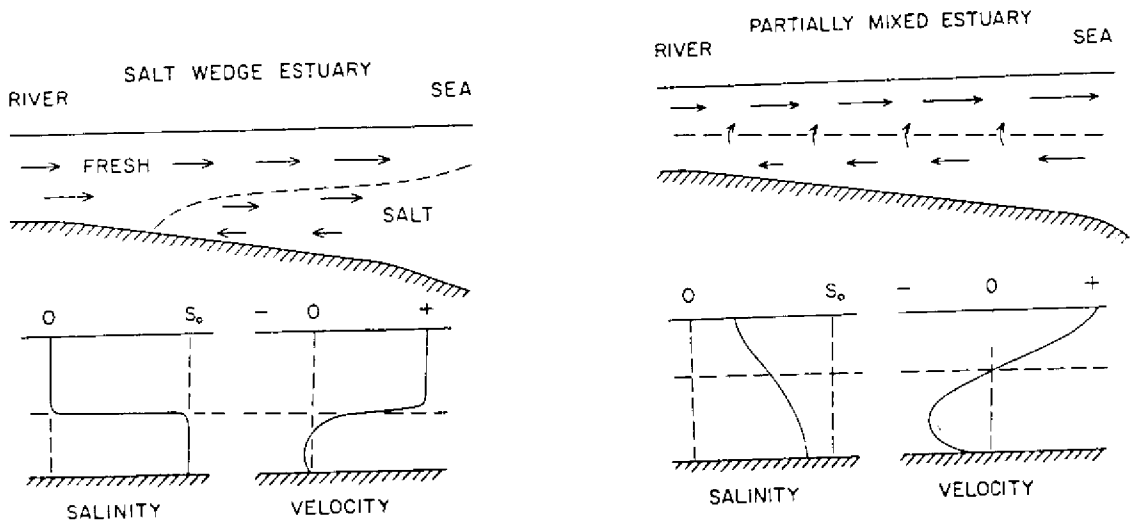

Figure 2. Salt wedge estuary and partially mixed estuary. Above: section along the estuary. Below: typical salinity and velocity profiles. From: Bowden, 1980. Reprinted by permission of John Wiley and Sons, Ltd.

Various types of estuaries can be differentiated according to their types of water circulation (Bowden, 1980); see Fig. 2. In a salt wedge estuary, the saline marine water extends as an underlying "wedge" into the river; this type of estuary is characterized by extreme vertical salinity and velocity gradients. The partially mixed estuary shows substantial vertical mixing due to the tidal currents, and consequently vertical velocity and salinity gradients are much more gradual than in the former case (Fig. 2). When the influence of tidal mixing relative to that of river flow is very strong, the estuary becomes well-mixed, with little vertical variations in salinity and in current flows.

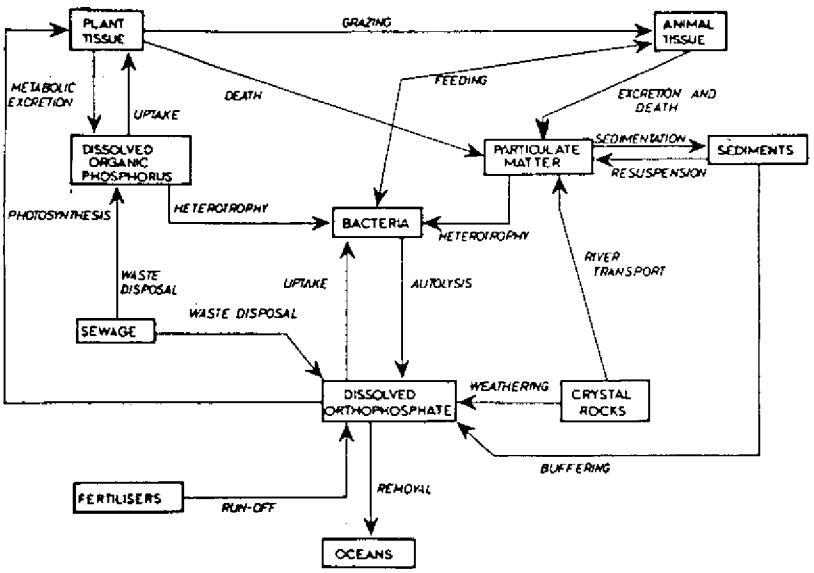

Figure 3. The phosphorus cyle in the estuarine environment. From: Aston (1980). Reprinted by permission of John Wiley and Sons, Ltd.

Fig. 3 shows the schematic phosphorus cycle in estuaries (Aston, 1980). Particulate and dissolved P, in inorganic and organic form, is brought into the estuary through geochemical weathering, run-off and wastewater discharges. Biological as well as physico-chemical conversion reactions take place in the estuary; most important representatives of the latter reactions are: estuarine mixing with nutrient-poor seawater, sedimentation of particulate matter, and P adsorption/desorption.

Graphs of *e.g.* P, Si, Fe concentrations versus corresponding concentrations of "conservative" elements (Cl^-, SO_4^{2-}) have often been used as a measure for checking the net source/sink behaviour of the former elements (Ketchum, 1967; Duinker, 1980; Fraser and Wilcox, 1981; Morris *et al*, 1981). Estuaries serve as efficient traps for particulate phosphorus, dominantly in the form of organically bound P and as absorbed Fe-Mn-OH-P complexes. Postma (1980) described the various mechanisms for sediment deposition in the estuarine environment. Sedimentation is the result of physical (*i.e.* reduced flow and wave actions; marine countercurrents) and physico-chemical (*e.g.* flocculation) processes upon the fine grained particles. In partially mixed estuaries the landward bottom flow is sufficiently strong to move suspended - both marine and fluviatile - sediment up the estuary to the head of the salt intrusion. Here a turbidity maximum is built up, acting as an efficient sediment trap, with up to 90% retainment values (Postma, 1980). Examples of this may be found in many European estuaries, like the French Gironde and Loire estuaries, and the Dutch Ems-Dollart estuary (Postma, 1967; 1980). Other factors like the relatively strong sediment entraining action of the flood tide relative to the ebb tide also favour a net accumulation of suspended material in this type of estuaries (Terwindt, 1967; Kelderman *et al*, 1984). In contrast, most suspended matter in a salt wedge type of estuary (*e.g.* the Mississippi, U.S.A.) can be carried into the sea together with the upper river water.

Co-precipitation of bound P onto particulate matter, as described earlier is a major sink mechanism for phosphorus in the estuarine environment, with P retainment values typically lying between 50 and 90% (Postma, 1967; Hobbie *et al*, 1975; Callender, 1982). The fate of the inorganic absorbed phosphorus is not yet fully understood. Adsorption/ desorption of the reversible Fe-P complexes are governed by environmental factors like: a) pH, whereby low pH values favour adsorption and b) salinity values, with Cl^- and SO_4^{2-} acting as competitors for PO_4^{3-} (and HPO_4^{2-}, $H_2PO_4^-$) adsorption. These factors seem to favour P adsorption towards the head rather than the mouth of the estuary (Aston, 1980; Duinker, 1980). With respect to this reversible Fe-P adsorption, investigations of Pomeroy *et al* (1965) and Bale and Morris (1981) suggested a buffering of dissolved phosphorus in estuaries between values of roughly 1.8 and 5.0 μmol $PO_4^{3-}.L^{-1}$. These findings, however, do not seem to be supported by the results of routine phosphorus monitoring programmes in the European estuaries.

Phosphorus settled onto the sediment may again be recycled into the overlying water. Benthic P regeneration takes place via two basic mechanisms: a: dissolution of inorganic Fe-Mn-OH-P complexes; here anoxic sediment conditions strongly promote P release through $Fe^{3+} \rightarrow Fe^{2+}$ conversion and subsequent P dissolution into the sediment interstitial water (Mortimer, 1941, 1942; Tessenov, 1972; Berner, 1980); b: microbial mineralization of phosphorus from organic rich material (Nixon *et al*, 1980; Klump and Martens, 1981). The strong temperature dependence for both processes can thus account for the

seasonal variations in benthic P regeneration rates (Berner, 1980; Klump and Martens, 1981; Kelderman, 1984).

Callender (1982), in a study of benthic P regeneration in the Potomac River estuary (U.S.A.) found an overall 50% P regeneration fraction (cf. Fig. 4), *viz.* varying between 10% for the upper, oxidized river region and 80-90% for the frequently anoxic lower estuarine zone. The author calculated that, of the phosphorus amount released, roughly half came from degradation of organic matter, half from dissolution of inorganic sources in the sediment.

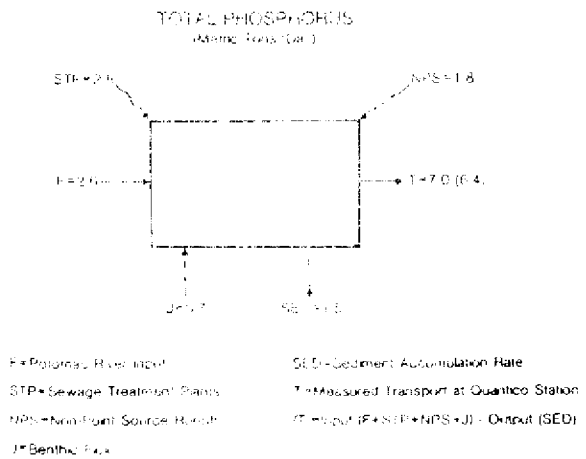

Figure 4. Input-output model of total phosphorus in the tidal Potomac River for the summer of 1979 (Callender, 1982)

Biological P cycling in estuaries, as depicted in Fig. 2 includes uptake of dissolved inorganic phosphorus by phytoplankton under favourable light conditions. Grazing by zooplankton and benthic filter feeders, and subsequent die-off eventually leads to release of PO_4-P back into the estuarine water. Biological P cycling in algae may be extremely rapid, with turn-over times of ca. 10 minutes (Correll *et al.*, 1975). Fresh sedimentation of planktonic material gives rise to enhanced P release rates from the sediment (Nixon *et al*, 1980); under extreme conditions anoxia of the sediment will mediate physico-chemical P dissolution, as described earlier.

Primary production values in European estuaries are in the order of 50-200 g $C.m^{-2}.year^{-1}$ for the pelagic phytoplankton and 30-150 g $C.m^{-2}.year^{-1}$ for benthic microalgae (Wolff, 1980). These values are equivalent to P uptake figures of 1-4 g $P.m^{-2}.year^{-1}$. In localized areas (e.g. the Grevelingen estuary, the Netherlands) seagrass as Zostera marina and Spartina alterniflora may substantially contribute to the overall primary production values. Additionally, these plant species may serve as an efficient "P-pump", excreting sediment phosphorus from the roots via the leaves into the overlying water (McRoy *et al.*, 1972).

In general, biological activity does not play a major role in the overall P budgets of estuaries. Due to the large supply of phosphorus into the estuary (including sediment P release) limiting conditions for primary production will virtually never be reached for this element; instead nitrogen, silicon or light have been shown to act as limiting factors for primary production in estuaries (Jaworski, 1981; Owens, 1984).

Coastal seas. After passing through the estuary the brackish water is directed towards the marine environment. Here, a very gradual mixing between the estuarine and marine waters take place. Distinct regions of low(er) salinity may thus be differentiated: the coastal zones, or semi-enclosed brackish seas like the Baltic Sea. Due to density differences, mixing between the exported brackish estuarine water and the surrounding seawater only proceeds rather slowly. In many cases a distinct coastal environment of characteristic qualities may be defined. According to Nixon (1981) the main features of coastal waters compared to the ocean proper are: a) high benthic mineralization figures (25-50% of the total production figures), b) frequently occurring P maxima in summer due to P sediment release and c) low N:P ratios. The latter implicates that often factors other than P will limit primary production in coastal waters (Parsons *et al.*, 1977; Jaworski, 1981; Wafar *et al.*, 1983). Denitrification is probably responsible for the major loss of nitrogen in the coastal environment (Nixon, 1981).

Case studies of phosphorus cycles in european estuaries and coastal seas

Estuaries

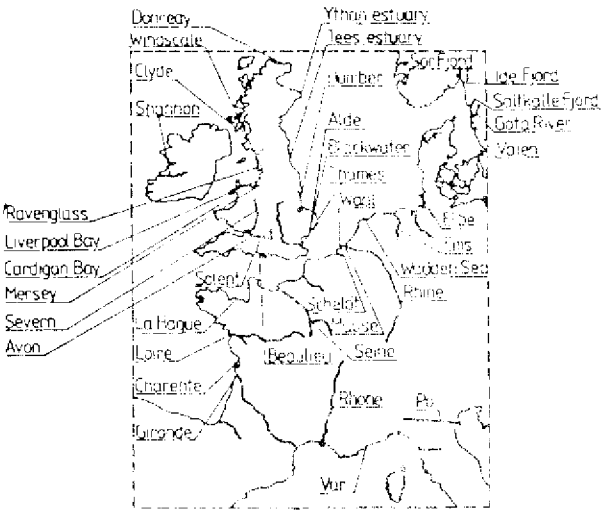

Figure 5. Estuaries in Europe (detail). From: Olausson and Cato (1980). Reprinted by permission of John Wiley and Sons, Ltd.

Fig. 5 shows a map of the region under consideration. Up till now, case studies of phosphorus budgets in European estuaries are rather scarce and incomplete. Owens (1984) calculated a PO_4^{3-}-P load into the Severn estuary (U.K.) of roughly 500 x 10^3 kg P per year, attributable for ca. 35% to rivers and streams, 15% to domestic sewage and 45% to industrial waste water discharges. Ortho-phosphate versus salinity profiles showed a conservative behaviour; concentrations of phosphate decreased from 50 μmol $PO_4^{3-}.L^{-1}$ in the head, to 6 μmol.L.$^{-1}$ in the mouth of the estuary (background correction for the receiving North Sea water *ca.* 1.5 μmol.L^{-1} (Topping,1976)). No data were given on the particulate phosphorus contents. Budget calculations were further complicated by the erratic in-estuarine P loadings through wastewater discharges. Similar difficulties have been encountered in P budget calculations for *e.g.* the Thames estuary, U.K. (annual discharge *ca.* 13,000 x 10^3 kg P) and the Tyne estuary, U.K. (1200 x 10^3 kg P per year) (Jaworski, 1981), as well as

for the river Elbe estuary, F.R.G. (*ca.* 25,000 x 10^3 kg P per year; *Anonymus*, 1982a) and river Rhine estuary, the Netherlands (*ca.* 45,000 x 10^3 kg P per year; cf. *Anonymus*, 1985). Detailed monitoring of the downstream stretches of the latter two estuaries have shown rather constant P levels of 15-50 μmol $PO_4^{3-}.L^{-1}$ overall, even at the high salinity river mouths.

In a study of the less disturbed Ems-Dollart estuary, Postma (1967) observed a marked sink of mainly inorganic particulate P near the turbidity maximum of the estuary, see Fig. 6. Here maximum total PO_4^{3-} contents of 30-50 μmol.L^{-1} were reached. Levels at the mouth of the estuary had gone down to 3-6 μmol.L^{-1}.

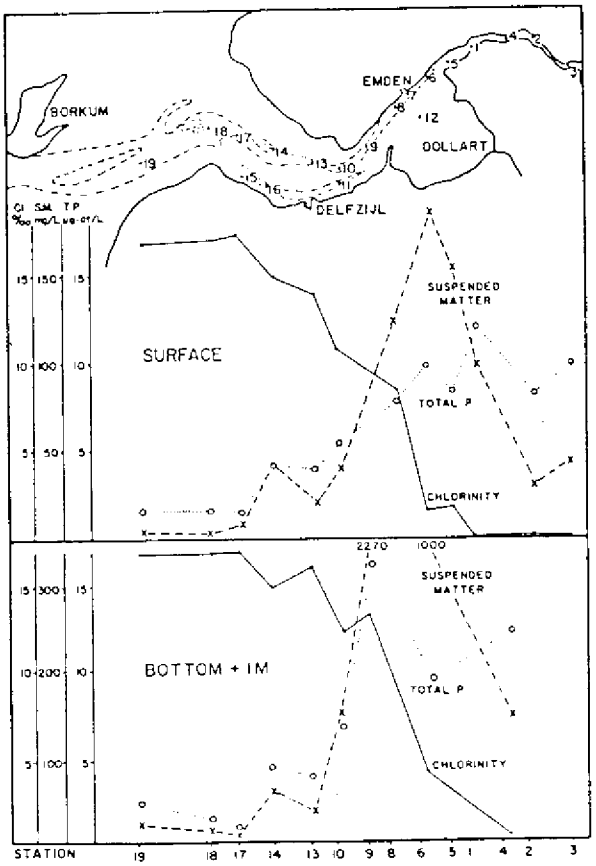

Figure 6. Turbidity maximum in the Ems Estuary (suspended matter in mg.L^{-1}). Observations at the surface and near bottom (bottom + 1 m). (Postma, 1967)

As mentioned before, the phosphorus budget in an estuary is largely determined by the deposition of riverine particulate material. Partially mixed estuaries as the French Gironde and Loire estuaries are characterized by a maximum turbidity region (Postma, 1980); the turbidity maximum moves upstream and downstream with the tide and may be pushed out of the estuary at strong river flows. Another extreme is formed by the (*e.g.* Norwegian) fjords, *i.e.* the deep, nearly stagnant basins closed off on the seaside by a shallow sill; fjords may serve as a nearly 100% entrapment of particulate and dissolved phosphorus and other nutrients (Bowden, 1980).

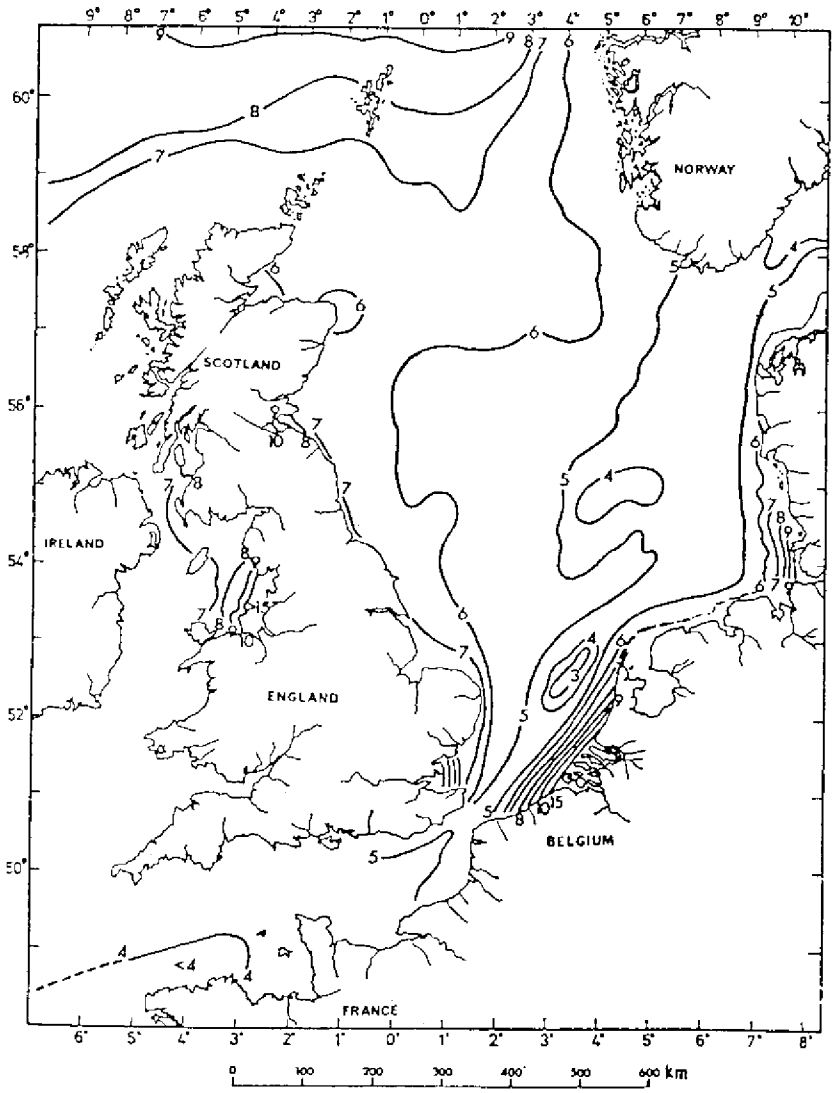

Figure 7. Winter phosphorus (10^{-1} μgat PO_4^{3-}-P.L^{-1}) in North Sea (multiply by 3.1 for μmol PO_4^{3-}.L^{-1}). (Topping, 1976)

Coastal seas of Europe.

a. North Sea. The North Sea (Fig. 7), has a surface area of approximately 575,000 km^2 and a total volume of ca. 54,000 km^3. Residence time of the North Sea water is 1-2 years overall. Fresh water from rivers and estuaries is mainly discharged into the Southern North Sea forming low(er) salinity coastal water that moves towards the Skagerrak with a velocity of 1.5 - 2 km per day (Topping, 1976). The North Sea receives an annual P load of 100-150 x 10^3 kg P, *i.e.* 0.2 μmol PO_4^{3-}.L^{-1}.$year^{-1}$ (Jaworski, 1981; Postma, 1985). Table I presents a survey of the different P discharges into the North Sea, and specifically into a narrow coastal strip (20 km width) off the Dutch coast. The table clearly shows the relatively strong P imission into the coastal waters.

Table I. Survey of P discharges into the North Sea, and into the Dutch coastal zone in 1980 and 1990. Compiled from: *Anonymus* (1986).

	Sources (x 10^6 kg P.yr^{-1})				
	Atmosphere	Rivers	Discharges off the coast	Additional sources	Total
North Sea, 1980	10	96	25	9	140
Dutch coastal zone, 1980	2.5	67	3.5	2	75
Dutch coastal zone, 1990	2.5	49-62	1.5	1.5	55-68

Over the years phosphorus (as ortho-phosphate) concentrations in the North Sea proper have remained relatively unchanged, in the order of 1.5 μmol.L^{-1}, whereas coastal P concentrations may easily attain values > 3 μmol.L^{-1}, or more (Fig. 7). The last few decades have shown a marked increase in the P concentrations of the coastal waters, with multiplication factors of 2.0 in 20 years for the Southern Bight, 1.5 in 20 years for the German Bight (Lancelot *et al.*, 1987) and a factor 2.5 in 20 years (*i.e.* from 2.2 to 5.0 μmol PO_4^{3-}.L^{-1} dissolved organic + inorganic phosphate) for the Dutch part of the Wadden Sea (De Jonge and Postma, 1974; Postma, 1985; Cadée, 1986). These strong P increases may directly be connected to the *ca.* ten fold increase in freshwater P discharges between 1950 and 1980 (Postma, 1985). Future trends point to a 10-20% decrease in these discharges in 1990 (Table I).

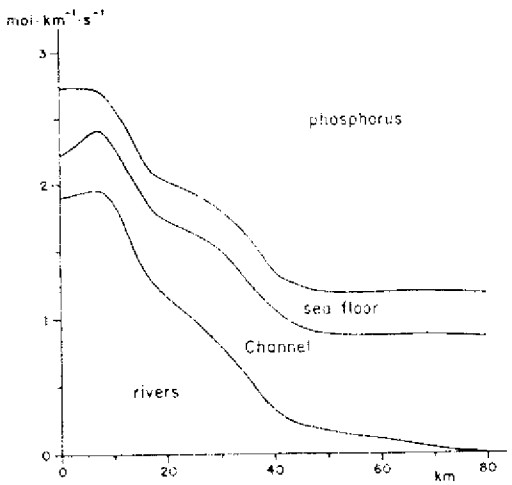

Figure 8. Composition of phosphate inputs (mol PO_4^{3-}.km^{-1}.s^{-1}) to the Southern Bight of the North Sea as a function of offshore distance. River and English Channel inputs were calculated for a section perpendicular to the Dutch coast at about 51°30' N. (Rutgers van der Loeff, 1980)

Benthic regeneration may be an important factor in the P cycle of coastal waters, especially under anaerobic conditions. In a study of the sediments of the Southern Bight, Rutgers van der Loeff (1980) found marked differences in the sediment and interstitial water qualities between coastal zone sediments (organic carbon contents 0.8 - 1.2%; PO_4^{3-}-P 100-150 $\mu mol.L^{-1}$) and off-shore sediments (organic carbon 0.4 - 0.8%; PO_4^{3-}-P 20-30 $\mu mol.L^{-1}$). From the calculated P release rates, the role of benthic P regeneration in the total phosphorus budget of the Southern Bight of the North Sea is evident (Fig. 8). Increasing nutrient loads, however, have not yet led to widespread anaerobic conditions in the coastal zone of the North Sea, with the exception of localized areas in the Dutch Wadden Sea and the German Bight.

b. Baltic Sea. The Baltic Sea, with a surface area of around 100,000 km^2 and a water volume of ca. 21,000 km^3, is a brackish sea (salinity < 10°/oo) under strong influence of the fresh water discharges from the surrounding lands and atmosphere (Voipio, 1981). Residence time of the Baltic Sea water is around 35 years. Due to temperature and density differences a permanent summer stratification has evolved in the deeper parts (> ca. 20 m) of the Baltic Sea.

In the surface water total phosphate concentrations showed an overall increase from around 0.5 $\mu mol.L^{-1}$ in 1959 to 1.5 $\mu mol.L^{-1}$ in 1975 (Grasshoff and Voipio, 1981). In the anoxic deeper parts, phosphate concentrations may easily reach values > 10 $\mu mol.L^{-1}$. Accordingly, 50-60% of the phosphorus present in the oxic surface layer is directly derived from the P pool in the anoxic bottom layer (Sen Gupta and Koroleff, 1973). Tentative budget calculations for phosphorus in the Baltic Sea (Table II) suggest a 50% unexplained net term between the P sources and sinks, this term being the net P uptake into the sediment. It may be expected that, in view of the ever increasing fraction of permanently anoxic sediments (at present 10-15%; Sen Gupta and Koroleff, 1973), the future P buffering capacity of Baltic Sea sediments will substantially be diminished.

Table II: Tentative P budget for the Baltic Sea.
Compiled data from: AMBIO 14 (1985): 10-14 (untitled paper)

	$\times 10^6$ kg $P.yr^{-1}$
P DISCHARGES	+ 71.4
ATMOSPHERIC CONTRIBUTIONS	+ 5.5
LOSSES:	
By fishing	- 3
Through the Danish sounds	- 1.5
ACCUMULATION IN THE FREE WATER MASS	- 15
UNEXPLAINED NET, INCLUDING SEDIMENTATION	57.4

c. Coastal zones of the Mediterranean. Up till now the effects of P discharges into the Mediterranean are limited to some localized coastal zones and bays in the region, e.g. the Northern Adriatic (Italy) and the Eubiokos Gulf (Greece).

Phosphorus contents in the Eubiokos and Saronikos Gulf, Greece, showed values of ca. 4 x the normal background levels (Friligos, 1985; Satsmadjis, 1985); however these areas have exceptionally high P discharges compared to the general situation in the Mediterranean.

Especially the Northern part of the Adriatic Sea has shown marked eutrophication phenomena since about 1970, mainly due to the nutrient discharges of the river Po. Over the whole of the Adriatic Sea, 34,000 x 10^3 kg P per year were discharged in 1980, of which 28,000 x 10^3 kg P in the Northern part only (Chiaudani *et al.*, 1982). This means a roughly five-fold increase over the last 50 years. The area is highly sensitive to nutrient discharges due to the long water residence time in this semi-enclosed basin, and frequently occuring thermal stratification. Local events of sediment anoxia have rapidly increased over the last few decades giving rise to enhanced benthic P regeneration rates from (especially organically bound) phosphorus (Giordani and Angiolini, 1983; Justić, 1987). Present phosphorus concentrations in the area are in the order of 2-3 μmol $PO_4^{3-}.L^{-1}$ on average, with peak values (*Anonymus*, 1982b) near 20 μmol.L^{-1} at the mouth of the river Po. In the open sea, PO_4^{3-} concentrations are generally below 1.0 μmol.L^{-1}.

Conclusion

Compared to the phosphorus flows in the world's seas and oceans, global estuarine and coastal P cycles only play a minor role (cf. Pierrou, 1976). However, recent and future P trends in the latter regions deserve special attention in view of their importance as highly productive ecosystems (e.g. as "breeding grounds" and commercial fishery zones).

Domestic and industrial discharges have caused a 2-3 fold increase in the P levels of the European estuaries and coastal seas over the last few decades. Quantitative input/output data for these systems are often lacking. It is evident that estuaries serve as a sink for dissolved and particulate phosphorus, especially through the large buffering capacities of estuarine sediments. In view of the ever increasing anoxic conditions, future P buffering capacities may substantially be diminished.

As pointed out by Postma (1980) estuaries are, in a geological time scale, very temporary structures, with present ages measured rather in thousands instead of millions of years. Filling up of the estuaries by land-based sediments is a key process when considering the future developments of the estuaries as geological systems. Long term changes in sediment supply are, amongst other, influenced by anthropogenic factors as deforestation, increased erosion by extensive land use and construction of hydroelectric power plants. These factors must be included when evaluating the global phosphorus cycles in estuaries and coastal seas.

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Inventory of Phosphorus in the North Sea

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Synopsis

The North Sea receives annually about 120 000 t P from terrestrial sources. The bulk of this is anthropogenic in origin. Due to the particular circulation pattern this input is confined mostly to coastal areas and strongly affects the intensity and species composition of phytoplankton blooms. Qualitatively the most important component of the P pool appears to be reactive inorganic phosphate with particulate P playing only a minor role. The importance of dissolved organically bound P is still largely unknown. Wadden Sea sediments represent an intermediate sink from which P can be easily remobilized. Sediments of the Skagerrak basin are the only mayor long-term sink. Despite considerable research efforts, the available data are still insufficient for budget calculations.

Introduction

Phosphorus is an essential element of life. It serves in ATP to transfer energy, in phospholipids to form membranes and in nucleic acids to store genetic information. Its total amount available to living organisms is - compared to the other macronutrients carbon, nitrogen and silicon - rather limited on Earth. Mobilized by weathering in the thin regolith layer of the continents or by hydrothermal leaching, the maximal phosphorus concentration in the aqueous phase theoretically is controlled by various mineral equilibria. One of these is apatite (calcium phosphate), which -in the present Ca-rich ocean- would limit build-up of phosphate concentrations to roughly 10 $\mu mol \cdot kg^{-1}$.

However, life processes are even more efficient in extracting phosphorus and the average phosphorus concentration reaches 2.3 $\mu mol \cdot kg^{-1}$ seawater (Broecker et al. 1982). Numerically, the following factors govern this overall average: (i) rate of input from rivers and submarine hydrothermal sources, (ii) rate of upwelling of deep ocean water to the euphotic zone, (iii) rate of remineralization and speed of sinking particles, and (iv) burial rate of phosphorus in sediments. A change in the rate of any of these processes would alter the average oceanic concentration as well. Generally speaking is phosphorus the ultimate limiting compound for oceanic life: Silica is not essential to many marine phytoplankters, nitrate can be produced enzymatically by cyanobacteria from dissolved nitrogen, and carbon is always present in excess of all other nutrients.

On average, marine plankton produces organic matter with a C/N/P molar ratio of 105/15/1, the so-called Redfield ratio. Heterotrophic degradation releases these elements at about the same ratio to the deep oceanic waters.

The molar ratio of dissolved nitrate to phosphate in the ocean is 15/1, giving rise to the hen-and-egg question: has life adapted to the oceanic ratio or is life determining this ratio? Broecker and Peng (1982) argue in favor of the latter simply because biogenic nitrification can overcome nitrate limitation. Curiously enough, rivers also deliver nitrate and phosphate at about this ratio to the ocean (Kempe 1982), suggesting that concentrations of N and P compounds in continental aqueous systems are also regulated biologically.

The North Atlantic surface water is the end of the global oceanic "conveyor belt" circulation, i.e. here the warm surface waters arrive after they have been thoroughly depleted in nutrients during their voyage from the Pacific through the Indian and into the Atlantic ocean. One might therefore expect that the North Sea does not receive appreciable amounts of nutrients and does therefore not have the capacity to sustain high primary production. Due to several circumstances this is, however, not at all the case: (i) At the eastern side of the Atlantic upwelling occurs, and water from a depth of several hundred meters, which is -compared to the Atlantic surface water- relatively rich in nutrients, feeds the marginal seas; it enters the North Sea from the north and circulates counterclockwise in it thereby forcing all marginal fresh water inputs to flow along the coasts; (ii) shallow seas act as traps for nutrients because the nutrients consumed by phytoplankton and settled to the bottom can be remobilized by storms, nutrients therefore can serve several phytoplankton blooms before they are finally removed from the shallow sea; (iii) the North Atlantic coastal areas receive above normal precipitation and hence experience enhanced weathering and phosphorus mobilization in the adjacent continental tributary areas; and (iv) they receive increasing amounts of anthropogenically liberated nutrients. All these factors suggest that the North Sea should be an area of high productivity and, indeed, it contributes 6 % of the global fish catch even though its area ($545 \cdot 10^3 km^2$) amounts to only 0.15 % of the global ocean.

Phosphorus input to the North Sea, natural and anthropogenic sources

All rivers entering the North Sea are heavily polluted. Particularly their nutrient concentrations exceed the global average considerably. Concentrations are up to two orders of magnitude higher than in pristine rivers (Kempe 1982). Because this increase in nutrients began well over 100 years ago with the industrialization of the British Islands and Central Europe and the advance of sewage channelization and artificial fertilization, it is difficult to reconstruct the pristine loads of European rivers. Zobrist and Stumm (1981) refer to a chemical analysis of a water sample taken from the Rhine at Arnheim in 1854 and conclude that the NaCl load has risen 13 times since then. Similarly the nitrogen and phosphorus loads increased by at least a factor of ten (Van Bennekom and Salomons, 1981). From 1963 to 1978 the annual load of PO4-P increased in the Rhine (Figure 1) from 8,000 to 25,000 t (correlation with time $r = 0.80$, $n = 16$ years, sign. > 99.9%; Kempe 1982). In contrast to this the record of the PO_4-concentration in the Elbe River at Hamburg, which starts in 1955, does not show a significant increase with time. Values have been high throughout the entire record. There is another difference in the behavior of the two rivers (Figure 2). In the Rhine most of the phosphorus is transported as dissolved phosphate (RDP = reactive dissolved P) (76 % of total phosphorus (TP) in 1984), while in the Elbe river only the

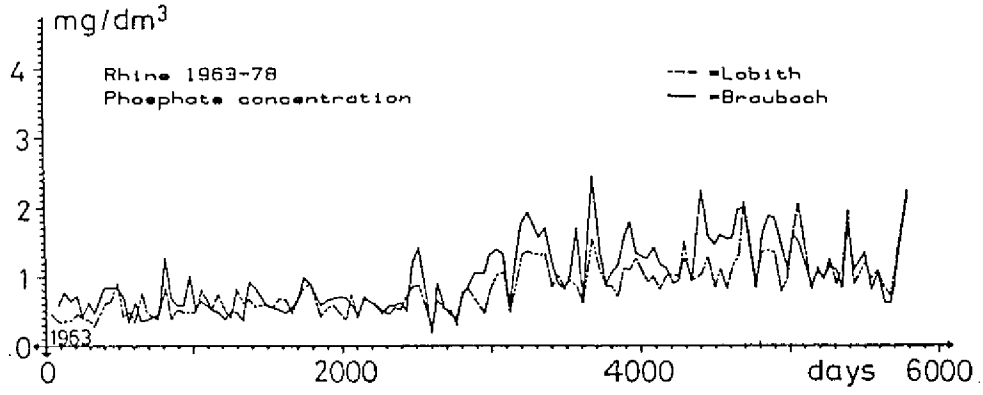

Figure 1. Increase of concentration in dissolved phosphate in the Rhine River as measured at stations Lobith (Dutch/German Border) and Braubach between 1963 and 1978. Dimension of X-axis is days starting in 1963 (Kempe 1982).

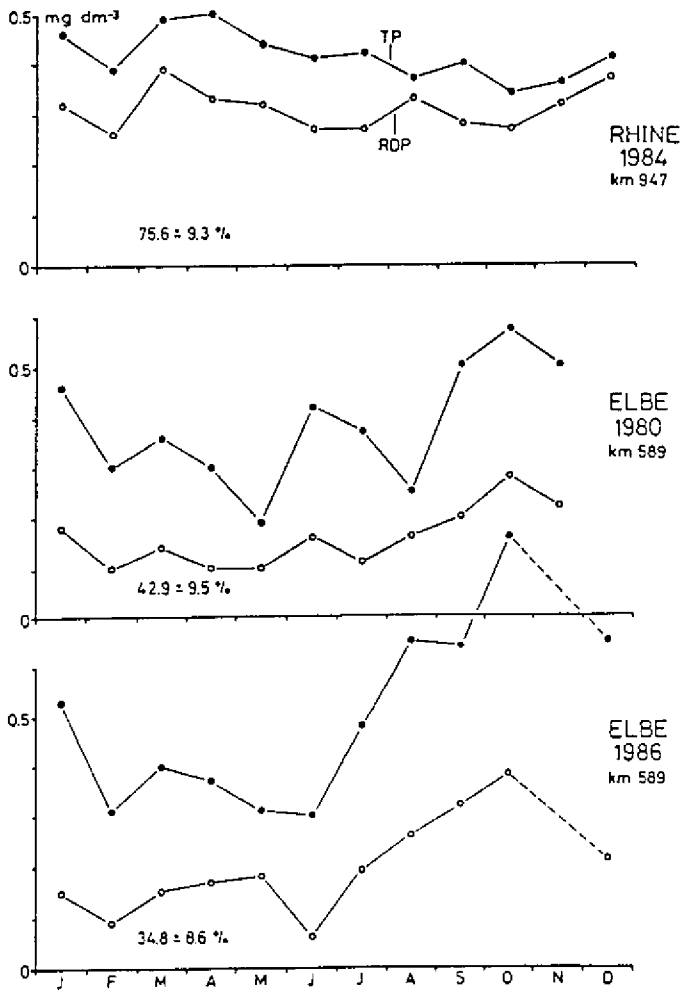

Figure 2. Seasonal variation of total phosphorus concentrations (TP) and of dissolved inorganic phosphate (RDP) in the Rhine and Elbe rivers (data from Rijkswaterstaat 1984 and Arge Elbe 1981, 1987, resp.). Note that in the Elbe less phosphorus is transported as RDP than in the Rhine.

smaller fraction is RDP (43 % in 1980 and 35 % in 1986). In the Elbe transport of phosphorus in the particulate phase or as dissolved organic P is therefore more important than in the Rhine. These differences originate most probably from differences in sewage treatment procedures between the GDR and the CSSR in case of the Elbe and the FRG, France and Switzerland in case of the Rhine.

Because of the large interannual variability of river transports and the assumptions made in calculating these loads from a few analyses spaced unevenly with regard to time and discharge, it is impossible to exactly calculate the phosphorus transport into the North Sea for a specific year (Kempe et al. 1989). Nevertheless, an estimate of this transport can be given within reasonable limits of accuracy.

Table 1. Nutrient transport of rivers tributary to the North Sea and the Channel, according to various sources (after Kempe et al. 1989)

Name/Station	Years	Source	NO_3-N	NH_4-N	PO_4-P	TP	Q
			$10^3 t \cdot a^{-1}$				$km^3 \cdot a^{-1}$
Elbe/Geesthacht	1979-80	GEMS 1983	86	60		10.7	28.5
Elbe/total		Calson 1986				14	
Weser/Mittelsbueren	1978	Kempe 1982	38		5.4		
Weser/Intschede	1979-80	GEMS 1983	52	1.7		5.9	10.3
Weser/total		Calson 1986			8.6		
Ems/Herbrum	1979-80	GEMS 1983	16	2.55		1.5	2.94
Ems/total		Calson 1986			3.1		
Rhine/Dutch frontier	1979-81	GEMS 1983	350		35		90.0
Rhine/Lobith	1963-78	Kempe 1982	200		17.4		
Rhine/Lobith	1978	Kempe 1982	250		25		
Rhine/Bimmen	1979-80	GEMS 1983	284	74		33.2	80.0
other German rivers		Calson 1986			1.2		
Maas/Eijsden Pontoon	1979-81	GEMS 1983	24.4		2.5		8.7
Great Britain discharges (rivers+sewage+industrial)							
to the North Sea and Channel		IOE 1984	184 (N_{tot})		24.5	41.0	
rivers East Coast only			111 (N_{tot})		3.44	30.92	
rivers Channel only			26.24 (N_{tot})			0.84	8.06
Thames/Teddington Weir	1979-81	GEMS 1983	21.7	0.73	1.12		3.15
Thames		IOE 1984	31.28 (N_{tot})			0.11	4.83
Humber		IOE 1984	41.54 (N_{tot})			0.58	5.68
Tees		IOE 1984	1.75 (N_{tot})			0.22	0.53
Tyne		IOE 1984	0.88 (N_{tot})			0.19	1.07
Forth		IOE 1984	0.82 (N_{tot})				3.20
Exe/Thorverton	1980-81	GEMS 1983	1.2	0.027	0.017		0.54
Seine/Paris	1975-79	Kempe 1982	36.7		1.6		7.1
Seine/Paris	1979-80	GEMS 1983	47	4.1	2.7		11.76

Table 1 lists transport estimates for rivers entering the North Sea according to a variety of sources. If one adds the maximal estimates for total P transport for the rivers Elbe, Weser, Ems, Rhine, other German rivers, Maas and the British North Sea rivers then a total transport of 66,000 $t \cdot a^{-1}$ is calculated. The largest source is the Rhine (33,000 $t \cdot a^{-1}$) followed by the Elbe (14,000 $t \cdot a^{-1}$). The total N transport (NO_3-N + NH_4-N) for the same set of rivers amounts to 704,000 $t \cdot a^{-1}$. The N/P molar ratio is then 24.

However, rivers are not the only sources of anthropogenic nutrients to the North Sea. Especially Great Britain discharges large amounts of sewage and industrial waste directly into the North Sea. Table 1 shows that the ratio of sewage and waste P-discharge to river P-discharge is 4.7 for the British Channel and North Sea coasts (IOE 1984). Thus about 5 times more phosphorus enters the Sea by direct input than through rivers. For nitrogen this ratio is much lower, i.e. 0.34. If one adds these direct phosphorus and nitrogen inputs to the total river inputs (119,000 $t \cdot a^{-1}$ for N_{tot} and 27,000 $t \cdot a^{-1}$ for TP, ICES 1978) then the N/P input molar ratio becomes 19.6.

In Table 2 the ICES estimate of nutrient input to the North Sea is given. It arrives at a somewhat higher river input than the above estimate (86,000 $t \cdot a^{-1}$ versus 66,000 $t \cdot a^{-1}$ of P). This difference gives a feeling for the size of the error which one should assign to any of these numbers: values can easily be off by plus or minus 30%. In the ICES estimate the total N and P inputs amount to 968,000 and 116,000 $t \cdot a^{-1}$, corresponding to a N/P molar ratio of 18.5.

Table 2. Nutrient input (rivers + sewage + dumping) to the North Sea grouped according to countries where the respective estuaries are located

Country	N $10^3 t \cdot a^{-1}$	P $10^3 t \cdot a^{-1}$
Norway	24	3
Sweden	1	2
Denmark	21	1
Fed. Rep. Germany	142	26
Netherlands	580	58
Belgium	2	< 1
England	186	27
Scotland	8	-
Sources		
Rivers	839	86
Sewage direct	119	27
Dumping of sewage sludge	10	3
Total	968	116

Another source of uncertainty in the input data is the amount of dredge spoils dumped in the North Sea. Since most of these spoils derive from harbours in the estuaries, they are a mixture of imported marine and fluvial matter. Because the transports of P given in Table 1 refer to stations above these harbours, it must be assumed that these figures include already most of particulate P later recovered in harbour spoils. Thus dredging of estuary shipping channels and harbour basins is just a short cut to the sea for this material but not a true net-source of P for the North Sea. Schwedhelm and Irion (1985) assume a P input of 51,000 $t \cdot a^{-1}$ and add that to the total river transport, thereby biasing the net P-input to the high side.

Another unresolved question is the input of pollutants from aerosols. Estimates of up to 10,000 $t \cdot a^{-1}$ of P have been suggested, but it is unresolved how much of that is simply recycled seaspray.

The anthropogenic portion of the fluvial P-load derives -according to an estimate by Gerlach (1983)- to 27 % from fecal matter, to 40 % from polyphosphates in detergents and to 33% from fertilizers. It is very difficult to estimate, how much of the P input is to be accounted for by natural sources. If the P-flux has increased by a factor of 10 over the last century, then about 10 % should be natural. The exact size of the present contribution from weathering is difficult to assess. The North Sea tributary area belongs to the temperate humid climate zone where weathering rates are high. Europe as a continent delivers 7.4 % of the global runoff but contributes only 6.9 % to the total continental area (Baumgartner et al. 1975). Due to the humid climate and due to the young morphology, Europe has the highest rates of chemical weathering of any continent: 12.6 % of all dissolved solids reaching the ocean derive from Europe, twice as much as one would expect from its relative area (Kempe et al. 1989). Large parts of the Alps, Central Europe and the British Islands consist of metamorphic and igneous rocks relatively rich in phosphate minerals. One should therefore expect that the specific P-loads of the European rivers in preindustrial times were higher than those derived from deeply weathered basins like those of the Zaire, Orinoco or Amazon. Today, Central European and British rivers transport the same load of nutrients as the Amazon but with just 3 % of its water volume (i.e., ca. 180 $km^3 \cdot a^{-1}$ versus ca. 6000 $km^3 \cdot a^{-1}$).

In spite of the impressive anthropogenic nutrient mobilization one has to realize that the natural nutrient input to the North Sea is still comprising more than 90% of its annual budget. More then 90 % of the North Atlantic water which enter the North Sea comes from the north, only 10 % passes through the British Channel. These waters have an average PO4 concentration of 0.5-0.7 $\mu mol \cdot kg^{-1}$ (Bockmann 1987), equivalent to the concentration found at depths of 400 to 600 m in the open North Atlantic (Broecker et al. 1982). These inputs are estimated to amount to 790,000 and 96,000 $t \cdot a^{-1}$ of P respectively (IOE 1984).

Phosphorus distribution in the North Sea

The residual currents in the North Sea follow in principle a counterclockwise circulation. Atlantic water entering from the Shetland Strait will flow south along the British E-coast and mix with British effluents. Water entering from the Channel and from the rivers Rhine, Weser, Elbe, will occupy the southern North Sea and will flow along the Dutch, German and Danish coasts towards the Skagerrak (Jütland Current) (e. g., Eisma and Kalf 1987). At its western fringe it mixes with Atlantic water and flows northeastward. After mixing with the outflow from the Baltic Sea and from fjords in Norway the water leaves the North Sea along the Norwegian coast (Norwegian Coastal Current). The overall flushing time of the North Sea is roughly 36 months. Chemically, the North Sea water can be described as a mixture of three endmembers: North Atlantic water, Baltic Sea water and a composite river water (Pegler et al. 1988).

The circulation pattern described can be modelled numerically (De Ruijter et al. 1987, Backhaus 1984). Figure 3 shows the P distribution one of these models generates on basis of the estimated P inputs. It is evident that the input from rivers is confined largely to a narrow strip along the Dutch, German and Danish coasts. Since modelling cannot account for effects of biological utilization the actual P distribution is, however, different. In winter, when phytoplankton activity is low, the southern and northern parts of the North Sea show distributions comparable to those predicted by modelling (Figure 4). There is, however, a large area in the central North Sea were values drop below 0.5 $\mu mol \cdot kg^{-1}$, i.e. below the concentration values of the inputs. Thus phosphorus is removed here from the water column by biological processes. The central North Sea and the Dogger Bank have long been known to sustain phytoplankton blooms even in winter (e.g. Kalle 1937). In this area the water is relatively shallow and clear so that even the winter insolation provides enough light for plankton to grow in the water column.

In summer, the distribution becomes even less similar to the conservative mixing distribution. Throughout all of the southern North Sea the phosphate has been consumed and the high concentration fringe has disappeared altogether. Only along the British coast areas of high concentrations occur. There, dump sites are located where phosphate is obviously supplied much faster to the bottom waters than it can be dispersed upward and removed by phytoplankton.

In the northeast of the North Sea bottom waters have high concentrations throughout the year. In this area the floor of the North Sea dips into the Skagerrak basin and into the Norwegian Trough, basins which are more than 200 m deep. At this depth phosphate cannot be consumed by phytoplankton. In the surface waters of this area, phosphate concentrations do however also drop to very low values in summer.

In comparing the distribution of theoretical TP concentrations (Figure 3) with those of measured RDP concentrations (Figure 4) is to a certain extent misleading because one has to establish first, if RDP is in fact representative of the bulk of the phosphorus present in the water column. In Figure 5 such an estimate is made. It graphs distribution of TP in the inner German Bight in January/February 1985 (Figure 5a) (DHI 1986) and compares it with the percentage of RDP (Figure 5b). TP concentrations increase significantly towards the innermost fringes of the German Bight while at the same time the percentage of RDP in TP seems to be relatively low (< 70 %) nearcoast, relatively high (> 90%) in intermediate areas and rather irregular in areas further offshore. If one plots (Figure 5C) RDP percentage versus salinity, then the lower salinity values follow a significant linear regression. Since the Elbe (see Figure 2) discharges phosphorus with a relatively low RDP fraction, this regression could describe the liberation of bound phosphorus to the dissolved phase in the Elbe plume with increasing salinity. The RDP fraction of the high salinity samples do not correlate with salinity and possibly represent patchiness in the distribution of open water plankton or resuspended fine-grained sediment.

The non-RDP fraction of TP could either be associated with the particulate phase (TPP, total particulate P) or with dissolved organic complexes (DOP, dissolved organic P). The distribution of TPP is given for the winter situation of the North Sea in Figure 6 (compare Figure 4 for RDP

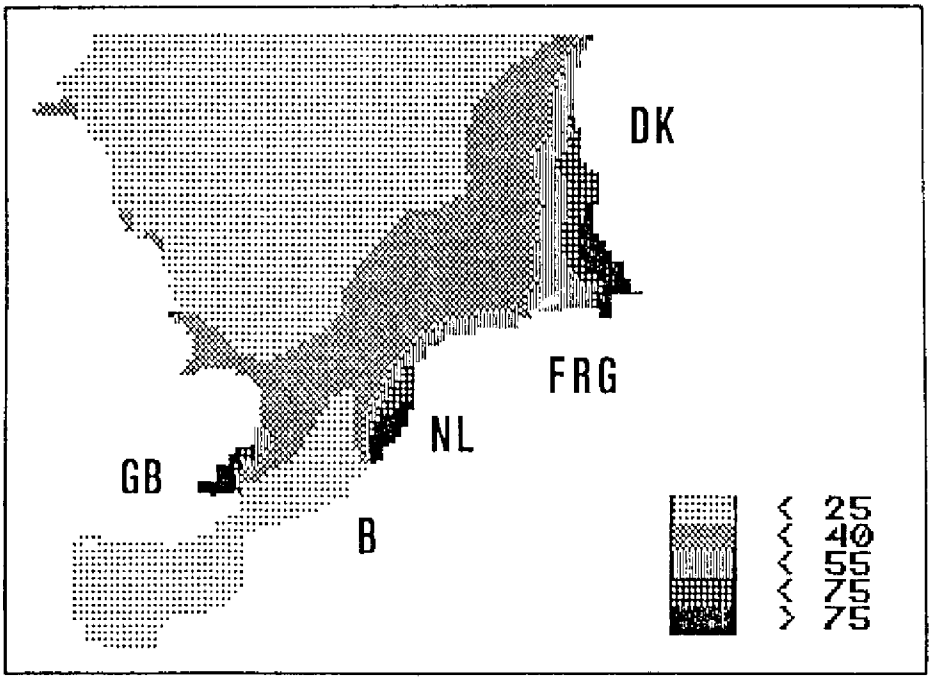

Figure 3. Theoretical distribution of the total phosphorus concentration in the North Sea as established by conservative transport with the average residual current system. This distribution was calculated using the Rijkswaterstaat model of North Sea circulation (Rijkswaterstaat 1986).

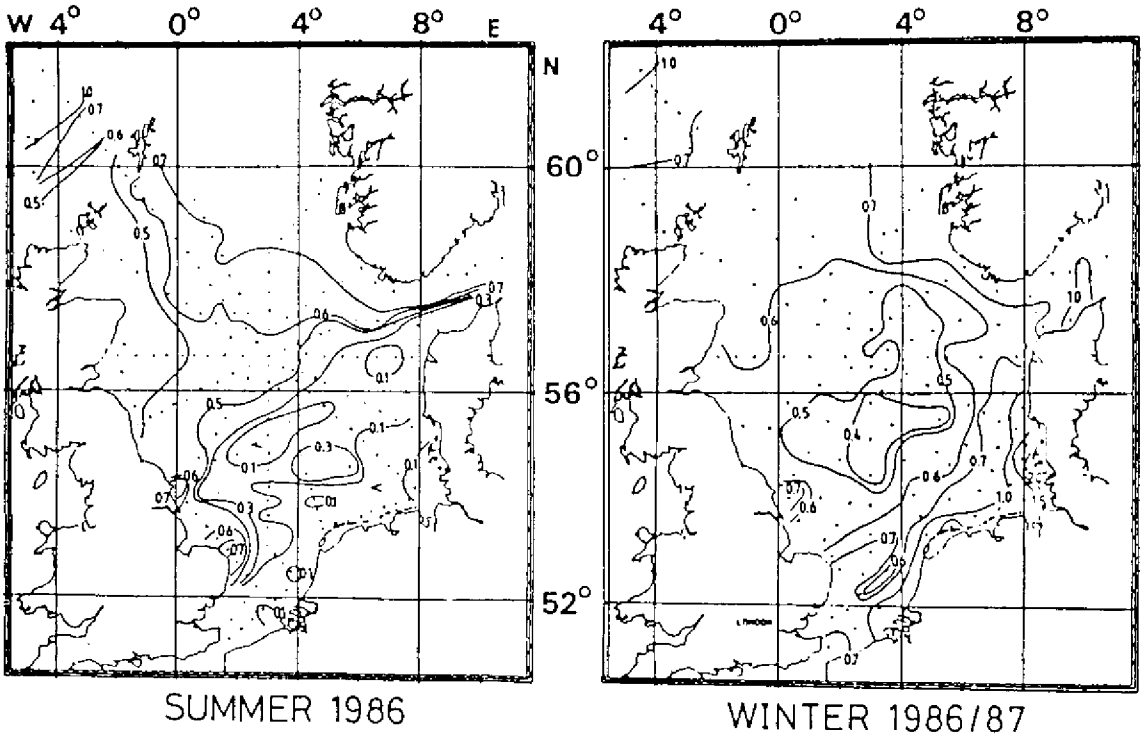

Figure 4. Actual distribution of phosphate concentration in the North Sea above the bottom in summer 1986 (left) and in winter 1986/1987 (Bockmann 1987).

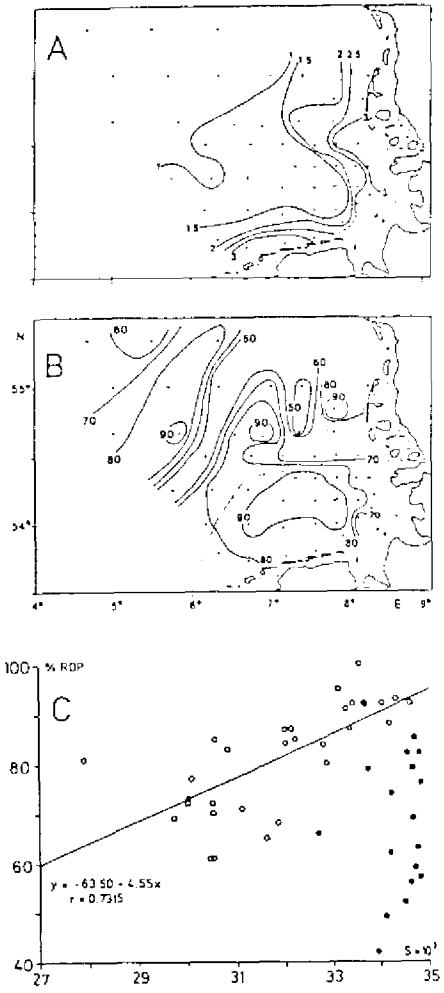

Figure 5. A: Distribution of TP concentration in the German Bight for January, February 1985 in $\mu mol \cdot kg^{-1}$. B: RDP percentage of TP. The samples to the right of the dotted line (salinity < 33.8 per mil) are used for the regression in C. C: Graph of RDP % of TP versus salinity and regression for samples of the inner German Bight (open circles). Note the positive and significant correlation with increasing salinity. North Sea samples (of high salinities) (solid dots) do not follow this correlation but seem to indicate a different water mass highly patchy with regard to RDP percentage (DHI 1986).

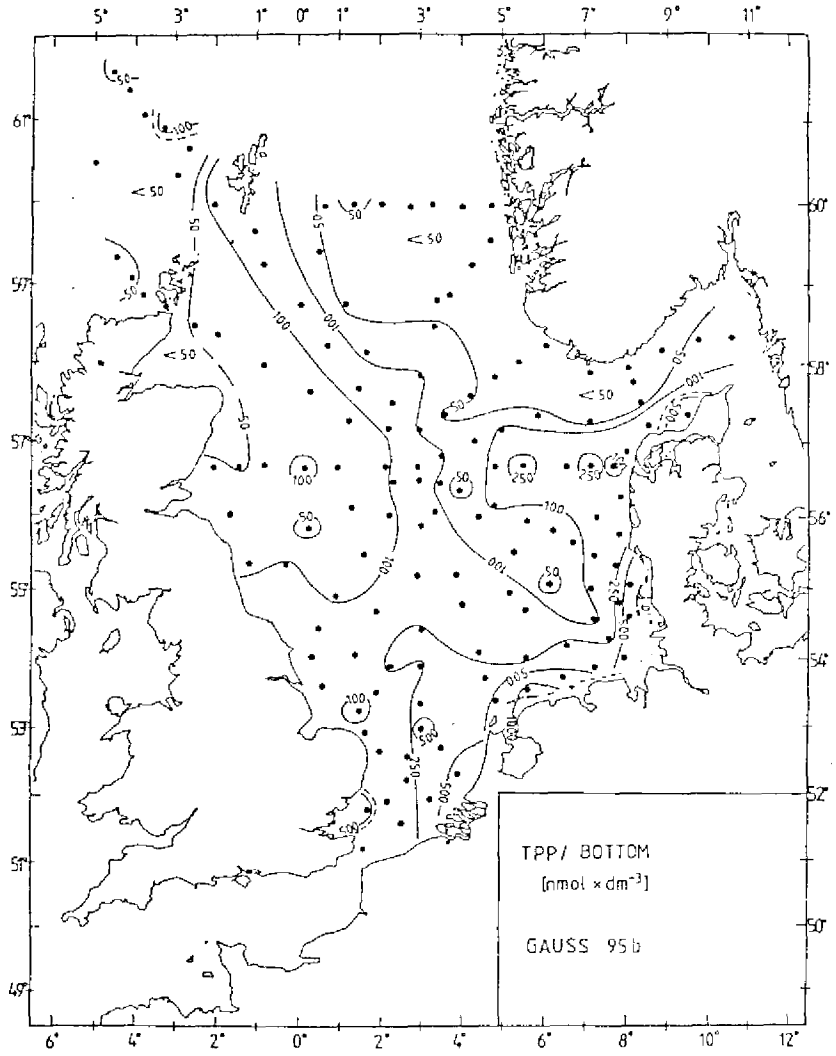

Figure 6. Near-bottom distribution of total particulate phosphorus concentration in January-February 1987 in the North Sea (Schröder 1987).

concentrations of the same stations). Concentrations increase significantly towards the southern coastal fringes compared to the central and northern North Sea by a factor of 10 while RDP concentrations change only by a factor of 5. Thus relatively more particulate P exists near shore than in the inner North Sea and the percentage of TPP in TP varies from 10 to roughly 25 percent.

The question of how much P is contributed by DOP is largely unresolved. Our preliminary data suggest that in the inner German Bight up to 0.3 - 0.4 $\mu mol \cdot kg^{-1}$ are present as DOP and that it mixes conservatively with the North Sea water. Further out values decrease to 0.1 $\mu mol \cdot kg^{-1}$. It is interesting to note that in the deep waters of the Pacific similar DOP concentrations as in the open North Sea were found (Liebezeit 1989). It is suggested that this DOP is associated with refractory organic compounds such as humic acids. Possibly the 0.1 $\mu mol \cdot kg^{-1}$ found in the North Sea are associated with such refractory material as well. Some of that matter may derive from river input with passes unaltered out to sea.

Figure 7 gives the fractionation of P for some typical North Sea samples. The concentration of TP is highest in the inner German Bight, and low in the open North Sea and the Skagerrak because the samples were taken during the first plankton bloom in April 1986. In the inner German Bight and in the open North Sea RDP is the most important fraction, but in the Skagerrak DOP constitutes the bulk of the phosphorus. TPP is highest in the sample from the open North Sea while the water extractable fraction is highest in the Skagerrak sample. High concentrations of water extractable P (up to 50% of TPP) were also found near the Elbe mouth. This P seems to be associated with highly soluble Fe-phosphate coatings and with easily degradable organic compounds like ATP. These examples show how variable the phosphorus composition can be even during the same season. They also show that the RDP distribution can still serve as a rough representation of the total P present but that DOP may play a more important role than assumed so far. Certainly TPP is, in terms of its contribution to TP, only of secondary importance.

In Figure 8 the seasonal variation of RDP and TPP is graphed for a station in the Wadden Sea. In April-May, during the main plankton bloom, we find a considerable drop in the RDP concentration and a concurrent rise in the P content of the suspended matter representing the transfer of phosphorus from the dissolved to the particulate phase. In June and August massive remineralization seems to have taken place which triggered a second plankton bloom in August/September, again increasing the P content of the particulate fraction. This pattern of a double plankton bloom was also recorded in the sediment trap studies in the Skagerrak and in the Norwegian Trough (Kempe and Jennerjahn 1988). Here the first bloom is caused by diatoms and silicoflagellates and the second bloom by coccolithophorids. At Helgoland (Figure 9) the long-term average seasonal variation in the RDP concentration (Radach and Berg 1986) also shows a massive removal of RDP from the water column in April/May and very low values in June/July. Then a rise in concentration occurs at the end of July and early August and a small secondary bloom seems to depress the RDP concentration in late August, early September before the annual maximum concentration is reached in October/November.

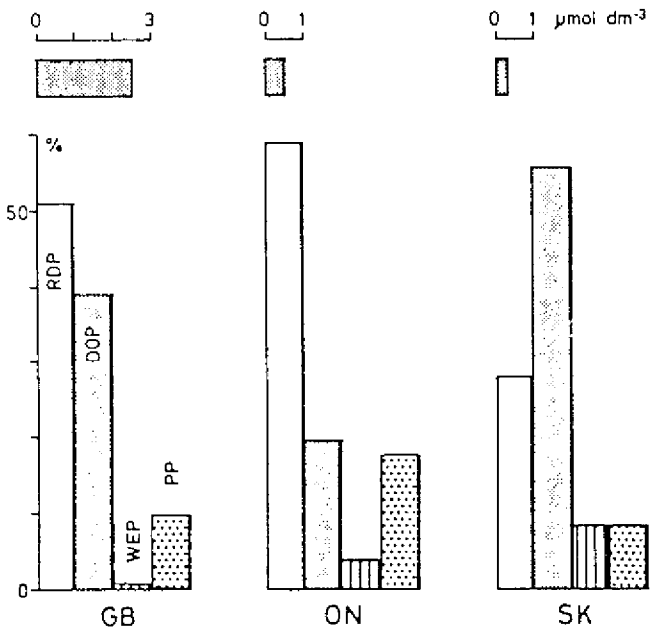

Figure 7. Speciation of total phosphorus in percent for three samples representing characteristic areas of the North Sea: German Bight (GB), open North Sea (ON) and Skagerrak (SK). Total P concentrations are indicated as bars on top. RDP = reactive dissolved phosphorus, DOP = dissolved organic phosphorus, WEP = water extractable particulate phosphorus, PP = particulate phosphorus (residual).

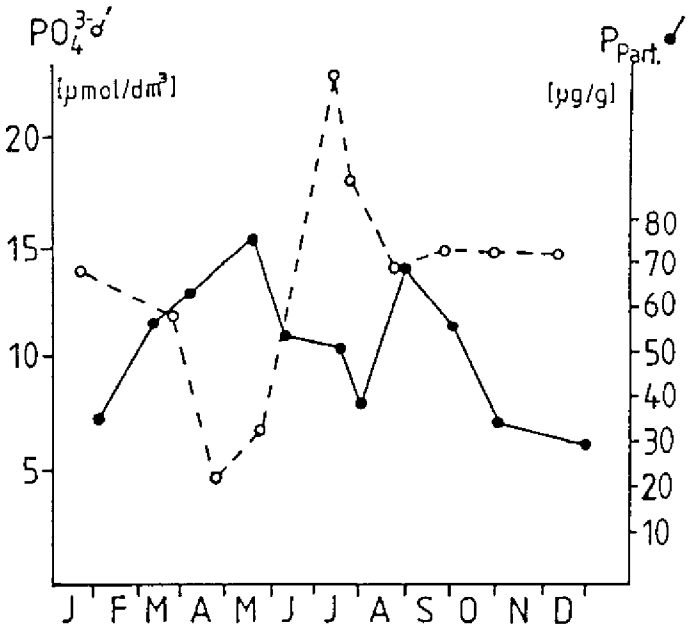

Figure 8. Annual cycle of phosphate and particulate phosphorus concentrations in the western part of the Dutch Wadden Sea 1971, modified after De Jonge and Postma (1974) by Schwedhelm and Irion (1985).

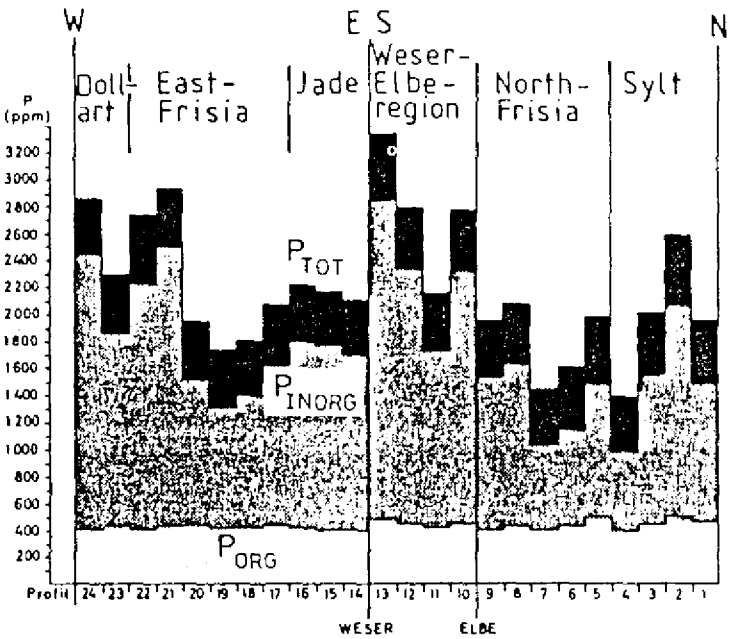

Figure 9. Concentrations of total phosphorus, inorganic phosphorus and organic phosphorus in the < 2 µm fraction of Wadden Sea sediments in a profile along the entire German coast from the Dutch border to the east (left) to the Danish border in the north (right) (Schwedhelm and Irion 1985).

Sinks for Phosphorus

During the spring and summer plankton blooms RDP is almost quantitatively removed from the euphotic zone of the North Sea. Since the southern North Sea is very shallow, this means that RDP is essentially removed from the entire water column (compare summer distribution in Figure 4). It is transformed into DOP and into TPP. TPP in turn is incorporated into sinking particles which very quickly reach the sea floor. Sinking speeds of 20 $m \cdot day^{-1}$ for flocculated matter have been measured in sediment trap experiments of the North Sea (Kempe and Nies 1987, Kempe and Jennerjahn 1988).

The nature of the particulate matter in the water column is quite variable. During winter 1987 the average C/P ratio of a large sample set of particulate material was 240 at the surface, 80 at a depth of 10 m and 96 above the ground (Schröder 1988). Thus phosphorus seems to be enriched in resuspended nearbottom fine particulates. In the western Skagerrak the sinking material had C/P ratios of between 120 and 1160 (average 352) in winter of 1985/86 and of between 60 and 240 (average 140) in summer 1985. In the Norwegian Trough values between 89 and 650 (average 256) were recorded in winter 1985/86 (Kempe et al. 1988).

The total downward flux of phosphorus in the year 27.03.85 to 27.03.86 as intercepted by a sediment trap in the Skagerrak at a depth of 263 m was 3,660 $\mu mol \cdot m^{-2}$. The bulk of this amount (85 %) sank with the spring and summer blooms between 27.03. and 14.09. The total flux is equivalent to stripping all phosphorus from a water column 7.3 m thick which had an initial P-concentration of 0.5 $\mu mol \cdot kg^{-1}$. The trap at the Norwegian Trough (210 m

deployment depth) intercepted a flux of only 390 $\mu mol \cdot m^{-2}$ during the year 27.09.85 to 21.09.86.

Undoubtedly high vertical P-fluxes similar to those in the Skagerrak occur also in the shallow southern North Sea after plankton blooms. However, the southern North Sea is not a net deposition area. Its bottom is composed of sands with only small contributions of fine-grained (< 20 µm) material. The settling flocs and fecal pellets form a fluffy layer at the floor as can be seen with in-situ video inspection. This layer serves as the food base for the benthos. Storms will, however, resuspend this material and subject it to further transport. Thus the fine-grained matter and the associated particulate phosphorus move episodically through the southern North Sea. The transport of phosphorus should therefore be much slower than that of water and a P cumulation must result in the southern North Sea. This in turn establishes a south-north concentration gradient which should be steeper than the one expected from the conservative transport model.

Fine-grained matter and its associated phosphorus can only be permanently deposited in the deep basin of the Skagerrak (Kempe et al. 1988, Salge et al. 1988). Here a thick veneer of Holocene sediments has formed, the upper layers showing increased concentrations of pollutants (e.g., Lohse 1988).

Total P concentrations in these sediments vary from 200 to well over 1000 $\mu g \cdot g^{-1}$. A close connection with the fine grain size fraction is evident (Liebezeit, unpubl. results). Up to 40 % may be present in organic form. However, no clear trend is to be seen in the geographic distribution of Porg. The few core profiles analyzed suggest enrichment in the upper sediment layers. Whether this is due to anthropogenic input or remobilzation and transfer to the interstitial waters in underlying suboxic sediments cannot be ascertained on the basis of the available data.

Another, albeit more temporary sink is furnished by the sediments of the Wadden Sea. Muds accumulating here show increased concentrations of phosphorus (Figure 10). Because of lateral erosion and fast redeposition an ever increasing volume of sediment is equilibrated with today's high phosphorus concentrations. However, remineralization is fast and porefluids are drained regularly at low waters, recycling large quantities of the deposited phosphorus to the water. As can be seen in Figure 10 most of the phosphorus in the sediment is present in inorganic form, possibly associated with easily reduceable Fe-Al- phosphates. Highest concentrations are found near the largest sources of phosphorus, i.e. in the area of the Elbe and Weser estuaries and in the Ems estuary (Dollart).

Neither of the three sediment compartments, the North Sea coarse bottom sediments, the Wadden Sea muds, and the Skagerrak sediments, have, however, been integrated as to their overall phosphorus mass. It is therefore not possible as yet to formulate even a simple box model in order to describe the time constants of mass transport with regard to phosphorus. Certainly residence times of P in the North Sea are larger than those of water and certainly both the coarse bottom sediments and the Wadden Sea muds form a temporary buffer for the high anthropogenic P-inputs to the southern North Sea.

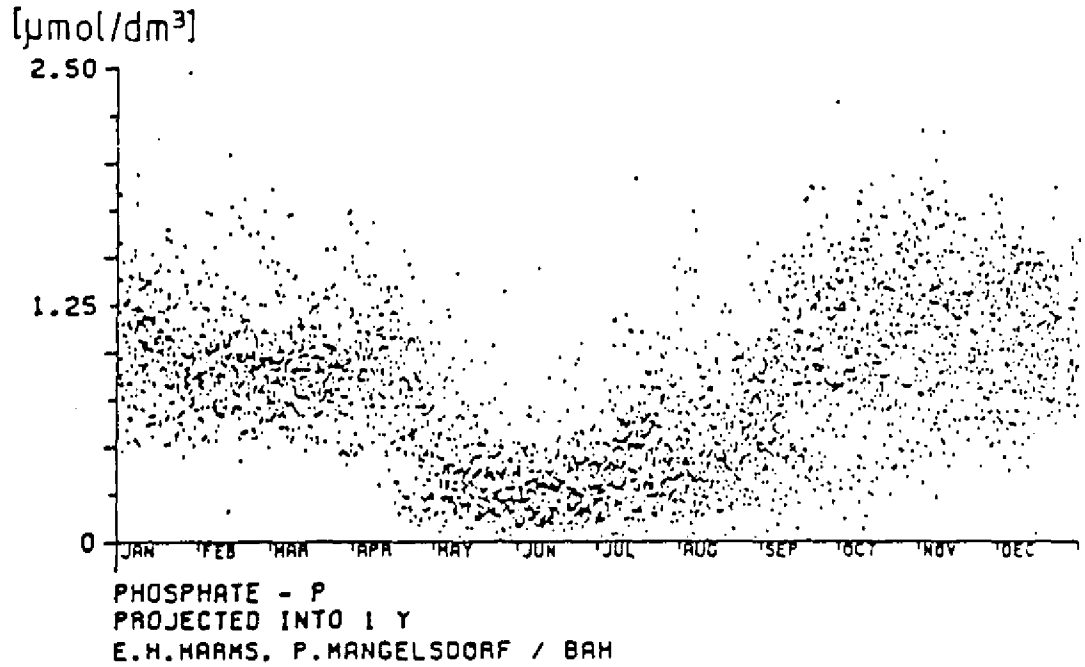

Figure 10. Scatter plot of long-term reactive dissolved phosphorus record at Helgoland projected into one year (Radach and Berg 1986, data by Lucht and Gilbricht 1978).

Long-term effects

At Helgoland, a small island situated in the inner German Bight, hydrochemical and biological parameters have been monitored regularly since 1962 by the Biological Institution Helgoland (Gilbricht, Harms, Mangeldsdorf). These records, which comprise a singular data set worldwide, have been evaluated for time trends by Radach and Berg (1986): Figure 11a graphs the development of the RDP concentration using all samples and Figure 11b shows the RDP concentrations for the winter months (Nov.-March) when primary productivity is low. Both records show a highly significant increase in concentration. The regression for all samples indicates an increase in the annual average concentration from 0.55 (1962) to 0.97 (1984) $\mu mol \cdot kg^{-1}$, while the winter concentrations increased from 0.77 to 1.20 $\mu mol \cdot kg^{-1}$. If one inspects only the winter data of low salinity (which are indicative of the freshwater sources) the increase is even higher, suggesting that much of the phosphate derives from the Weser/Elbe system. Even the summer concentrations have increased, indicating that plankton blooms today cannot remove all of the phosphorus from the water column. The phytoplankton records clearly indicate that flagellates have become the main primary producers, increasing their productivity two to three fold. Diatoms in contrast could not increase their share, mainly because the silica concentration is not influenced by direct anthropogenic input and has therefore not increased during the time of record. Nitrate and nitrite values have, however, also increased, but not as significant as RDP which lead to a rapid decrease of the average N/P ratio in dissolved nutrients (Figure 12). The annual variation in the N/P rate indicates preferential consumption of nitrate or its bacterial denitrification in summer. By October the N/P ratio falls below the Redfield ratio and nitrate limitation may occur. This change in the N/P ratio could be the

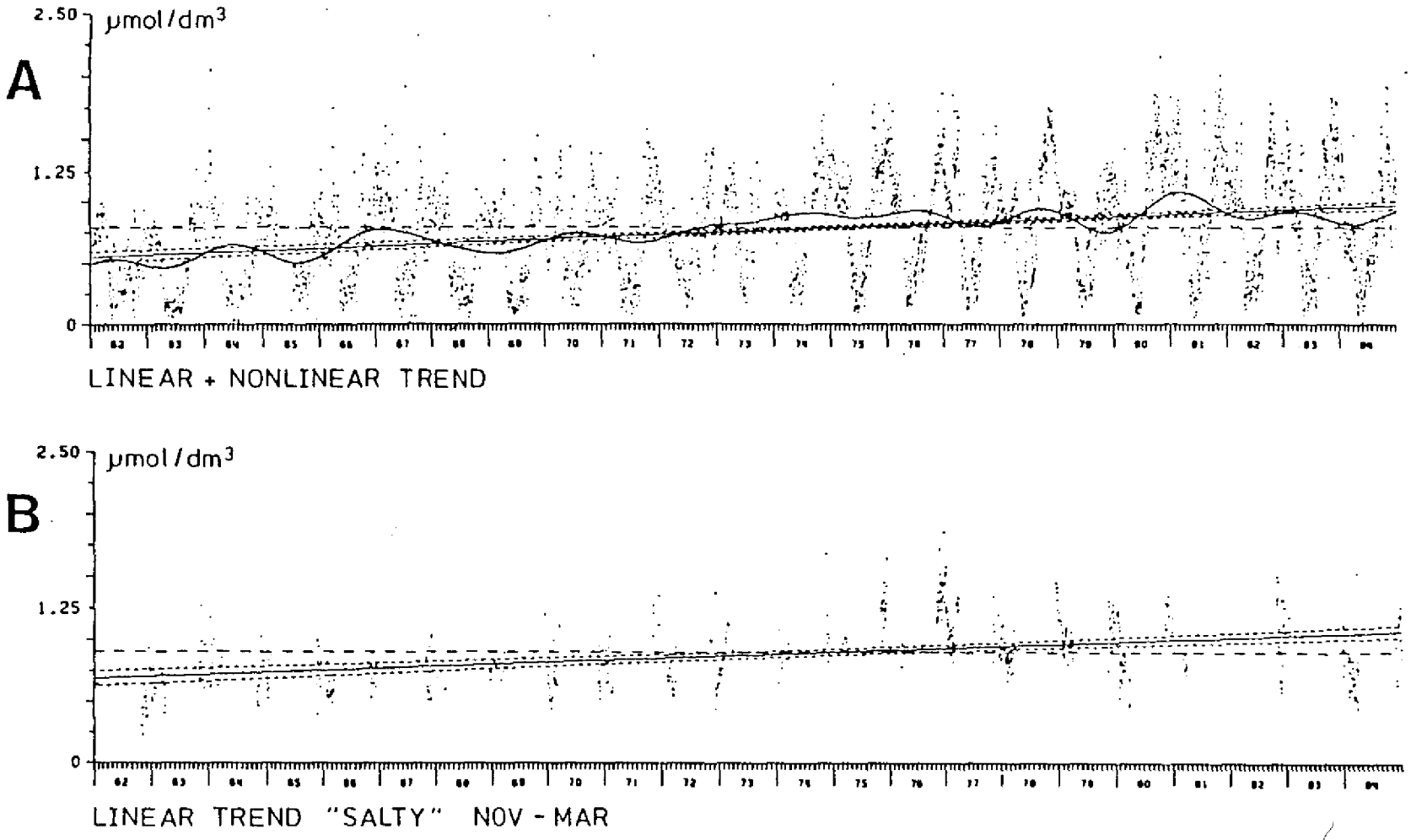

Figure 11. Trend analysis of the reactive dissolved phosphorus (phosphate) record by Radach and Berg (1986) as measured at Helgoland, German Bight, by Lucht and Gilbricht (1978). Heavy, dashed line marks the long-term average. Solid straight line marks the linear regression with time; light, dashed lines mark the 95% confidence intervals of the linear regression. Wavy, heavy line marks the non-linear trend excluding frequencies < 0.5 a^{-1}. A: Record including all measurements. B: Record including only the winter measurements of the more salty samples (trend for North Sea water body).

expression of the accumulation of phosphorus in the inner German Bight, which would be stronger than the nitrogen accumulation since nitrate can be destroyed by denitrification in the oxygen-poor sediments.

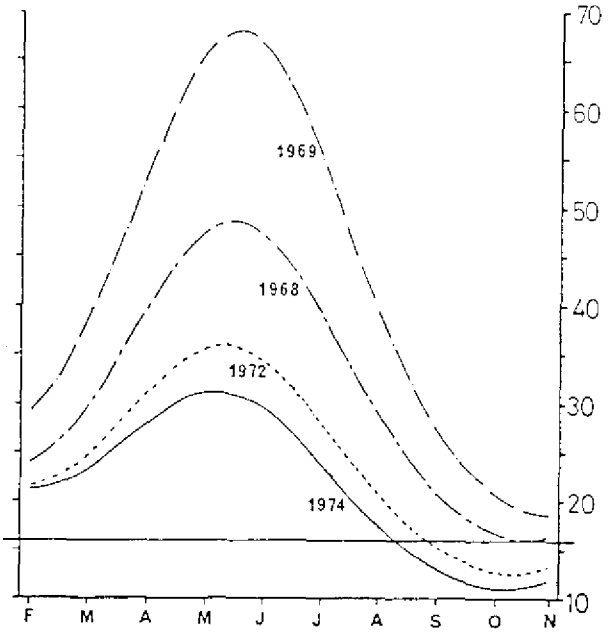

Figure 12. Annual cycles of the N/P molar ratio standardized to S = 32 per mil as calculated from measurements at Helgoland, German Bight for various years. Horizontal line marks the Redfield ratio of marine plankton nutrient requirement (N/P = 16) (Lucht and Gilbricht 1978).

If one compares the present distribution of nutrients in the inner German Bight with conditions reported fifty years ago (Kalle 1937, Lammers 1987, Lammers and Liebezeit 1988), then an increase in concentrations of up to 300 % of its original value is evident (Figure 13). During the same time the concentration in silica decreased significantly to 50 or 60 % of its original value. This decrease may have several reasons. Seawater and rivers may lose most of this nutrient before they reach the sampling area because eutrophication occurs all along the Dutch and German coast and in the rivers themselves, or the remineralization of the settled diatom frustrules is hampered because of an increase in their aluminum concentration (Van Beusekom 1989). The effect for the ecosystem in the inner German Bight is clear: diatom blooms become less prominent and flagellates can produce super blooms. Grewe and Parsons (1977) suggested that the decrease in the diatom/flagellate ratio favors the growth of small copepods. In turn medusa, which feed on small copepods, replace the original stock in small fish, which prefer large copepods.

These flagellate blooms (mainly Phaeocystis pouchetii) have become notorious in the German Bight and in their aftermath oxygen deficiency has become a common threat to fish and shellfish in summer (Bockmann and Eberlein 1986). Figure 14 graphs the extent of these oxygen depletion areas in recent years. It is conceivable that in the near future and with the inevitable further increase in phosphorus these zones become a real threat to all of the higher life in the German Bight.

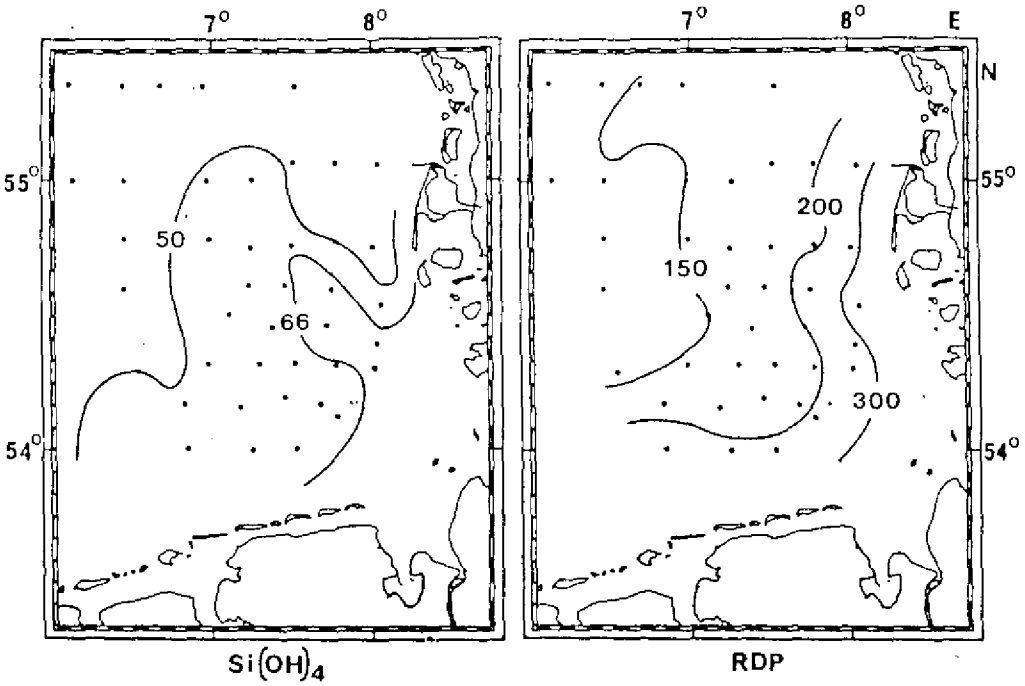

Figure 13. Distribution of dissolved silica concentrations (left) and reactive dissolved phosphate concentrations (right) as measured during the R/V Anton Dohrn cruise 138 in December 1984 in percent of measurements in February 1936 by Kalle (1937) and Lammers (1987).

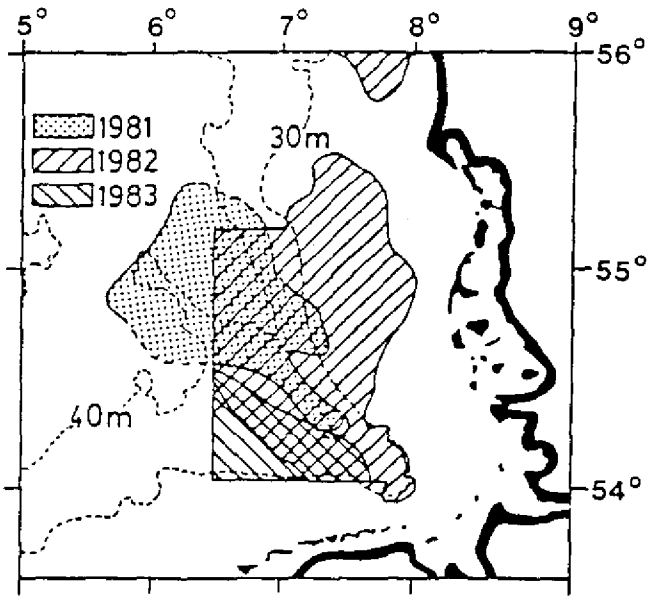

Figure 14. Areas of oxygen depletion in the German Bight in 1981, 1982 and 1983 (Bockmann and Eberlein 1986, according to data of von Westernhagen and Dethlefsen 1983, and Rachor and Albrecht 1983).

Conclusions

The bulk of the phosphorus entering the North Sea is derived from the North Atlantic water. However, at its western and southern fringes rivers deliver increasing amounts of anthropogenic phosphorus to the ecosystem of the North Sea. Because of the circulation pattern of the North Sea, these nutrients stay in a rather limited coastal zone where eutrophication is noticeable and phosphate concentrations in winter are up to 300 % higher than fifty years ago. Especially flagellates proliferate and produce so much organic matter that the inner German Bight is suffering a marked oxygen depletion in summer.

The final sink for all anthropogenic phosphorus is most likely the sedimentation basin of the Skagerrak. However, due to the uptake and particularization of phosphorus by phytoplankton, the residence times of phosphorus in the North Sea are larger than the flushing times of the North Sea. I.e., phosphorus behaves non-conservatively and will tend to increase in concentration in the southern North Sea. Fine-grained matter in the otherwise coarse bottom sediments and the muds of the Wadden Sea offer only temporary sinks because from both environments phosphates are easily remineralized or resuspended and returned to the water column for the usage of phytoplankton.

Acknowledgements

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