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MEDITERRANEAN ACTION PLAN

Training course on Mediterranean river monitoring

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STRATEGIC ACTION PROGRAMME

GUIDELINES FOR

RIVER (INCLUDING ESTUARIES) POLLUTION MONITORING PROGRAMME
FOR THE MEDITERRANEAN REGION

In cooperation with

GEF

FFEM

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PREFACE

The monitoring of rivers' pollution, due either to point or to diffuse sources of pollution, is compulsory as never before. This could be accomplished by a General Master Plan, of general acceptance, which will be implemented step by step, within the criteria of the categories and the amount of hazardous pollutant as also the bodiness of each river.

On the other hand monitoring of rivers pollution must be included in a wider Master Plan of each river's Integrated Water Resources Management at a hydrological basin level.

The problem of integrated water resources management in a hydrological basin level is very complicated because it combines many aspects such us technical, economical, institutional, legal, environmental, social etc.

This problem becomes even greater when we deal with transboundary rivers and the cooperation between the riparian countries is required in order to agree for a common general master plan.

In this context, a strategic vision of each river basin integrated management plan should elicit from the following long-term goals:

- To assist participating countries in the development, the conservation and the rational use of the waters of their transboundary rivers in an integrated and sustainable manner through basin-wide cooperation for the benefit of all.
- To assist participating countries in the determination of the equitable entitlement and obligations of each riparian country to the use and protection of each transboundary river waters.

Short-term goals:

- To assist participating riparian countries to develop for each transboundary river Short-Term Action Programs and its integration into national Master Plans.
- To assist participating riparian countries in developing the appropriate infrastructure, capacity building and techniques required for the management of the transboundary river basin water resources.

The elaboration of completed studies for the Integrated Water Resources Management at a hydrological basin level must be done based on specific Term of Reference agreed by all interested countries for each transboundary river.

The incorporation of Decision Support Systems (DSS) in the overall process is considered as a prerequisite tool for both categories of management options, as by definition it is an essential element of any integrated water resources management approach.

This document can constitute an element for a constructive convergence of exchanged prospects between the countries of the Mediterranean Sea in order to develop the concept of river basin management throughout the region.

1.   INTRODUCTION

The Mediterranean Sea is subject to pollution (including chemical and bacterial contamination and the spread of pathogenic micro-organisms) and eutrophication, mainly from inputs from rivers, especially along the European southern and African northern coasts. The problems are mainly in semi-enclosed bays (e.g. North Adriatic sea), some of which still receive large amounts of untreated sewage. Discharge of nitrogen and phosphorus is probably the cause of the phytoplankton blooms, the 'red tides' that are now frequent in certain parts of Mediterranean (UNEP/MAP 1996). The rapid increase of human activities in the Mediterranean Sea Area, particularly in the fields of industrialization and urbanization, as well as the seasonal increase in the coastal population due to tourism is a major threat to the environment and biodiversity in much of the area

2.   STATUS OVERVIEW OF THE MAJOR MEDITERRANEAN RIVERS AND ESTUARIES

Pollution mainly reaches the Mediterranean Sea through its major river systems: the Po, the Ebro, the Nile, and the Rhone, which carry substantial amounts of **agricultural and industrial wastes**. As the Mediterranean is almost entirely landlocked, its waters have a **very low renewal rate (80 to 90 years)** making them excessively sensitive to pollution.

About 80 rivers contributing significantly to pollution inputs to the Mediterranean Sea have been identified. The 40 major are presented in Table 2.1.

The pollution from land-based sources and the serious problems primarily due to the release of untreated, insufficiently treated or in no way treated wastes, disposed of domestic or industrial discharges, in now wide recognized as a great danger posed to the marine environment and to human health.

2.1 Hydrological characteristics

Mediterranean basin hydrology is in fact very heterogeneous, ranging from alpine regime with early summer maximum, to typical Mediterranean regime with winter high flows and summer low flows, to semi arid regime of the South Coast with gradual increase of summer drought and development of episodic floods. Except for alpine rivers and for the Nile, in its natural condition, the Mediterranean rivers regime is typically characterized by very high variations of day-to-day and year-to-year discharges.

Water inputs to the Mediterranean Sea have dramatically decreased over the last 40 years. The most dramatic decrease is noted for the Nile. Prior to the construction of the High Aswan Dam the water discharge was estimated to more than 83km^3/yr. The construction of the High Aswan Dam led to a decrease of this figure due to the reservoir evaporation. In addition to these losses the major water use in Egypt is by far irrigation and water is not returned to the main river branches, the Rosetta and Damietta branches in the Delta, but to canals reaching the Mediterranean Sea or the Delta lakes. As a result the Nile river discharge to the Mediterranean Sea was on the average around 2 km^3/yr this last decade.

Other reductions of water discharge have been observed in many major rivers of the basin such as the Rhone river (diversion of the Durance, one of its main tributaries), and the Spanish rivers (Segura, Jucar, Mijares, Ebro, Llobregat, Tuna) Similar decrease are most likely for Southern Italian, Greek, Turkish, and Northern African rivers due to evaporation in reservoirs, diversion, and generalized use of water for irrigation.

The present reduction of river water discharge for the whole basin, taking into

account the near-complete reduction of the Nile inputs, is estimated between 30 and 40%. South Levantin, Alboran, South West Aegean, Central and North Levantin basins are probably those most affected by this reduction.

Few Mediterranean rivers still exist in pristine conditions: their levels of nutrients, fecal coli, or metals are practically those found in river of other continents without any human activities. This is due to the very low population density, limited agriculture and absence of industries. Krka and Neretva (Croatia), Var, Argents and Tavignano (France) are examples of such conditions. It must be remarked that such basins have also none or little number of existing dams and have also a high ecological values for this reason.

Table 2.1: Major Mediterranean Rivers in decreasing order of present water discharge to the sea

Rivers	Qact Km³/yr	Area 10³ km²	Passing through Countries	Outfall Country
PO	48.90	70.00	Italy	Italy
RHONE	48.07	95.60	France, Switzerland	France
DRINI	11.39	14.17	Albania	Albania
NERETVA	11.01	10.02		Croatia
BUNA	10.09	5.19	Albania	Albania
EBRO	9.24	84.00	Spain	Spain
TEVERE	7.38	16.55	Italy	Italy
ADIGE	7.29	11.95	Italy	Italy
SEYHAN	7.20	20.00	Turkey	Turkey
CEYHAN	7.10	20.50	Turkey	Turkey
EVROS	6.80	55.00	Bulgaria, Greece, Turkey	Greece /Turkey
VIJOSE / AOOS	6.15	6.71	Greece, Albania	Albania
ISSER	6.12	31.60		Algeria
AKHELOOS	5.67	5.54	Greece	Greece
MANAVGAT	4.99	1.32	Turkey	Turkey
AXIOS	4.90	24.70	FYROM, Greece	Greece
BUVUK MENDERES	4.70	19.60	Turkey	Turkey
MATI	3.25	2.44	Albania	Albania
VOLTURNO	3.10	5.50	Albania	Albania
SEMANI	3.02	5.65	Albania	Albania
NAHRELASI	2.70	22.60	Turkey	Turkey
STRYMON	2.59	16.50	Bulgaria, Yugoslavia, FYROM, Greece	Greece
GOKSU	2.50	10.10	Turkey	Turkey
BRENTA	2.32	1.56	Italy	Italy
LAMAS	2.20		Turkey	Turkey
ARNO	2.10	8,228	Italy	Italy
SHKUMBINI	1.94	2,45	Albania	Albania
GEDIZ	1.87	15.62	Turkey	Turkey
PESCARA	1.70	3.10	Italy	Italy
KRKA	1.61	1.98		Croatia
MOULOUVA	1.58	51.00		Morocco
VAR	1.51	1.83	France	France
RENO	1.40	3.40	Italy	Italy
AUDE	1.31	1,794	France	France

Rivers	Qact Km^3/yr	Area 10^3 km^2	Passing through Countries	Outfall Country
CHELIFF	1.26	43.70		Algeria
JUCAR	1.26	21.60	Spain	Spain
ALIAKMON	1.17	9.50	Greece	Greece
NESTOS	1.03	5.74	Bulgaria, Greece	Greece
NILE	0.30	28.70	Burundi, Congo, Kenya, Rwanda, Sudan, Tanzania, Uganda, Eritrea, Ethiopia, Egypt	Egypt
LITANIS			Lebanon	Lebanon
ORODES			Lebanon, Syria, Turkey	Syria / Turkey

2.2 Chemical characteristics

2.2.1 *Organic pollution*

Although not completely documented, organic pollution is not a major problem in documented Mediterranean rivers. Po and Rhone rivers present a remarkable improvement during the last 15 years, but few small rivers are still heavily contaminated when BOD$_5$ are considered. Levels of DOC are generally quite low, due to low contribution of humic substances but level of POC may reach 25 mg/L and up, during major floods, although this material is derived from natural erosion.

Many small rivers can still be considered as highly polluted and their pollutants sources should be controlled as Qued Martil, the Besos and Kishon. Adige, Po, Ceyhan and Seyhan are still somewhat polluted. The Po River is now much less polluted than during the peak of pollution, which occurred in 1977-78.

2.2.2 *Nutrients*

Nutrient levels for the Mediterranean rivers are about 4 times less than in Western Europe rivers Some rare pristine levels can still be found on the Dalmatian coast and some islands, but most rivers are now impacted. Nitrate is increasing in all documented cases. Phosphate may increase dramatically (Greece), or steadily (France). In Italy a marked decrease is observed as the result of efficient P restriction measures (P ban in detergent). Although some local coastal eutrophication may occur, the main body of the Mediterranean as a whole is not yet seriously threatened with eutrophication over the last decades (Vollenweider, 1996). Ammonia levels have been decreased as a result of domestic and industrial waste collection and treatment.

The concentration range is enormous, over an order of magnitude for NO$_3$ and more for NH$_4$ and P0$_4$. Nutrients are water quality determinants most sensitive to human impacts. Ammonia is still very high in some rivers (Llobregat, Ter, Tet, Tevete) and levels in the Besos are extremely high, i.e. similar to those found in sewage effluent. Nitrate levels are much less (2 to 10 times) than those commonly found in Western European rivers.

2.2.3 *Heavy metals*

Mediterranean rivers are also less contaminated with heavy metals that most other Western European rivers. But this may be the result of dilution of urban and industrial sources by high levels of suspended solids in highly erosive environment. Metals are very much linked with particulates, which constitute the proper medium to be investigated. When

considering the growing storage of particulates in reservoirs it can be said that net metal fluxes to the Sea are actually decreasing even if trends of contamination of river basins are steady of deteriorating.

Budgets of heavy metal inputs from rivers to the Mediterranean are quite difficult to be set up. Many rivers are still unmonitored for particulate metals, or not adequately monitored, water inputs have been changed, sometimes drastically as for the Nile and river sediments including their attached load of metals are now retained behind reservoirs.

Some major points can be made: (i) most metal fluxes are still associated with particulate matter. (ii) reservoirs are probably storing much of the metals originating from human activities. (iii) due to this retention the net inputs to the Mediterranean Sea are stable for the cadmium, or may decrease (copper, lead, zinc). However the mercury inputs are increasing due to a major contamination of particulates for this metal.

2.2.4 *Organic micropollutants*

Organic micropollutants discharged by rivers are not correctly monitored in order to assess loads, even within orders of magnitude. This type of finding is not specific to the Mediterranean Basin. Contamination by industrial products is documented on great rivers (Po, Ebro, Rhone) for Polychlorinated Biphenyls, Poly aromatic Hydrocarbons, and solvents. Evidence of pesticide high concentrations (concentrations > 1mg/L) has been found in some specific studies, as in Greece, and is believed to occur in many small rivers with intensive agriculture but was not found during the Rhone pilot study. Type of pesticides found in rivers may greatly vary from one country to another and probably from one river to the next. The new pesticides generation (atrazine and others) are not much transported by rivers: only 0.2 to 3 % of the products applied to cultivated land are exported.

2.3 Microbiological characteristics

Bacterial contamination is a problem mainly in semi-enclosed bays, some of which still receive large amounts of untreated sewage Although little documented for the whole Basin, bacterial contamination ranges from none in few basins sparsely populated, to dramatic in some Southern rivers. In major Greek and Italian rivers the contamination is real although generally not severe. If the improvement noted for the Po river, which has variable levels of contamination along its course, is extrapolated to other Northern rivers, where sewage collection and treatment is known to have occurred in the last two decades, the bacterial contamination should not be any more a major problem in the Northern part of the Basin; but in the Southern part its actual status should be set up.

2.4 Physical characteristics

Mediterranean Rivers Physical characteristics are not seem to have significant impacts in much of the area of the sea environment. In enclosed bays or the estuaries thermal discharges could cause serious damage to the ecosystem while turbidity can affect in fish population.

Thermal pollution occurs, when river water is used as coolant in power plans or industries. The increasing amount of power produced by fossil fuel and nuclear power plants makes it pressing to establish the real impact of heated effluent discharge from power stations on the marine environment. River temperature monitoring along the river course will allow the detection of the portion of the original thermal load reaching the sea and how this affect on the sea thermal condition. It is also of great importance to figure out thermal power plans adjoin to rivers in order to determine the major rivers that receive thermal discharges.

Domestic waste discharges can cause turbidity while the major source is erosion. A measure of turbidity increment could be land cover changes detection such as deforestation. The kind of wastes, reaching each river, detection as well as turbidity monitoring in major river estuaries are also important tasks to evaluate the impacts to the sea environment.

Industrial wastes, color rivers water, affecting mostly the estuaries and also causing aesthetic diminution. The impact of water coloring to the sea environment is not correctly assessed. In order to assess these impacts, even within coarse lines a watercolor monitoring must be carried out as well as industrial wastes sources recording.

3. ORGANIZATION OF SAMPLE COLLECTION PROGRAMMES MONITORING AND SAMPLING TECHNIQUES

3.1 River monitoring strategy

River monitoring, as an effort to obtain information on the quality of water and sediment, always suffers from the lack of a clear information goal. With monitoring it must not just water and sediment quality being checked against some standard, but information on status and trends of a whole water body must be provided. Therefore, for the purpose, of this guideline, monitoring can be viewed as a sequence of related activities (a system), which, when all performed in an integrated manner, will produce the desired understanding of pollution of the whole river watershed. These related activities, in sequence, are:

- sampling the water and related factors to measure the physics, chemistry and microbiology of the surface water and sediments of the watershed
- measuring specific characteristics of the physical, chemical and microbiological samples in the field and in the laboratory
- entering and storing the resulting data into a computer data base for recalling later when enough observations have been collected to support data analysis
- analysing the stored data using statistical and/or modeling approaches
- writing a report (or preparing an oral presentation) in which the information gathered from the analysis is presented in easily understood formats
- information utilisation from the report or oral presentation for managerial purposes and decisions

In case the existing river sampling network is considered necessary for reviewing, the following steps have to be followed:

- start with the existing programme
- identify sites required for statutory purposes
- examine remaining sites and remove obvious redundant and anomalous locations
- examine remaining sites using a *statistical tool* and remove those that do not significantly contribute to overall information
- carry out further adjustments according to priority need to achieve guideline target change for region
- confirm National Monitoring Programme, draw up inventory of sites and costs

A tailor-made sample collection strategy for water, wastewater and sediment aims at:

- quality control
- making forecasts
- determination of the extent of pollution damage

Most tests fall within the framework of quality control, and are in most cases prescribed by legal regulations. For forecasts, data are determined for planning purposes or to recognise trends. This is important in the construction of sewage treatment plants, e.g. where future discharge of wastewater into bodies of surface water needs to be estimated. In estimating damage, the causes and extent of the damage due to pollution are considered important.

The most important prerequisite for proper sampling is the satisfactory qualification and training of the surveillance personnel, parallel with the representativeness and validity of the samples for the population to be tested. This means that they must be collected and stored in such a way that the parameters determined in the final sample correspond to the true values over the population of the water, wastewater and sediments. The location and time of sampling should be chosen in such a way that the samples reflect the temporal or local variance during the period of investigation.

Each sample collection campaign depends to a certain extent on chance and is therefore subject to an inherent error. The smaller the sample, the less representative it is of the population. In addition, the information contained in the result from a random sample depends on the variation of the particular parameter measured. In order to be able to generalize empirical results, the size of the random sample error must be known. This error is the difference between the parameter of a random sample (e.g. arithmetic mean) and the real value of the whole population. The size of the random sample error depends on the sample population. Above a certain number of samples error becomes so small that an increase in the number of samples can no longer be justified.

The variance in the overall analysis procedure (S_{total}), consisting of sampling, sample processing and analysis, is produced by addition of individual variances, according to the error propagation law: $S^2_{total} = S^2_{sampling} + S^2_{sample\ processing} + S^2_{analysis}$ (3.1)

With a sampling error of 25%, a processing error of 10% and an analysis error of 5%, the total error comes out to be 27%. If the processing and analysis errors are cut into half, the total error is only decreased by 2%. Therefore considering how representative the results of the analyses are, it can be seen that the accuracy of the laboratory measurement is of minor importance when the errors in sampling and processing are considerable higher that the errors in measurement. This reveals how important and sensitive is the procedure of sampling. An effective sampling strategy takes the following into consideration:

- statistical aspects of the work
- standardised instructions for sampling, labeling, transport and storage
- training of personnel in sampling techniques

Representative and valid samples can be taken according to the scheme presented in Table 3.1. The following sampling procedures are to be used:

- *Random sample:* An individual sample is taken manually at a specific time, describing therefore the water status at this very moment only
- *Qualified random sample:* This is a variant of the random sample where at least five random samples are taken at intervals of not less than 2 min, over a maximum total period of 2 h and then combined to give a *pooled sample*
- *Time-dependent sample:* In the chosen sampling period, samples of the same size are taken at the same time intervals and are combined to produce a pooled sample. The result obtained is thus strongly dependent on changes in flow and pollution level of the water
- *Volume-dependent sample:* At this case, constant volumes are taken at variable time intervals determined by the volume of flow and are combined to give a pooled

sample. If there are large variations in both the pollution level and flow (small discharges), this sampling procedure should not be chosen

▪ *Flow-dependent sample:* Samples are taken at uniform time intervals, which are of different sizes depending on the flow at that particular moment, and are combined to create a pooled sample. This type of sampling hands over exact results even if high
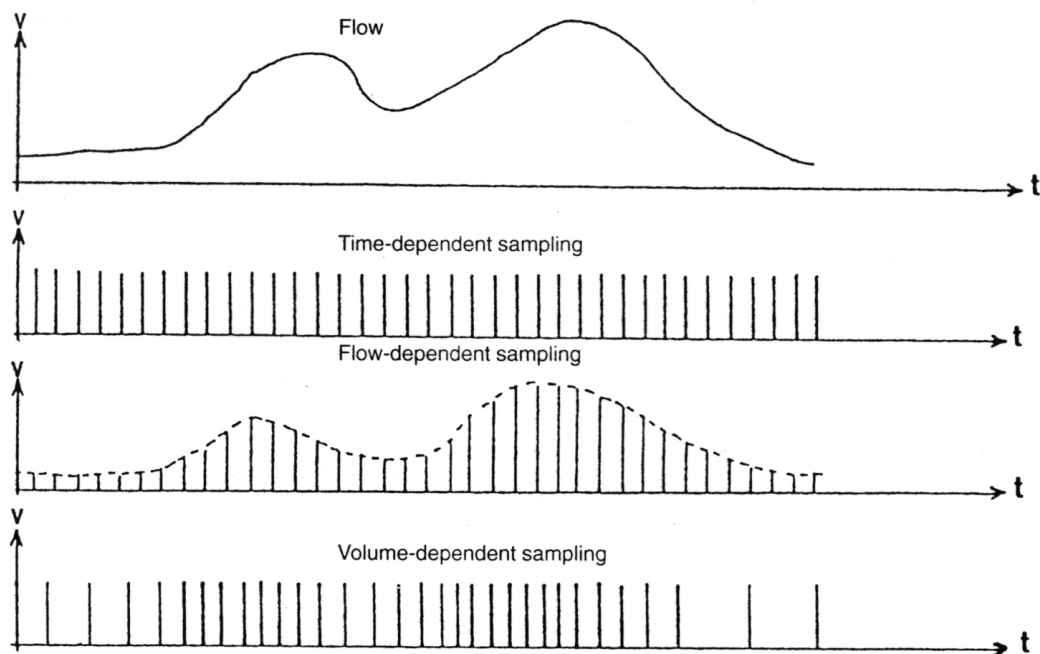
variations in flow and pollution levels are observed

▪ *Incident-dependent sample:* Every time exceeded threshold values needs to be documented, this kind of sampling has to be employed. Sampling only takes place when an incident has occurred; otherwise the sampler is only on stand-by. All continuously measurable parameters can be used to initiate sampling if a given measurement signal is exceeded

▪ *Time-, flow and incident sample:* This type of sampling is the most versatile combination of the different techniques. The priorities can be laid down e.g. in the following: incident-dependent, quality-dependent, time-dependent. The process produces considerable demands on the sampling instrument and its control. A single instrument can deal with several tasks simultaneously, e.g., continuous monitoring of a body of water (time- and volume-dependent sampling) at the same time as responding to incidents or faults (incident-dependent sampling).

Figure 3.1: Graphical presentation of possible techniques for sampling of water and wastewater.

Table 3.1: A preliminary procedure for choosing a sampling method for water and wastewater

Concentration fluctuation	Small	Flow variation Large
Small	(Qualified) random sample	(Qualified) random sample
Large	Time – dependent pooled sample	Volume – or flow-dependent pooled sample

Volume- or flow– dependent pooled samples can also be prepared manually afterwards, by combining several random samples comprising of various quantities of water (flow measurements necessary). Table 3.2 presents an example.

Table 3.2: Calculation example of a manually collected quantity-dependent pooled sample

Time	Momentary flow (m³/sec)	Proportion of random sample in the pooled sample (l)
8	1	0.1
9	2	0.2
10	1.5	0.15
11	4	0.4
12	0.5	0.05
13	1	0.1
14	2	0.2
15	1.5	0.15
16	0.5	0.05
	Σ	1,41

With sediments, there is the danger that because of the granular nature of individual fractions, proportions are determined which are either too large or too small. The sample error S_s for a measured parameter is given as follows:

$$Ss = [(1-x)/x]^. (m/m_s) \qquad (3.2)$$

where: x content of component 1, m average mass of a particle and m_s mass of the sample.

The sampling error increases as the content of x decreases, with decreasing sampling area and with the increasing average mass of a particle. By increasing the number of samples, the total error will decrease more sharply than by making a larger number of parallel measurements. The conditions become more complex with mixtures of components with more than two different particle sizes.

3.2 Organisation of sampling networks

For the organisation of sampling networks, planning is very important including preliminary tests. The planning has to be carried out carefully, as the network will have to be used for a long period and subsequent future modifications will lead to difficulties in comparing analytical data. Since larger catchment areas or drainage systems of larger cities consist of individual, and in most cases of heterogeneous subsystems, measuring networks and sampling points must be planned taking this into consideration. Special attention must be paid also to favourable transport connections and ease accessibility to sampling points independent of the weather conditions. Area photographs topographic maps and thematic maps have to be used in every field survey.

3.2.1 *Point source monitoring*

Where samples of contaminated ground water are to be taken (effluent stream), there should be at least two measuring points. The first should be in the ground water exit stream of the contamination source. The distance of this point from the contamination should be <10% of the flow distance of the ground water below the source. The second measuring

point is in the feed channel of the contamination.. This distance from the to the contamination should be ca. 50% of flow distance of the ground water below the source of contamination. The connecting line between the two measurement points should be perpendicular to the actual ground water level. In order to examine the extent of pollution caused by old waste deposits more accurately, a sealed sampling network must be set up downstream. It is a good idea to set up measurement points perpendicular to the direction of ground water flow at regular intervals of not more than 50 m.

3.2.2 *Non point and storm water monitoring*

For non point (river systems) and storm water monitoring partial catchment areas must sometimes be taken into account when planning sampling networks (Fig. 3.2).

Figure 3.2: Catchment area of a river system for non point monitoring.

Here the total area can be divided into five sections, whose water quality is determined at a particular measurement point. Depending on the requirement, a further subdivision can be made. Critical areas in larger rivers systems lie below the junctions with strongly polluted tributaries and large wastewater inflow points. In addition, less contaminated places should also be included in order to determine the natural composition of the water. Measurement points are often set up in rivers on both sides of a political border to resolve conflicts regarding water use. Generally one sampling point for every area of 100 to 200 km^2 is sufficient, except in industrial areas where more are required. A section of the catchment area of a body of water is shown in Fig. 3.3. Measurement points at which possible changes in water quality might be expected are shown as circles. Populated areas have been shaded and wastewater entry points (including entries of storm water) are marked by arrows. In addition to the major measurement points, regular checks can also be made at these entry points.
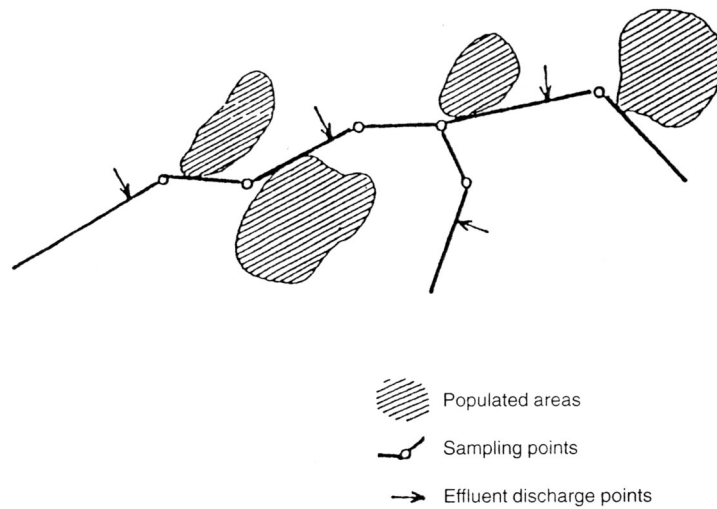
Populated areas

Sampling points

Effluent discharge points

Figure 3.3: Schematic Part of a river system with effluent discharge points including storm water.

Figure 3.4 is a schematic representation of a network for wastewater disposal in towns. It contains the street channels, collectors, main collector, collection shaft, overflow chamber and overflow channels as well as the sewage plant with an outlet into the body of water. Measurement points in the drainage system should be set up where individual industrial plants discharge wastewater into the network, where main collectors meet and at sewage plant outlets. If a discharge of pollutants is suspected, the guilty party can be traced along his branch of the network. Sampling points in large rivers or water channels should be located such that waters entering above the sampling points are completely mixed. If this is not the case two sampling points can be positioned, one on each side of the waterway. Figure 3.5 shows how the mixing of waters from tributaries and wastewater inlets is very slow when there is laminar flow. Here a permanent sampling point should not be placed before position 5.
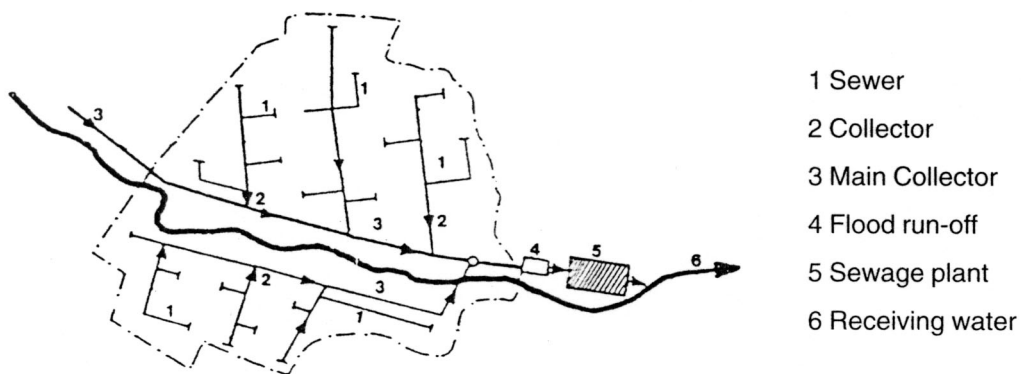

1 Sewer
2 Collector
3 Main Collector
4 Flood run-off
5 Sewage plant
6 Receiving water

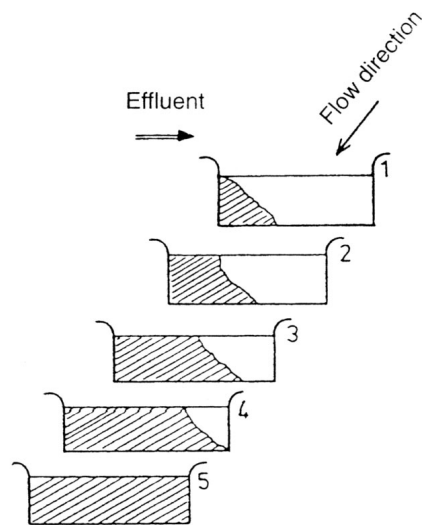**Figure 3.4: Scheme of a sewage network**

Figure 3.5: A presentation of effluent mixing in flowing water systems

In addition to the choice of a representative spatial sampling network, the choice of a suitable sampling timetable is also important. If concentration fluctuations are high, samples are taken more frequently, but if they are low, sampling at intervals of a few months can be sufficient for an assessment. Where cyclic variations in days, months or years are known, the sampling interval must be made more flexible in order to avoid repeated measurement of a high or low value (Fig. 3.6).
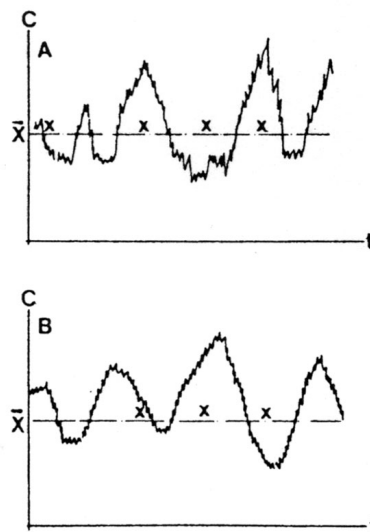

Fig. 3.6: Effect of concentration fluctuations on values predicted from random samples.

After a longer period, the most important statistical parameters, such as mean values, extreme values, variances and correlations should be calculated. Cyclic concentration fluctuations can easily be detected graphically. The sampling frequency can then often be decreased without loss of important information.

3.3 Determination of sample quantities

As stated in detail in chapter 4, the quantity for 1 liter of liquid is sufficient for water or wastewater samples and 1 kgr of solid sample for sediments.

3.4 Sampling devices

For Surface water and wastewater, buckets are used as manual devices for the sampling of water from or near the surface and seeable ladling devices (Ruttner buckets) for deeper layers. Automatic sampling devices are mainly used for water and consist of the following parts:

- Delivery system
- Control mechanism
- Sample apportionment and metering
- Sample storage

Delivery is accomplished using hose pumps or eccentric screw pumps. A system with a free falling water device is shown schematically in Fig. 3.7. In this way a sample is diverted from a continuous water stream using an impulse circuit (time – or quantity – dependent) so that a partial sample can be taken. This type of sampler is easy to use and clean. A cooling unit should be incorporated for longer sampling periods. Figure 3.8 shows the sampling phase of a system within a free- falling water device coupled with a constant sample feed device. In this way, a constant sample volume is always obtained. Highly contaminated wastewater can lead to blockage of the feeding container. Short-scaled pipes, high delivery velocities, and elimination of light are required to minimize changes in the nature of the sample. Regular cleaning and maintenance avoid deposit formation and ensure the reliability of the system.

Lifting   Feeding   Lifting
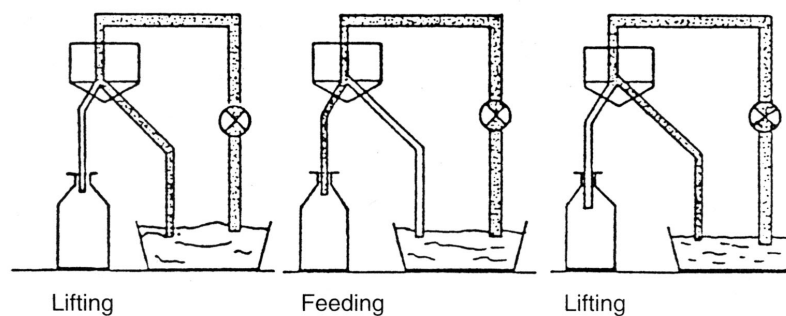
Figure 3.7: Schematic representation of an automatic free – fall sample

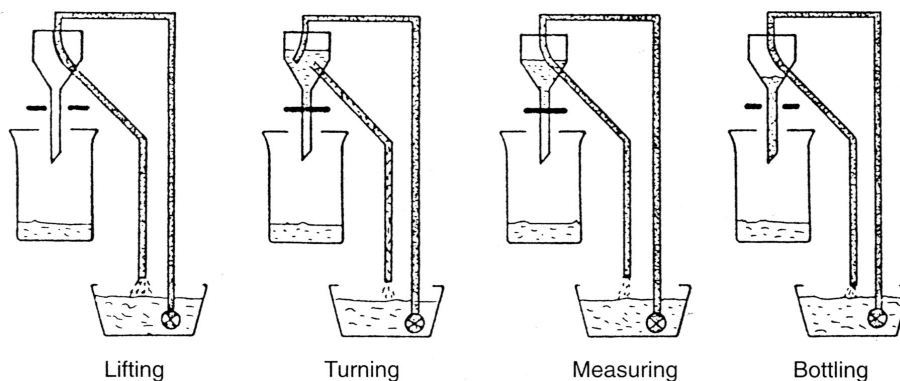Lifting   Turning   Measuring   Bottling

Figure 3.8: Schematic representation of an automatic free-fall sampler coupled with a fixed quantity-feeding device

Sediment and suspended matter is normally collected with water samples such as the Van Dorn, Ruttner, Kemmerer, or Friedinger samplers (Golterman et al., 1978). These have an open tube of one to three capacity with a higher lid at each and. The lids may be closed by a messenger. The Ruttner tube is made of Perspex (- plexiglass), while the Kemmerer is made of cooper. The Friedinger is similar to the Ruttner and Kemmerer types, but its lids are held open at 90 º parallel to the axis of the sampler, and do not seriously impede water flow. Another method makes use of pump samplers. In these types, weighed rubber or plastic tube is lowered to the desired depth and a pump sucks up a continuous stream of water with which the water sampler is first rinsed and then filled. Bottom deposits usually a depth of 0,5 to 1 m can be also sampled by grab samplers or dredges, such as the Ekman or Petersen dredge (Fig. 3.9).
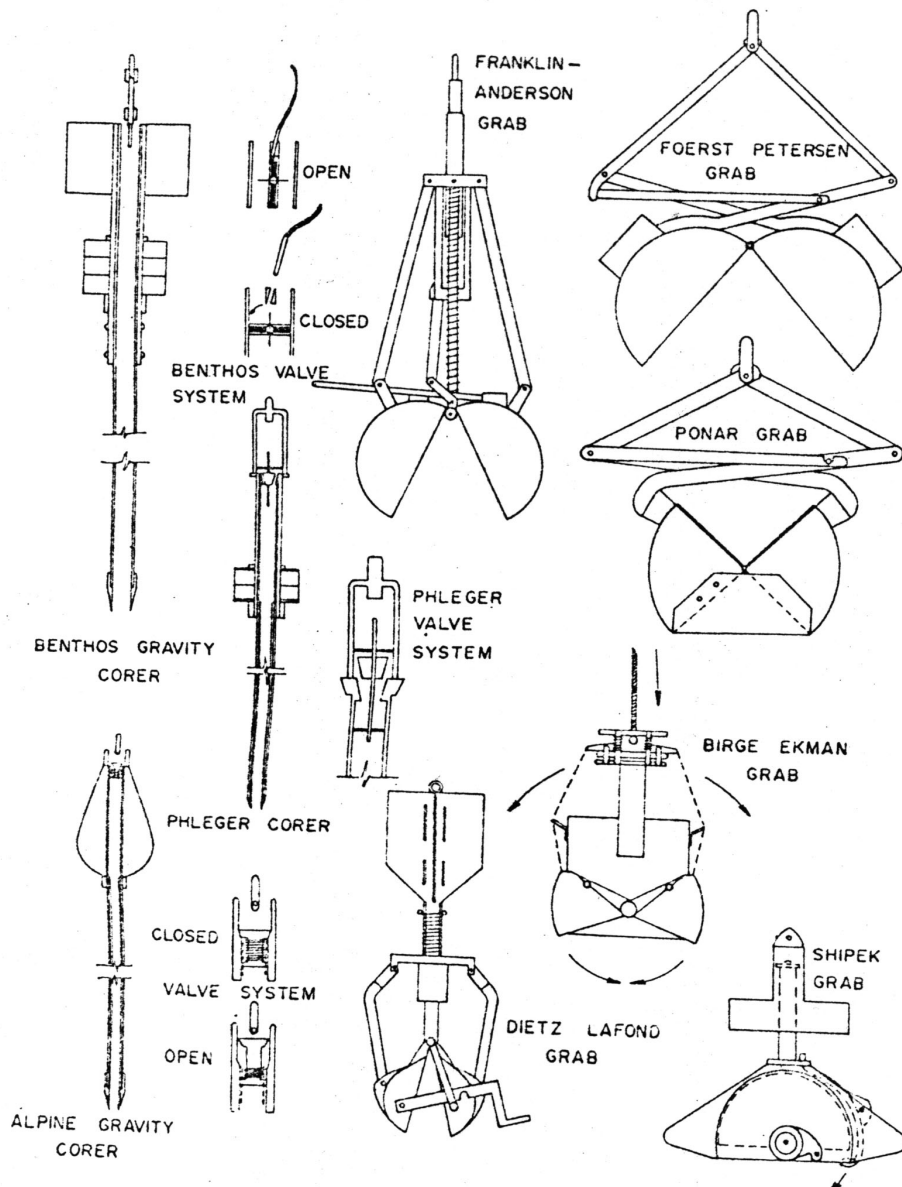

Figure 3.9: Miscellaneous bottom sediment samples.

3.5 Preservation, transport and storage of samples

The contents of water samples can alter at different rates. As only a few parameters can be measured during collection, pretreatment or stabilization is often necessary. This allows tests to be carried out even after long periods of time have elapsed. Most inorganic components do not require additional measures for transport and storage, but some can undergo changes, for example through reduction, oxidation or precipitation. If the sample contains organic material and there are favourable conditions for the development of micro-organisms, rapid changes often occur. In these cases stabilization is necessary. This is defined as blocking or delay of biochemical processes whereby the difference in content between the original and preserved sample should be less than 10%. Water and wastewater samples are cooled during transport and storage, particularly at high external temperatures, as otherwise the rate of biochemical processes increases. Reactions generally take place in waste and surface water samples more quickly than in ground or drinking water samples.

The following changes are possible:

- oxidation of components by dissolved oxygen (e.g. Fe^{2+}, S^{2-}),
- precipitation and coprecipitation of inorganics through changes in the medium (calcium carbonate, metal hydroxides)
- adsorption of dissolved trace components on the container walls,
- Changes in parameters as a result of microbiological activity (pH value, oxygen, carbon dioxide, biochemical oxygen demand, trace organics).

Some suitable preservation methods are listed in Table 3.3.

Table 3.3: Preservation of substances present in water

Parameter	Preservation	Maximum storage time
Trace metals	5 ml HNO_3 per l	Several weeks
DOC, TOC, COD, BOD_5	Cooling at 4° C or freezing at - 18° C	One day or several weeks respectively
NH_4, total N	5 ml HNO_3 per l	A few days
Hg	2 ml $HNO_3/K_2Cr_2O_7$ solution per l (0,5 g $K_2Cr_2O_7$ in 100 ml 30% HNO_3)	A few days
Cyanides	Basify to pH =8	1 day
Fe(II)	Addition of 2,2' - bipyridine	1 day
S^{2-}	2 ml 10% Zn acetate solution per l	1 week
Phenols	5 ml $CuSO_4 \cdot 5H_2O$ per 1	1 week

The methods are only recommendations. Usually examination immediately after sampling makes preservation unnecessary. Particularly with relatively pure water, cooling to 4 ° C is sufficient even for longer storage periods. If wastewater has to be tested for COD or BOD_5 only after a long storage period, it can be frozen at ca. - 18° C in plastic bottles. Rapid freezing and thawing are important. Soil samples should be dried as quickly as possible, provided that tests in the original state are not necessary. For the testing of nitrate, the sample should be cooled during transport and then frozen in a plastic bag at - 18° C.

Concerning sediment samples freeze-drying provides a relatively quick and simple means of sample preparation for long-term storage. Wet sample materials are placed in special glass containers, which are partially immersed in a bath of freezer coolant and quickly cooled to about - 40ºC. Although the samples can be frozen in dry ice in ordinary

vacuum flasks, it is best to use shell freezers, in which the special glass containers are rotated as they freeze. This has the effect of coating frozen sediment over most of the inner surface of the glass containers and provides a more easily dried sample. After freezing, the glass containers are connected to a source of high vacuum and the samples are dried as the ice is lost in vapour form under the vacuum. This technique leaves a clean dry powder which is ready to be stored in clean dry vials. Properly sealed vials (to exclude moisture) can be stored for many years without significant degradation of the sample material. The technique is not suitable for the preservation of volatile compounds or gases dissolved in the interstitial waters, and analyses must be completed on these components before treatment by freeze-drying. Particle size analyses should also be completed before freeze-drying.

3.6 Sample collection procedure

3.6.1 *Surface water*

The collection of surface water samples normally presents no serious technical difficulties. The choice of sampling technique depends on the reason for and the goals of the test. Samples, which are taken after pollution incidents or for quality control, are usually random samples. For further information on water quality longer series of samples are necessary, which can be taken manually or preferably with automatic samplers. For still bodies or water or slow flowing rivers the collection of depth –or area-integrated samples is a good idea. This involves continuous (pump) or discontinuous (buckets) removal of individual samples at various depths and locations. Sometimes individual samples are combined to give average samples. The determination of positions of sampling points on the water used to be more expensive than it is now because easy to handle and cost – effective GPS (global positioning satellite) devices are available.

For surface water which is used as crude water for the preparation of drinking water, the frequency of sampling and testing is regulated by the EC guideline 79/869 and supplements to it referring to individual European states. In principle the minimum frequency is greater than larger the quantity of water to be prepared for drinking and the number of inhabitant to be served. The frequency must also increase if the risk to health is increased by a lowering of crude water quality. If smaller quantities of water are used, up to 3 sampling a year are sufficient. For larger quantities and decreased crude water quality, at least 12 are required.

To collect samples, a bucket or sample bottle is simply dipped into the water. In flowing waters the container movement should be against the stream. Here the proximity of still water zones by the bank and stretches of fast running turbulent water often leads to concentration gradients in the content of oxygen and suspended particles. Also a river is not completely mixed below wastewater entry points or the joining of tributaries. During the filling of bottles stoppers or lids should be put down in a clean place. On sampling at bridges attention should be paid to the possibility of Whirlpools near the supports affecting the water quality. Samples for bacteriological examination are collected by dipping the sterile container into the water with the opening against the current. In still water the container is pushed through the water in such a way that the hands has no contact with the water in front of the opening.

3.6.2 *Wastewater (effluents)*

The representative collection of crude water samples with their variable quantities of suspended materials presents problems, especially where automatic devices are employed. Therefore, either exact determination of the solids is dispensed with, or pooled samples are prepared from representative random samples. Where organic substances from a separate phase, only manual sample collecting can be used.

The sampling of purified wastewater is, however, relatively easy and is similar to that of surface water. Random or average samples can be collected either manually or automatically. Modern automatic sampling devices usually permit the programming of different sampling methods and are therefore flexible to use.

Official monitoring of wastewater requires a qualified random sample and a two-hourly pooled sample for assessment according to the laws governing water and, in particular, waste disposal. Furthermore, the regulations concerning the location and frequency of wastewater sampling depend on size and technology used in the sewage treatment plant. For manual sampling 15 min pooled samples from several random samples are usually sufficient. For quality assurance two – hourly or daily-pooled samples are usually combined. To avoid dividing samples in the laboratory, several bottles are usually filled if possible.

High-polluted water leaking from waste dumps is normally collected from waste shafts or drainage pipes. This water should flow for a longer period through a glass funnel into the overflowing collecting bottle so that the effect of the surrounding air is lowered. If the drainage pipes from a dump open into wastewater channels, an automatic sampler can be used to collect time –or flow-dependent individual samples, which can then be pooled.

For representative sampling from wastewater pipes with continuous turbulent flow a sampling tube is held in the middle of the main stream. In case of laminar flow or strongly fluctuating flow rates a perforated tube is placed in the cross section of the pipe and water is collected manually by opening a valve.

Particular attention should be paid to the hygienic problems involved with wastewater sampling.

3.6.3 *Sediments*

The soil sample must be representative of the whole area to be examined. This requirement is not easy to satisfy even on mixing many individual samples, because spatial heterogeneity can be much more extreme than in case of water. For collection a random distribution of sampling points would be ideal, but in relatively homogeneous sediment pooled samples of almost equally good quality can be obtained with less effort by reducing the sampling area. Suitable sampling methods are illustrated in Fig. 3.10
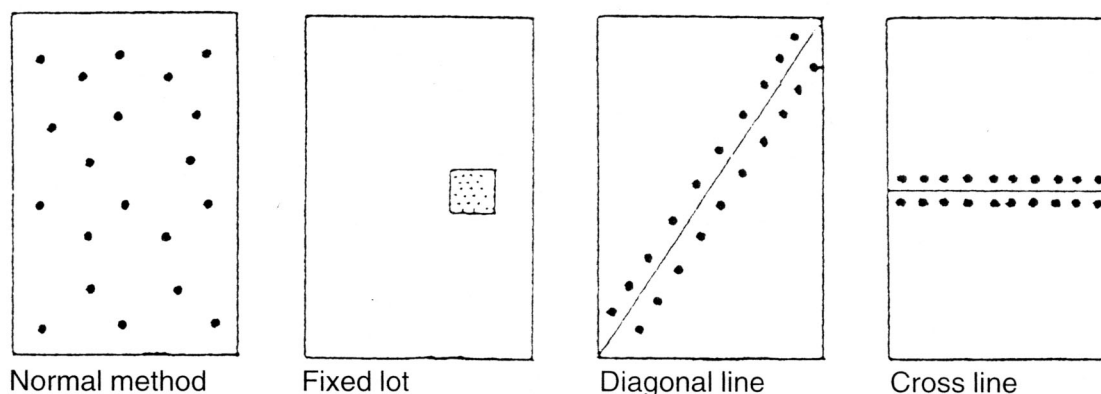
Figure 3.10: Sampling of sediments

3.7 Measurements of chemical, physical and biological parameters

In this chapter are presented the physical, chemical and biological parameters that have to be monitored. It is obvious that the above-mentioned parameters as well as the methodologies that will be applied must be agreed by the stakeholders in order for the results to be comparable and compatible.

Suggestively, the most usual sampling and measurement methodology for each of the above-mentioned quality parameters monitoring are given, as an example for the reader to have an illustration off the whole work.

3.7.1   Water and wastewater

3.7.1.1 Field measurements

The definitude of test results depends to a large extent on the completeness of the information collected in the field, in addition to sample collecting itself. A check list makes measurements easier and avoid subsequent time – consuming work. The results of field measurements of rapidly changing parameters are an important part of necessary information.

A checklist makes subsequent processing of information easier, particularly when sampling and measuring conditions are difficult. The list shown in Table 3.4 is not necessary complete but it acts as memory aid for planning the work. The data obtained are entered into the sample collection report.

Table 3.4: Check List for sampling and inspection

Parameter	Ground water	Surface water	Drinking water	Waste water	Soil
Sampling location (O,M)	x	x	x	x	x
Entry of co-ordinates (C)	x	x	x	x	x
Geological conditions (C,O)	x	x			x
Catchment area (O)	(x)	x	x	x	
Surface structure (O)	x	x		x	x
Soil use, vegetation (O)	x	x	x	x	x
Flow velocity (O,M)	(x)	x	x	x	
Outlet, flow (O,M)		x	x	x	
Sedimentation (O,M)		x		x	

Parameter	Ground water	Surface water	Drinking water	Waste water	Soil
Description of bodies of water (O)					
- *Discharge point /effluent inlet*		x		x	
- *Organisms*	x	x	x	x	
- *Eutrophication*		x			
- *Visible contamination*	x	x	x	x	
- *Type of spring or well*	x	x			
- *Sings of corrosion*	x	x	x	x	
- *Gas evolution*	x	x		x	
Soil description (O)					
- *Colour*					x
- *Nature*					x
- *Type*					x
- *Compression*					x
- *Root penetration*					x
- *Humidity*					x
Measurements (M,O)					
- Air temperature	x	x		x	
- Air pressure	x	x		x	
- Colour, odour	x	x	x	x	x
- Taste	(x)		(x)		
- Turbidity	x	x	x	x	
- Visible depth		x		x	
- Sedimentable materials	x	x		x	
- Precipitation	x	x	x	x	
- pH value	x	x	x	x	x
- Redox potential	x	x	x	x	
- Electrical conductivity	x	x	x	x	x
- Oxygen	x	x	x		
- Chloride			x		
- Carbon Dioxide	x		x		
- Agression	x	(x)	x	(x)	

M = measurement

O = observation

C = chart

3.7.1.1.1   Organoleptic Examination

The organoleptic examination should take place during sampling because changes in the sample can occur during transport and storage. This test includes odour, taste, transparency, turbidity, and coloration. Soil samples should be tested for odour, colour and consistency on rubbing the moist sample between the fingers.

The *odour* is tested immediately after sampling. Odour strengths and types may be designated as follows:

Odour strength: very weak, weak, clear, strong and very strong,

Odour type: earthy, mossy, peaty, musty, putrid, reminiscent of manure, fisfy, aromatic, or characteristic of a particular substance.

The qualitative test involves smelling a half-filled, previously shaken bottle.

The *colour* can be tested by viewing the sample in daylight. The designation is as follows: colourless, very weakly coloured, weakly coloured and strongly coloured. The corresponding colour tone is also given.

The examination of *taste* is only carried out when it is certain that no infectious bacteria or polluting substances are present. Taste sensations can be designed as follows: tasteless, salty, bitter, alkaline, sour, astringent, metallic, repulsive. The degrees of taste may be differentiated by the terms weak, clear and strong.

The *visible depth* of water is defined as the depth at which a white disc let down with a line or pole into the water is just visible. Down to 1 m the values are given in cm intervals, at more than 1 m, 10 cm intervals.

The simple test of *turbidity* involves filling a clean 1 l glass container about two thirds full with the water sample, shaking well and comparing against a black and then a white background. The following degrees of turbidity are determined: clear, opalescent, weakly turbid, strongly turbid, opaque.

3.7.1.1.2   *Physicochemical parameters*

a.   Temperature

b.   Sedimentable Material

Sedimentable material can be found in some surface water and in untreated wastewater. The determination should be carried out in the field immediately after sampling to avoid errors through flocculation. The method is suitable for the determination of sedimentable material above 0,1 ml/l.

c.   pH Value

The pH value is the negative logarithm to base 10 of the hydrogen ion activity (mol/l) and is the 7,0 in pure water (neutral point). This value changes in the presence of acids and alkalis and through the hydrolysis of certain salts. Strong bases and weak acids raise or lower it. Acidification of soil can be due to hydrolysis of iron or aluminium salts or by the formation of humic acid during the degradation of organic matter.

In natural water the pH is usually between 6,5 and 8,5. The presence of free carbon dioxide or humus lowers the pH. Biogenic decalcification in surface water, which occurs when there is high CO_2 depletion by algae, can cause the pH to rise to ca. 10.

d.   Redox Potential

Like pH values, redox potential control many chemical processes in water. In bodies of water and wastewater anaerobic processes are characterized by low redox potentials. Oxygen enters the surface or still water by diffusion. This creates an aerobic environment in the upper water layer, while as a result of poor mixing there can be an anaerobic environment in the lower layers or in the sediment. The redox potential measures the competing processes of electron donation (reduction) and acceptance (oxidation).

e.   Electrical Conductivity

The electrical conductivity is a total parameter for dissolved, dissociated substances. The results do not give any information on the nature of the ions. The concentration of dissolved electrolyte can be calculated from the conductivity when the ionic composition and

equivalent conductivities are known. In sediment examinations conductivity provides information on the proportion of soluble salts and thus on the suitability of the sediment for agricultural use.

f.   Oxygen

Oxygen is essential for the survival of most organisms in water. This also applies to the metabolic pathways of aerobic bacteria and other micro-organisms, which are responsible for the degradation of pollutants in water and utilize oxygen as an electron acceptor for this purpose. Oxygen reaches the water via surface diffusion and by photosynthesis in algae and submerged plants. When plant growth is prolific, as with the recent algae blooms, supersaturation by oxygen can occur. In drinking water oxygen concentration of at least 4 mg/l is necessary to prevent corrosion of the carrier pipes. Oxygen can be determined amperometrically or titrimetrically using the modified Winkler method.

g.   Chlorine

Chlorine is used as a disinfectant for the treatment of drinking water, bathing water and, in special cases, also for wastewater. Chlorine in the form of dissolved elemental chlorine, hypochlorous acid and hypochlorite ions is known as free chlorine. Chlorine compounds which are formed by reaction of hydrochlorite ions with ammonium or organic compounds containing amino groups are known as bound chlorine. Both together are known as active chlorine, free chlorine being the stronger oxidizing agent. Active chlorine should be determined at each stage of drinking water treatment, both in the mains and at the point of and at the point of consumption to guarantee bacteriologically impeccable water. 0,2 to 0,5 mg/l active chlorine should be present in drinking water. A field method using a comparison and the titrimetric DPD method (N,N-diethyl-p-phenylenediamine, $C_{10}H_{16}N$) are described below.

3.7.1.2 Laboratory measurements

Water and wastewater samples generally require a very careful collection and processing of water. It is generally desirable to carry out analyses as soon as possible after sample collection, in order to avoid falsifications of results. In some samples heavy metals can be complexed to humic substances in varying degrees. In these cases it is recommended that nitric acid or a nitric acid – hydrochloric acid mixture (3:1) added to the sample. It should then be carefully evaporated to a smaller volume to break down these complexes. This also allows the detection limit to be lowered, provided that matrix problems related to increased salt concentration do not arise. Metals adsorbed on *to suspended particles* are usually oxidised and brought into solution by this type of pretreatment. It should be stated whether the sample was tasted in the original state or homogenized, *sedimented*, centrifuged or filtered. A magnetic stirrer has to be used for homogenization of the sample.

In this guideline the 23 chemical parameters whose analytical methods described in a synoptic form in this paragraph are recommended for measurement.

3.7.1.2.1   Chemical Analytical Methods

a.   Adsorbable Organic Halogen Compounds (AOX)

Chlorinated hydrocarbons are the most important organohalogen compound. In wastewater, particularly that of industrial origin, concentrations of > 1 mg/l are not uncommon. Certain organhalogen compounds are discharges directly into bodies of water or wastewater. The analytical method is based on the adsorption of organohalogen compounds on activated charcoal.

b.   Ammonium

Ammonium ions can be formed in water and sediment both by microbiological degradation of nitrogen containing organic compounds and by nitrate reduction under defined conditions. Considerable ammonium concentrations of up to 50 mg/l are present in household wastewater and very high concentrations of up to 1000 mg/l in water seeping from waste dumps

c.   Biochemical Oxygen Demand

For the BOD_5 measurement is used a reaction time of 5 days. In the dilution method the sample is treated with oxygen – saturated water. Manometric measuring systems are commercially available and give useful results. It is not permissible to convert results obtained for a particular incubation period into results for other lengths of time except with considerable limitations.

d.   Calcium and Magnesium

Calcium and magnesium ions are in all natural water and are often cited as cause of hardness. Both elements can be determined with the complexometric method.

e.   Chloride

Chloride is present in all natural waters at greatly varying concentrations, depending on the geochemical conditions. Particularly high concentrations occur in water near salt deposits. Large amounts of chloride reach wastewater thought faecal discharge. The volumetric determination with silver nitrate using potassium chromate as the end point indicator.

f.   Chromate

As salts of chromic acid (H_2CrO_4), chromates are important industrial chemicals. On acidification of chromate – containing solutions dischromates are first formed and under strongly acidic conditions, polychromates. The analysis is based on DIN 38 405, part 24. It can be used to determine Cr(VI) concentrations of up to 3 mg/l. The procedure involves the oxidation of 1,5 – diphenylcarbazide to 1,5 –diphenylcarbazone, which forms a red dye complex with chromium.

g.   Cyanides

Cyanides are used in some industrial and manufacturing processes and are liberated. They can reach wastewater or bodies of water as a result of incidents. The presence of cyanides in groundwater, surface water and drinking water indicates a discharge of wastewater or seepage from a dump and should always be followed up with an investigation and remedial measures. In crude water for drinking water processing and in drinking water itself, cyanide concentrations may not exceed 0,05 mg/l.

h.   Iron

Under anaerobic conditions the content of Fe^{2+} can be several mg/l, particularly in groundwater and wastewater, while in most aerobic surface waters the concentration seldom exceeds 0,3 mg/l. Fe^{2+} ions are oxidized fairly rapidly by atmosphere oxygen. First yellow – brown colloidal iron(III) hydroxide is formed, which then precipitates as the brown hydroxide. Iron is an undesirable component of drinking and industrial water because iron hydroxide can form deposits in pipes and cause problems in usage at higher concentrations.

i.   Fluoride

Fluorides can occur in wastewater from the aluminium, ceramics, glass, enamel and semiconductor manufacturing industries. Increased fluoride concentrations can be present in some groundwater as a result of geology of the area. Its use as drinking water can lead to fluorosis.

j.   Dissolved Organic Carbon (DOC)

DOC is the dissolved part present in the sample. In addition water usually contains carbonates, which is either removed before the determination or determined separately and subtracted from the total carbon determined.

k.   Potassium

The concentration of potassium in natural water seldom exceeds 20 mg/l whereas in some wastewater and especially seepage from waste dumps, very high concentrations can be found, even exceeding the sodium level.

l.   Silicic Acid

Silicon occurs in all rocks and sediments. Silicon compounds, such as silicic acid, can be dissolved from these materials by weathering processes and thus reach the water cycle. Silicic acid can be found in dissolved, colloidal or suspended form and it is only stable for a short period at pH 3,2. Otherwise it is transformed by dehydration into orthosilic acid, then into polysilicic acid and finally into metasilicic acid. Its solubility decreases with increasing molecular size and degree of dehydration.

m.   Hydrocarbons

Contamination by hydrocarbons can occur in surface water and wastewater and, after certain pollution incidents, also in ground water. According to DIN 38409 a distinction has conventionally been made between the following: a) Involatile lipophilic substances with boiling point >250º C, b) All substances which can be extracted into 1,1,2-trichlorotrifluoroethane ($C_2Cl_3F_3$) and which remain after removal of polar materials, c) All substances which can be extracted into 1,1,2-trichlorotrifluoroethane and which can be separated directly by gravity. The procedures generally do not give any information on defined component classes or individual compounds.

n.   Copper

In natural unaffected waters the concentration of copper does not exceed a few µm/l. In bodies of water contaminated with cooper, concentrations of 0,1 to 0,2 mg/l can be toxic to lower water organisms. Higher concentrations in drinking water are generally a result of corrosion of cooper pipes.

o.   Sodium

Sodium is one of the major components of many natural waters with high concentrations in domestic wastewater, some industrial wastewater, seepage water from waste dumps and in sea water. Detectable concentrations are also found in rainwater, depending on the distance from the coast. In sediments in arid regions the content of sodium ions plays an important role in the problem of oversalting.

p.   Nitrate

Nitrate is found in many natural waters at concentrations of between 1 and 10 mg/l. Higher concentrations often indicate the effects of nitrogen – containing fertilizers since the nitrate ions is only poorly adsorbed in soil and easily reaches the ground water. Nitrate concentrations are found in outflows from modern sewage plants because ammonium nitrogen is partially or completely nitrified microbiologically. However nitrate concentrations in untreated wastewater are low.

q.   Phenol Index

Phenols are found in small quantities in natural waters because, as components of plants, they are liberated during degradation and humification processes. Certain types of untreated industrial wastewater contain considerable phenol concentrations. The toxicity of phenols depends on the nature and arrangement of functional groups in the molecule.

r.   Phosphorus Compounds

Natural unaffected waters mostly contain total phosphorus at concentrations of less than 0,1 mg/l. Contaminated surface water, however, contains higher phosphorus concentrations caused by the discharge of wastewater and the washing out of fertilizer residues used of fields. Too much phosphorus in still bodies of water often leads to eutrophication, lowering of the oxygen concentration and problems in water treatment. Phosphorus compounds are adsorbed on to soil particles to such an extent that the danger of seepage into the deeper layers or even into the ground water is relatively slight.

s.   Sludge Volume and Sludge Index

Sludge volume and sludge index are two important parameters for the characterisation of sewage sludge, predominantly activated sludge. The sludge volume is defined as the volume in ml of the sludge – water mixture in the activating basin of a sewage plant, after a sedimentation time of 30 min.

t.   Heavy Metals by Atomic Absorption Spectrometry (AAS)

Heavy metals are usually present in water and soil in very small concentrations as a result of contact with certain minerals. Through human activity the concentrations can increase considerably, giving rise to toxic effects on organisms. Regulations for the protection of bodies of water and soil therefore always contain threshold values for heavy metals.

u.   Sulfate

Sulfate ions occur in natural unaffected waters at contaminations of up to 50 mg/l though concentrations of up to more than 1000 mg/l or more can be found in water in contact with certain geological formations. In anaerobic groundwater aquifers the concentrations are

usually low while those of hydrogen sulfide are higher as a result of sulfate reduction. Contaminated bodies of water and wastewater normally have high sulfate concentrations, usually as a result of industrial discharges, waste dumps or fertilizers.

v.   Surfactants

Surfactants are synthetic surface – active substances, which generally consist of mixture of isomeric or homologous individual compounds. The surfactant molecule always has one or more hydrophobic and hydrophilic groups. The former give the molecule its surface – active properties and the later a degree of water – solubility. Depending on the nature of ion formation, one can differentiate between anionic, cationic, nonionic and amphoteric surfactants. Surfactants are used in the home and industry.

w.   Zinc

Zinc is present in natural waters up to a concentration of 50 µg/l. Higher concentrations in mains drinking water pipes are generally caused by corrosion of galvanized steel. After a long-standing time concentrations of up to 5 mg/l are not unusual. Zinc contamination can occur in bodies of water as a result of wastewater discharges. Concentrations of more than 0,5 mg/l are toxic to some species of fish.

3.7.1.2.2   *Microbiological analysis methods*

The monitoring of drinking, industrial, bathing and other waters is carried out using microbiological water tests. The tests involve the determination of the total count of virulent organisms and identification of special organisms, which are indicative of hygienically suspect contamination or are pathogens themselves. The species Salmonela, Shigella and Escherichia, the so-called coliform bacteria and Proteus, Yersinia and Erwinia belong to this family. In hygienic water testing mainly the presence of these bacteria is tested. In addition the eggs of various parasites can be present in water.

3.7.2   *Sediment and suspended solids*

Sediment is a general term which is used to describe both suspended and deposited material.

3.7.2.1 Chemical analysis

Refer to paragraph 3.7.1.2 for chemical analysis of suspended mater.

3.7.2.2 Physical analysis

Accepted laboratory methods and procedures for determining the sediment concentration of the water – sediment mixture, the particle – size distribution, the specific gravity, and the unit mass of deposited sediments are needed for the measurement of those physical properties necessary for the computation of sediment – discharge and sediment – accumulation rates and amounts.

3.7.2.2.1   *Sediment concentration*

Though the quantity and character of sediment in a sample may vary over a range of concentrations and particle sizes, suspended – sediment samples seldom exceed 50,000 g/m^3 or contain particles coarser than fine gravel (4.0 mm); they usually contain considerable silt and clay. It is easier and more convenient to work with the mass of samples rather than their volumes; therefore, the concentration is normally determined as a ratio of the dry

sediment mass to the mass of the water – sediment mixture and stated in the laboratory as parts per million. Sediment concentration should generally be expressed in grams per cubic meter, although sometimes milligrams per liter is used. Conversion from parts per million to grams per cubic meter or milligrams per liter is easily accomplished. It is recommended that data be reported to the nearest $1g/m^3$ for concentrations to $1,000$ g/m^3 and to 3 significant figures for higher concentrations. Special procedures would need to be adopted where it is desirable to determine concentrations to the nearest 0.1 g/m^3.

Evaporation and filtration are the most frequently used methods for determining sediment concentration. Many laboratories need the capability of using both methods. The filtration method is faster if the quantity of sediment in the sample is small and/or relatively coarse grained. When the Gooch crucible is used with a suitable filter, a dissolved – solids correction is not needed. Laboratory procedures for both methods are well documented.

3.8 Eco-auditing

Since April 1995 commercial enterprises, including laboratories, in EC countries can undergo a voluntary eco-audit, based on the eco-audit regulation of July 1993. The aims of the audit are:

- setting up an environmental management system,
- self monitoring by regular audits,
- external communication through an environmental declaration,
- external monitoring by environmental assessors.

Auditing involves the following steps:

- environmental testing
- building up equipments for environmental protection,
- testing operations for the effect on the environment,
- an environment declaration,
- certification.

The first environmental test is the recording of the actual state and has the aim of creating a secure database for all environmentally relevant processes in the laboratory. Technical equipment, material balances and available authorizations are recorded, subdivided into the areas of water, sediment and air and the records drawn up as existing documentation. The functions of the existing infrastructure and waste disposal organisations are ascertained and analysed.

On this basis equipment for environmental protection is developed. Besides technical and product-based aspects, the overall organization is included. The documentation regarding the equipment is produced in the form of environmental handbook.

In the environmental operating test, which is the actual audit, the environmental protection equipment is tested and evaluated regularly and systematically. Environmental aims and the environmental programme of the company are brought up to date and measures for the further development of the environmental management system are proposed.

In an environmental declaration the general public is informed, for example, about the environment protection aspects of the plant operations. A summary of the consumption of raw materials, energy and water, emission of pollutants and generation of waste, supplement the data.

An authorized independent environmental assessor carries out certification of the company. He checks the statements in the environmental declaration and the adherence to the instructions of the EC regulation. After successful certification the company receives the eco-audit symbol and is included in the list of audited companies. This is published once a year in the EC official gazette.

4. QUALITY CONTROL ASSURANCE

4.1 General

Quality control measures must always be part of the analytical work. The basic principle is that the measurements should be as comprehensible, as plausible and as accurate as possible, or at least interpretable. Only those analysis results having verifiable accuracy and precision can be compared.

Measurements on "same samples " frequently differ. Therefore all external influences on the results must be taken into account to avoid significant errors in the individual steps of test procedures. Figure 4.1 depicts the problems encountered in judging and checking errors of measurement. Two types of errors can be identified: systematic and random errors. Sampling, sample conservation, sample transportation, sample storage, sample preparation/processing, measurement, data evaluation and test report form the steps in a test procedure of an analytical quality assurance system.

4.2 Implementation of analytical quality assurance

Implementation of analytical quality assurance entails the following:

- **Optimisation of personal resources.** The following requirements should be fulfilled when establishing a test: engagement of properly qualified personnel; the superintendent of the test should be qualified at university level; all co-workers performing the test should undergo an inducement with regard to their tasks and obligations; possibilities for further training.
- **Optimisation of technical equipment:** The technical equipment for a test should be acclimatized to the problem under investigation and should be of satisfactory quality. Particular attention should be paid to ease of handling, susceptibility to faults, amplitude of application and sensitivity. In addition, any appropriate construction and waste disposal modifications should be performed in accordance with the regulations and be ensured.
- **Selection of suitable test procedures for the point at issue:** It should be certified whether the test procedure selected is befitting for the problem and is sufficiently sensitive. The maximum tolerable total error of the process should be estimated. This estimation considers the random error, which affects the precision of the process, and the systematic error, which affects the accuracy (see Figure 4.1).
- **Determination of the parameters of the test procedure applied:** During routine analyses, the chemical constituents of both standard and actual samples have to be determined. The processes employed, including possible modifications, should be recorded together with the calculated constituents, i.e. *recovery rate*, *standard deviation of reproducibility, coefficient of variation of reproducibility*, *standard deviation of repeatability and coefficient of variation of repeatability.* The definitions of these parameters can be traced in DIN 38402, part 42. Analytical chemistry methodologies require calibration procedures. In the most straightforward cases, values of concentrations of standard solutions and corresponding measurements can

be plotted graphically. For a linear regression model three assumptions must be satisfied: *linearity over a wide range; stability of variation of measured values over the whole range; and, normal distribution of data.* The calibration function in such a case is:

$$y = a + b \cdot x \tag{5.1}$$

where: a is the calculated zero value and b is the gradient of the calibration function (representing the sensitivity of the measurement technique), which depicts the smallest possible deviation of all the data points from the straight line function.

The actual calibration function lies within a range of reliability (confidence interval). The confidence interval depends on the deviation of the calibration points from the curve (*residual standard deviation s_y*) and the gradient b of the calibration function. A parameter which clearly shows the quality of the calibration function, is the methodological standard deviation s_m, which is calculated from:

$$s_m = s_y / b \tag{5.2}$$

The s_m must be used to compare different analytical procedures over the same working range and with the same number of calibration points. The F-test has to be employed for numerical comparison of s_y values.

Every standard solution must be considered making use of the same analytical procedure as the actual sample. As a minimum demand for background quality control, it is advised that single or duplicate laboratory determinations be performed on several sequential days. In these determination should be included: *blank values; standard solutions with high and low concentrations within the working range; real samples; and, real samples after spiking.*

Observations should be recorded over a period of 10 to 20 days. The stability of the system is then tested by calculating: *the standard deviation within the batch (s_w); the standard deviation between batches (s_b).* The values of s_w and s_b are then compared using the F-test at a predetermined level (e.g 95%). Only when this test reveals a significant difference between s_w and s_b, must a separate calibration be carried out for each batch.

- **Performing internal quality assurance procedures**
- **Participation in external quality assurance procedures:** Regular participation in national and international collaborative tests with synthetic samples of known content or with real samples of unknown content is important. With the latter matrix-dependent errors must always be reckoned with. The results of collaborative tests are usually recorded by the collaborative test managers and made available to the participants, often with appropriate recommendations.
- **Evaluation and documentation of the quality assurance procedures used:** The quality assurance procedures used with the test should be recorded in detail (e.g. in an analytical quality assurance handbook). These records should be made available at the request of interested parties (clients, national monitoring organizations, or other departments within a large company). Insufficiently documented quality assurance procedures or those only carried out sporadically are of little value.
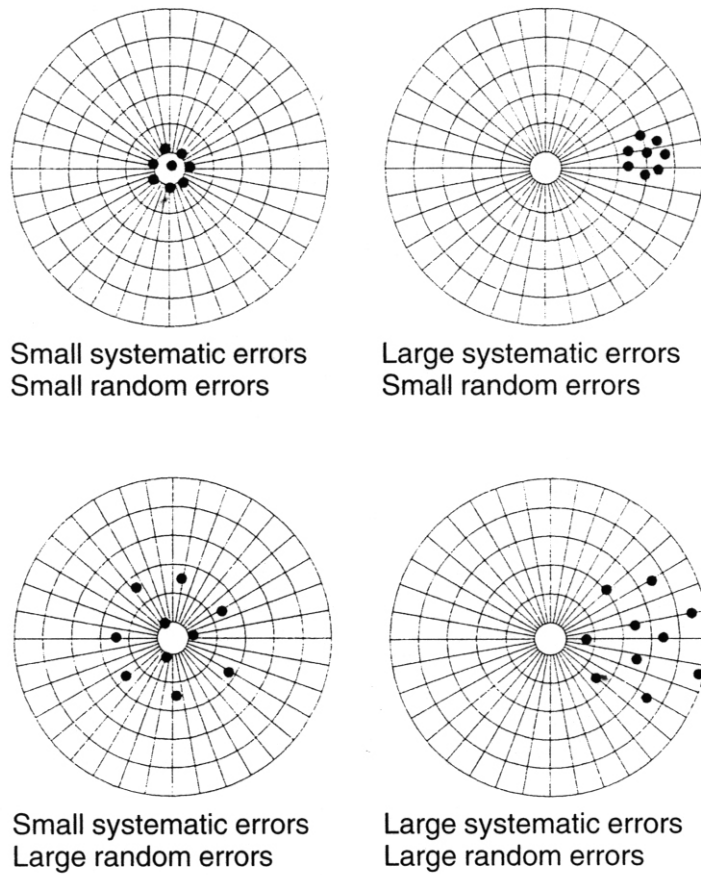
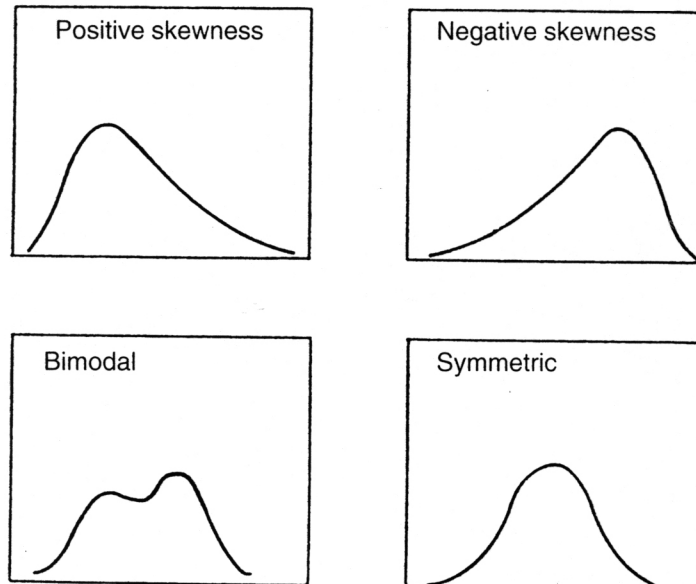**Figure 4.1: Different types of error in laboratory measurements**

Figure 4.2: Distribution curves occurring from the evaluation of time – dependent water source data

4.3 Statistical tests

Whenever an analysis repetition is performed on the same homogeneous sample, identical analytical results are not obtained each time but a variety of results whose distribution can be presented by a histogram. If a satisfied number of such measurements is available, a distribution curve can be constructed, which is often a normal Gaussian curve. This curve represents the relationship between the numerical value of an analytical result and the probability of occurrence. *The relative error or the coefficient of variation* is expressed as:

$$V = \frac{(m/x)}{s} 100\% \qquad\qquad (5.3)$$

where: m is the mean and s is the standard deviation.

But not always normally distributed data are expected. Other distribution curves can appear, particularly in the evaluation of time –dependent water source data (e.g. river water quality analyses including samples from flood waters) or in measurement of the same sample by various laboratories during collaborative tests (Figure 4.2). A coefficient of variation V of a value > 100% indicates that the data do not follow the normal distribution. Such results reveal the non-existence of compatible statistical populations (e.g. more than one water type) or of systematic errors of measurement. In such cases the different data sets must statistically be subjected into separate tests, since otherwise mean and standard deviation values will otherwise lead to unadjusted conclusions (see Figure 4.3). In such case two populations exist, since after about 1981 significantly higher values were observed than before. The continuous curve represents the mean values, each calculated from five single measurements.

Also special attention has to be paid to trends in data interpretation procedures. In Figure 4.4, the graphs (a) and (b) exhibit the same mean and standard deviation, although the measurements in (a) follow a periodical variation while in (b) a trend. It can be stated with clearness that additional support from graphs and other statistical evaluation methods cannot be relinquished.

Before the processing of the experimental data, extreme or peripheral values must be classified and, if necessary, eradicated since most statistical techniques demand a normal distribution. Statistical tests can provide objective clarification of such situations. In other words test parameters are calculated using established equations and can then be compared with values published in tables. Important test methods, such as the F-test, the t-test and the outlier test are described in specialised statistics literature. For some time efficient and PC-compatible statistics packages have been commercially available and permit the processing of all types of data. These can be stored in a format belonging to the same system or exported to other formats, such as Excel or dBase. Other formats allow the export of data for other applications. Also a large number of simple and varied statistical processes and graphical representations are available in the market. Such complex statistical packages include SPSS, STATISTICA, SYSTAT and UNISTAT.
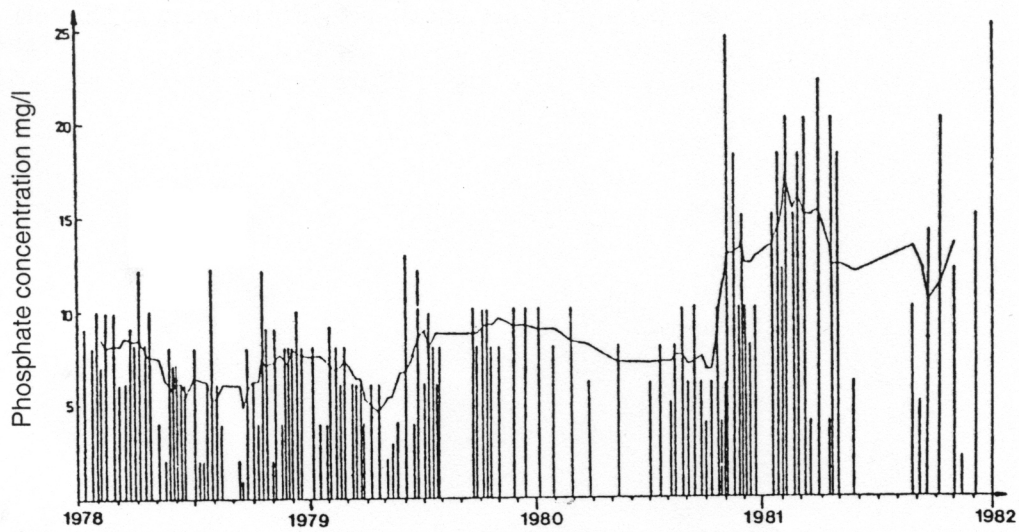
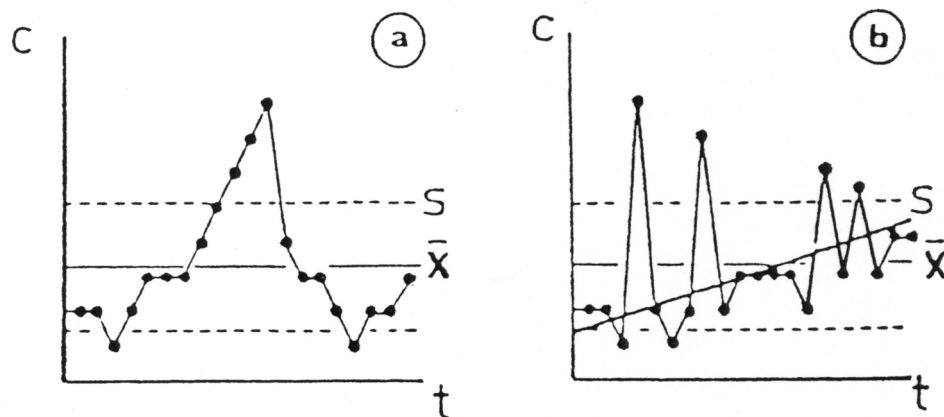**Figure 4.3: Time series of the phosphate concentration in a Greek river**

Figure 4.4: Time series of concentration of a particular chemical constituent in surface water: (a) cyclic and (b) trend.

4.4 Quality assurance systems

The EN 45000 system (1989) European Standard

Specialists in the European Community (EC) drew up the EN 45000 series of standards (including the DIN EN 45000 system). For test settings up, such as laboratories, they provide criteria in the form of an auditing, which must be fulfilled in order to obtain a statement of technical competence through accreditation. These criteria are valid for the operation of test laboratories (EN 45001), their assessment (EN 45002) and the authorities, which accredit the test laboratories (En 45003) and certify the products (EN 45011), the quality assurance systems (EN 45012) and the personnel (EN 45013).

The first step for a laboratory is the application to a licensed accreditation authority in order to fulfill the criteria of DIN EN 45001. The laboratory can only be accredited after being successfully examined by the accreditation authority. Part of the accreditation involves the occasional checking of the correct use of quality assurance procedures.

The ISO 9000 system (1994) International Standards

Companies, enterprises, organisations and not least authorities produce material and non-material products. For these products to be economical and of high quality, a quality assurance system is required. The ISO 9000 series provides a framework, but it is designed to be so general that it can be applied to the widest spectrum of organisations. The central feature of this standard, which deals with quality management, elements of quality assurance system, and stages in the proof of quality assurance, is the company and not the laboratory.

In order to remain competitive, companies aim to achieve certification, which states that their development and production are carried out according to the quality requirements of ISO 9000. An independent authority tests this and may include the laboratory of a company, depending on the planned extent of the certification. In this case the laboratory must fulfill the quality assurance requirements stipulated in the standard in addition.

If the laboratory wishes to carry out the work for an external customer, the criteria of EN 45001 must be fulfilled.

5. DESIGN CRITERIA FOR EARLY WARNING MONITORING

The objectives for early warning monitoring must be must be the following:

- *warning and alarming* in case of an accidental pollution rendering river water unsuitable or harmful for a specific use (e.g. for drinking water preparation)
- *signaling* river pollution incidents, as a form of monitoring, to identify and trace all the "wrong happenings" leading to deterioration of water quality.

The design criteria for depicted early warning stations must be:

- when something harmful and toxicant is passing by, an alarm should be initiated, and a relevant selection of parameters should be measured and recorded. This is putting a lot of emphasis on the development of new methods in the last fifteen years, concerning a combination of chemical and biological early-warning systems.
- ideally, no trace of pollution should be missed. Sampling frequencies should be such that no pollution slips through. Therefore operation should be around the clock throughout a week. Besides that, from computations of critical situations in rivers such as Danube and Rhine, it was found that the minimum sampling frequency must be around two times a day.
- the alarm should be in time. The response time of the alarm should be shorter than the transit time of the pollution in the river.

All river water monitoring stations should be equipped with a reliable data logging and processing system with advanced communications options. Experience has shown that small portable devices with low power consumption and designed for long periods of unattended use, can help keep the running costs low by allowing for unmanned installations. The offered systems should have an open architecture and be flexible enough to adapt to advances in software technology and provide the widest possible compatibility with the majority of the related measuring instruments and analyzers.

Functionally, the system should be capable of continuously monitoring all measured parameters and performing complex calculations in order to extract data trends that will be necessary for alarms and early warning messages. Alarm conditions and data trends should be user defined (by authorized users) from a remote computer. Special care must be taken to ensure broadest connectivity (PSTN, GSM, Inmarsat etc) with telecom networks. This

could prove extremely important, as appropriate sites for monitoring often tend to be away from populated areas, with limited or even no access at all to PSTNs. A broad range of alarm and early warning notification methods is recommended in order to achieve the maximum compatibility with telecommunications equipment found in research centers, national institutes, academia etc. Such methods should include technologies like FAX, SMS, e–mail, and use strategies for multiple recipient lists ensuring that important alarm notifications will get the proper attention.

A very important aspect of this system is the ability to communicate with a wide variety of measuring instruments and analyzers. Most of them have a serial interface and therefore the data logger should be able to communicate via the vendor's serial protocol, while at the same time provide at least a dozen inputs for standard voltage ($\pm$ 100 mV, $\pm$ 1 V, $\pm$ 5 V, $\pm$ 10 V etc) and current (0 – 20 mA, 4 – 20 mA etc) interface.

Although typical data logging requirements do not demand very short sampling periods, research workers and scientists on this field often need and appreciate a more detailed set of data, and recent experience on this field shows that periods in the order of one (1) hour are more appropriate. After all, advances in hardware are such that the memory capacity, of a modern, small sized, data logger is adequate for nearly one year's data at the aforementioned rates. All data log files should be kept in a standard ASCII format so that it will be easy for scientists to process them using any spreadsheet application.

6.   POLLUTANT LOADS AND FLUX CALCULATIONS

6.1 General

Monitoring programs of the water quality in rivers are normally based on the comparison of average concentrations with standard concentration ranges, which are considered to reflect the different pollution states of rivers. In many cases, however, the average loads better represent the real degree of pollution, since they reflect the total amount of pollutants being released into the riverine environment, or being mobilized by the river transport. Relatively high concentrations can also be the result of natural levels during low discharge periods, whereas relatively low concentrations can originate from the dilution of pollutants with high rainfall and river discharge. The determination of reliable average pollutant loads, both in the form of the total fluxes (e.g. in t yr^{-1}) and in the form of the specific fluxes (total fluxes divided by the drainage basin area, e.g. in t km^{-2} yr^{-1}) should therefore be one of the priorities in the design of studies on the water quality in rivers.

6.2 Water discharge

The transport of pollutants and natural compounds in rivers is strongly coupled to the water discharge in general. Fluxes are calculated as the product of concentrations and water discharge, and even if the concentrations in the rivers have been followed with high precision, the reliability of the calculated fluxes can only be as good as the reliability of the estimated water fluxes. For many compounds, the temporal variability of the concentrations in rivers is less important than the temporal variability of discharge, giving the monitoring of water discharge a dominant role in the determination of river fluxes. This is especially true for the Mediterranean rivers, where the ratio of peak discharge on mean annual discharge is frequently about one order of magnitude greater than for rivers in Non-Mediterranean areas (Estrela et al., 2001).

Continuous discharge measurements nowadays exist for a great number of rivers worldwide. As for climatic and meteorological data, national monitoring services are in charge with the task of the collection of river discharge measurements, and the data are normally centralized in national hydrological services from with they can be obtained by different means (online access via the internet, distribution of paper copies on demand, publication in hydrological yearbooks, etc.). Monitoring studies on the water quality in rivers can often rely on these hydrological measuring networks and do not require the proper monitoring of the river discharge in the framework the water quality monitoring study. If no water gauging stations exist, however, the monitoring of water discharge must be implemented

One has naturally to ensure that the selected stations for the water quality sampling correspond to the existing water gauging stations, and that there is no water gain or water loss between the two stations due to additional tributary river contributions and/ or water extraction for irrigation and other forms of water consumption. Moreover, one has also to verify that the discharge measurements correspond to good quality measurements. Discharge is normally monitored via continuous measurements of water height, together with the fitting of empirical relationships between water height and individual measurements of instantaneous discharge during different hydrological conditions. The nature of these relationships can change over time when the morphology of the river bed evolves and they are only valid within their calibration ranges. The latter might be especially problematic during floods when the rivers enter into the floodplains and the water height/ discharge relationships loose their validity.

6.3 Determination of average loads

6.3.1 Methods for flux calculations

The total load over a given period, such as a hydrological or calendar year is given by integration of instantaneous flux, i.e. the product of concentration C and discharge Q. In practice, continuous and exact measurement of the streamflow and concentration required to calculate mass fluxes is not possible, principally due to lack of continuous concentration records. As mentioned above, river flow is recorded with high temporal resolution, even if in some circumstances uncertainty in streamflow data can be appreciable. Concentration data are still commonly the limiting factor on the quality of river flux estimates. Uncertainty may therefore come from both the measurement of the concentration and the temporal integration of instantaneous fluxes.

A frequent starting point for the determination of average fluxes is the availability of more or less continuous river discharge data (e.g. in a daily temporal resolution) together with a certain number of instantaneous concentration measurements, which spread in about regular time intervals over one or several calendar years. For example, many national water quality monitoring programs take samples in monthly time intervals. Although these intervals are normally longer than the time slice over which concentrations vary significantly, the average fluxes can be determined with rather good precision when the sense of the concentration changes is predictable. In fact, in may cases concentration do not evolve independently from discharge and the methods for flux calculations often rely on this fact. This can be seen in the Table 5.1, which presents some of the commonly used formulas for the calculation of average river loads of pollutants and natural compounds.

Method 1 is based on the average arithmetic concentration mean. This method may be useful when the riverine concentrations are rather stable and/ or when the flux calculation should be used for an order-of-magnitude-estimate of the average loads, e.g. for the comparison of different rivers. In many cases, however, this method may considerably fail compared to the real values.

Method 2 is based on the determination of the discharge-weighted mean concentrations. It gives very realistic results when the evolution of concentrations is highly correlated, or anti-correlated, with the evolution of water discharge.

Method 3 determines the average fluxes between two sampling events by using the average arithmetic mean of both concentrations, and by summing up these fluxes for the time period for which the average fluxes should be determined (e.g., one year). The power of this method naturally depends on whether the sampling intervals fit with the major concentration changes (e.g., during floods). An advantage of this method is that it can also take into account major concentration changes that are not related to the river discharge (e.g., temporal variable pollution, etc.).

As a modification of this method, one often also linearly interpolates the concentration evolution between to sampling events to the time units in which the discharge data exist (method 4). This mostly corresponds to a daily time step resolution. The average fluxes are then calculated by summing up the individual products of daily discharge and concentration.

Method 5 is very close to method 3, but it uses the discharge-weighted concentration between two sampling events. This method fits well when the concentration evolution is generally controlled by discharge, but both parameters do not evolve synchronously.

Table 5.1: Commonly used approaches and formulas to calculate mean annual river fluxes

(A)	$$C_{av} = \frac{\sum_{i=1}^{n} C_i}{n}$$ (B) $F_{annual} = C_{av} \times Q_{annual}$	**M1 - Arithmetic mean:** Calculation of an average concentration (C_{av}) on the basis of n samples of instantaneous concentrations (C_i), and multiplication with the annual discharge total (Q_{annual}).
(A)	$$C_{dw} = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i}$$ (B) $F_{annual} = C_{dw} \times Q_{annual}$	**M2 – Discharge weighted mean:** As A, but calculation of a discharge weighted mean concentration (C_{dw}) on the basis of n samples of instantaneous concentrations (C_i) and instantaneous discharge values (Q_i)
(A)	$$C_j = \frac{\sum_{i}^{i+1} C_i}{2}$$ (B) $F_{annual} = \sum_{j=1}^{m} C_j \times Q_j$	**M3 – Partial fluxes (a):** Calculation of average concentration (C_j) for each period j between two sampling events. Multiplication of this concentration with the total discharge corresponding to this period (Q_j) and summing of the fluxes of the m periods covering one hydrological year ($m = n - 1$).
(A)	$$C_{th-dx} = \frac{(d_x - d_i) \times (c_{i+1} - c_i) + c_i \times (d_{i+1} - d_i)}{d_{i+1} - d_i}$$ (B) $F_j = \sum_{l=1}^{L} C_{th-dx} \times Q_{dx}$	**M4 – Partial fluxes (b):** Calculation of an average theoretical daily concentration (C_{th-dx}) for the l days d_x in the period j between the two sampling events i and $i+1$ (=> C_i and C_{i+1}). Multiplication of these concentrations with the daily

		discharges (Q_{dx}) and summing of the fluxes to the partial (F_j) and annual fluxes (F_{annual}).
(C)	$$F_{annual} = \sum_{j=1}^{m} F_j$$	
(A) (B)	$$C_j^* = \dfrac{\sum_{i}^{i+1} C_i \times Q_i}{\sum_{i}^{i+1} Q_i}$$ $$F_{annual} = \sum_{j=1}^{m} C_j^* \times Q_j$$	**M5 – Partial fluxes (c):** Calculation of a discharge weighted mean concentration (C_j^*) for each period j between two sampling events. Multiplication of this concentration with the total discharge corresponding to this period (Q_j) and summing of the fluxes of the m periods covering one hydrological year ($m = n - 1$).
(A) (B) (C) (D) (E)	$\log(C_i) = a \times \log(Q_i) + b$ $\log(C_i) = a \times \log(Q_i)^2 + b \times \log(Q_i) + c$ *(or similar models)* $$F_{annual}^* = \sum_{d=1}^{365} C_{th-d} \times Q_d$$ $$s^2 = \sum_{i=1}^{n} \dfrac{\log(C_i) - \log(C_{i-th})}{n-2}$$ $c_f = \exp(2.651 \times s^2)$ $F_{annual} = F_{annual}^* \times c_f$	**M6 – Regression model:** Determination of an empirical regression model between instantaneous concentrations and discharge values (often in logarithmic form). Calculation of a theoretical daily concentration (C_{th-d}) and multiplication of theses values with daily discharge for all days of the year. In the case of logarithmic relationships with large scatter, this method tends to underestimate real fluxes and should be corrected according the method proposed by Ferguson (1986, 1987).

Method 6 is based on the establishment of empirical relationships between concentrations and discharge. These relationships can then be applied to the daily discharge records in order to calculate theoretical values for daily concentrations. This method is normally applied to elements and compounds that depict a similar variability of concentrations compared to the variability of discharge.

In most cases the relationships are established on a log/ log unit basis, which reduces the dominant impact of extreme values on the regressions. However, log/ log relationships tend to underestimate the real values in relationships with large scatter and the results should be corrected according to the method proposed by Ferguson (1986, 1987).

6.3.2 Dissolved compounds

The variability of the levels of dissolved compounds in rivers is generally less important than the variability of discharge, although concentrations often vary in close relationship with discharge. Many natural elements resulting from the weathering reactions in the river drainage basins, such as the major cations (Ca^{2+}, Na^+, Mg^{2+}, K^+) and anions (HCO_3^-, Cl^-, SO_4^{2-}), are negatively correlated to discharge, and the method 2 for the flux calculations yields realistic results.

For dissolved nutrients (NO_3^-, PO_4^{3-}, …), clear concentration-discharge relationships are often missing. Except for very pristine rivers, nutrients are mainly introduced into surface waters by anthropogenic activities, which overwhelm the natural mobilisation processes. Moreover, due to the reactivity of nutrients in biogeochemical cycles, concentrations can be strongly influenced by the terrestrial and aquatic metabolism and vegetation cycles, or by climatic parameters such as temperature. This makes that the evolution of concentrations

may follow marked seasonality, but not necessarily in direct connection with the water runoff. As a consequence, the methods 3 and 4 often yield good results for the flux calculations. However, since the seasonality of vegetation and climate may show some coincidence with the seasonality of water discharge, also method 2 can still result in reliable fluxes.

For certain elements and compounds, the maximum concentrations in the rivers are observed during the high water stages, but the concentration peaks precede the peak of water discharge. This so-called "flushing effect" can be explained by the depletion of a given reservoir, characterized by elevated concentrations, via the rising precipitation and water levels. The flushing of dissolved organic carbon (DOC) from the soils is a typical example for this phenomenon. In this case, the method 5 may be well adapted for the determination of the average fluxes.

6.3.3 Particulate compounds

The levels of particulate matter in general, commonly measured as total suspended solids (TSS), can evolve very rapidly in rivers. Their variability may be greater than the variability of discharge, which implies that the monitoring of TSS in rivers should be done in the same temporal resolution as water discharge (almost continuously) in order to obtain reliable fluxes.

Continuous monitoring of TSS requires the installation of sophisticated instrumentation at the sampling stations (auto-samplers, turbidity sondes, etc.), which may be beyond the financial possibilities of the water quality program. Regular manual sampling is therefore still the most frequent approach to obtain data. In this case, the quality of the flux calculations strongly depends on the sampling frequency during floods, which account for by far the greatest part of the overall TSS transport in rivers. In the Mediterranean region, TSS are almost exclusively transported during the often short and violent floods.

When the floods have been sufficiently covered by sampling, the methods 3-5 may give realistic estimates for the resulting fluxes, although one has to be aware that the errors can be much greater than in the case of the monitoring of dissolved compounds. Also the method 2 can give correct results. In many cases, however, method 6 is used to determine riverine TSS fluxes. TSS and discharge often correlate, but due to scattering of the data, one mostly fits log/ log relationships. One advantage of the method 6 is that it can also be applied to longer time series of discharge records compared to the sampling period in order to determine an estimate on the long-term average fluxes. Sampling during relative short periods (e.g. one year) may not be sufficient to determine representative fluxes.

The determination of reliable TSS fluxes is a crucial point for the monitoring of water quality in rivers, since the transport of many pollutants is highly associated with the transport of TSS. This concerns, for example, the transport of heavy metals and/ or organic pollutants, but also the transport of some inorganic and organic nutrients, such as particulate inorganic phosphorous. This means that the fluxes of these compounds cannot be coupled to water discharge alone, and their calculation requires first of all the determination of reliable TSS fluxes in general. For example, the average percentages of heavy metals in TSS can be rather constant, and the average heavy metal fluxes can hence be determined by a multiplication of these percentages with the total sediment fluxes. In other cases, the percentages of the particulate compounds and pollutants in TSS may vary in a regular but predictable manner. Exemplary for this are the fluxes of particulate organic carbon (POC). POC is strongly coupled to TSS, but the percentages of POC clearly decrease with increasing TSS concentrations.

6.4 Modelling

Fluxes are often needed for budget calculations in the context of an evaluation of the potential impacts of the riverine inputs on a given ecosystem. The transport of nutrients to the coastal sea of to lakes that suffer from eutrophisation may be examples for this. When the drainage basins of the receiving ecosystems are large, it may be impossible to monitor the overall river inputs, and the establishment of empirical models that predict the river fluxes may be used in order to refine the budgets. Of course, these models have to be established and calibrated on the basis of observed data from the concerned systems and should not be applied to different systems outside the study areas.

It could been shown that the fluxes of dissolved inorganic nutrients, especially nitrate, or dissolved inorganic nitrogen in general, are often highly correlated to the human activities in the corresponding drainage basins. Population densities alone are already a good predictor for these fluxes. Including other data such as N-fertilizer spreads, wastewater inputs and/ or atmospheric N deposits from industries and cars may still improve the models. Also the fluxes of organic nutrients, such as dissolved organic carbon (DOC), may be related to the environmental characteristics of the drainage basins, such as drainage intensity, carbon storage in the soils or the steepness of morphology. Collecting these data and including them into geographical information systems (GIS) can hence be very useful for modelling purposes.

Also the fluxes of TSS may be predicted in a similar manner. But TSS fluxes are not only temporarily but also spatially highly variable, which requires extreme care in the calibration of the models to the applied systems. The great spatial variability of the TSS fluxes can be the result of a combination of different environmental factors, which means that the resulting variability may be much greater than the variability of the individual factors alone. One example for the use of such a modelling approach is the universal soil loss equation (USLE, Wischmeier et al., 1958), which is frequently applied for small-scale predictions of soil erosion and the resulting TSS fluxes on agricultural fields. The USLE predicts the sediment mobilization as the product of several factors concerning rainfall frequency, soil texture, slope length and others. Similar approaches were also successfully applied to determine the TSS fluxes at much larger scales, such as the global scale (e.g., Ludwig and Probst, 1998).

One additional problem for the prediction of particulate river fluxes is the fact that the transport of suspended matter between different points is not necessarily conservative because basin internal sediment retention via sedimentation processed may occur. This has to be considered for flux calculations and modeling approaches of TSS. Especially the sediment retention in reservoirs and lakes may be important. The phenomenon of sediment retention may be quantified when knowing the average residence time of the water in the reservoir, e.g. by using the following relationship (Vörösmarty et al., 1997):

$$R = 100 \times \left(1 - \frac{0.05}{\sqrt{T_r}}\right)$$

R is the sediment retention in %, and T_r the mean annual residence time of the water in years. Although a generalization of such type of relationships is naturally difficult, one can note that an average residence time of only ten days already provokes a sediment retention of about 70%. This underlines the important potential impact of this phenomenon on the riverine transport of particulate matter.

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