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PROCEDURES AND METHODS FOR INTEGRATED GLOBAL BACKGROUND MONITORING OF ENVIRONMENTAL POLLUTION

F. Ya. Rovinsky, USSR, and G. B. Wiersma, USA

ENVIRONMENTAL POLLUTION MONITORING AND RESEARCH PROGRAMME NO. 47

GLOBAL ENVIRONMENT MONITORING SYSTEM (GEMS)

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W O R L D M E T E O R O L O G I C A L O R G A N I Z A T I O N

U N I T E D N A T I O N S E N V I R O N M E N T P R O G R A M M E

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F O R E W O R D

"Integrated Monitoring" has been defined at a WMO/UNEP expert meeting in 1980 as follows:

- Integrated monitoring is the repeated measurement of a range of related environmental variables or indicators in the living and non-living compartments of the environment, and the investigation of the transfer of substances or energy from one environmental compartment to another with the aim of assessment and prediction of the environmental status.

- Monitoring becomes truly integrated when the measurement of different variables or of the same variables in different compartments are co-ordinated in time and space to provide a comprehensive assessment of the system under study. The variables might include chemical substances (e.g. pollutants), geophysical parameters (e.g. wind, ocean currents), biological characteristics (e.g. primary productivity) or other variables as may affect man, his natural resources and the climate.

Other formulations given in the text and outlining the term 'integrated monitoring' are consistent with the above definition.

The procedures described are the result of several years' studies implemented in the USA, the USSR and, within a UNEP/WMO pilot project, in a biosphere reserve in southern Chile.

The governing bodies of WMO appealed to Members to add the monitoring of pollution in media other than air to their background pollution monitoring programmes, e.g. at suitably located BAPMoN and at biosphere reserve stations.

This manual is the first publication of its kind. It reflects the state-of-the-art in integrated monitoring and is to provide the necessary advice on how to carry out integrated monitoring.

NOTE: The reader may sometimes get the impression that the authors of the manual regard IGBM as a new independent activity. For clarification, it should be understood that all IGBM is an activity within the WMO BAPMoN, and therefore also within the UNEP Global Environment Monitoring System (GEMS).

I. PREFACE

Large-scale consequences of anthropogenic activity spreading over vast territories of the globe which involve the atmosphere as a whole and threatening the biosphere, have been attracting the attention of scientists in various countries and lately that of many national governments. The ever increasing environmental emission of numerous wastes has already changed the chemistry of air, water, soil and biota. Overexploitation of renewable resources not only results in the extinction of flora and fauna species, but can also change the functioning of many ecosystems. Thus, anthropogenic activity might disturb matter and energy relations and fluxes and threaten the biosphere sustainability unless it is regulated according to the interests of mankind, on the one hand, and the need for biosphere conservation, on the other.

The above environmental issues that arose in the second half of the twentieth century have attracted the close attention of the United Nations (UN) and various specialized international organizations, such as the United Nations Environment Programme (UNEP), the World Meteorological Organization (WMO), the United Nations Educational, Scientific and Cultural Organization (Unesco), The Intergovernmental Oceanographic Commission (IOC), the International Union for the Conservation of Nature and Natural Resources (IUCN), etc.

The UN Conference on the Human Environment (Stockholm, Sweden, 1972) discussed the necessity of establishing Earthwatch, an observation system whose major ideas were later considered at the UNEP Intergovernmental Meeting on Monitoring (Nairobi, Kenya, 1974).

The basic principles of a new information system - integrated background monitoring, to be created within the framework of the Global Environment Monitoring System (GEMS) - were broadly discussed at a number of UNEP and WMO supported international meetings of scientists and experts:

- First International Symposium on Integrated Global Monitoring of Environmental Pollution (Riga, USSR, 1978);
- Inter-agency Consultation on Integrated Monitoring (UNEP, Nairobi, Kenya, 1980);
- Expert Meeting on the Operation of Integrated Monitoring Programmes (WMO, Geneva, September 1980);
- Second International Symposium on Integrated Global Monitoring of Environmental Pollution (Tbilisi, USSR, 1981);
- Third International Symposium on Integrated Global Monitoring of the State of the Biosphere (Tashkent, USSR, 1985).

In the 1970's a number of prominent scientists , such as Professor Yu.A. Izrael, Professor R.E. Munn and others, formulated the basic ideas and principles of integrated monitoring and

substantiated the need in its practical implementation (Izrael, 1979; Munn, 1980; Gwynne et al., 1980; Rovinsky et al., 1980; Izrael, 1980).

The Geneva expert meeting (1980) discussed and developed the Pilot Project on Integrated Monitoring to be carried out at a network of biosphere reserves in temperate mixed forests. At present, the project is being realized in the U.S.A. and in Chile (Wiersma, 1985).

Since 1977 the CMEA (Council for Mutual Economic Assistance) countries Bulgaria, Czechoslovakia, German Democratic Republic, Hungary, Poland, Romania, and USSR, on the basis of multi-lateral scientific and technological co-operation have been working to establish a background integrated monitoring network with a unified programme and methodology to evaluate the background state of the environment in the region of the co-operating countries (Rovinsky and Buyanova, 1982; CMEA, 1986). At present, information obtained is published in annual Bulletins of Background Environmental Pollution in the Region of the East Europe CMEA Member Countries (CMEA, 1985)[1]. In both cases, background integrated monitoring stations are preferably established in biosphere reserves.

The aforementioned activity in North and South America, Europe and Asia should answer complicated and interrelated questions, such as:

- What are the state and trends of background pollution of ecosystem components?
- How do the natural systems under study function under conditions of background pollution?

Thus, it can be stated that, by now, the foundations of a Global Background Integrated Monitoring Network (GBIMN) have been laid. It should be emphasized that actions taken to create GBIMN proceed from the experience gained in establishing the WMO Background Air Pollution Monitoring Network (BAPMoN; WMO, 1970) and that the XXVIth Session (1974) of the WMO Executive Council urged WMO Members to create integrated background monitoring stations within this activuty.[2]

As was noted in the Recommendations of the Third International Symposium on Global Integrated Monitoring of the State of the Biosphere, "the principal task of global integrated monitoring is the earliest possible detection of signs of disturbance

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1 The participation of the USSR makes it possible to describe the background environmental state in parts of Asia as well.

2 Before the Riga Symposium (1978) the term "multi-media monitoring stations" was used.

of biosphere sustainability. It would be desirable to develop within GEMS a specialized program for monitoring characteristics of the state of the biosphere, oriented toward control of human environmental components impact on large-scale biosphere processes and large biosphere elements. The solution of the problem requires efforts to develop methods, standardization and intercalibration, as well as to study anthropogenic impact and to develop the concept of ecological sustainability of the biosphere, including further expansion of research and monitoring on the Global Biosphere Reserve Network (MAB/UNESCO, 1985)."

The aim of the present paper is to formulate the basic principles of integrated background monitoring, and to describe procedures and methods of integrated background monitoring with respect to observation of background pollution of environmental components. Materials included in the paper are based on the practical experience of integrated monitoring gained both while implementing the Pilot Project in America and in the course of multilateral cooperation in Europe (and Asia). It is important that in both cases scientists and experts came into contact and shared opinions at numerous meetings and discussions and developed a common basis of approaches to, and activities on, many essential aspects of integrated background monitoring.

2. INTRODUCTION AND SCOPE

Protection of human health and well-being against possible negative implications of economic activity has grown into a particularly urgent problem all over the world in the last decades. The scope of such negative implications has been increasing, and eventually a large-scale threat to the environment has arisen. All this has an international response and a global character.

It is very important under the conditions of increasing anthropogenic impact to have objective information on the actual state of ecosystems, to predict their future state, and to know critical factors of anthropogenic impact and critical (most vulnerable) elements of the biosphere. In this connection it has become necessary to create specialized systems for environmental monitoring, including global ones.

The primary task of such an information system is to distinguish man-induced changes in the environmental state from the background of its natural variability. It should also allow one to assess and predict the state of the environment. Thus, monitoring is a multipurpose information system and, in this context, it is an indispensible link in environmental quality management, though a monitoring system does not directly include any management elements.

Several definitions of a monitoring system or, to be more exact, a system for monitoring anthropogenic changes in the

environment have been formulated.

R. E. Munn (1973): a system of recurrent purposeful observations of environmental elements in space and time in compliance with a prearranged programme.

According to Yu. A. Izrael (1974), monitoring includes the following activities:

- observation of the environmental state and factors affecting the environment;
- assessment of the actual environmental state and impact factors;
- prediction and assessment of the future state of the environment.

The two definitions are in agreement with respect to "observation" though the second one envisages a wider scope of activity. Observations are the basis of monitoring and of its first stage.

Impact monitoring is required to detect and prevent local problems. For instance, urban air pollution monitoring systems are meant to protect human health, and to prevent possible damage to various materials and constructions, including historical and cultural monuments. Other systems belonging to this type are surface and drinking water monitoring systems. As a rule, impact monitoring deals with a relatively limited though variable range of sources and impact factors, with environmental quality assessment based on common criteria, such as maximum permissible concentrations or quality standards established for man. Environmental state prediction and quality management are rather simple and closely connected with sources in a given area (city, industrial complex, etc.).

Regional monitoring, though having the same task, is related to more complicated processes and involves much larger territories. The variety of impact factors decreases while the number of sources increases and the relationship between these factors and environmental quality becomes more complex. This fact considerably complicates the development of predictions and recommendations concerning environmental quality management. The situation becomes still more complicated when the region considered includes several countries and, hence, there is a need for coordinated efforts at the international level. Usually the most difficult task of regional monitoring (within the framework of one or several states) is the development of criteria of environmental quality, since in this case it is necessary to standardize the impact on natural complexes and not only the impact on man. A typical example of the application of regional monitoring is the acid rain programmes in North America and Europe.

Global monitoring is required to detect and prevent negative effects on the biosphere on a planetary or hemispheric scale. In

this case the number of impact factors can be less than in the regional approach, though the number of sources significantly increases (it corresponds to integral economic activity). The complexity of relations between the environmental quality and impact sources grows still further.

Anthropogenic impact on a global scale has some peculiarities. First, such processes are associated with relatively small concentrations with large-scale effects. In this connection it is necessary to study and evaluate the background state of the biosphere. Second, these processes are always associated with long-range pollutant transport, mainly in the atmosphere, but sometimes in the hydrosphere. Third, global anthropogenic impacts may have a long lead time before detrimental impacts may be noticed.

Most often anthropogenic impact is not confined to the change in physiochemical properties of environmental components only. The major anthropogenic impact factor, including that on a global scale, is the emission and dispersion in the atmosphere, hydrosphere and at the earth's surface of huge amounts of various wastes and other substances, e.g., fertilizers or toxic chemicals. Certain large-scale implications of combined anthropogenic activity have already been universally recognized, such as climate impact, impact on the ozone layer, etc.

The consequences of accumulation in ecosystems of toxicants contained in anthropogenic wastes and involved in large-scale processes of spreading, dispersion and biogeochemical turnover are less studied. These toxicants include sulfur and nitrogen compounds, various heavy metals, organochlorine compounds (e.g., 3,4 benzo-a-pyrene and petroleum products[1]) All of these substances (or their transformation products) are capable of cycling in the environment for a long time, accumulating in living organisms and affecting them. Threshold accumulation of the substances in ecosystems on a global level, the excess of which evolves certain implications, has not been studied well enough. However, it is clear that we cannot allow an uncontrollable increase in toxicant concentrations in biosphere elements.

People can experience negative consequences of global background pollution of the biosphere both through direct and indirect impact. THe direct impact consists of increased input of toxicants to human organisms from ambient air, water and food. The indirect impact is related to changes in terrestrial and aquatic ecosystems, disturbance of their sustainability, structural simplifications, genetic effects, reduced bioproductivity, etc. The above effects are strongly intensified when

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1 Important mainly for the aquatic environment

combined with other large-scale consequences of anthropogenic activity - soil and forest degradation, desertification, and species extinction or reduction.

For the human population it could involve adverse effects on health and well-being, including aesthetic and psychological damage from reduced possibility of keeping contact with nature. Social implications are also quite evident: changes in food quality and quantity, changes in economy and conditions favorable for societal development.

Thus, a necessity has arisen to complement the available global monitoring systems with a specialized observation system which would enable one to evaluate and predict background environmental pollution and its ecological consequences. This system has been named Integrated Global Background Monitoring (IGBM). It should tackle both global and many large-scale regional problems.

As has been emphasized in Munn et al., 1980 and Izrael et al., 1980, the basis of integrated monitoring is formed by recurrent measurements of a number of interrelated environmental variables and indicators in the biotic and abiotic environmental components, as well as by studies of cross-media transport of substances. To obtain a comprehensive picture of the system investigated, the measurements should be correlated in time and space. The list of variables to be measured consist of chemical (including pollutants), geophysical and biological characteristics, and other parameters capable of affecting man and natural resources.

The IGBM program should be divided into two separate though interrelated blocks:

- monitoring of background pollution of ecosystem components, including biota;
- monitoring of ecological consequences.

Monitoring of ecological consequences on the background level (IGBM biotic subprogram) is an essentially new and very complicated task. At present it is impossible to make a real-time assessment of background pollution impact on biota using field observations (Izrael et al., 1980; Izrael et al., 1983). Such parameters as dose-response relations for individual populations (let alone individual ecosystems) have not been studied well enough. That is why the present guideline material pays much attention to the establishment and focuses on the first IGBM component - monitoring of background pollution of ecosystem components, including biota. Methodological bases of biotic monitoring would require a specialized guide to be compiled. However, even at the present stage of IGBM system establishment, it is essential to provide an opportunity for implementing biotic monitoring; defining the creation of IGBM stations in biosphere reserves or at similar sites as the most

important recommendation. It should also be envisaged that the section of the IGBM program related to background pollution would, as much as possible, reflect interests of the biotic subprogram.

It is evident that the IGBM system can be established only on the basis of international cooperation and should become part of GEMS along with the five currently operating programs: climatic monitoring; monitoring of long-range pollutant transport; health monitoring; ocean monitoring; and monitoring of renewable land resources. Thus, the establishment of the IGBM system is mainly the responsibility of UNEP, WMO and UNESCO.

In 1973, the Unesco Programme on Man and the Biosphere (1973) recommended that a global network of biosphere reserves be established. This was accomplished in 1974 (Program on Man and the Biosphere, 1979). One of the purposes of the reserve system was to serve as potential baseline sites for environmental monitoring.

The recognition of the need for a global monitoring system for pollutants in remote or background areas preceeded the establishment of the Biosphere Reserve system by several years. Lundholm (1968) called for the establishment of a global early warning system which would be based on long time series of environmental data collected on background areas.

The Swedish Natural Science Research Council (Ecological Research Committee, 1970) and the United States AdHoc Task Force on the Global Network for Environmental Monitoring (1970) also called for the establishment of a global background monitoring system.

In 1976, the International Environmental Programs Committee of the U.S. National Research Council recommended that the terrestrial component of the Global Environmental Monitoring System (GEMS) be incorporated and coordinated with the Biosphere Reserve system. Franklin (1977) also listed the biosphere reserves as a component of GEMS. In 1978 the International Co-ordinating Council of the Unesco Programme on Man and the Biosphere (Anon., 1978) officially recognized the link between GEMS and the Biosphere Reserve system. They recommended:

1. That coordinated monitoring activities on biosphere reserves be carried out in conjunction with UNEP/GEMS and WMO.
2. That UNEP provide support to developing countries to enable them to undertake appropriate monitoring activities on biosphere reserves.

At a UN interagency meeting in Geneva, steps to effect these recommendations were taken. UNEP/GEMS agreed to explore the use of three biosphere reserves as part of the terrestrial component

of GEMS. A tentative design for monitoring was established, including basic ecological processes as well as pollutants.

Further progress on integrating the biosphere reserve system with the WMO Background Monitoring Stations (BAPMoN) was discussed at a meeting in Geneva in April, 1980 and plans were laid for beginning programs in the global cycling of trace metals (WMO, 1980).

Wiersma (1981) at the request of UNEP/GEMS conducted a preliminary analysis of the biosphere reserves as of 1978 to determine which of the then existing 176 biosphere reserves were suitable for background monitoring. Finally, in 1984 a pilot project was initiated under the auspices of UNEP/GEMS, UNESCO and WMO. Two pilot sites were started - one at Olympic National Park in the United States, and the second at Torres del Paine National Park in Chile. Concurrent with these activities, a significant effort was underway in the Soviet Union on background monitoring on Soviet biosphere reserves.

The scope of this paper is limited to dealing with sampling methodology associated with integrated monitoring on background areas. The methodologies mentioned in this report have all been field tested under a variety of conditions in different parts of the world including the United States, the Union of Soviet Socialist Republics, European CMEA-member countries and Chile.

The recommended procedures are based on over 10 years of experience in at least 10 biosphere reserves. The report is not intended to be a review of all possible sampling techniques appropriate to integrated background monitoring. However the techniques described do work and have produced reliable results over the years.

The pollutants covered are primarily those that have or are suspected to have long range transport capabilities. As such, the methodologies concentrate heavily on atmospheric particulates, including trace elements, sulfates and nitrates and selected organic compounds such as DDT and benzo-a-pyrene.

The report also emphasizes monitoring activities that are associated with remote area sampling. This is because the current emphasis in integrated monitoring is on sampling in remote natural areas. Furthermore, virtually all of those natural areas that have been investigated to date have also been Biosphere Reserves. Indeed this manual starts from the premise that as integrated monitoring programs are implemented, the International Biosphere Reserve system will be the original universe from which initial sampling locations will be chosen.

By definition, integrated monitoring is a multi-media effort. Therefore, the emphasis will be on sampling and analytical techniques for air, water, soil, and biota with the emphasis in the last category being on vegetation sampling.

Finally, an attempt has been made throughout this manual to describe relatively simple procedures for monitoring of environmental components. Also the manual is written in the fashion of a step by step procedures manual. We recognize that local conditions will cause these procedures to vary at times, nonetheless, the procedures in this manual appear to us, from our experience, to be reasonable first approaches to multi-media sampling in an integrated monitoring program.

Integrated monitoring programs almost by definition, have a strong ecological component associated with the sampling program. However in the interest of time and space they are not included in this manual. We have restricted ourselves to abiotic measurements only, although many of these measures are made in biological environmental components.

3. OBJECTIVES, GOALS, TASKS AND PRINCIPLES OF INTEGRATED GLOBAL BACKGROUND MONITORING (BACKGROUND ENVIRONMENTAL POLLUTION)

The IGBM system should provide the identification of anthropogenic changes against the background of natural variability. One of the essential IGBM components is collection of data on the initial (baseline) state of the environment, its current background pollution and rates of pollutant spreading in the biosphere, and trends in environmental quality changes. These data are required to understand major physiochemical and biological processes and to improve our knowledge of pollutant and toxicant effects on ecosystems.

The objectives of an integrated global background monitoring program are to:

1. Establish baselines of compounds that have both natural and anthropogenic sources. These baselines are established simultaneously in several environmental media.

2. Serve as an early warning system to detect the spread of anthropogenic compounds that have transported beyond their points of emission or use. Examples of pollutants that have only anthropogenic sources that have permeated the entire biosphere in a way not anticipated by their developers or users are DDT and polychlorinated biphenyls. It is anticipated that by a wise choice of analytical methodology, screening for these man-made chemicals (mostly organic chemicals of one kind or another) is not only technically feasible but is demanded both by past history and by the quantities of such chemicals currently being used and introduced.

3. Establish ecological baselines to serve as reference levels against which data from similar ecosystems in

more impacted areas can be compared.

4. Identify current and future trends of pollutants on background areas as well as selected ecosystem functions.

Tasks of an integrated background monitoring program are to:

1. Establish a database of pollutant measurements in different media readily available by all users and operators of background sites. This database should be operated and coordinated by the World Meteorological Organization (WMO).

2. Establish a similar database for ecosystem parameters.

3. Set up a formal alerting system based in the WMO to alert global, regional and local governments about the spread of pollutants.

4. Serve as a mechanism for communication between scientists engaged in trying to understand global contamination problems.

5. Serve as integral component of ICSU/SCOPE's proposed International Geosphere Biosphere Program as that program becomes operational.

6. Assess anthropogenic contribution to background environmental pollution.

7. Determine pollutant fluxes and migration pathways in ecosystems.

8. Investigate pollutant transformations in the environment and assess the impact of transformation products (secondary pollutants).

9. Detect trends in background pollution of environmental and biotic components on the basis of long-term observations as soon as possible.

10. Identify spatial regularities in background pollution spreading over continents.

11. Assess pollutant budgets and identify critical areas of pollutant accumulation in the biosphere.

The realization of the above objectives and tasks requires the fulfillment of certain principles while establishing and implementing IGBM:

1. All pollutants should be measured in a coordinated fashion along with measurements of the appropriate

physical and biological processes that help interpret the results.

2. Maximum possible correlation of all types of observations in time and space, i.e., they should be carried out at the same time and at the same sites.

3. A unified observation program for all the stations. The program can be divided into two parts: basic (practical) one, and an optional (research) program. The basic part of the program is implemented at all stations, the optional one only at a number of them.

4. Unified methods of observation and sample analysis; an application of unified standards and regular intercomparison of the results to ensure high quality and compatibility of data.

5. A systems approach to the IGBM arrangement; the establishment of a global system of stations, within the framework of which regional subsystems are singled out and regional centers (laboratories) are created to provide methodological guidance for the stations, to carry out sample analysis and data quality assessment and generalization on a regional scale.

6. A systems and hierarchical approach to data collection, processing, generalization, assessment, and publication and elaboration of recommendations; establishment of a leading center (laboratory) to guide the regional centers (laboratories).

7. All inadequately studied types of monitoring or those which currently do not have satisfactory research methods should be excluded from the IGBM system.

8. Identification of trends in background pollution of the biosphere requires information on its past state. Such studies should be envisaged.

9. The possibility of the occurrence of new IGBM goals and new improved methods and instruments calls for the conservation and long-term storage of currently collected samples.

4. REVIEW OF INTEGRATED GLOBAL BACKGROUND MONITORING

Integrated monitoring systems, including integrated global background monitoring systems, by definition, involve multi-media sampling. Traditionally, monitoring systems have been single media oriented, such as air or water (Barth, et al.) With the notable exception of radioactive pollutants, efforts to develop multi-media monitoring programs were minimal until the mid

1970's. At that time, the difficulty of making exposure estimates based solely on single medium measurements was becoming apparent, and efforts were undertaken to develop multi-media environmental monitoring systems. The term commonly used to describe these systems was integrated monitoring. Schuck and Morgan (1975) stated that environmental assessments required integrated monitoring systems that linked pollutant sources with a defined critical receptor. These integrated monitoring systems had to consider all media a pollutant could interact with; the transport mechanisms; and the biological, chemical and physical interactions that the pollutant underwent.

Munn (1973) also recommended integrated monitoring systems and emphasized the importance of measuring processes as well as pollutant levels. Behar et al. (1979) further expanded on the need for integrated monitoring in a report entitled "Integrated Exposure Assessment Monitoring". The title included the words exposure assessment to focus attention on the purpose of the monitoring system. They recommended a systems approach. The approach described, however, appeared complex, and no specific paradigm was developed that could easily be applied to the design of environmental systems.

Lindell (1978) proposed that the application of the commitment concept used in radiation exposure estimates be applied to nonradioactive pollutants. Bennett (1981) further expanded on the idea and gave examples of its application using lead and cadmium. The commitment approach is simple to use and can provide estimates of the relative pathways of exposure to a critical receptor. But the approach depends on the ratio of the steady state or integrated exposure level of a pollutant in the sending compartment to the similarly derived pollutant level in the receiving compartment. Therefore it does not help the investigator focus on problems affecting transfers between compartments. Also feedback loops are difficult to deal with using this method.

A more useful approach is one proposed by Eberhardt et al. (1976). They suggested that simple kinetic models describing pollutant movement and distribution among the various environmental compartments of interest would be a useful technique for designing monitoring programs. They admitted that the simple first order reactions used tended to yield poor fits to field data, but the strength of this method was in helping to conceptualize complex systems by means of a schematic. The simplistic set of equations served as a basis for developing more complex but more accurate models.

Of importance to this approach to integrated monitoring is elucidation of the fundamental processes that define the movement of pollutants between compartments. A series of articles by Mackay has addressed selected mechanisms of determining mass transfer coefficients based on basic principles. Specifically, articles have appeared relating bioconcentration factors and

water solubilities (Mackay, 1982). In addition, experimental observations have been made with respect to volitalization of organic compounds (Mackay and Yeun, 1983) and hydrophobic materials (Mackay et al., 1979).

This manual uses a systems approach (Wiersma et al. 1984) to help plan and design integrated background monitoring networks and also to help in the interpretation of the data.

In the 1970s-1980s many international publications appeared containing data on background environmental concentrations of various pollutants. These studies covered wide geographic areas, including the Antarctic Continent and high seas. Some of the measurements had been performed in the 1960s.

However, generalization of these data is complicated by a number of principal difficulties, such as:

1. Observations cannot be extrapolated to other areas beyond the geographical location of an observation. In most cases information about the possible impact of local sources on observation results is not available.

2. A relatively short observation cycle in each particular case; only in a few cases, has it covered a period of several months at one site.

3. Conditions and statistical representativity of measurements can be absolutely different in different countries and continents. It is impossible to take into account meteorological and climatic characteristics as measured by different authors. It is also impossible to take into account the geochemical background in various regions under study, which can have a particularly strong effect on environmental objects, such as soil, surface water and biota.

4. The comparison of data from various studies cannot always be justified due to differences in methods and instruments applied.

5. Different authors were interested in different anthropogenic substances.

The above difficulties would undoubtedly be overcome if global background pollution could be described with the help of a sufficiently long series of observations carried out at the IGBM network according to a unified program and using unified methods, and if IGBM stations were sited on the basis of identical principles and recommendations. In one case this condition is fulfilled, namely - some East European countries have created an IGBM network with observation series 4-6 years (sometimes up to 10 years) long. The results have been used in the present

outline.

The present analysis deals with substances most frequently measured when studying the background. To a certain extent, this characterizes their priorities. In addition, when performing the analysis, we gave preference to studies using the most up-to-date measuring methodologies to exclude systematic errors, if possible.

Besides, there are also specific limitations in the application of observation analysis to particular environmental objects. These will be considered later.

4.1 Atmosphere and Precipitation

Generalized data on background pollution of the atmosphere and precipitation are given in Table 1 (Rovinsky et al., 1982a; Rovinsky et al., 1982b; Rovinsky et al., 1982c; Egorov, 1984; Yushkan et al., 1984; Afanasyev et al., 1984; Petrukhin et al., 1986; Afanasyev et al, 1986; Pastukhov, 1986). In this case the atmosphere is characterized by mean daily concentrations. Many publications present only mean hourly concentrations for ozone (this is noted in Table I), which cannot be fully compared with mean daily values, due to specific diurnal variations of atmospheric ozone concentrations. For some substances, the atmospheric state of aggregation is particularly important. Mercury exists in ambient air mainly in a vapor state (90-95%) (Petrukhin et al., 1982). Therefore, 10-20 fold values of mercury aerosol component should be taken to compare data obtained by various authors. The same refers to DDT (with metabolites) whose distribution between the solid and vapor phases is about uniform (Rovinsky et al., 1982; Afanasyev et al., 1984; Afanasyev et al., 1986); here the uncertainty factor is approximately equal to 2.

As seen from Table 1, there exists a conformity to one principle: background atmospheric pollution (in terms of every indicator) in Europe, North America and Asia is higher than in South America, Africa and Australia. The minimum background pollution values are observed over the oceans and Antarctic Continent. This conclusion is most evident when based on maximum boundary values within the ranges given. At the same time the range of the minimum background values between various parts of the globe as a whole is less significant.

Evidently, the measured minimums are close to natural atmospheric concentrations of the substances under study, though these should vary from region to region. For example, for the group of heavy metals, natural concentrations depend on their content in the underlying soil and bedrock, as well as on weathering conditions. Of course, this assessment does not concern DDT, which is a purely anthropogenic substance.

Regular daily observations carried out at the IGBM network

Table I
Background Pollution of the Atmosphere and Precipitation

Pollutant	Units of measurement	Europe	Asia	North America	South America	Africa	Australia	Antarctic Continent	World Ocean
1	2	3	4	5	6	7	8	9	10
					Ambient air				
Sulfur dioxide	ug/m^3	0.02-22	0.01-19	0.5-15	0.05-3.2	0.8-6.1	-	0.05-0.5	0.04-4
Sulfate	ug/m^3	2-11	2.2-5.9	2.6-18	0.1-0.3	1.5-1.8	-	0.01-1.6	1-3.9
Nitrogen dioxide	ug/m^3	0.6-6	-	2-25	1-10	-	0.1-0.5	-	0.3-1.2
Ozone	ug/m^3	40-90	-	40-115	-	4-80**	24-66xx	40-70	70
Lead	ng/m^3	2-125	2-51	0.2-72	1.9-11	15-77	-	0.1-0.6	0.02-1.9
Mercury	ng/m^3	5-49	2-42	0.5-50	0.05-0.07***	0.4-0.7***	-	-	0.4-3.5
Cadmium	ng/m^3	0.05-13	0.03-1.2	0.2-2	0.02-1.1	<1.2	-	0.02	0.01-0.6
Arsenic	ng/m^3	0.2-5.4	0.6-3.7	0.2-2.5	0.1-1.6	0.6-1.7	-	0.01	0.02-0.2
DDT*	ng/m^3	0.07-3.5	0.1-0.2	0.1-19.5	-	-	-	0.02-0.2	0.001-3.9
3,4-benzo-a-pyrene	ng/m^3	0.02-2.3	0.06-0.5	0.01-2	0.03-0.06	-	-	0.0001-0.001	0.0002-0.2
					Atmospheric precipitation				
Lead	ug/l	0.3-64	0.5-20	0.3-39	-	<13	4.7	0.005-0.2	0.01-9
Mercury	ug/l	0.03-1.5	0.05-1.8	0.01-2.2	-	<0.3	-	0.03	
Cadmium	ug/l	0.02-3.4	0.1-4.9	0.01-1	-	<1.3	-	0.003-0.03	
Arsenic	ug/l	0.5-3.9	0.4-6.1	0.02-4	-	<1.4	-	0.008-0.03	0.02-0.03
DDT*	ng/l	1-250	1-215	-	-	-	-	0.2-8	0.1-13
3,4-benzo-a-pyrene	ng/l	3-6	3-13	0.1-3.1	-	-	-	-	-

Notes: * DDT is given with its metabolites (DDE, DDD);
** mean hourly concentration;
*** aerosol mercury

in Eastern Europe and Asia (Bulletin of Background Environmental Pollution in the Region of the East European CMEA Member Countries, 1983, 1984, 1985; Rovinsky et al., 1983; Izrael and Rovinsky, 1985; Rovinsky et al., 1985; Petrukhin et al., 1986) have shown that background pollution is a constant parameter at one site, but is subjected to intra-annual and seasonal variations. In winter the concentrations of sulfur dioxide and 3,4 benzo-a-pyrene are 4-10 times higher than in summer, and those of lead, cadmium and arsenic are 1.5-3 times higher. The variations of suspended particulates and mercury concentrations have an opposite seasonal trend, i.e., their maxima are observed in summer. Ozone content is hghest in the spring/summer period.

The above dependences are associated with the major source of the atmospheric input of these pollutants. The first group of substances (sulfur dioxide, 3,4-benzo-a-pyrene, lead, cadmium, arsenic) is closely related to power stations and heating systems whose emissions increase in the cold season. Dust and mercury sources are dependent on the state of the underlying surface; their emissions increase in summer. The annual maximum of ozone is associated with the period of the most intensive air mass exchange between the stratosphere and troposphere.

Background pollution of atmospheric precipitation is less studied than that of ambient air, especially in the southern hemisphere. On the whole, background pollutant concentrations in the atmosphere and precipitation are well correlated. Analysis of glacier layers presented in a number of papers (e.g., Nikolishin et al., 1979) shows that heavy metal content in precipitation of the northern hemisphere has noticeably increased over the last decades. At the same time, recent studies of glacier layers in the Antarctic Continent have not revealed an equally significant trend in the southern hemisphere (Boutron et al., 1984; Boutron, 1982). Recently, Wiersma and Davidson (1986) reviewed the literature from the last 10 years on trace element concentrations in background atmospheres.

4.2 Surface Waters, Soils and Biota

Unlike the atmosphere where pollutants have rather short lifetimes, terrestrial surface waters are a more conservative element of the biosphere. Pollutant content in background surface waters depends on both geochemical peculiarities and anthropogenic impact which manifests in the global or regional chain of transport:

1) atmosphere → surface waters
2) atmosphere → catchment soils → surface waters

The first pathway is typical of lacustrine water bodies, the second one is a characteristic of rivers.

River runoff is formed by surface and subsurface runoff and

determines discharge of substances beyond the landscape limits and, eventually, into seas and oceans. At present there are hardly any big rivers in the world which are not exposed to direct pollution (discharge of industrial, agricultural or municipal wastewaters). International reported data on water and sediments from background areas for lakes, river heads, and rivers in sparsely populated areas, are rather scarce. Table 2 summarizes such data obtained from the aforementioned reviews. It can be seen that the variation ranges of the substances considered are as wide as for the atmosphere and precipitation, and that the northern hemisphere is described much better than the southern one.

Due to a relatively rapid sorption and sedimentation, pollutants find their way to bottom sediments which, compared to water, are usually enriched by these pollutants.

The variations in the background content of heavy metals in soils (only the upper several cm-thick horizon is considered) must be primarily related to soil formation processes and geochemical conditions of a given area. To a lesser degree pollutant content in soils depends on the atmospheric input. However, for DDT the role of the atmospheric input is exceptionally important, since DDT is a completely man-made substance. The modern background soil concentration of lead in industrially developed countries is 35 mg/g (Bowen, 1979) which is 3 times as high as the Clark value determined more than 30 years ago (Vinogradov, 1957). Lead increase in the surface soil layer is caused by anthropogenic input from the atmosphere.

Data on pollutant content in biota (flora and fauna) are most difficult to generalize. Pollutants enter vegetation both via root nutrition system and directly from the atmosphere. So the variations in background pollution of vegetation depend not only on the variations typical of the atmosphere and soil, but also strongly depend on species composition of plants. In one and the same region pollutant content in the sequence grass-leaves-needles-lichens-mosses increases by 2-3 orders of magnitude (for the extreme members of the sequence). Generalization of data on background pollution of fauna samples is a still more difficult task since pollutant content in living organisms is dependent not only on environmental variations, but also on ecological peculiarities of species.

4.3 Major Anthropogenic Sources of Pollutant Input to the Atmosphere

As has been mentioned above, the present guidance is meant for establishing a global network of IGBM stations. All other conditions being equal, the network density also depends on the global distribution of atmospheric pollution sources. Since we are speaking about terrestrial continental stations, pollutant input to such ecosystems might be attributed to atmospheric sources. Based on UNEP (1982), Ostromogilsky et al. (1985) and

Table 2. Background pollution of surface waters, soils and vegetation

Pollutant	Units of measurement	Europe	Asia	North America	Africa	Australia
			Surface Waters			
Lead	ug/l	0.06-9	0.2-9	0.2-36		1-10
Mercury	ug/l	0.01-6.5	0.01-1.3	0.01-5		0.01-0.
Cadmium	ug/l	0.05-10	0.03-1.9	0.01-3.8	0.4-0.6	0.02-3
Arsenic	ug/l	0.02-6.3	0.2-9	0.08-7.5		
DDT	ng/l	2-300	2-90	4-400	10-73	
3,4 benzo-a-pyrene	ng/l	0.01-25	0.1-3	0.3-77		
			Freshwater sediments			
Lead	mg/kg	1-110	10-76	2-70		23
Mercury	mg/kg	0.01-11	0.01-0.8	0.06-2.1		0.13
Cadmium	mg/kg	0.04-5.7	0.06-2.1	0.2-12	0.1-13	
Arsenic	mg/kg	0.4-13	3-11	1.3-13		
			Soils			
Lead	mg/kg	2.8-80	2.5-40	5.2-73	0.1-71	14-20
Mercury	mg/kg	0.001-0.3	0.004-0.3	0.002-0.2		
Cadmium	mg/kg	0.01-2.1	0.02-3.2	0.05-0.6	0.01-0.8	0.05-0.2
Arsenic	mg/kg	0.01-8.6	0.02-12	1-7.5	5-6	
DDT	ug/kg	2-100	1-15	20	10	
3,4 benzo-a-pyrene	ug/kg	0.3-15	0.1-15	1-40		
			Vegetation*			
Lead	mg/kg	0.3-22	0.4-12.6	2-37		
Mercury	mg/kg	0.01-0.6	0.004-0.9	0.03-0.8		
Cadmium	mg/kg	0.01-1.2	0.02-0.4	0.05-1		
Arsenic	mg/kg	0.01-0.8	0.05-1.4	0.5-1		
DDT	ug/kg	2-85	1-64			
3,4 benzo-a-pyrene	ug/kg	1-65	0.7-48			

* Including all major types of terrestrial vegetation: mosses, lichens, coniferous, deciduous and herbaceous species.

Suess (1976), one can assess the distribution of anthropogenic sources of a number of pollutants between the northern and southern hemispheres (see Table 3).

Table 3. Anthropogenic pollutant input to the global atmosphere; thousand tonnes per year

Hemisphere	SO_2	Pb	Hg	Cd	As	DDT	3,4 BP
Northern	190,000	400	5.8	8	33	16	4.5
Southern	10,000	25	0.6	1.5	7.3	4	0.7

These estimates show that the atmospheric input of anthropogenic pollutants in the northern hemisphere is 4-19 times greater than in the southern one. Taking into account a poor air mass exchange between the hemispheres, it should be considered that in the northern hemisphere the anthropogenic input of these substances to ecosystems is greater, as well. This, on the one hand, accounts for a better understanding of background pollution in the northern hemisphere and, on the other, indicates the need for a greater detailization when organizing the IGBM system in the northern hemisphere.

5. ESTABLISHING INTEGRATED GLOBAL BACKGROUND MONITORING STATIONS

5.1 A Standard IGBM Program

The development of a standard IGBM program is an important stage; the program should meet the tasks and objectives of the IGBM system. When establishing a program for integrated global background monitoring of environmental pollution, one should identify:

- a list of priority pollutants of anthropogenic origin;
- objectives (or environments) exposed to large-scale pollution impacts;
- recurrence (or frequency) of observations;
- concommittant (or supplementary) observations.

To our minds, to establish the list of priority pollutants is the most complicated task. Only few of many thousands of pollutants emitted into and dispersed in the environment should be selected for the IGBM program. The selection criteria were considered at the Intergovernmental Meeting on Monitoring in 1974 (UNEP, 1974). They included various characteristics of pollutants such as: abundance, persistence, toxicity, transformation into more harmful compounds (products), transport along food chains, and accumulation in organisms. These criteria have preserved their significance to the present moment.

Persistent application of these criteria to large-scale processes makes it possible to specify the list of priority pollutants now that some important problems (impact on climate and ozone layer, acid rains and their ecological consequences, mass forest suppression and degradation far from pollution sources) are better investigated.

The lists of priority pollutants compiled in the USSR and the USA are almost identical (see Table 4).

Table 4. List of priority pollutants of anthropogenic origin

Pollutant	USSR[1]	USA[2]
Atmospheric suspended matter (dust)	+	+
Turbidity (of the atmosphere)	+	+
Ozone (tropospheric)	+	+
Carbon monoxide	+	+
Sulfur dioxide, sulfate	+	+
Reactive hydrocarbons	+	+
Freons	–	+
DDT and other organochlorine compounds	+	+
3,4-benzo-a-pyrene	+	–
Lead	+	+
Mercury	+	+
Cadmium	+	+
Arsenic	+	+

1. Rovinsky et al., 1977
2. Morgan et al., 1979

Substances from Table 4 are still of vital importance. However they should be commented on from the viewpoint of their inclusion in the IGBM program.

First, observations related to a possible impact on climate and ozone layer:

At present, the list of substances and indicators of the state of the atmosphere that are to be studied from the viewpoint of climatic consequences has been considerably extended. It includes radiatively active trace "greenhouse" gases – CO_2, N_2O, CH_4, freons, and ozone. Freons, N_2O and some other substances are also important as those affecting the ozone layer. In this connection monitoring of the integral content of ozone and its density in the ozonosphere is an essential parameter. We believe that such measurements should be carried out at a specialized WMO network. At the same time some IGBM stations can perform these

types of monitoring as an optional program, when expedient.

Second, observations related to a possible growth of the tropospheric ozone and its impact on natural ecosystems and agrosystems:

In this case, it is considered advisable that the basic IGBM program should include monitoring of tropospheric ozone, and an optional measurement carried out at some IGBM stations monitoring of C and reactive hydrocarbons, which could be associated with the genesis of the anthropogenic component of tropospheric ozone.

Third, observations related to the long-range (including transboundary) pollutant transport, acid rain formation, mass forest decline and other ecological consequences:

In this case it would be expedient to include the BAPMoN and EMEP programs in the IGBM program to complement (or to combine) the above programs and to have a possibility of assessing ecological effects. Besides, the IGBM program should include a number of anthropogenic substances that might get involved in natural cycles, accumulating in critical ecosystem objects, and causing large-scale ecological consequences. Therefore, the IGBM program should include not only measurements of pH of various media, sulfur and nitrogen oxides, but also measurements of substances like some heavy metals, 3,4-benzo-a-pyrene, DDT, and other widely used organochlorine pesticides.

Another important part of the IGBM program requires us to determine environments and environmental objects to be monitored. To determine them, one should obtain information both on the spacial and temporal distribution of pollutants, and on their migration, cycling and crossmedia transport; besides, it is necessary to identify critical ecosystem links. Consequently, the objects to be monitored are ambient air, atmospheric deposition, soil, surface waters, flora and fauna species. When the territory of a background station (or any territory that might be referred to it) offers an adequate monitoring object, e.g., a lake, the optional program should include monitoring of bottom sediments. All non-biological environments are rather easy to unify. The unification of biological objects is a complicated or even impossible task within the framework of the whole global IGBM network. However, it is partly possible for individual regions, though it would require additional research with the participation of botanists and zoologists and consideration for the ecological peculiarities and ecosystem relations of a given region.

Determination of the recurrence (or frequency) of observations is an integral part of the IGBM program. Ambient air and atmospheric deposition are the most labile component from the point of view of IGBM. Experience shows that in ambient air monitoring, in general, 24 hours would make quite a satisfac-

tory period for averaging a primary measured value. When solving large-scale problems, diurnal variations of parameters measured can be neglected, since they are not significant, as a rule. Ozone might be a noticeable exception, especially when air masses are transported from urbanized zones, but its mean daily concentration in the atmosphere can be determined with a sufficient reliability. The information obtained in about 300 measurements a year might seem abundant from the viewpoint of revealing multiyear (mean annual or mean seasonal) trends. However, one should allow for the real loss of information due to various accidents and, first and foremost, for the fact that pollutant content in the atmosphere at one site can strongly depend on air mass history (Rovinsky and Cherkhanov, 1983; Izrael et al., 1984). As for monitoring of atmospheric deposition, the averaging period can be taken equal to a week based on WMO experience with the implementation of the BAPMoN program.

Surface waters are a less labile medium than the atmosphere and precipitation. Observation frequency should be confined to major hydrological phases: The minimum frequency would be 3 times during floods (rise, peak, fall) and once in the low water period. To prevent accidental losses of information, all samples should be doubled.

Bottom sediments and soils are the most conservative environments. The sampling frequency should be twice a year, with samples taken at some fixed time, e.g., in spring and in autumn. Flora and fauna observations depend on species peculiarities and should not be more frequent than twice a year. Sample doubling is obligatory.

Meteorological, hydrological and other observations, used to interpret results obtained, make up an indispensable part of the IGBM program. Measurements of ambient temperature and atmospheric pressure are required to estimate the volume of air forced through pumps while collecting samples on filters and sorbents. In a broader context, the estimates would require meteorological information to trace back air mass trajectories when measurements would show anomalous pollutant concentrations in the atmosphere. To estimate pollutant fluxes from the atmosphere to the underlying surface, one would need data on precipitation amount.

Hydrological (standard) observations of brooks, rivers, and lakes are required not only to determine hydrological phases and sampling periods, but also to calculate pollutant budgets within a catchment or water body.

Observations of pollutant concentrations in biotic objects, e.g., autotrophic vegetation, require data on the biomass to estimate the total pollutant input. The IGBM program discussed above is presented in Table 5.

Table 5. The program for stations of integrated background monitoring of environmental pollution[1]

Environment (objects)	Basic program	Optional program	Observation frequency
1	2	3	4
Ambient air	Suspended particulate matter (dust), sulfur dioxide, atmospheric turbidity, ozone, nitrogen oxides, sulfate, lead, mercury, cadmium, arsenic, 3,4-benzo-a-pyrene, DDT, HCCH[2], PCBs	CO_2,N_2O,CH_4,CO, freons, reactive hydrocarbons, Other heavy metals (V, Ni, Zn, Ag, Sn, Sb)	Daily (300 times/year
Atmospheric precipitation and deposition	pH, anions, cations (according to BAPMoN program), lead, mercury, cadmium, 3,4-benzo-a-pyrene, DDT, HCCH, PCBs	Other heavy metals (V, Ni, Zn, Ag, Sn, Sb)	Weekly (50 times/year
Surface waters	pH, lead, mercury, cadmium, arsenic, 3,4-benzo-a-pyrene DDT, HCCH, PCBs	Other heavy metals (V, Ni, Zn, Ag, Sn, Sb), methyl mercury	Up to 8 times/year (3 times during the flood and once during the low water period.)
Soils, bottom sediments	pH, lead, mercury, cadmium, arsenic, 3,4-benzo-a-pyrene DDT, HCCH, PCBs	Other heavy metals (V, Ni, Zn, Ag, Sn, Sb)	Twice/year
Biota	Lead, mercury, cadmium, arsenic, 3,4-benzo-a-pyrene, DDT, HCCH, PCBs	Other heavy metals (V, Ni, Zn, Ag, Sn, Sb)	Twice/year

1. Analytical chemistry techniques allow simultaneous detection of a large number of trace organics and trace elements.
2. HCCH - hexachlorocyclohexane, component of the pesticide lindane

5.2 Recommendations for Site Selection for Integrated Global Monitoring Programs

In order to select background monitoring sites for integrated global background monitoring, it is necessary to follow a consistent set of guidelines. This will help ensure uniformity and consistency in sites making up the integrated global background monitoring system.

The most appropriate siting criteria would seem to be those established for the WMO BAPMoN stations as modified in 1979 (WMO, 1980).[1] These are:

1. The site should be located in an area where no significant changes in land-use practices are anticipated for at least fifty years within 100 km in all directions of the station. For mountain stations well above the surface mixing layer, this criteria can be relaxed somewhat.

2. The site should be located away from population centers, highways and air routes, preferably on small isolated islands (uninfluenced by sea spray) or on mountains above the tree line.

3. The site should experience only infrequent effects from local natural phenomena such as volcanic activity, forest fires, dust and sandstorms.

The criteria are vague concerning what a background measurement is, but the report seems to imply that a local pollutant source was acceptable provided it did not affect the instruments greater than 60% of the time. Taken literally, this would be unacceptable for an integrated background monitoring site because many of the parameters measured (vegetation, soil, litter) are integrating in nature, i.e., they cannot be turned off. Any pollution sources, therefore, even if they affected the source only 40% of the time, would still be a serious source of contamination.

A second set of site selection criteria was presented in the WMO report, Environmental Pollution Monitoring Programme (WMO, 1980). With the removal of references to specific sites which are not appropriate for this manual, these criteria were:

1. The area should be typical of the region in terms of the following physiogeographical characteristics: relief, climatic factors (nature of the atmospheric circulation, thermal regime in the atmosphere, amount of precipitation, etc.), nature and state of the soil, and plant cover and the hydrologic system.

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[1] For additional history see WMO (1976)

2. The area should not be subject to the direct influence of any major pollution sources (i.e., industrial pollution sources) Small human settlements, agricultural holdings, road, air routes, etc. should also be minimal.

3. The areas should be located in a minimum amount of economic activity, and there should be no substantial anticipated change in the nature of this activity in coming decades.

4. The area should have a reasonably restricted core area.

5. The area should be in a region that is relatively easy to access.

6. The area should have a relevant research institute nearby and a good set of existing background data.

This list appears to be more directly related to the selection of background monitoring sites than the previous list and will serve as an initial set of criteria for site selection in this manual. The International Biosphere Reserve System will serve as the initial universe from which to draw the baseline sites.

Based upon the above, the selection criteria that could be suggested for use in identifying an integrated global background monitoring site are listed below. This list is divided into two categories: mandatory criteria and desirable criteria.

Mandatory criteria are:

1. Size - the size of the reserve can help to ensure that several of the WMO site selection criteria can be met. For example, adequate size will help minimize local influences. It would help ensure that an adequate core exists and would help shield it against changes in economic activity.

   With this in mind, a size criteria is set at 20000 hectares. However this requirement may, of necessity, be altered to meet local conditions.

2. Access - the area should be reasonably accessible without allowing large numbers of automobiles, buses, etc. equally easy access.

3. Protection - the area should have institutional protection (i.e., government, state)in perpetuity. This will not only help the core area, but in some cases could significantly alter economic development in the surrounding areas.

4. Staff - the site should have a permanent staff. This will increase the likelihood, but not guarantee, that the following services will be available:

   - Protective oversight
   - Scientific studies
   - Logistical staging areas
   - Personnel available to provide sampling support

5. Biological system type - the reserve should have a biological system representative of a major biogeographical type in the world.

Desirable criteria are:

1. Undeveloped surrounding area - this will help ensure a buffer zone and increase the undisturbed nature of the site.

2. No history of disturbance - this attribute will help to increase the natural condition of the reserve.

3. Park staff greater than five - this is based on the premise that the larger the resident staff, the greater is the possibility that the area will have suitable facilities and ongoing activities that will be useful to the monitoring program.

4. Scientific research underway - three kinds of research are envisioned:
   - pollutant monitoring
   - impact studies
   - basic ecology studies

5. Data availability - examples of data that will be nice to have are:
   - Meteorological
   - Hydrological
   - Geophysical
   - Soils
   - Geohydrology
   - Biological, including such things as species lists, forest type maps, census data, etc.

5.3 Technical Requirements for Stations and Regional Laboratories

The cited requirements mainly stem from methodological recommendations of observations, sample collections, and analysis to be described later in Sections 6 and 7.

Based on their complexity and labor consumption, demand for

sophisticated instruments and qualified personnel, observations and measurements envisaged by the IGBM program are divided into three categories:

1. Manual or automated observations and measurements carried out directly at the observation site.

2. Observations or sample analysis which require rapid processing or measurements with the help of a relatively simple equipment.

3. Measurements whose methodologies allow the transportation of preserved samples and require more sophisticated instruments and highly qualified personnel.

Therefore, primary data acquisition and sample collection and initial treatment require us to establish observation sites and a small, logistical support base at the site. The more sophisticated support laboratory that will be required does not necessarily have to be on the site.

To implement a program of ambient air and atmospheric deposition monitoring one needs a standard meteorological test site (50 x 50 m) to install air and precipitation samplers, automatic gas analyzers, a turbidimeter and a set of standard meteorological instruments.

The test site must be located in an even, uniform landscape open to horizons, with due regard for siting criteria for meteorological observations.

To implement a program of surface water monitoring, it is necessary to organize a standard hydrological (river or lake) gauging-station which would enable one to perform standard hydrological observations and water and sediment sampling. The site of stationary hydrological observations should be representative and provide continuous observations all year round. The size of the river basin, its discharge, alimentation regime, and natural water chemistry must correspond to a given hydrological area. There should be no water reservoirs, drainage and irrigation systems, extended water supply, wastes and effluents discharge in the basin of the water body under study.

To implement a program of soil and vegetation monitoring within a landscape under study it is necessary to select a 100 x 100 m site with a typical soil and vegetation cover. There can be several sites of this kind depending on the diversity of soils and their representativeness for the given natural zone. The selected sites should be intact; no economic activity is allowed there.

Not far from the air monitoring/meteorological site (at about 500 m), ideally there should be a small building with an area of 75-125 m^2 designed for carrying out activities of the

second category. It must be electrically heated to prevent local atmospheric pollution. The building should include working rooms for observers, gas analyzer chambers, storage space for nonexposed and exposed filters and sorbents, rooms for water sample initial treatment (conservation), rooms for soil, sediment or biota sample treatment (drying, milling), rooms for weighing or simple analyses, for example, using a photoelectric colorimeter. The building must also be equipped with refrigerators to store certain samples prior to their transportation to the regional laboratory. All activities resulting in atmospheric emissions of pollutants capable of affecting the monitoring program carried out are forbidden. The number of workers and their stay in the building must be limited. Adequate power supply and a hard-coated road to the observation site and laboratory building are requisite. However, in places in the world these ideal conditions cannot be met and appropriate adjustments have to be made to get the samples to the regional laboratories.

Analysis of air, sediment, water, soil and biota samples for background concentrations of inorganic and organic substances requires rather sophisticated methods and instruments, as well as highly qualified personnel. So it is impossible and inadvisable to carry out these types of analytical measurements directly at an IGBM station.

Each group of IGBM stations should be provided with a regional laboratory which would receive both primary data obtained at IGBM stations and representative pretreated samples. The regional laboratory performs final sample measurements, provides quality assurance of all data obtained at IGBM stations, carries out data analysis generalization and publication. The functions of the IGBM center can be performed by one of the regional laboratories.

5.4 Monitoring Systems Design

Munn (1973) states that it is essential that GEMS be designed in such a way that interactions between media can be studied, permitting delineation of the pathways of biogeochemical cycling. The integrated background monitoring network discussed in this paper will very likely become a significant component of GEMS and shares many of the goals of GEMS. Therefore, a systems approach to the design of the site specific monitoring program is essential. A promising technique for accomplishing this is the use of kinetic models. Theoretical bases for these models have been described in detail by O'Brien (1979), Miller and Buchanan (1979), and Barry (1979). Wiersma (1979) has applied the approach to the design of the biosphere reserve monitoring project in the Great Smoky Mountains National Park, USA, as well as other national parks in the US and Chile.

This approach starts with a schematic representation of the system to be monitored. It must be emphasized at the outset that what is intended is not a predictive model, but merely a tool to

help design and evaluate the system of interest. The kinetic approach does this by forcing one to consider the system as an entity at the time the monitoring program is being conceived. Doing this also sets up a procedure for carrying out the data analysis.

Normally, a group of people with expertise concerning the various aspects of the system at hand get together and develop the schematic relationship which depicts the environmental system of concern. Usually just this exercise is a tremendous assist to logically evaluate the environmental system of interest.

Once the schematic is in hand, a series of equations can be developed that further help to describe the system. The derivation of these equations and their use will not be covered in this report but are readily described in the papers cited in the introduction to this section.

Advantages to using this type of an approach are:

1. It forces the designer to consider the system as a whole and not a series of distinct environmental components.

2. It forces an analysis and consideration of the physical, chemical, and biological factors influencing pollutant transport and distribution in the system.

3. It sets up analytical procedures for the data analysis at the time the monitoring system is designed.

4. It shows the functional relationship between pollutant levels in different environmental media.

5. It identifies points where the sampling design could be changed to provide for a more efficient monitoring system.

6. It identifies gaps in the current knowledge of physical, chemical, and biological factors influencing the transfer of pollutants and provides guidance to controlled studies addressing pollutant kinetics.

Some disadvantages to this approach are:

1. A very large data base may be required.

2. The unwary user may be lulled into believing the answers produced by the equations are predictive in nature.

3. This method will not result in optimization of sampling locations.

6. REPRESENTATIVE SAMPLING OF ENVIRONMENTAL OBJECTS AND BIOTA: SAMPLE PRETREATMENT, PRESERVATION AND STORAGE

6.1 Air Sampling

6.1.1 Principles and characteristics of the method[1]

Air samples to be analyzed for suspended particulate matter (dust), heavy metals, sulfate, 3,4-benzo-a-pyrene, DDT, and HCCH are commonly collected using forced air filtration. Air is filtered by air samplers. An air sampler consists of an air pump, air flowmeter, filter holder protected from atmospheric deposition, and a solid sorbent cell (for DDT and HCCH detection).

Sampling is carried out by different types of filters which pass no more than 10 per cent of particles below 0.3-0.5 um. The type of filter is selected according to the purpose of the sample collected and method of sample analysis. Depending on the method of analysis applied, the analytical laboratory specifies the volume of daily air samples required to define the aforementioned compounds. The air flow and filter holder cross-section are calculated on the basis of the sample volume specified and the range of the permissible linear flow rate through the selected type of filter.

The IGBM observation program envisages collection of diurnal air samples to be analyzed for pollutant concentrations. To this end, filters are changed on a daily basis at a definite hour (in the morning). When preparing air samplers, filters are taken from their package by tweezers, put on the filter holder screen and fixed by a clamp. When the exposure is over, the operations are performed in the reverse order.

To define the atmospheric content of DDT and HCCH, aerosol and gas/vapor components are sampled. For this purpose the air sampler should be equipped with a solid sorbent cell mounted in the air duct behind the filter. The cell with a diameter of 30-50 mm contains 20-50 cm^3 of adsorbent (silochrome S-80 or S-120).

Filters inserted in an air sampler meant for collecting samples to be analyzed for dust should be preliminary dried to a constant mass and weighed.

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1 See also WMO (1974)

6.1.2 Equipment and materials needed:

Air Samplers
- dust;
- heavy metals;
- 3,4-benzo-a-pyrene
- DDT and HCCH
- NO_3
- sulfate
Filter materials for sample collection and dust analysis
Adsorbants: silochrome S-80 and S-120 (pretreated fractions from 0.3 to 0.5 um)
Clean bags
Scissors
Tweezers
400 ml glass jars with air-tight plugs

6.1.3 Sample collection and storage

To collect samples, air samplers are located at the observation site in a 1.5 m space. The air inlet is elevated to a 2 m height and oriented horizontally upward which prevents an effect from wind direction and speed on sampling efficiency.

When the filter exposure is over, the air sample volume is measured and then reduced to normal conditions by the following formula:

$$V_o = \frac{273\ P \times V}{(273+t)\ 760} = 0.359\ \frac{P \times V}{273+t} \qquad (1)$$

where
P - mean atmospheric pressure during filtration, mm Hg;
V - sample volume, m^3;
t - mean air temperature over the sampling period, degrees C.

Exposed filters are packed into labeled clean bags and the exposed adsorbent is placed into a labeled glass jar with an air-tight plug. Samples are stored in a dry room or in a refrigerator to be analyzed for DDT, HCCH, and 3,4-benzo-a-pyrene.

Three unexposed filters and sorbents from each set are sent to the analytical laboratory for the determination of background component concentrations in filters and sorbent. Methodological instructions on ambient aerosol sampling for detecting the above ingredients at specific IGBM stations are based on the aforementioned general principles with due regard for specific sampling devices, selected types of filters and methods of sample analysis applied.

6.2 Sampling of Atmospheric Precipitation and Deposition (including snow cover)[1]

6.2.1 Sampling of atmospheric precipitation

Samples of atmospheric precipitation are considered representative if the initial content of substances analyzed is not changed at the moment of sampling, during storage and transportation to the place of analysis.

Considerable distortion of data on the concentrations of components under study can result from the contamination of the absorption surface of the precipitation sampler by dry deposition in the absence of rains, from the inherent availability of substances under study in the material of the absorption surface, or from inadequately cleaned glassware. In this context great importance is attached to precipitation sampler design and construction material, and sterility of chemical utensils used.

In accordance with the program of background precipitation pollution monitoring, samples are analyzed for a number of inorganic and organic substances.

The absorption surface of a precipitation sampler for collecting samples to be analyzed for inorganic pollutants (heavy metals, anions, cations) can be made of polyethylene, Yenaor pyrex-type glass, or teflon. In sample collection for determining organic substances, the absorption surface can be made of glass or enamelled metal.

The best precipitation sampler recommended for IGBM stations is an automatic precipitation collector with a lid that opens to a sensor signal. The signal is generated when the first raindrops fall on the sensor.

If automatic precipitation collectors are not available, one can use polyethylene or enamelled cylinders not less than 30 cm high. Another version of a nonautomated precipitation collector can be designed as a welded polyethylene or stainless steel cone connected to a receiving vessel.

Precipitation collectors are installed at the sampling site either on wooden table-like mounts or fixed by tension devices 2m above the underlying surface.

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1. WMO Operations Manual No. 491 contains detailed recommendations on precipitation and deposition sampling. These recommendations should be used in IGBM station operations whenever possible.

The area of the collector's receiving surface (S) which ensures the required volume of a weekly sample is calculated on the basis of mean multiyear weekly sum of precipitation J(mm) for a given region and sample volume specified, V(l):

$$S(m^2) \quad \frac{V(l)}{J(mm)} \qquad (2)$$

Samples to be analyzed for each type of pollutant are taken by individual precipitation samplers. In compliance with the observation program, four samples are collected simultaneously:

- sample to be analyzed for lead, cadmium and arsenic;
- sample to be analyzed for mercury;
- sample to be analyzed for anions and cations (BAPMoN program);
- sample to be analyzed for 3,4-benzo-a-pyrene, DDT, and HCCH.

6.2.1.1 Equipment and Materials Needed:

Precipitation collectors with polyethylene receiving surface
Precipitation collectors with an enamelled or steel receiving surface
Polyethylene bottles (0.5 and 1L).
Glass bottles (2L)
Measuring cylinders (100, 1000 and 2000 ml)
Pipettes (5 ml)
Superpure concentrated nitric acid.
Twice-distilled n-hexane
Chemically pure potassium bichromate

6.2.1.2 Sample collection, preservation and storage

Precipitation collectors installed at the observation site are to be clean. To this end, the receiving surface is treated with detergents, rinsed with water and then distilled water. If a background station has a stationary working regime, precipitation samples are taken every day at a fixed time. In the absence of precipitation, the receiving surface of nonautomated collectors is rinsed with distilled water and kept exposed for 24 hours. After that, the operations are repeated.

To obtain a total weekly precipitation sample, daily samples are accumulated. Diurnal precipitation from collectors is transferred to relevant bottles (flasks) whose volume should 1.5-2 times exceed sample volume required for analysis.

Samples to be analyzed for inorganic substances are stored in polyethylene bottles and acidified; those to be analyzed for organic substances are stored in glass ones.

The bottles are labeled in accordance with the defined precipitation components:

- lead, cadmium, arsenic;
- mercury;
- anions, cations;
- 3,4-benzo-a-pyrene, DDT, HCCH

Weekly precipitation sample volume required for the analysis of each component is specified by the analytical laboratory depending on the method of analysis applied. The minimum volume can be as follows:

- for lead and cadmium	0.2 - 1.0 L
- for arsenic	0.2 - 0.5 L
- for mercury	0.1 - 0.5 L
- for 3,4-benzo-a-pyrene, DDT, HCCH	1.0 - 2.0 L
- for anions and cations	about 1.0 L

Precipiation samples to be analyzed for heavy metals are preserved immediately after sampling using 5 ml of concentrated nitric acid per 1.0 L of the sample. Samples to be analyzed for mercury are treated not only with nitric acid, but also with 0.2g of potassium bichromate per 1.0 L of the sample.

Precipiation samples to be analyzed for organic substances are preserved after the required sample volume is accumulated, i.e., an aliquot of a mean weekly sample is preserved using 20 ml of twice-distilled n-hexane per 1 L of the aliquot.

At negative air temperatures, snow collected in the sampler is transferred to some clean chemical vessel and melted at room temperature. All subsequent operations are similar to liquid sample treatment.

Weekly precipitation samples to be analyzed for heavy metals are stored in a cool dark place; samples to be analyzed for organic matter are stored in a refrigerator.

6.2.2 Weekly sampling of (total) atmospheric deposition

Heavy metals and organic substances deposited from the atmosphere on the earth's surface with dust and precipitation are sampled by a collector with a horizontal surface.

The sampler is either an 0.08 m^2 polyethylene cell with 10-15 cm high edges or a high-walled cylinder with the cross-section diameter of 30-40 cm.

The bottom of the cell or cylinder is covered with acidified distilled water (10 ml of nitric acid per 1.0 L of water). The water layer depth is 1-2 cm.

6.2.2.1 Equipment and Materials Needed:

Sampling cell or polyethylene cylinder mounted on a special support
Measuring cylinders (100, 1000 and 2000 ml)
Polyethylene bottles (0.5 and 1 L)
Pipettes (5 ml)
Distilled water
Superpure concentrated nitric acid
Chemically pure potassium bichromate
Twice-distilled n-hexane

6.2.2.2 Sample collection, preservation and storage

A sampling device is installed at the observation site at a 2 m height and exposed during one week. If the station is located in an area with a deficit of atmospheric precipitation, the water level in the cell or cylinder is kept constant by adding distilled water. After the exposure, the sample volume (distilled water with atmospheric precipitation) is measured, and aliquots to be analyzed are taken. The aliquot volume to be analyzed for inorganic and organic substances, and conditions of preservation, storage and labeling are the same as in 6.2.1.2.

In winter, the samples of atmospheric deposition are collected in a high-walled polyethylene vessel without distilled water. After exposure, snow is melted at room temperature, the volume is measured, and the sample is preserved as indicated in 6.2.1.2. If there was no precipitation during the period of exposure, dry deposition is washed out of the vessel by acidified distilled water.

6.2.3 Sampling of Dry Atmospheric Deposition[1]

Sampling of dry atmospheric deposition is based on the application of an organic film as a collecting surface. The sampler is exposed only in the absence of precipitation.

6.2.3.1 Equipment and Materials Needed:

Dry deposition sampler
Celluloid or collodion
Chemically pure isoamyl acetic ester (isoanyl acetate)
Distilled water
Tracing paper
Polyethylene film
Scissors
Analytical balance with weights
Rubber bulb
Cement

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1. The method is not adequately tested yet.

6.2.3.2 Sample collection, preservation and storage

The sampling assembly consists of a crystallizer inserted into a wooden container with 30 cm high edges. A ring with an 8-11 cm diameter is placed at the bottom of the crystallizer. The walls of the ring are 0.2-0.4 cm thick and 3-5 cm high. The ring is made of teflon or plastic. The walls of the ring are punched in 2 or 3 places (diameter of the holes is 0.4 cm). The crystallizer is filled with distilled water so that the ring is completely submerged. A drop of 2 per cent isoamyl acetate solution of celluloid or collodion is pipetted on the water surface forming a thin surface film.

The water level in the crystallizer is lowered with the help of the rubber bulb until the film rests on the ring. This prevents its deformation in strong winds and ensures uniformity of the exposed area. Samples are taken at a 2 m height. To carry out a simultaneous sampling, one crystallizer can house two or three rings.

The dry deposition sampling period is one day. After exposure the film is removed with a needle, rolled into a ball and placed on a 3 x 3 cm polyethylene base; then it is dried at room temperature, covered by another polyethylene base of the same size, and stored in an envelope between two sheets of tracing paper. Daily samples are combined into weekly ones.

When sampling is carried out in winter, distilled water is replaced by a saturated solution of antifreeze.

6.2.4 Sampling of Snow Cover

Snow cover sampling is performed at the observation site of an IGBM station during the time of maximum water content in the snow. Whole-depth snow cores are taken at several points of the observation site in unaffected snow cover using a snow gauge. Care must be taken to avoid contamination of the lower part of the core by soil particles. The number of sampling points is determined from the required sample volume, its water content, and a uniform coverage of the selected sampling area. The collected sample is transferred into an enamelled vessel which is then dosed and delivered to the laboratory, where the sample is melted at room temperature. The sample is allowed to settle, after which is is decanted or filtered through a paper filter, poured into polyethylene and glass bottles and preserved in a way similar to atmospheric precipitation samples.

The filter with collected particulate matter is dried in the air, then folded with the exposed surface inside, inserted into a tracing paper envelope and stored there until it is analyzed.

6.2.4.1 Equipment and Materials Needed:

Snow gauge
Enamelled vessel with a lid
Glass and polyethylene bottles (0.5-1.0 L)
Superpure concentrated nitric acid
Chemically pure potassium bichromate
Twice distilled n-hexane
Ashless paper filters
Filtering device with a pump

6.3 Surface and ground water sampling

6.3.1 Surface water sampling

Water is one of the important pathways in which pollutants transport. It is also a life supporting medium in its own right. Therefore, it is a critical environmental medium to sample in any integrated monitoring program.

Sampling site location has been addressed in a general sense in a previous section. Specifically, it is recommended that all sampling be tied to a discrete watershed. Therefore, the water sampling locations will be determined by the original watershed selection. In general, a sampling site in a stream should be located as near to the exit point of that stream from the watershed as possible.

If there is a lake or pond in the watershed, it will be helpful to sample around that lake or pond. In general this sampling should include at least a sample at the input to the lake and one at the exit.

6.3.1.1 Equipment and Materials Needed:

Hach water sampling kit (or equivalent)
Field pH meter and conductivity meter
Appropriate buffer solutions (pH 4 and pH 7)
A plastic bottle with a drip snout to hold and dispense Ultrex nitric acid (or other very clean nitric acid). The addition of pure nitric acid to the sample helps prevent trace element adsorption to the walls without adding contamination to the sample.
Precleaned acid-washed sampling bottles. Note these are only for trace element analyses. Samples taken back to the laboratory for pH, sulfate, nitrate and other similar analyses should not be placed in acid-washed bottles. In this latter case, a distilled

water wash is sufficient.
Syringe and 0.45 micron filters
Sample forms
Marking pen

To sample water, follow the procedures outlined below.

1. Without the 0.45 micron filter attached, draw about 50 cc of water into the syringe.

2. Attach the 0.45 micron filter to the end of the syringe.

3. Rinse out the sample bottle with the filtered water and discard the rinse water.

4. Remove the filter and refill the syringe from the stream or lake that is being sampled.

5. Add about 1 to 5 ml of Ultrex nitric acid and seal the bottle.

6. Reattach the filter and filter about 100 ml of stream or lake water into the bottle.

7. Label the bottle with the time, date, and location of sampling, the fact that the sample has been filtered, and that it was acidified.

8. If during the above procedure the filter becomes clogged, remove it and throw it away, and replace it with a new filter.

9. Rinse out a new sample bottle from the stream or lake and then collect a second sample directly from the stream or lake without using the syringe or the filter. Collect no more than approximately 100 ml of water.

10. Add 1 to 5 ml of Ultrex nitric acid to this sample and seal with the cap.

11. Label the bottle as before, except note that it is an unfiltered sample.

The section that follows describes how to take a pH and conductivity sample under field conditions. These instructions are for a pH - temperature, SpC - multimeter. The techniques are similar for other models but the manufacturer's instructions should be consulted. Also it should be pointed out that measuring pH in certain types of low alkalinity lakes (<150 micro equivalents) is rather difficult under field conditions, and may be better performed under laboratory conditions.

1. Place the pH buffer solutions in the stream/lake and allow the buffer solution to equilibriate with stream/ lake ambient temperature. Note that you should use at least two buffer solutions, one at pH 4 and the other at pH 7.

2. Be certain to anchor the buffer solution bottles in the stream or they may float away.

3. Place the temperature, specific conductivity (SpC), and pH probes in the water to be sampled and allow them to equilibrate.

4. Record the temperature on a sample form (see example, Figure 1).

5. Take a SpC reading and record that on the sample form. Note that on some types of instruments this reading will appear in the same location as the temperature and pH readout. This is the case with the multimeter used as an example in this manual. A mode indicator switch lets you select the appropriate readout. Other instruments may vary. Also many of these instruments will have a scale indicator. Be sure you are reading in the appropriate scale.

6. Calibrate the pH electrode by putting it into the pH 7 buffer. Correct this for temperature effects using the supplied table that comes with your instrument. Now place the pH electrode in the pH 4 buffer. Record the measured pH for the pH 4 buffer and record on the sample form. Rinse the probe thoroughly in the stream.

7. Place the pH electrode in the stream and allow it to equilibrate with the stream temperature.

8. Record the pH and check stability by remeasuring the pH 7 buffer: if you are off by more than .05 pH units from the original calibrated pH 7 buffer reading, recalibrate the instrument and do the procedure over again.

WATER SAMPLING FORM

Location of the sample:_____
Date of the sample:_____
Time of the sample:_____
Name of the field person who took the sample_____
_____
Filtered:_____Unfiltered:_____
Water Temperature:_____Specific conductivity:_____
pH 4 buffer reading:_____Sample pH:_____

Figure 1. Example of a water sampling form.

Under certain circumstances, it may be necessary to include alkalinity measurements in the standard water measurements.

6.4 Biota Sampling

Vegetation is an important part of the environmental system, forming the first trophic layer on which all heterotrophs eventually feed. Vegetation can, under certain circumstances and in certain species, serve as an important accumulator of various types of pollutants. For example, mosses are known to be effective indicators of atmospheric particulates, and lichens presence or absence have been shown to be good indicators of certain types of gaseous air pollutants such as SO_2.

However, sampling of vegetation must be done carefully to accurately reflect the true pollutant conditions. This is particularly true for airborne particulates that are deposited on vegetation. Because of rain washoff, vegetation samples may give extremely variable results, since many airborne particulates adsorb to the surface of the plants rather than being absorbed into the plant itself.

The primary purpose of plant sampling is as an indicator of airborne contamination as well as an indicator of general plant contamination. In order to accomplish this, we have chosen to restrict ourselves to sampling for mosses and lichens, although in many integrated monitoring programs other forms of plant life may be desired for sampling.

Plant identification is important. A taxonomist familar with local species of lichens and mosses, as well as other vascular plants, should be available to the monitoring project. In the case of both lichens and mosses, species identification can be difficult, and identification to genus may be necessary. Scientific Latin names should always be used. Obviously, the same species (genus) should be collected at each plot on each of the sites.

The plot layout will be as shown in Figure 2. In general, try to sample at each of the subplot layouts in the same way as for soil and litter. However, it may be difficult to find the desired species in the immediate vicinity of the soil/litter plot. You may have to move a considerable distance away to obtain the correct chosen species. The important point to remember is to spread the vegetation sampling around the plot to ensure that a representative sample is collected.

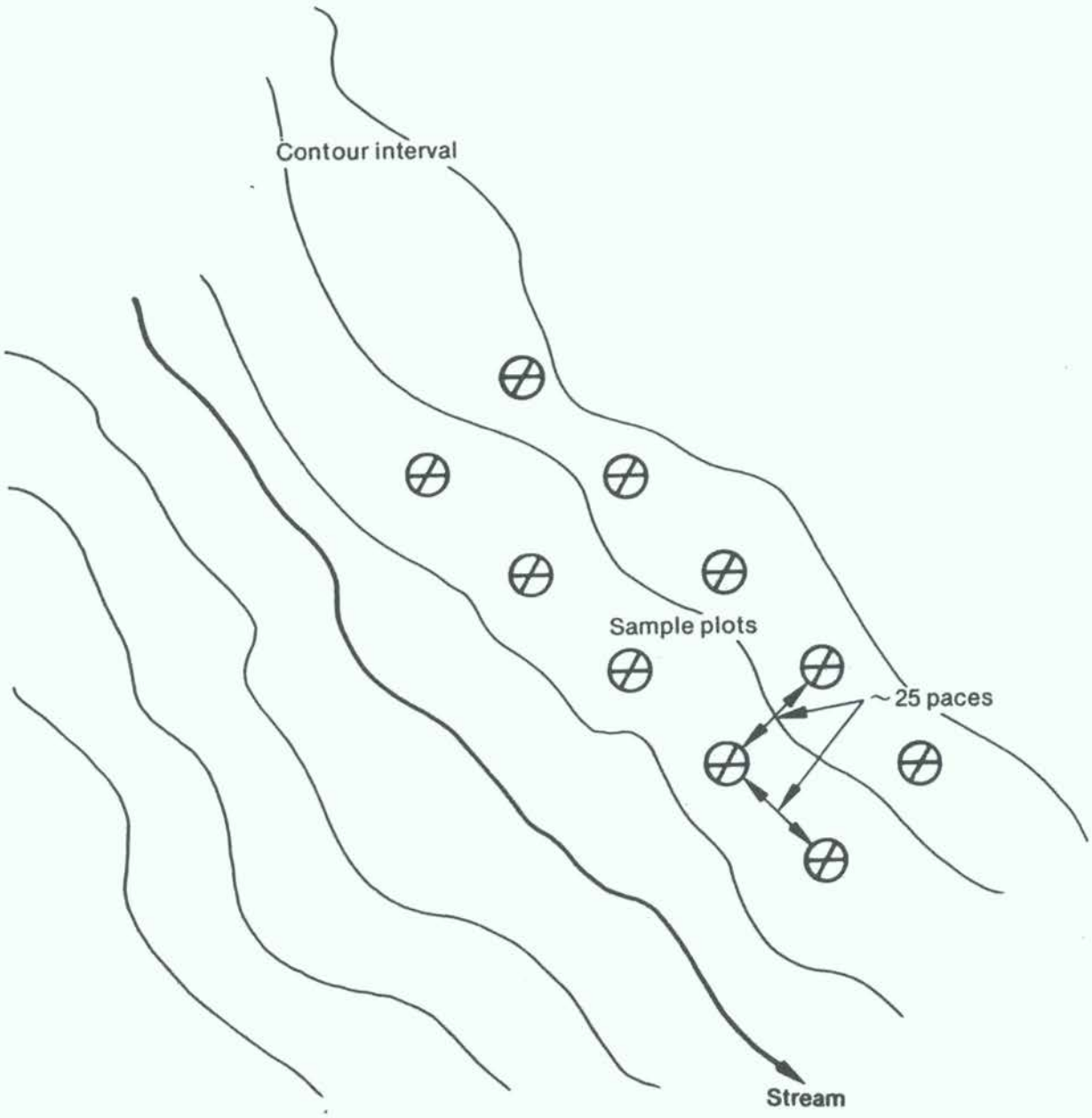

Figure 2. Diagram of how sample plots are laid out in the field

6.4.1 Equipment and Materials Needed:
Disposable plastic gloves[1]
Plastic bags
Marking pens
Tape (such as masking tape)
Vegetation clipper

The sampling procedures will be as follows:

1. In general, sampling will be coordinated at each plot with the subplot as described for soil and litter. However, as discussed above, some adjustments will have to be made in the event the appropriate species of vegetation is not readily available near the soil/litter subplot.

2. Put on a pair of new latex disposable gloves.

3. Pick a moss sample from a log, tree trunk or rock near each subplot. Place this in a new plastic bag (Figure 3).

4. Try to avoid collecting moss or lichen samples directly from the soil surface. The soil can contaminate the moss or lichen sample and also cause interferences in the chemical analyses.

5. Continue around the circumference of the plot until you have collected about 50 to 75 grams for the sample.

6. Using a separate clean plastic bag and a new pair of disposable gloves, repeat the procedure for the next species of vegetation to be collected.

7. Never mix species in the same bag.

8. Always change the plastic gloves between plots and when a new species is being collected at the same plot.

9. Label and fold the bags as described .

If it is desired to collect other plants, particularly woody vegetation, it may be easier to use clippers to make the collection. Plastic gloves should still be worn. Normally, this year's growth of leaves are collected. Approximately the same mass as for other species of vegetation should be collected as was for the moss and lichens.

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1. Plastic gloves which have talcum powder or a similar compound inside should not be used because of the possibility of contaminating the samples

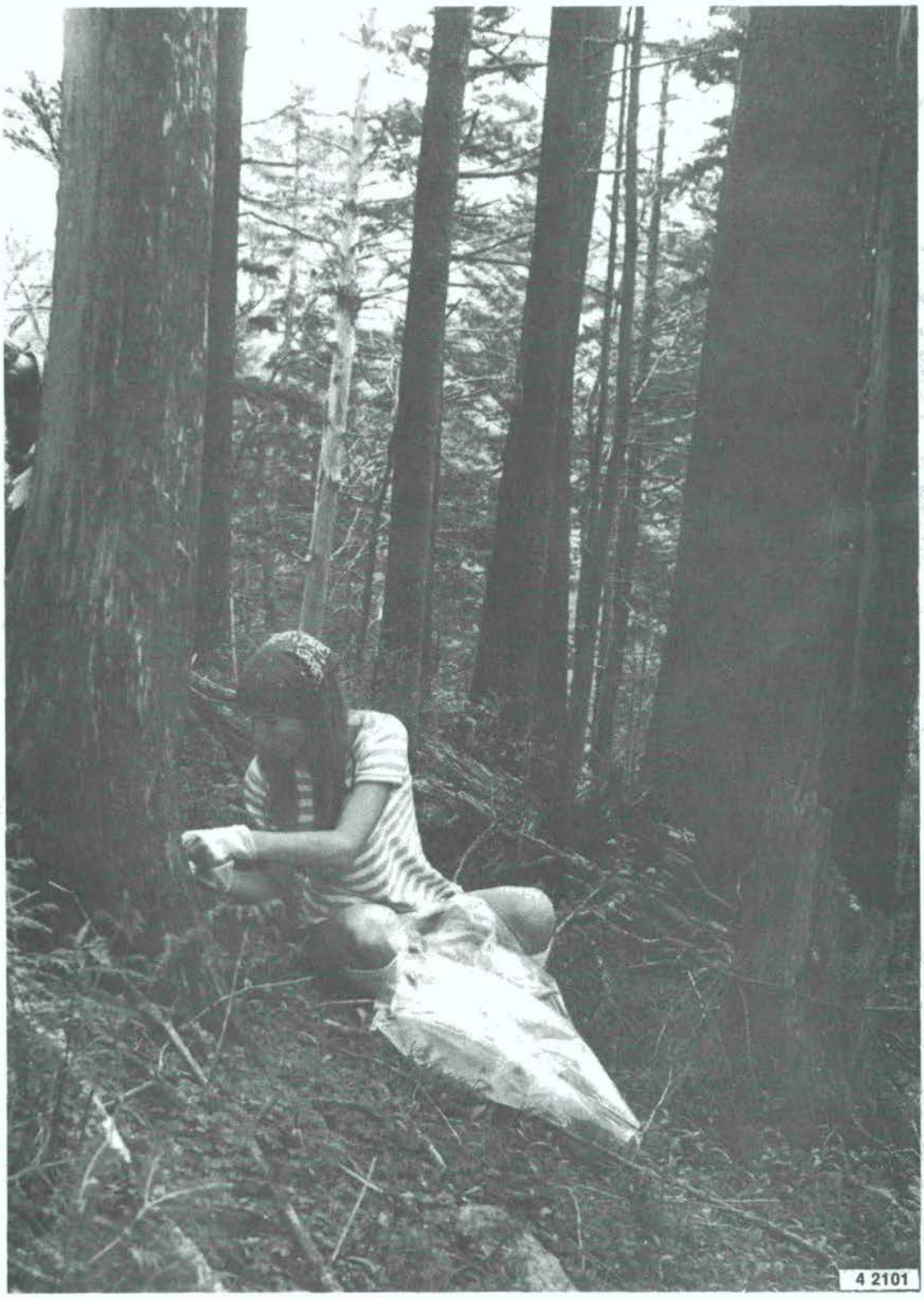

Figure 3. Sampling vegetation.

Sampling mammals, fish, birds, etc., may be an important part of an integrated monitoring program. However, since the sampling techniques are so varied and change almost on a case by case basis, detailed sampling procedures are not given in this manual.

6.5 Soil Sampling

Soil is an important sink for many pollutants such as heavy metals and certain organic compounds. It is also a critical environmental compartment for the cycling of many trace elements and nutrients.

In many forested ecosystems, litter or the forest floor, a component of the soil system, is also a very important compartment to sample. Litter receives input both directly from dry and wet deposition, from throughfall, and also from leaf and twig drop; and, as such, it is an important accumulating point for a large number of compounds of concern. Also, because this compartment has a relatively rapid turnover as well as a relatively small mass, detection of certain trace elements is made easier than in other compartments.

Descriptions for sampling litter and soil will be given separately in the following pages.

Sample plot layout is as shown in Figures 2 and 4[1]. The litter sample should be collected at the same locations as the soil samples. It is important, however, not to get any soil from the soil plot mixed in with the litter sample.

Normally, forest litter is composed of three layers:

1. Fresh litter (recently fallen) which in this document will be called the L layer.

2. Partially decayed litter, which is called the F or fermentation layer.

3. Decomposed litter, partially incorporated with soil, which is called the humus layer (H layer).

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1. The reader should be reminded that the suggested sample plot layout and number of samples are only recommendations. Modifications may have to be made to the recommendations to meet varying environmental situations.

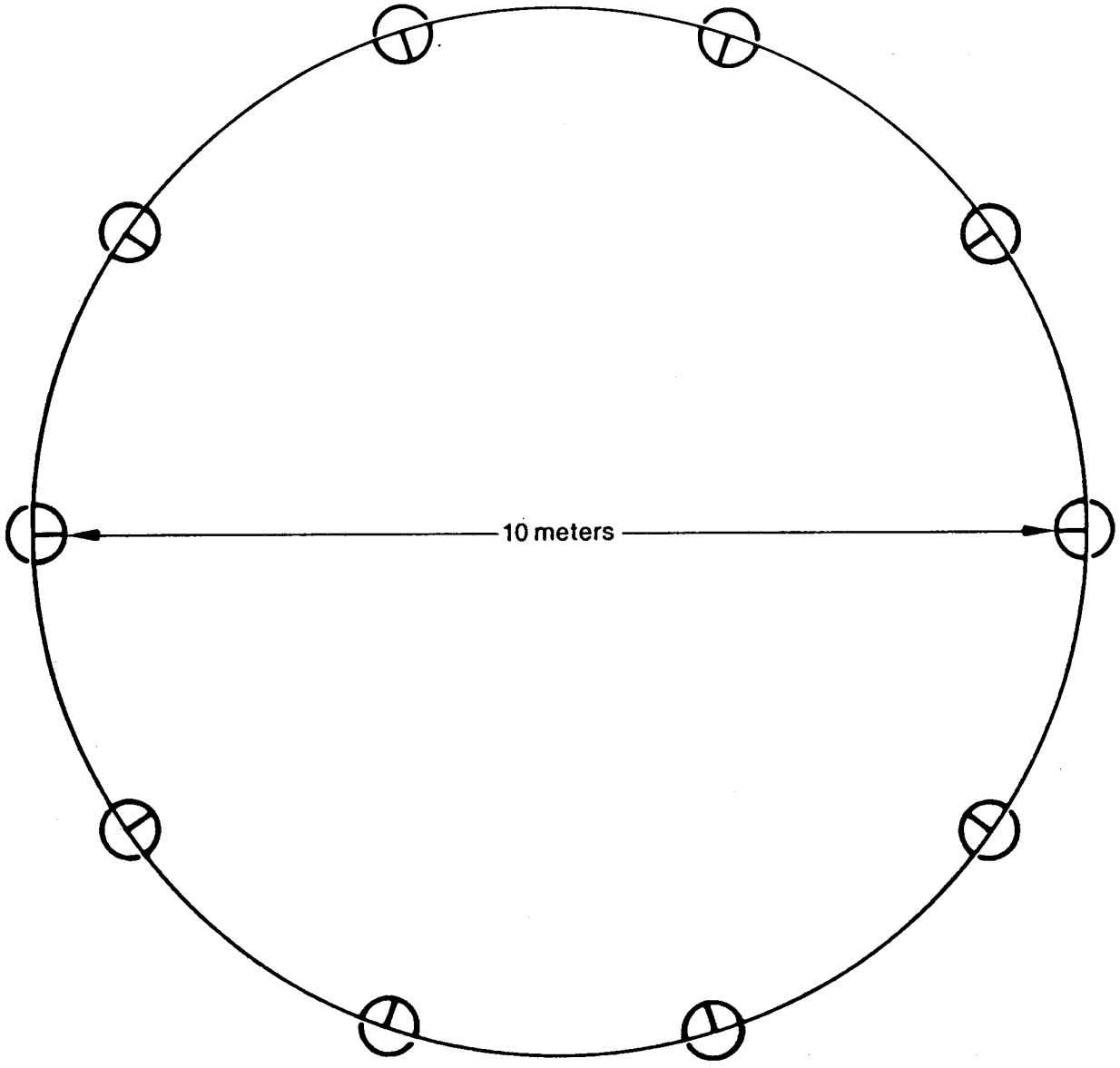

Figure 4. Illustration of how subplots are laid out in the field

In this manual, litter is taken to include both the L and H layers. The humus is considered to be part of the soil and is included in the soil sample (Figure 5). However, this convention can be changed to meet varying needs or circumstances. But once changed, consistency should be maintained throughout the sampling protocol.

6.5.1 Equipment and Materials Needed

Disposable plastic gloves
Clean plastic bags
Marking pens
Roll of tape
Garden Trowel

Sampling procedures will be as follows:

1. Locate plots

2. At each plot, lay out a circle of 10 m diameter (Figure 4). This circle does not have to be marked on the ground.

3. Be careful not to walk on the litter prior to sampling.

4. Put on disposable latex gloves. Change gloves between each plot but not between each subplot.

5. Ten litter samples will be collected at approximately equally spaced intervals around the circumference of the circle.

6. At the first soil pit, remove about 25 to 50 g of the L and F layers (Figure 6). Be careful not to include any soil from the soil pit. Do not sample the humus layer.

7. Place the litter in a clean unused plastic bag.[1]

8. Repeat the process at each of the ten subplots.

9. When all subplot locations are sampled, label the bag in the upper left corner with the appropriate sampler number (Figure 7).

---

1. Note: Do not use plastic bags if you are sampling for organic pollutants such as pesticides or chlorinated hydrocarbons. For these samples, use specially cleaned glass or teflon containers. Do not touch these samples with the latex gloves, use the metal trowel only.

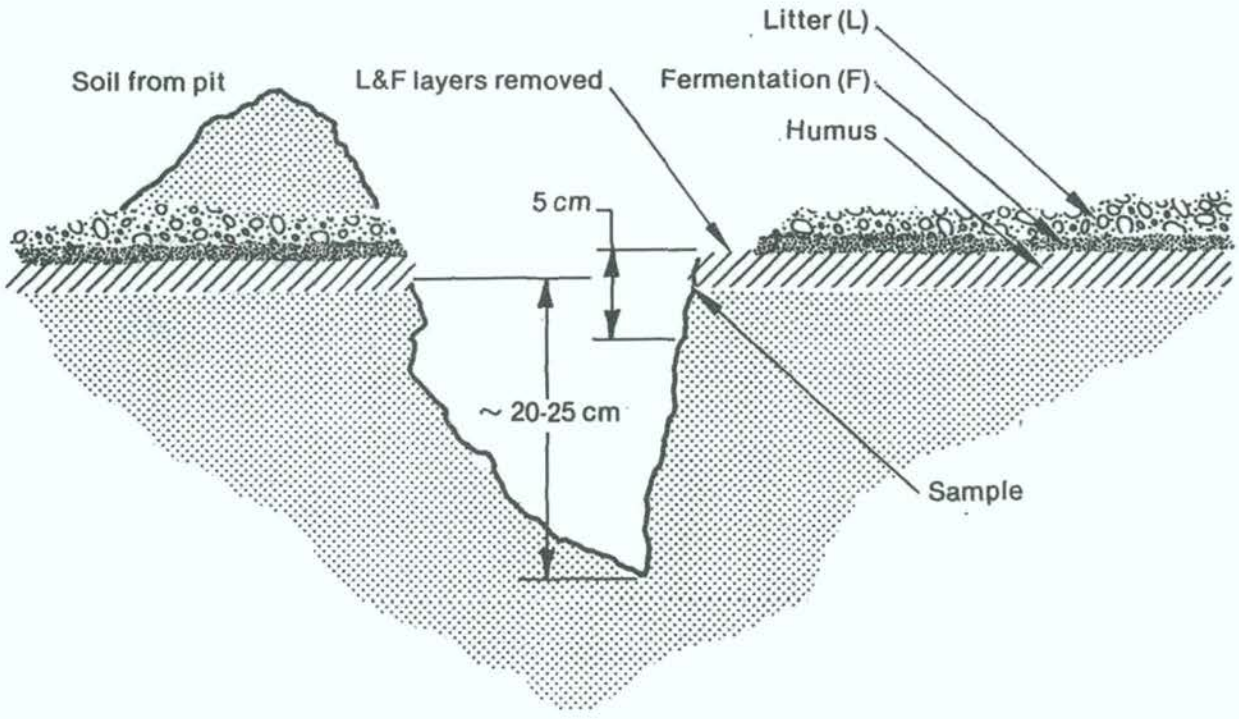

Figure 5. Side view of a soil pit.

Figure 6. Sampling litter.

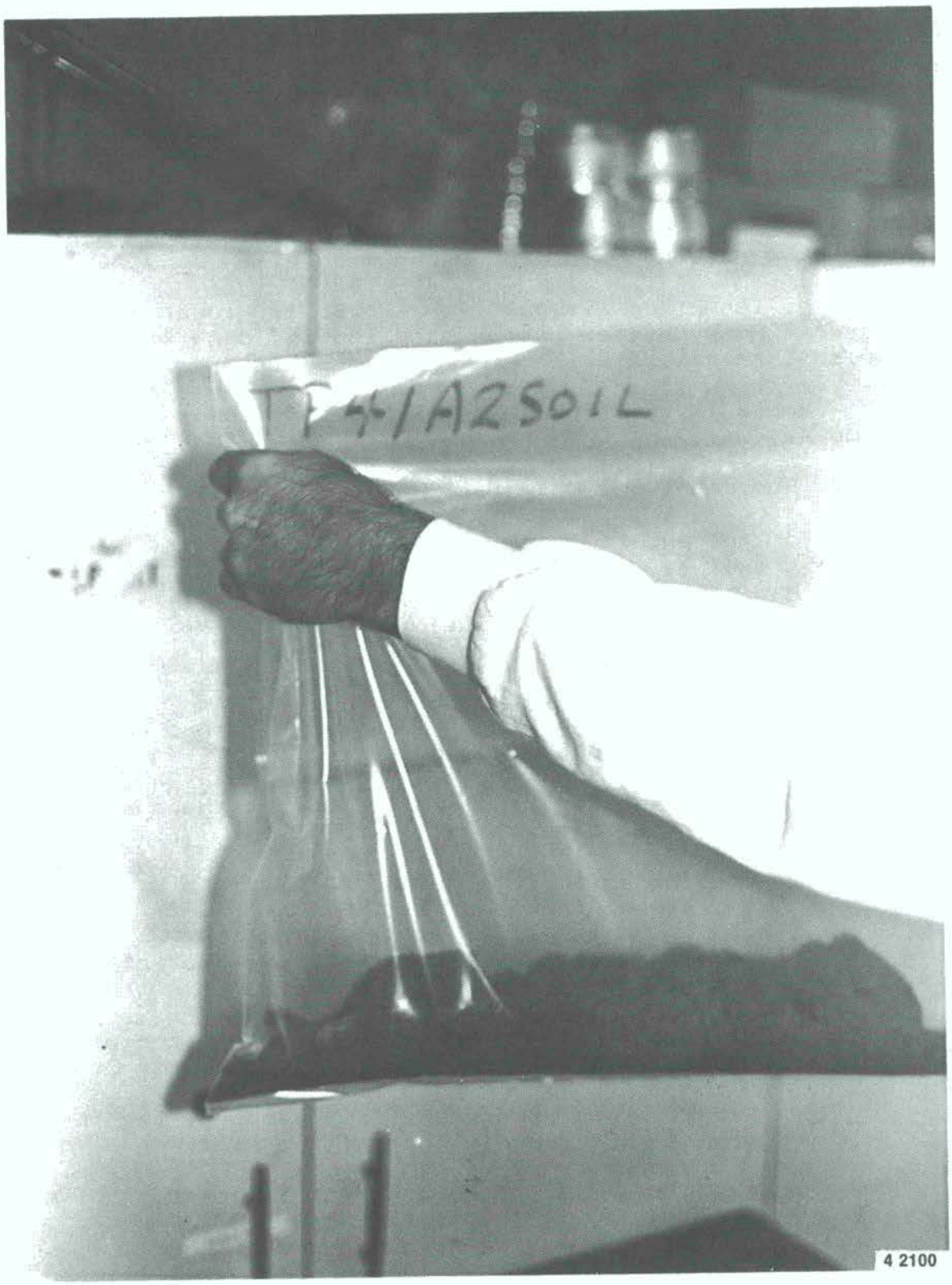

Figure 7. Soil in the bottom of the sample bag.

10. Shake the bag so the litter is in the bottom (Figure 7).

11. Roll the bag around the litter and seal with the masking tape around the middle.

The sampling layout for soil is identical to that for litter. However, the litter sampling is done first, followed by the soil sampling.

Sample layout for soil will be the same as shown in Figures 2 and 4.

6.5.2 Equipment and Materials Needed:

Shovel or entrenching tool
Garden trowel
Cleaning cloths or other cleaning materials (i.e., paper towels, "Kimwipes")
Plastic sampling bags
Roll of tape
Marking pen

Sampling procedures will be as follows:

1. Soil samples are collected at the same locations as litter samples.

2. Dig the soil pit as shown in Figure 5 with a shovel or an entrenching tool.

3. At each soil pit, use the trowel to collect the upper 5cm of soil as shown in Figure 8.

4. Place soil sample collected with the trowel in a clean plastic bag.

5. Repeat this procedure at each of the ten soil pits around the circumference of the plot.

6. Shake the bag so the dirt is all located in the bottom (Figure 7).

7. Mark the bag in the upper left hand corner with the appropriate sample number (Figure 7).

8. Roll up the bag around the soil in the bottom of the bag and seal with tape around the middle.

Figure 8. Sampling soil.

7. METHODS FOR DETERMINING PRIORITY POLLUTANTS IN ENVIRONMENTAL SAMPLES

Methods described in this section are meant for substances included in the IGBM basic program (see Table 5). Each substance contained in environmental samples can be determined by a variety of methods described in the international literature. The present guide includes methods most suitable for the IGBM network due to their simplicity and required sensitivity. To achieve the highest performance and data quality, preference is given to methods that are either based on automatized continuous measurements, e.g., using sensitive gas analyzers; or make it possible to preserve samples so that their mass analysis can be performed in regional laboratories equipped with the required equipment, including precision instruments, with standards, and highly qualified personnel. In this case a high-level data quality control can be achieved, since analytical procedures can be closely correlated with the analysis of observation series. Besides, strictly observed principles of sample (or their aliquot) duplication would always ensure recurrent measurements, if any doubts occur.

The description of measurement procedures will include the following analytical characteristics:

Detection limit - the lowest concentration which allows detection of the component under study in a sample or its extract, using a given procedure, with a specified confidence level. It is determined with the help of the calibration characteristic by the minimal detectable analytical signal;

Sensitivity factor or sensitivity - the value of the first derived calibration function at a given concentration measured. For calibration charts plotted without transformation of the analytical signal and analyzed concentration, the sensitivity factor is equal to the calibration plot scope;

Range of concentrations measured - the value domain defined by a given method. The range of concentrations measured can be prescribed by the boundary values of the analytical signal.

Whenever expedient, references will be made to the WMO Manual - No. 491 (WMO, 1978).

7.1 Aerosol Turbidity of the Atmosphere

These measurements should be based on WMO Recommendations No. 491 (WMO, 1978).

7.2 Atmospheric Particulate Matter (Dust)

7.2.1 Principles of the Method

The essence of the method is the filtration of a definite air volume through a filter and determination of dust concentration of the sample by gravimetry.

7.2.2 Characteristics of the method

The detection limit is 0.1 ug/m^3, air volume being 1000 m^3; 10% error.

7.2.3 Equipment and Materials Needed:

Filter fan device (electric aspirator)
Analytical balance
Filters or material for filter fabrication
Drying oven
Tracing paper
Desiccator (i.d. 25-30 cm)
Melted calcium chloride
Medical forceps
Scissors
Cement

7.2.4 Determination of Procedure

Concentrations of the atmospheric particulate matter (dust) are determined with the help of various filters. In the case of fiber filters, it is important to avoid losses due to a possible adherence of the filtering material to storage bag walls.

Dust is sampled as described in 6.1

To determine the atmospheric concentration of dust, daily samples are taken. The sample volume can vary from 40 to 1000 m^3, depending on the type of filter and parameters of the filtering unit.

The filter is weighed before and after exposure. Prior to this, filters are brought to a constant mass determined with an accuracy of 0.1 mg. To this end, fiber filters are exposed in the desiccator with melted calcium chloride for 24 hours, and then for an hour in a room where they are weighed afterwards. Porous filters are dried in the oven at 80° C for 72 hours and stored in the desiccator until weighing.

7.2.5 Calculation

Dust amount in a sample is derived from mass difference between the exposed and unexposed filter. Atmospheric concentra-

tion of dust is calculated by the following formula:

$$C = \frac{(m_2 - m_1) \times 10^3}{V_o} \quad ug/m^3 \qquad (3)$$

where C - dust concentration, ug/m^3;
m_1 - mass of unexposed filter, mg;
m_2 - mass of exposed filter, mg;
V_o - air volume reduced to normal condition, m^3

7.3 Atmospheric Sulfate

Sulfates are present in the atmopshere as aerosol particles. Sulfates, usually ammonium sulfate, are produced from sulfur dioxide oxidation. The latter is released into the atmosphere from organic fuel combustion and forms as a result of oxidation of reduced sulfur compounds, such as hydrogen sulfide, carbon bisulfide, dimethyl sulfide and others. Sulfate particles are always present in the background atmosphere. The range of background sulfate concentrations is given in Section 4. The sensitivity of the method applied should be satisfactory for the given range, and the method itself must undoubtedly be selective, since the atmosphere contains quite a variety of sulfur compounds. Quartz based filters are preferred since artifact formation is eliminated.

Filters can be analyzed for sulfate both at the background station and regional laboratory.

7.3.1 Turbidimetry

7.3.1.1 Principles of the Method

The method is based on measuring the intensity of clouding of solutions containing sulfate ions in the presence of barium salts. To stabilize the resultant suspension of barium sulfate, glycerine or ethylene glycol is introduced into the reaction mixture, and to reduce residue solubility, ethyl alcohol is added.

The optical density of solutions is measured at 364 nm wavelength.

7.3.1.2 Characteristics of the Method

The detection limit is 0.1 ug/m^3, the air volume being 500 m^3. The measurement error is 10-15% at sulfate concentrations in the atmosphere above 1 ug/m^3, and up to 30% when the sulfate concentration is under 1 ug/m3.

The sensitivity of the method is 0.25 mg SO_4^{2-}/l, the range of sulfate ion concentrations measured being 0.5-40 mg/l. The

measurement error is ± 0.05 mg/l. The linear dependence between the optical density of the solution and sulfate concentration remains within the range of 0-80 ug of sulfate ion in the sample volume analyzed.

7.3.1.3 Inteferences

Measurements are interfered with by suspended particulates, carbonate and bicarbonate. Suspended particulates are remoted from the solution by sample centrifuging or filtration through a glass filter. To remove carbonate or bicarbonate, samples are acidified with hydrochloric acid and heated.

7.3.1.4 Equipment and Materials Needed:

Photoelectric colorimeter
Cells with the working layer depth of 30 and 50 mm
Centrifuge (3-5 thousand rpm)
Centrifuge test tubes (500-1000 ml)
Analytical balance with weights
Apparatus for bidistilled water production
Electric heater
Water bath
Scissors
Tweezers
Measuring flasks (100, 500, and 1000 ml)
Pipettes (1, 5, 10, 25, and 50 ml)
Heat resistant beakers or cone flasks (100 ml)
Watch glass
Graduated test tubes with ground-glass stoppers (20 ml)
Glass filters No. 4

7.3.1.5 Reagents and Solutions

Bidistilled water
Chemically pure concentrated hydrochloric acid
5 per cent solution of chemically pure barium chloride
Analytically pure glycerine or ethylene glycol
Ethyl alcohol
Chemically pure potassium sulfate

Reagent mixture: 100 ml of 5 per cent solution of barium chloride, mixed with 300 ml of glycerine (or ethylene glycol) and 300 ml of alcohol. The pH value is brought to 2.5-2.8 by acidification with concentrated HCl. Then the mixture is kept for 2 days, after which it is filtered through a glass filter. The reagent mixture is applicable for 6 months.

Standard solutions

a) standard solution No. 1 containing 1 mg SO_4^{2-}/ml - 1.814 g of potassium sulfate (dried at 120-150 degrees C for 3 hours) dissolved in distilled water in a measuring flask (1000 ml);

b) standard solution No. 2 containing 0.1 mg SO_4^{2-}/ml is prepared by dissolving 50 ml of standard solution No. 1 in bidistilled water in a measuring flask (500 ml)

7.3.1.6 Sampling

Sulfate aerosols are sampled on quartz based filters by air pumping during 24 hours; the air sample volume being 500-600 m^3.

7.3.1.7 Analytical Procedure

The substrate (if any) is removed from the filter, put into a 100 ml heat resistant beaker or flask, wetted with 2 ml of alcohol, after which 50 ml of bidistilled water and 1 ml of concentrated HCl are pipetted into the vessel. Cover the beaker with a watch glass and heat in the water bath up to 80 degrees C with periodical stirring with a glass rod. Three-four hours after the sample cools down, the solution is passed through the centrifuge or porous glass filter to remove suspended matter. Part of the sample (about 10ml) is transferred into a test tube with a ground stopper for further analysis. The aliquot (0.5-2 ml) is transferred into a test tube with a ground glass stoppper (20-25 ml) and diluted by bidistilled water up to 10 ml. Add 1 drop of HCl and 5 ml of the reagent mixture and shake the solution. A reference solution ("0" solution - 10 ml of bidistilled water, 1 drop of HCl and 5 ml of the reagent mixture) is to be prepared for each sample series.

Half an hour after adding the reagent mixture, the optical density of solutions relative to distilled water is measured in cells with 30 mm-thick working layer at 364 nm wavelength. The amount of sulfate ions in the sample is determined using the calibration plot by the difference between the optical densities of the sample solution and zero solution.

The optical density of the zero solution should not exceed 0.030. If it is higher than that, the cleanliness of the chemical utensils and measuring cells, as well as the water and reagent mixture quality, must be checked on. If the optical density of the sample is beyond the limits of the calibration plot, duplicate analysis of the same sample is to be carried out, with the aliquot reduced twice or more. If the optical density of the sample approaches that of the zero solution, the aliquot is to be increased.

Sulfate concentrations in unexposed filters (filter blanks) are determined for each set of filters, but no less than once per three months. While analyzing unexposed filters, the aliquot is taken equal to 10 ml.

7.3.1.8 Calibration Plot

To plot a calibration curve, a series of standard solutions is prepared in 10 ml measuring flasks, as directed in Table 6. Solutions are diluted by bidistilled water up to the mark.

Table 6. Standard scale for sulfate determination

Nos. of standards	0	1	2	3	4	5	6	7
Std. solution No. 2 (0.1 mg SO_4^{2-}/ml), ml	0	1	2	3	4	6	8	10
Amount of SO_4^{2-} in a sample, ug	0	10	20	30	40	60	80	100

To obtain the scale of standards, 10 ml of the respective solution, 1 drop of concentrated HCl, and 5 ml of the reagent mixture are to be poured into each test tube, shaken and allowed to stand for 30 minutes. The calibration curve is plotted by mean values calculated from 3-5 measurements of the scale (by the difference between the measured optical densitites of standard and zero solutions).

The calibration curve should be checked when the reagent is changed, but no less than once per three months.

7.3.1.9 Calculation

Atmospheric sulfate concentration (C) is calculated by the following formula:

$$C = \frac{\frac{V}{V_1}(q - q_b)}{V_o} \quad ug/m^3 \qquad (4)$$

where q - sulfate content in the sample aliquot analyzed, ug (to be determined by the calibration plot);
V - volume of the dissolved sample, ml;
V_1 - volume of the sample aliquot taken for analysis, ml;
V_o - air sample volume reduced to normal conditions, m^3;
q_b - mean sulfate content in an unexposed filter calculated by formula (5):

$$q_b = \frac{V}{V_2} q_b \quad ug \qquad (5)$$

where q_b - mean sulfate content in the sample aliquot analyzed (unexposed filter), ug;
V_2 - volume of the aliquot taken for analysis, ml

7.3.2 Thorin Method

The method is recommended in WMO-No. 491 (WMO, 1978) for sulfate determination in atmopsheric precipitation. The procedure can be applied after the dissolution of sulfates collected on filters.

7.4 Sulfur Dioxide in the Atmosphere

The range of sulfur dioxide concentrations in the atmosphere from background regions is given in Section 4. The lower limit can be very small (fractions of ug/m^3) which prevents the application of automatic gas analyzers. However, we are currently field-testing a battery-operated SO_2 monitor with lower detection limits of 0.3 ppb. The manual techniques recommended in the present guide have been comprehensively tested by way of practical background measurements; it has the required sensitivity and can be successfully applied by background station personnel. From the chemical viewpoint is is a modified West-Gaeke method.

7.4.1 Pararosaniline-Formaldehyde Method

7.4.1.1 Principles of the Method

Atmospheric sulfur dioxide is absorbed by disodium tetrachloromercurate (TCM). The addition of acid pararosaniline (or fuchsin) and formaline to the absorbing solution produces pararosaniline methylsulfonic acid which has its own color. Its concentration in the solution is determined by spectrophotometry.

7.4.1.2 Specifications of the method

The detection limit is 0.05 ug/m^3, the air volume being 2 m^3. The error of measurements is 6-30 percent.

Samples are collected on glass beads impregnated with absorbing solution, which forms sorption tube packing.

7.4.1.3 Interferences

Interferences might be due to nitrogen oxides, ozone, heavy metals, and suspended particulates. To eliminate the influence of nitrogen oxides, the absorbing solution is to be treated with sulfonamic acid; the influence of ozone is compensated by allowing samples to stand before photometric determination; that of heavy metal salts is compensated by adding trilon B and phosphoric acid; the influence of suspended particulates is eliminated by sample centrifuging prior to measurement.

7.4.1.4 Equipment and Materials Needed:

Photocolorimeter or spectrophotometer
Centrifuge

Gas meter or rotameter (the error does not exceed 2.5 percent)
Compressor or another air suction inductor with air flow rate up to 3 l/min.
Glass sorption tubes (8-20 mm) with two porous partitions filled with 1-2 mm glass beads to a 50 mm length
Measuring flasks (100, 250, 500, 1000 ml)
Pipettes (1, 2, 5, 10, 25, 50,100 ml)
Burettes (25 ml)
Separating funnels (100, 1000 ml)
Beakers (100, 200, 500 ml)
Graduated test tubes (10 ml)
Electric heater

7.4.1.5 Reagents and Solutions

Analytically pure (yellow) mercuric oxide
Chemically pure sodium chloride
Chemically pure trilon "B"
Chemically pure concentrated hydrochloric acid (10 N, 1N, 0.1 N)
Chemically pure sulfonamic acid, 0.03 percent
Chemically pure concentrated orthophosphoric acid, 3 M
40 and 0.2 percent water solutions of formaldehyde
Pure pararosaniline hydrochloride
Chemically pure sodium sulphite (or pyrosulfite)
Chemically pure sodium acetate
Newly prepared solution fo sodium thiosulfate, 0.01 N
Caustic soda, 0.1 N
Newly prepared solution of iodine, 0.01 N
Analytically pure glycerine
Analytically pure ethylene glycol
Analytically pure solube starch, 0.2 percent solution
Chemically pure n-butanol
Chemically pure mercurous iodide
Newly distilled water
0.04 M solution of sodium tetrachloromercurate: 8.7 g of mercuric oxide, 4.68 g of sodium chloride, and 0.07 g of trilon B are dissolved in 9 ml of 10 N hydrochloric acid when heated. The resultant solution is transferred into a flask containing 124 ml of 0.1 N solution of caustic soda and about 700 ml of distilled water. The solution is diluted by water up to 1000 ml, mixed and allowed to stand for 24 hours. The pH of the solution should be 5.4-6.4. When necessary, pH is brought to the required level using 0.1 N solutions of caustic soda or hydrochloric acid. The residue (if any) is filtered. The solution is to be stored in a refrigerator for 6 months.

The absorbing solution for sorption tubes: 1.6 g of sodium acetate is dissolved in 0.04 M TCM solution in a 100 ml flask. The resultant mixture is treated either with 15 ml of glycerine for air sampling at ambient temperatures above -5 degrees C or with 15 ml of ethylene glycol for air sampling at temperatures below -5 degrees C.

The basic 0.2 percent solution of pararosaniline (or fuchsin) 0.2 g of pararosaniline dissolved in 100 ml of 1 N solution of hydrochloric acid.

The working solution of pararosaniline (or fuchsin): a 250 ml measuring flask is filled with 200 ml of 3M phosphoric acid and 20 ml of basic pararosaniline (or fushsin) solution. The resultant mixture is to be brought to the mark using distilled water. The solution is stable for 6 months if kept in a dark place at room temperature.

0.2 percent solution of starch: 0.4 g of soluble starch and 1-2 grains (0.002g) of mercurous iodide mixed in a small amount of water are to be slowly added to 200 ml of hot distilled water and heated to boiling.

The standard basic solution: 0.400 g of sodium sulphite (Na^2SO_3) or 0.300 g of sodium pyrosulphite ($Na_2S_2O_5$) are dissolved in 500 ml of distilled water. The SO_2 concentration is determined by iodimetric titration, 20 ml of 0.01 N iodine solution and 10 ml of distilled water are pipetted into three cone flasks (200-250 ml), while each of three other flasks are filled with 20 ml of 0.01 N iodine solution and 10 ml of the standard basic solution. The mixtures in all the flasks are titrated with 0.01 N solution of sodium thiosulfate till a slightly yellowish color, after which 2 ml of the starch solution is added into each flask and the mixtures are titrated further till complete loss of color. The sulfur dioxide concentration in the standard solution is calculated by the formula:

$$C = (A-B).\ K\ ug/ml \qquad (6)$$

where A - mean volume of 0.01 N solution of sodium thiosulfate used for blank sample titration, ml
B - mean volume of 0.01 N solution of sodium thiosulfate used for standard solution titration, ml;
K - equivalence factor (K=32).

The standard working solution with 10 ug/ml SO_2 concentration is prepared in a 100 ml measuring flask immediately after titration of the standard basic solution. To this end, the calculated amount of the titrated solution is diluted to the mark by the absorbing solution. The standard working solution is to be prepared just before the application.

Sorption tube preparation. New sorption tubes are boiled in a hydrochloric acid solution(1:1) for 10-15 minutes, rinsed in running water and successively boiled in two portions of distilled water. Cleaned tubes are dried in a drying oven.

After analysis, exposed tubes are boiled in two portions of

distilled water for 10-15 minutes and rinsed with fresh water using a rubber bulb.

Beads in dried sorption tubes are treated with an absorbing solution. Excess solution is to be carefully blown out by the rubber bulb and the outer surface of the tubes rubbed with filter paper. Tubes filled with absorbing solution can be sorted in a dark and cold place (refrigerator) for a month.

7.4.1.6 Sampling

A sorption tube is mounted in a vertical position with the glass beads down, connected to an air pump providing air flow rate through the tube within 1-3 l/minute, covered by a light screen and exposed for 24 hours. At low atmopsheric concentration of sulfur dioxide (0.05-0.1 ug/m^3) the diameter of the tubes should be 14-20 mm, and the air flow rate is to be increased up to 8-16 l/minute. At ambient temperatures above + 30 degrees C and below -30 degrees C, losses of sulfur dioxide are possible.

Tubes with samples can be stored in glass test tubes with ground stoppers or polyethylene bags for 1-2 days in darkness without a refrigerator and up to 5 days in a refrigerator at 0 degrees C. For a longer storage (up to 30 days) sorption tubes are to be kept in a carbon dioxide or nitrogen atmosphere.

7.4.1.7 Analytical Procedure

Sorption tubes are placed into glass test tubes containing 6ml of 3 percent solution of sulfonamic acid. Using a rubber bulb, the sorbent with absorbed sulfur dioxide is washed off into the solution, after which the sorption tubes are removed from the test tubes and 5 ml aliquots are taken for analysis. Each aliquot is diluted with 0.4 ml of 0.2 percent formaldehyde solution and 1 ml of pararosaniline solution. The solutions are centrifuged for 10-15 minutes (3-4 thousand rpm) and optical densities are determined 30 minutes after adding pararosaniline. Measurements are carried out in containers with a 10 mm distance between the working edges within 560-580 nm wavelength band. A reference solution is to be prepared for each set of samples by applying an identical treatment of impregnated but unexposed sorption tube. The optical density of the reference solution should not exceed 0.030. If it does, the initial pararosaniline (or fuchsin) solution must be additionally purified by butanol and activated carbon.

The concentration of sulfur dioxide in a sample is determined using a calibration plot by the difference between optical density measurements of the sample and reference solution.

7.4.1.8 Calibration Plot (Standard Scale)

Standard solutions are prepared in 100 ml measuring flasks. Each flask is filled with 20-30 ml of distilled water and

standard working solution according to Table 7. 6.0 ml of absorbing solution is added to each flask and the resultant mixture is to be diluted to the mark by distilled water. To plot a standard scale 5 ml of each standard solution should be sampled into test tubes and all subsequent operations are carried out according to the analytical procedure. The calibration plot is based on mean values calculated from 3-5 measurements indicated in the standard scale.

The calibration and analysis temperatures should not differ by more than ± 2 degrees C. The calibration plot must be checked each time the reagent set is changed, but no less than once in 6 months.

Table 7. Standard Scale for Sulfur Dioxide

SO_2 concentration	Standard Nos. 1	2	3	4	5	6	7	8
Std. solution with sulfur dioxide concentration of 10 ug/ml, ml	0	0.2	1	2	4	8	12	16
Sulfur dioxide concentration in a 5 ml sample, ug	0	0.1	0.5	1	2	4	6	8

7.4.1.9 Calculation

Sulfur dioxide concentration C in the air under study is determined by the following formula:

$$C = \frac{1.2 \times q}{V_o} \quad \mu g/m^3 \qquad (7)$$

where q - amount of the substance in a 5 ml sample (determined from the calibration plot), ug
V_o - air sample volume reduced to normal condition, m^3
1.2 - factor for recalculating for the total sample volume (suflur dioxide is washed out from the sorption tube by 6 ml of sulfonamic acid and a 5 ml sample is taken for analysis).

Fuchsin purification: fuchsin is to be purified by n-butanol neutralized with hydrochloric acid. To prepare the purifier, a 1 L separating funnel is filled with 250 ml of 1 N hydrochloric acid and 250 ml of n-butanol. The solution is to be shaken for 10-15 minutes and allowed to stand. Four hours later the phases are separated and poured into cone flasks.

The hydrochloric solution (the lower phase) is used for preparing fuchsin solution. Dissolve 0.2 g of fuchsin in 100 ml of 1 N hydrochloric acid saturated with butanol. The solution is then transferred to a 250 ml separating funnel, treated with 30-50 ml of neutralized butanol, shaken for 5 minutes, and 10-15 minutes later the phases are separated. Contaminating impurities pass into the organic fraction which is discarded. The extraction is to be repeated 4-6 times with new portions of butanol. If the butanol phase is still violet after the sixth extraction, the application of the particular set of pigment is not advisable.

To further purify fuchsin, the solution is treated with 4-5g of activated carbon, mixed and passed through a dense filter. The purified reagent should be reddish-yellow.

Determination of formaldehyde content in formalin - a 50 ml measuring flask is filled with 1 ml of formaline and the solution is diluted to the marker by distilled water. After a thorough mixing, 5 ml of the solution is poured into three cone flasks (250 ml). Then 40 ml of 0.1 N iodine solution and 30 percent solution of caustic soda is pipetted into each flask until the mixture becomes weakly yellow. The flasks are plugged and left in a dark place for 10 minutes, after which 5 ml of hydrochloric acid (1.5) should be carefully added into each flask, and they are left in a dark place again. Ten minutes later, excessive iodine is titrated with 0.1 N solution of sodium thiosulfate adding 1 ml of starch near the equivalence point. Simultaneously a blank test is performed. The results of 3 measurements are

averaged. Calculation example. If the titration of 40 ml of 0.1 N iodine solution (blank test) required 40 ml of 0.1 N solution of sodium thiosulfate and sample titration consumed 14 ml of it, then 5 ml of formaldehyde solution interacted with 40-14-26 ml of iodine solution. One ml of 0.1 N iodine solution corresponds to 1.5 mg of formaldehyde. Therefore, 5 ml of diluted formaldehyde solution contains 1.5 x 26 = 39 mg of formaldehyde, while 50 ml of it (i.e., 1 ml of nondiluted formaline) contains 0.39 g. Thus, 100 ml of formaline contain 39 g of formaldehyde.

7.4.1.10 Battery Operated SO_2 Monitor

Currently in the U.S. IGBM project, we are testing a highly sensitive portable SO_2/oxidant meter. This meter, the electrochemical concentrate cell (EEC) oxident meter is a portable device capable of making oxidant measurements in very clean air. It is a highly portable instrument and operates from a 6 volt battery system. The EEC oxidant sensor uses an iodine-iodide redux electrode concentration cell (Additional details are available from W.D. Komhyr, 9th Methods Conference in Air Pollution and Industrial Hygiene Studies, Pasadena, California, Feb. 7-9, 1968.).

Because of the addition of a scrubber system, the instrument is capable of simultaneous measurement of oxidants and SO_2. Sensitivity of this instrument to oxidants is about 0.8 ppb and 0.2 ppb for SO_2. The instrument is currently being field tested in the United States and is not available commercially at this time. However, the instrument shows great promise to be of extreme value in IGBM stations because of its reliability, sensitivity, ease of operation, portability and power requirements.

7.5 Ozone (in the Atmospheric Surface Layer)

The range of background ozone concentrations is given in Section 4. The ozone detection limit of modern gas analyzers is 2 ug/m^3, therefore, it is preferable to use them for continuous ozone measurements at IGBM stations.

7.5.1 Chemiluminescence

7.5.1.1 Principles of the Method

The method is based on measuring chemiluminescence intensity during the gas phase interaction of ozone in the air sample and ethylene fed into the reaction chamber from a cylinder in a ten-fold excess. The chemiluminescence intensity is proportional to the concentration of ozone entering the reactor. This is a

relative method and the measuring equipment (gas analyzer) is to be calibrated before measurements.

7.5.1.2 Specifications of the Method

Detection limit is 2 ug/m^3. The error in the concentration range measured (10-200 ug/m^3) is 5 percent.

7.5.1.3 Interferences

This is a selective method for ozone determination. To prevent large dust particles in the reaction chamber the air to be analyzed is first filtrated through a teflon filter with pore diameter from 1 to 4 um.

7.5.1.4 Instruments, Equipment and Materials:

Automatic ozone analyzer
Ozone generator
Teflon hoses
Teflon filter (pore diameter from 1 to 4 um)
Filter holder (teflon or stainless steel)
Cylinder charged with ethylene (150 atm.)
Cylinder pressure regulator

7.5.1.5 Reagents

Ethylene

7.5.1.6 Sampling

Samples are continuously collected via a teflon hose 2 m above the ground throughout the day.

7.5.1.7 Calibration Plot

Gas analyzer is calibrated using ozone/air mixtures produced in an ozone generator. Ozone is produced by feeding preliminary purified air into the quartz cell of the ozone generator, which is irradiated by a mercury lamp with a regulated UV flux. Resultant ozone is diluted with purified air, and the ozone concentration in the ozone/air mixture is determined by iodometry. The ozone/air mixture with a known ozone concentration is used for gas analyzer calibration.

The calibration is carried out not less than twice a month.

7.5.1.8 Calculation

Ozone concentrations in ambient air are continuously

recorded on the recorder chart throughout the day. Mean daily concentrations are estimated by averaging mean hourly values which are determined from the recorded curve.

Ozone/air mixture calibration. The ozone/air mixture is fed from the ozone generator via the teflon air duct and bubbled through two sequential Richter absorbers containing 10 ml of absorbing solution (10 g of potassium iodide and 6.2 g of boric acid per 1 L of the solution) at the rate of 1-2 L/min. for 10-60 minutes. At ambient temperatures above 20 degrees C the absorbers are placed into an ice bath. When the above operation is over, the volume of the exposed solution is diluted to 25 ml by adding the absorbing solution and the optical density of the former is measured relative to the unexposed absorbing solution at 352 nm wavelength.

Ozone concentration in the solution is determined using the calibration plot, and that in the ozone/air mixture by the following formula: $C = \frac{q}{V_o}$ ug/m^3 (8)

where q - ozone amount in the solution determined from the calibration plot, ug;
V_o - air volume bubbled through the absorber and reduced to normal conditions, m^3.

To plot the calibration curve, a basic standard solution (0.1 must be prepared: 32 g of potassium iodide and 6.346 g of iodine are dissolved in bidistilled water in a 500 ml measuring flask). Prior to application, the solution is allowed to stand in a dark place for 24 hours. Iodine concentration in the solution is 12.692 mg/ml.

The working standard solution is prepared by sequential dilution of 5 ml of the basic standard solution with bidistilled water until the volume amounts to 100 ml. Then the diluted standard solution is diluted by the absorbing solution two times running (each time 5 ml of the preceeding solution is diluted to 100 ml). Iodine concentration in the working standard solution is 1.587 ug/ml. The scale of the standards is to be prepared from the obtained solution according to Table 8.

Based on the photometric analysis of the standards a plot of the solution optical density vs. ozone content in 25 ml of the absorbing solution is constructed, proceeding from the following ratio: 1 mole of I_2 corresponds to 1 mole of ozone absorbed by the solution.

Table 8. Standard scale

Standard No.	0	1	2	3	4	5	6	7
Volume of the working standard solution (1.587 ug/ml), ml	0	0.5	1.0	1.5	2.0	4.0	6.0	8.0
I_2 amount in a sample, ug/25 ml	0	0.793	0.587	2.381	3.174	6.348	9.522	126
Relative ozone content in a sample, ug	0	0.L5	0.3	0.45	0.6	1.2	1.8	2.4

Ozone detection limits for ozone/air mixtures is 0.15 ug of ozone in a sample. The relative error of the method is 5 percent. Interferences are as follows: sulfur dioxide at concentrations exceeding 10 ug/m^3 and nitrogen oxides at concentrations exceeding 20 ug/m^3.

To calibrate the ozone analyzer, the ozone/air mixture, already analyzed for ozone, is fed into the gas analyzer. The analyzer recorder indication is set in accordance with the ozone concentration measured in the ozone/air mixture.

To calibrate the gas analyzer it would be advisable to use ozone/air mixtures with ozone concentrations from 20 to 150 ug/m^3.

7.5.1.9 Battery Operated Ozone Monitor

(See section 7.4.1.10)

7.6 Atmospheric Nitrogen Oxides

Nitrogen compounds occur in the atmosphere in various forms. In the gas phase, they are ammonia, nitrous oxide, nitrogen monoxide and dioxide. Nitrogen monoxide and dioxide are of specific interest to the IGBM program. Usually these oxides are present in the atmosphere together. As a result of chemical and photochemical reactions, they undergo mutual transformations and eventually produce nitrate. Separate determination of these oxides at the background level is a difficult task. IGBM would need the determination of nitrogen dioxide. The range of background concentrations of nitrogen dioxide is given in Section 4.

The lowest values, below 0.5 ug/m^3, have been measured with the help of specific, rather complicated methods. A trade-off, less sensitive, though suitable for mass measurements in terms of all the other parameters, should be recommended for IGBM station network.

7.6.1 Chemiluminescence

The method is based on the application of an automatic gas analyzer; the detection limit is 1-2 ug/m^3. Under favorable conditions with sufficient background concentrations of nitrogen monoxide and dioxide, this method ensures their separate determination. The required procedures are described in the WMO Handbook No. 491 (WMO, 1978).

7.6.2 Nitrogen Dioxide Determination by the Interaction with Sulfanilic Acid and N-(I-naphtyl) Ethylene Amine

7.6.2.1 Principles of the Method

Atmospheric nitrogen dioxide is absorbed by the absorbing solution which forms a thin coat on glass beads. The interaction of nitrite ions with sulfanilic acid and N-(I-naphthyl) ethylenediamine produces a colored compound. The intensity of the solution color is proportional to the amount of nitrogen dioxide absorbed and is measured by photometry at 550 nm wavelength.

7.6.2.2 Specifications of the Method

Detection limits for nitrogen dioxide is 0.3 ug/m^3 in a 0.3 m^3 air volume. Measurement error is 5-30 percent.

7.6.2.3 Interferences

Ozone interference is eliminated by adding sodium arsenite into the absorbing solution. To eliminate solar radiation interference the sorption tube is to be screened.

7.6.2.4 Instruments, Equipment and Materials:

Electric aspirator with a capacity of 0.2-1 L/min.
Gas meter (error within ± 2.5 percent)
Sorption tubes filled with glass beads (2 cm^3) retained by a porous glass partition
Photoelectric colorimeter
Cells with 10-mm spaced working edges
Analytical balance with weights
Measuring flasks (50, 100, and 1000 ml)
Graduated pipettes (1, 5 and 10 ml)

7.6.2.5 Reagents and Solutions

Chemically pure potassium iodide

Analytically pure glycerine
Analytically pure ethylene glycol
Pure sodium arsenite
Chemically pure sodium nitrate
Chemically pure orthophosphoric acid, 70 percent solution
Analytically pure sulfanilic acid
Pure N-(I-naphtyl) ethylenediamine dihydrochloride
Chemically pure ammonium phosphate, twice-substituted
Analytically pure acetone
Distilled water

Absorbing solution for sorption tubes: 40 g of potassium iodide are dissolved in 35 ml of distilled water and diluted with 15 ml of blycerine (at temperatures above -5 degrees C) or 15 ml of ethylene glycol (at temperatures below -5 degrees C). Two g of sodium arsenite (Na_3 AsO_3) are separately dissolved in 10 ml of water. The two solutions are mixed together. The resultant solution remains persistent for a month. If Na_3 $HAsO_3$ is not available, other arsenous compounds can be used. When the twice-substituted salt (Na_2 $HAsO_3$) is used, sodium hydroxide is added: 2 g of Na_2 $HAsO_3$ per 0.46 g of NaOH. When arsenous anhydride is used, 1.5 g of NaOH should be added to each 1.2 g of A_sO_2.

Buffering solution: 125 g of twice-substituted ammonium phosphate are dissolved in 500 ml of distilled water, diluted with 170 ml of orthophosphoric acid and then the solution volume is brought to 1 L.

Sulfanilic acid, 1 per cent solution: 10 g of sulfanilic acid are dissolved in 500 ml of distilled water in a 1 L measuring flask. Then 200 ml of acetone are added and the solution is diluted with distilled water up to the marking.

N-(I-naphtyl) ethylenediamine dihydrochloride, 0.02 percent solution: 200 mg of N-(I-naphthyl) ethylenediamine dihydrochloride are dissolved in a small amount of distilled water. Then 400 ml of the buffering solution are added and the resultant volume is diluted with distilled water to 1 L. Reagent mixture (to plot the calibration curve): before the application the 1 percent solution of sulfanilic acid and the 0.02 percent solution of N (I naphthyl)-ethylenediame dihydrochloride are mixed together, as 1:1.

Reagent mixture (for sample analysis): before the application 1 part of 1 percent sulfanilic acid, 1 part of 0.02 percent N-(I-naphthyl)-ethylenediamine and 2 parts of distilled water are mixed together. (The absolute amounts of reagents introduced into solutions measured are the same, both when measuring samples and plotting the calibration curve).

Basic standard solution, 1 mg NO_2^-/ml: 0.15 g of sodium nitrite, dried at 60 degrees C for 2 hours, are dissolved in 100 ml of distilled water in a measuring flask. The solution is stored for

a fortnight.

The working standard solution containing 1 ug NO_2^-/ml is prepared by diluting the basic standard solution with distilled water in a 100 ml measuring flask. The solution is prepared just before application.

7.6.2.6 Sampling

Sorption tube preparation for exposure includes multiple rinsing of tubes with hot distilled water, drying in an oven and application of the absorbing solution on glass beads. The solution is applied with the help of a rubber bulb by sucking into the tubes until the beads are completely covered. The excess solution is blown out and the outer surface of the sorption tube is rubbed with filter paper. Sorption tubes are stored in an air-tight packing in a dark place for a month.

During sampling, sorption tubes are mounted in the vertical position, with the porous partition down, shielded by a sun screen and connected to an air pump providing an air flow rate within 0.2-1 L/minute.

The collected samples sealed in an air-tight packing can be stored in a dark place for a week.

7.6.2.7 Analytical Procedure

The exposed sorption tube is placed in a glass test tube where 5 ml of the reagent mixture (for sample analysis) is added. Blowing the rubber bulb (8-10 times), the sample is transferred into the solution and the contents of the test tube are mixed. Twenty minutes later, the optical density of the solution relative to water is measured. The measurement is carried out in cells with 10 mm-spaced working edges at 550 nm wavelength.

Simultaneously, the reference solution ("zero" solution) is prepared. To this end an unexposed tube from the same set is analyzed in the same way as the sample analysis. The amount of nitrogen dioxide in samples is determined using the calibration curve by the difference between the optical densitites of the sample and zero solutions.

7.6.2.8 Calibration Plot (Standard Scale)

The scale of standards is prepared in 50 ml measuring flasks. To this end, each flask is filled with 25 ml of the reagent mixture (for the calibration plot), the working standard solution (according to Table 9), 2 ml of the absorbing solution (the amount of the absorbing solution corresponds to the amount of the solution applied to the sorption tube) and the resultant volumes are diluted to the mark with distilled water. Measurements are carried out as described in the "Analytical Procedure".

Table 9. Standard scale for NO_2^- determination in samples

Standard No.	0	1	2	3	4	5	6	7
Working std. solution ($1\ ug\ NO_2^-/ml$), ml	0	1	2	4	6	8	10	20
NO_2^- content in a 5 ml sample, ug	0	0.1	0.2	0.4	0.6	0.8	1.0	2.0

The optical density of the zero solution should not exceed 0.05

7.6.2.9 Calculation

NO_2^- concentration in ambient air (C) is determined by the following formula:

$$C = \frac{q}{V_o} \quad ug/m^3 \qquad (9)$$

where q - NO_2^- content in the sample volume analyzed, ug;
V_o - air sample volume reduced to normal conditions, m^3

7.6.2.10 Battery Operated NO_2^- Monitor

The U.S. IGBM pilot monitoring project and related studies have recently begun using a highly sensitive, portable NO_2^- monitor made by Scintrex Corporation (Scintrex/Unisearch, 222 Snidercroft Road, Concord, Ontario, Canada, L4K 1B5). This instrument operates by detecting the chemiluminescence produced when the NO_2^- encounters a surface wetted with a specially formulated luminous solution. This instrument measures NO_2^- directly and does not require conversion of NO_2^- to NO prior to detection. The instrument requires a 250 ml solution bottle to keep the sensing wick wetted. This provides for about 80 hours of continuous operation before the solution has to be replenished. It is capable of detecting NO_2^- at or above 5.0 ppt.

The unit requires a calibration device. In our studies we have used a portable gas permeation calibrator made by CEA Instruments (SC-100 calibrator)(CEA Instruments, Inc. 16 Chestnut

Street, P.O. Box 303, Emerson, New Jersey 07630, USA).

We have operated this instrument strictly under battery and solar power for 3 days at a time in very remote sites (6 miles from the nearest road). The results have been good and very consistent. Because of the reliability, sensitivity, stability, ruggedness, portability and power requirements, we believe this instrument has great potential for use in IGBM sites around the world.

In November, 1986, this instrument plus the SO_2 monitor were operated successfully at Torres del Paine National Park. The system operated from solar power and batteries. The results indicate that oxidant levels were in the 20 ppb range, NO_2 levels less than 1.0 ppb were common, and SO_2 levels in the 1.0 to 3.0 ppb range.

7.7 Analysis of Atmospheric Precipitation (the BAPMoN Programme)

Procedures required for precipitation sample analysis are all given in the WMO Handbook No. 491 (WMO, 1978).

7.8 Lead and Cadmium

These elements, belonging to the group of heavy metals, are present in virtually all environmental objects and biota. Anthropogenic activity has caused an increase in natural lead and cadmium concentrations. And though at present, there is no evidence for direct biological danger due to chronic effects from the general growth of background concentrations, monitoring of these elements, as well as of other heavy metals, is quite an urgent task. Studies (Ostromogilsky, et al., 1985) have shown that the anthropogenic contribution of lead and cadmium to background atmopsheric pollution is rather significant. In the continental areas of the Northern Hemisphere, it is about 90 percent for lead and about 50 percent for cadmium. In the oceanic atmosphere it goes down to about 80 percent for lead and 10 percent for cadmium. In the Southern Hemisphere, the contribution to the continental atmosphere is lower, and to the oceanic atmosphere considerably lower. The range of background concentrations of lead and cadmium in environmental objects is given in Section 4.

7.8.1 Measurement in the Atmosphere and Precipitation

The considered methodology of using widely applied instruments based on atomic absorption spectrophotometry with flameless atomization is fairly simple and possesses high sensitivity.

7.8.1.1 Principles of the Method

Treatment of the solution for analysis includes drying,

ashing and atomization in a graphite cell by high temperature electric heating in an inert gas flow. Absorption of the resonance line of the emission spectrum of a lamp with a hollow cathode for a relevant element is proportional to the element concentration in the sample. Absorption of lead is measured at 283.3 nm wavelength, that of cadmium at 228.8 nm.

7.8.1.2 Specification of the Method

The detection limit for lead during electrothermal atomization in the graphite cell is 2 10^{-4} ng/m^3; for cadmium it is 1 10^{-5} ng/^{3}, the air sample volume being 1000 m^3. Detection limit in liquid samples is 0.25 ug/L for lead, and 0.02 ug/L for cadmium. Measurement error is 15 percent.

The method provides for lead and cadmium determination in non-enriched precipitation samples, as well as in dissolved solid samples (aerosols).

7.8.1.3 Interferences

In the case of incomplete digestion of the sample, lead and cadmium concentrations can be overestimated due to macrocomposition effects via non-selective absorption. Therefore, lead and cadmium concentrations should be measured using blank correction by a deuterium lamp.

To eliminate sulfate interferences in lead, determination in water samples is as follows: 5 ml of sample and standard solutions are each diluted with 0.5 ml of lanthanum nitrate solution.

7.8.1.4 Instruments, Equipment and Materials:

Atomic absorption spectrophotometer with electrothermal atomizer (graphite cell) and blank corrector
Graphite cells
Lamps with hollow cathodes for lead and cadmium
Compressed argon cylinder with pressure regulator
Electric heater with a sand bath
Bidistilled water generator
Filtering device with membrane or glass filters
Micropipettes with replaceable tips (10, 20, 50, 100, 500, 1000 ml)
Pipettes (5, 10, 50, 100 ml)
Graduated test tubes (5 and 10 ml) with ground stoppers
Heat resistant beakers (25, 50, 100 ml)
Glass and quartz cups (0 50 mm)
Measuring flasks (10, 50, 100, and 1000 ml)
Glass funnels
Polyethylene bottles (10, 25, 100, 500 and 1000 ml)
Cylinders (25, 100, 1000 ml)
Crucible tongs
Asbestos sheet
Rubber bulb

7.8.1.5 Reagents and Solutions

Superpure concentrated 1 N and 1 percent (by volume) nitric acid
Chemically pure or analytically pure 30 percent hydrogen peroxide
Chemically pure lanthanum nitrate. Solution with lanthanum concentration of 50 mg/ml is prepared by dissolving 5.8 g of La_2O_3 in 10 ml of concentrated nitric acid and the volume of the resultant solution is brough to 100 ml.
Chemically pure lead and cadmium nitrates
Bidistilled water
Standard solutions of lead and cadmium

Basic standard solutions of lead (1 mg/ml) and cadmium (1 mg/ml) are prepared from the standards or by dissolving 1.599 g of $Pb(NO_3)_2$ and 1.372 g of $Cd(NO_3)_2 4H_2O$ in a small amount of bidistilled water, and diluting the resultant solution with 1 percent nitric acid in a 100 ml flask. The solutions can be stored for a year. The working standard solutions of lead (0.1-5 ug/ml) and cadmium (0.01-05 ug/ml) are prepared by an adequate dilution of the basic solutions with 1 percent nitric acid and stored for no more than half a year.

All solutions are based on bidistilled water. Nitric acid is distilled in a quartz or siliciboride distiller.

7.8.1.6 Analytical Procedure

Concentrations are determined according to the instruction of the company-producer of the atomic absorption spectrophotometer. Optimum analytical conditions are selected experimentally by electrothermal decomposition and atomization of standard lead and cadmium solutions.

Techniques for dissolving solid samples are described below.

7.8.2 Atmospheric Aerosols (Dust)

Aerosols are sampled on various filters, therefore several ways of sample dissolution are suggested.

Fibrous filters with an organic base. After base separation, the exposed filter is placed in a porcelain crucible and ashed in a muffle furnace. The maximum temperature for filter ashing is 430 degrees C. Samples are processed at this temperature for no less than an hour (until the disappearance of black carbon mass). The temperature is continuously monitored by a calibrated thermocouple (or a 500 degree C thermometer). Crucibles are removed from the muffle furnace, and when they cool down, their contents are treated with 10 ml of nitric acid (1:1) while heated on an asbestos-coated electric heater. Evaporation should not be accompanied by boiling. Samples digested to wet salts are cooled, flushed with 10 ml of 1 percent nitric acid and thoroughly mixed. After settling, the solution is transferred

into a 10 ml test tube. The test tubes should be tightly plugged with ground stoppers and labeled, with the sample code indicated. Two blank tests are prepared for each batch of nitric acid and each set of filters.

Porous filters. The filter is placed into an evaporating cup (about 50mm), flushed with 10 ml of concentrated nitric acid, then evaporated until the sample is 2-3 ml. The cooled sample is treated with 1 ml of 30 percent hydrogen peroxide and carefully evaporated to dryness (do not allow the residue to turn brown). The residue is flushed with 1-2 ml of 1 percent nitric acid, heated to boiling, transferred into a 10 ml measuring flask upon cooling, and diluted to the mark with 1 percent nitric acid. The resultant solution is to be stored in a polyethylene bottle.

Glass fiber filters. The filters are treated with concentrated nitric acid (10 ml of the acid per about 10 cm^2 of the filter surface). The sample is evaporated to a pulp, cooled, diluted with 1 ml of 30 percent hydrogen peroxide and heated again for 5 minutes. After cooling, the sample is filtered and rinsed with water. Combined filtrates are carefully evaporated to dryness. The residue is dissolved in 1-2 ml of 1 percent nitric acid heated to boiling, then the solution is cooled, transferred into a 10 ml measuring flask, and diluted to the mark with 1 percent nitric acid.

Twenty ml of the sample solution under study are pipetted into the graphite cell with a micropipette and measured in compliance with a prescribed program.

7.8.3 Atmospheric Precipitation

Lead and cadmium are directly determined in the sample without any preconcentration. In this case, 20 ul of the sample under study are fed into the cell using a micropipette and measured according to a prescribed program. If the concentration of the metals analyzed is below the detection limit, they are concentrated by sample evaporation to wet salts which are then dissolved in 5 ml of 1 percent nitric acid.

To eliminate interferences due to nonspecific absorption occurring during the analysis with electrothermal atomization, the method of additions is used. Four aliquots are taken from the sample. The first is diluted with an equal volume of bidistilled water, the others with equal volumes of standard solutions of different concentrations. The concentrations of the standard solutions should be selected proceeding from the concentration expected in the sample analyzed, i.e., the concentration of the first standard solution should be about twice as low as the expected concentration; those of the second and third ones two and three times as high as the concentration of the first standard solution, respectively. Absorption of the four solutions is measured, and the height of the absorption peak is

plotted as a function of the concentration of the element added. The obtained straight line is extrapolated to the intersection with the concentration axis. The axis segment cut off by the line is equal to the concentration of the element in the initial sample.

The method of additions is applicable only when all absorption values are within the linear part of the calibration curve.

7.8.4 Calibration Plot (Standard Scale)

Calibration plots are constructed by 4-6 points. Standard solutions are used to prepare solutions with lead and cadmium concentrations of 1-10 ng/ml and 0.1-1 ng/ml, respectively, by dilution with 1 percent nitric acid. The newly prepared solutions are applicable for 3 days. Twenty ul of standard solutions are fed into the cell by a micropipette and measured according to the instructions for a given instrument. The calibration curve is plotted against element concentration, ng/ml, and the absorption signal value, after which the linear area of the ratio between the concentration and absorption is distinguished.

7.8.4.1 Calculation

Solution concentration is determined from the plot, since the volumes of the sample fed and standard solutions are equal to 620 ul. Atmospheric concentrations of lead and cadmium is calculated by the following formula:

$$C_{atm} = \frac{C \times V}{V_o} \quad ng/m^3 \qquad (10)$$

where C - metal concentration determined from the plot, ng/ml;
V_o - air sample volume reduced to normal conditions, m^3
V - dissolved sample volume, ml;

In the case of direct determination of lead and cadmium in atmospheric precipitation, their concentration is found from the plot. Lead and cadmium content in preconcentrated samples is calculated by the following formula:

$$C_{pr} = \frac{C \times V \times 10^{-3}}{n} \quad ug/l \qquad (11)$$

where C - metal concentration in the enriched sample determined from the plot, ng/ml;
V - concentrated sample volume, ml;
10^{-3} - conversion factor
n - concentration factor (above 1)

7.9 Arsenic

Arsenic, like lead and cadmium, is present in virtually all environmental objects. The anthropogenic contribution of arsenic to atmospheric pollution is intermediate, as compared to lead and cadmium, though it is closer to cadmium, i.e., in the continental areas of the Northern and Southern Hemisphere, the anthropogenic flux of arsenic to the atmosphere exceeds or equals natural source intensity. The range of background arsenic concentrations in environmental objects is given in Section 4.

7.9.1 Determination in the Atmosphere and Precipitation

This section deals with the methodology of using a Zeeman atomic absorption spectrophotometer with flameless atomization.

One of the main difficulties in arsenic determination by atomic absorption spectrophotometry is the unfavorable location of the resonance line in the UV skip band (193.7 nm). This involves problems of dust deposition on windows, optics quality and nonselective absorption effects. The application of a Zeeman atomic absorption spectrophotometer allows us to overcome the above difficulties and determine arsenic (as well as lead and cadmium in a single sample) both after acid digestion on the sample and by direct measurement of samples without any pretreatment.

7.9.1.1 Principles of the Method

The method allows us to analyze solid, as well as liquid samples. The sample under study is subjected to electrothermal atomization in argon flow. The absorption of the resonance line of arsenic emission spectrum is proportional to the element amount in the sample. Spectral interferences are corrected automatically using Zeeman effect.

7.9.1.2 Specifications of the Method

Detection limit is 0.1 ng/m^3 for an air sample volume of 1000 m^3. The detection limit for liquid samples is 10 ug/l. Measurement error is 15 percent.

7.9.1.3 Interferences

Zeeman effect provides for an automatic compensation for practically all spectral interferences.

To reduce arsenic losses in a sample after it has been fixed in the analysis boat, about 20 ul of 2 percent nickel nitrate solution should be added. The solution is added to liquid samples, as well, so that nickel nitrate concentration in the sample is about 0.1 percent.

7.9.1.4 Instruments, Equipment and Materials:

Zeeman atomic absorption spectrophotometer
Microbalance
Two-channel recorder
Graphite analysis boats
Micropipette with a 50 ul replaceable dosimeter
Compressed argon cylinder with reducer

7.9.1.5 Reagents and Solutions

Superpure concentrated and 1 percent nitric acid 1 N solution of chemically pure hydrochloric acid 1 N solution of chemically pure caustic soda
2 percent solution of nickel nitrate
Lacquer for sample fixation in the graphite analysis boat: 2 g of celluloid dissolved in sioamyl acetic ester diluted to 100 ml. The lacquer should not contain the analyzed elements.
Chemically pure arsenic trioxide
Bidistilled water

Basic standard arsenic solution with a concentration of 1 mg/m. The solution is prepared by dissolving 0.1320 g of arsenic trioxide in a small amount (1-2 ml) of 1 N caustic soda solution. The resultant solution is neutralized by 1 N hydrochloric acid and diluted to 100 ml with bidistilled water in a measuring flask.

Working standard solutions with As concentrations of 0.15 and 0.75 ug/ml are prepared by a relevant dilution of the basic standard solution with 1 percent nitric acid. The solutions are applicable for a month.

7.9.1.6 Analytical Procedure

Atmospheric aerosol. Part of the exposed filter (0.5-1cm^2), cut out by a special die, is placed into the graphite analysis boat and fixed with the lacquer. The boat is placed into the graphite furnace; the heating program is switched on and the integral absorption signal is recorded. One sample undergoes no less than 5 parallel measurements. The samples analyzed are flushed with about 20 ul of 2 percent solution of nickel ntirate.

Atmospheric precipitation. 10-40 ul of the analyzed sample containing nickel ions are introduced into the graphite analysis boat by a micropipette with a replaceable dosimeter. The boat is placed into the furnace and the heating program is switched on. When low-arsenic samples are analyzed, they undergo a 50-fold concentration by evaporation (care must be taken to prevent sample from evaporating to dryness).

Aerosol solutions (see 7.8.1.6). The sample solution is

diluted with nickel nitrate to bring its concentration to about 0.1 percent. 10-40 ul of the sample transferred into lacquer fixed graphite boat should be analyzed further according to the heating program of the furnace. In liquid sample analysis, the ashing temperature is to be set during the drying stage to skip the sample ashing stage.

7.9.1.7 Calibration Plot (Standard Scale)

To calibrate the instrument, 20 or 40 ul of the working standard solutions should be fed into the graphite analysis boat and fixed by the lacquer. The boat is placed into the graphite furnace and measurements proceed according to the prescribed program. To obtain the scale of standards, the standard solutions are diluted with dissolved nickel nitrate, as indicated above. The calibration curve is plotted against the concentration and the integral absorption signal upon deducting the blank test signal. Due to graphite furnace parameter variations in the process of operation, the working standard solutions should be periodically measured to correct the calibration curve.

7.9.1.8 Calculation

Arsenic concentration is calculated by the following formulas:

Aerosols: Solid samples $$C = \frac{q \times S_1}{V_o \times S} \ ng/m^3 \quad (12)$$

Liquid samples $$C = \frac{q \times V_s \times 10^3}{V_o \times V} \ ng/m^3 \quad (13)$$

where C - atmospheric concentration of arsenic, ng/m^3
q - amount of arsenic in a filter part or solution aliquot placed into the furnace determined from the calibration curve, ng/
S_1 & S - areas of the filter part analyzed and total working surface of the filter, respectively, cm^2;
V_s - total volume of the dissolved sample, ml;
V - aliquot of the dissolved sample taken for analysis, ul;
10^3 - recalculation factor
V_o - air volume reduced to normal conditions, m^3

Atmospheric precipitation

$$C = \frac{q \times 10^3}{V \times n} \ ug/l \quad (14)$$

where C - arsenic concentration in precipitation, ug/l;
q - arsenic amount in the sample aliquot placed into the furnace, determined from the calibration curve, ng;
V - sample volume taken for analysis, ul;
n - concentration factor (above I);
10^3 - conversion coefficient

7.10 Mercury

7.10.1 Determination in the Atmosphere

The range of background mercury concentrations is given in Section 4. There is no unanimous opinion concerning the anthropogenic contribution of mercury to background atmosphere pollution in the world literature; the estimates differ considerably. Recent studies have shown that atmospheric mercury occurs mainly in the gas phase (92-97%). In this connection it is determined separately from other heavy metals occurring in the form of atmospheric aerosol.

7.10.1.1 Principles of the Method

Cold vapor atomic absorption is the most selective and sensitive technique for the determination of mercury in various environmental samples. At room temperature mercury is present as a monoatomic vapor whose light absorption is measured at 253.7 nm wavelength using standard gas cells designed for UV spectrophotometry. The limit of mercury detection by this method is 0.1 ng.

Atmospheric mercury is accumulated on a silver or gold sorbent (amalgamator) by passing ambient air through the sorbent at a rate of 1.5 L/min. for 24 hours. Then the sorbents should be heated and the accumulated mercury transferred with a nitrogen flow to the calibrated measuring amalgamator whereupon mercury is transferred to the atomic absorption spectrophotometer cell.

7.10.1.2 Specifications of the Method

Detection limit is 2 ng/m^3 at the air sample volume of 2 m^3. Measurement error is 10%.

7.10.1.3 Interferences

The method is specific, there are no interferences in background samples.

7.10.1.4 Instruments, Equipment and Materials

Dual-beam atomic absorption spectrophotometer with a hollow-cathode mercury lamp (or a specialized MAS-50 instrument for mercury determination).

The cell with 200-250 mm optical base and 10-20 mm internal diameter is to be made for the atomic absorption spectrophotometer (except specialized instruments) and installed along the optical axis of the instrument.

Laboratory recorder with a sensitivity of no less than 0.2 mV/cm.

Microcompressor, suction rate up to 2 L/min.
Electric tube furnace for trace analysis
Thermocouple with a measuring device for temperatures within 0-900 degrees C
Rotameters, rheometers
Stopwatch or contact watch regulated within a range of 1-60 seconds
Nitrogen cylinder with reducer
Laboratory thermometers for 0-50 degrees C with the least division of 0.1 degrees C, and for 0-500 degrees C with the least division of 1 degree C
Medical syringe (10 ml)
Polyethylene bottle (1 L)
Thermostat
Filter holder
Silicone and rubber hoses
Glass wool
Fibre or membrane filters
Silver wire of 0.05 - 0.1 mm diameter
Silver-plated glass beads
Gold wire of 0.01 mm diameter
Silver and/or gold amalgamators
There are two types of silver amalgamators used:
- measuring amalgamators (Figure 9);
a quartz glass tube is filled with a spiral silver wire of 0.05 - 0.1 mm diameter (the spiral diameter is 1.5 mm, length 1-2 mm);
- sampling amalgamators; a quartz glass tube is filled with silver-plated glass beads (0 0.9-1 mm). The inlet and outlet of the tube are plugged with glass wool or porous glass plates.

Silver plating of glass beads is carried out using a "silver mirror" reaction. To this end, three solutions should be prepared: solution 1 - 4 per cent silver nitrate solution; solution 2 - 9.5 percent potassium hydroxide solution; solution 3 - 1.1 g of tartaric acid and 9.5 g of sugar are dissolved in 100 ml of distilled water, the solution is boiled for 5-10 minutes, cooled and treated with 20 ml of alcohol.

Before silver plating, solution 1 is to be treated with a concentrated ammonia solution to dissolve the precipitate (but without excess) and mixed with solution 2. In case of silver hydroxide precipitation, ammonia solution is added drop by drop (without excess) to dissolve the precipitate formed; the resulting solution is quickly mixed with solution 3 and poured into a plating vessel with glass beads predegreased with a chromic acid mixture. During silver plating, the vessel is placed into hot water (70-80 degrees C). Then the solution is drained, the beads are rinsed with water and dried.

Before sampling, the amalgamators undergo a 2-hour heat treatment in the tube furnace with the nitrogen flow (0.5 L/min) at 300 degrees C. Afterwards the sampling amalgamators are tested for residual mercury.

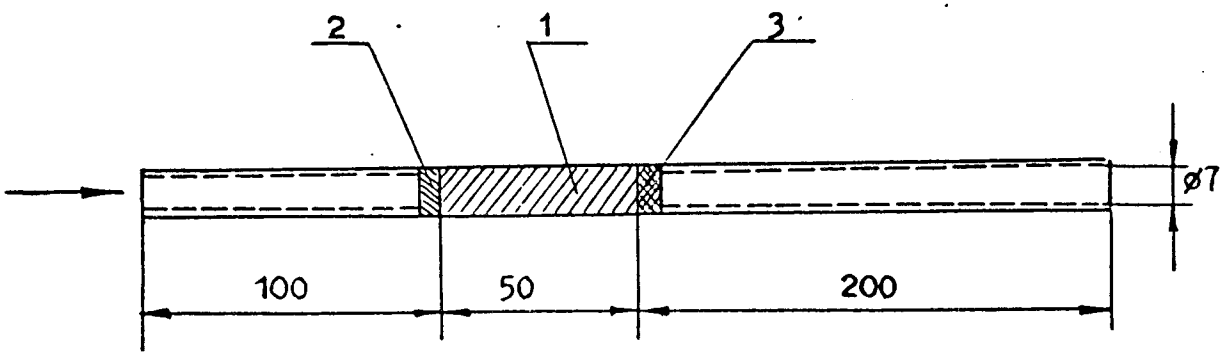

Figure 9. Measuring amalgamator (mm)

1 - silver; 2 - glass wool; 3 - porous glass partition

Sampling amalgamators are standardized by performance monitoring. A sampling system consisting of 3 sequential sampling amalgamators is installed in a laboratory or any other room (on condition that mercury concentration in the air does not exceed 0.3 ug/m^3). Air is passed through the system for 24 hours at a rate of 1.5 L/min and mercury concentration is measured in each amalgamator. Then mercury catch efficiency (%) in the first amalgamator is calculated relative to the total amount of collected mercury. A sampling amalgamator is considered applicable if it catches no less than 90% of mercury. The date of its production and testing, as well as mercury catch efficiency (%) and the number of operation cycles are registered (an operation cycle implies sample collection and measurement). Performance monitoring is carried out once in 20 cycles.

Once sealed by glass rods via silicone couplings, unexposed sampling amalgamators can be stored up to one year.

Gold measuring amalgamators are made of 25 cm long (8 mm internal diameter) quartz tubes filled with gold wire (0 0.01 mm). The filling length is 8 cm, gold wire weight is 1.5 g.

Gold sampling amalgamators are made of 15 cm long quartz tubes 4 mm in diameter (filling length is 5 cm, gold wire weight is 0.5 g).

7.10.1.5 Reagents and Solutions

Metallic mercury
Activated carbon
Chemically pure silver nitrate
Chemically pure potassium hydroxide
Chemically pure tartaric acid
Sugar
Ethyl alcohol
Chemically pure ammonia, 25 percent aqueous solution
Magnesium perchlorate

7.10.1.6 Analytical Procedure

Sampling. Daily samples are collected by passing about 2 m^3 of air through sampling amalgamators. Figure 10 shows a scheme of an air sampling unit. During sampling the tubes are mounted in a vertical position; air flow rate should be 1.2-1.5 L/min. The amalgamators should not be exposed to direct sunlight. When sampling is over, the amalgamators are sealed and can thus be stored for up to 2 months.

Figure 11 shows a convenient sampling unit. The sampling amalgamators mounted on a frame are connected with each other via Chaco taps with an inlet and rheometers. Ten single or five parallel samples are collected by switching over taps without amalgamator rearrangement. In parallel sampling partial flows

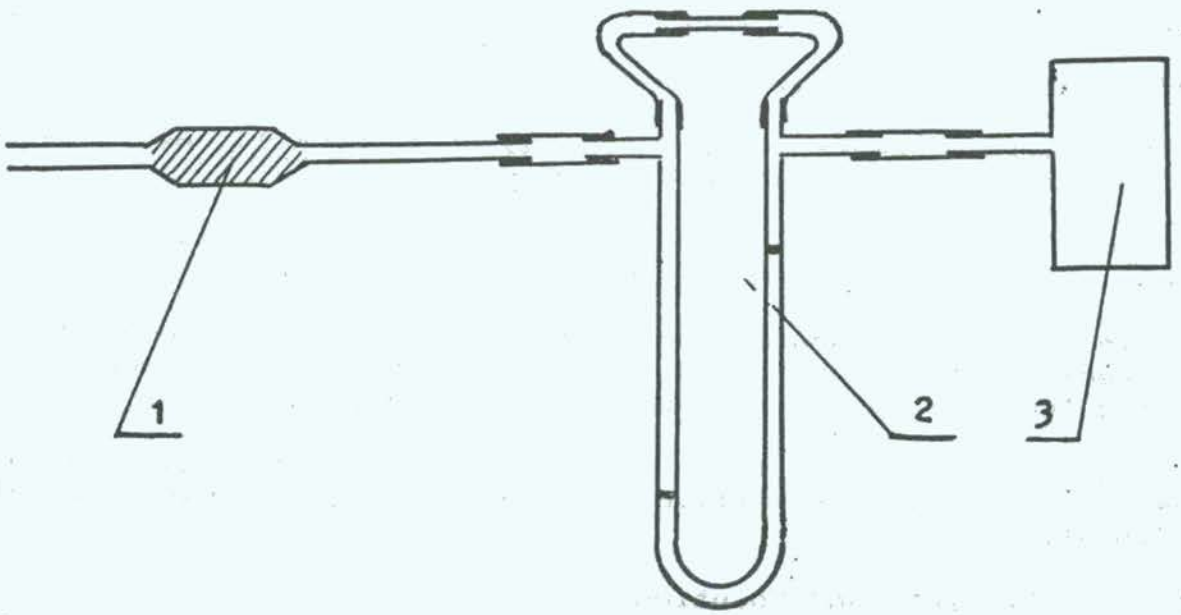

Figure 10. Air sampling device

1 - amalgamator; 2 - rheometer; 3 - microcompressor or pump

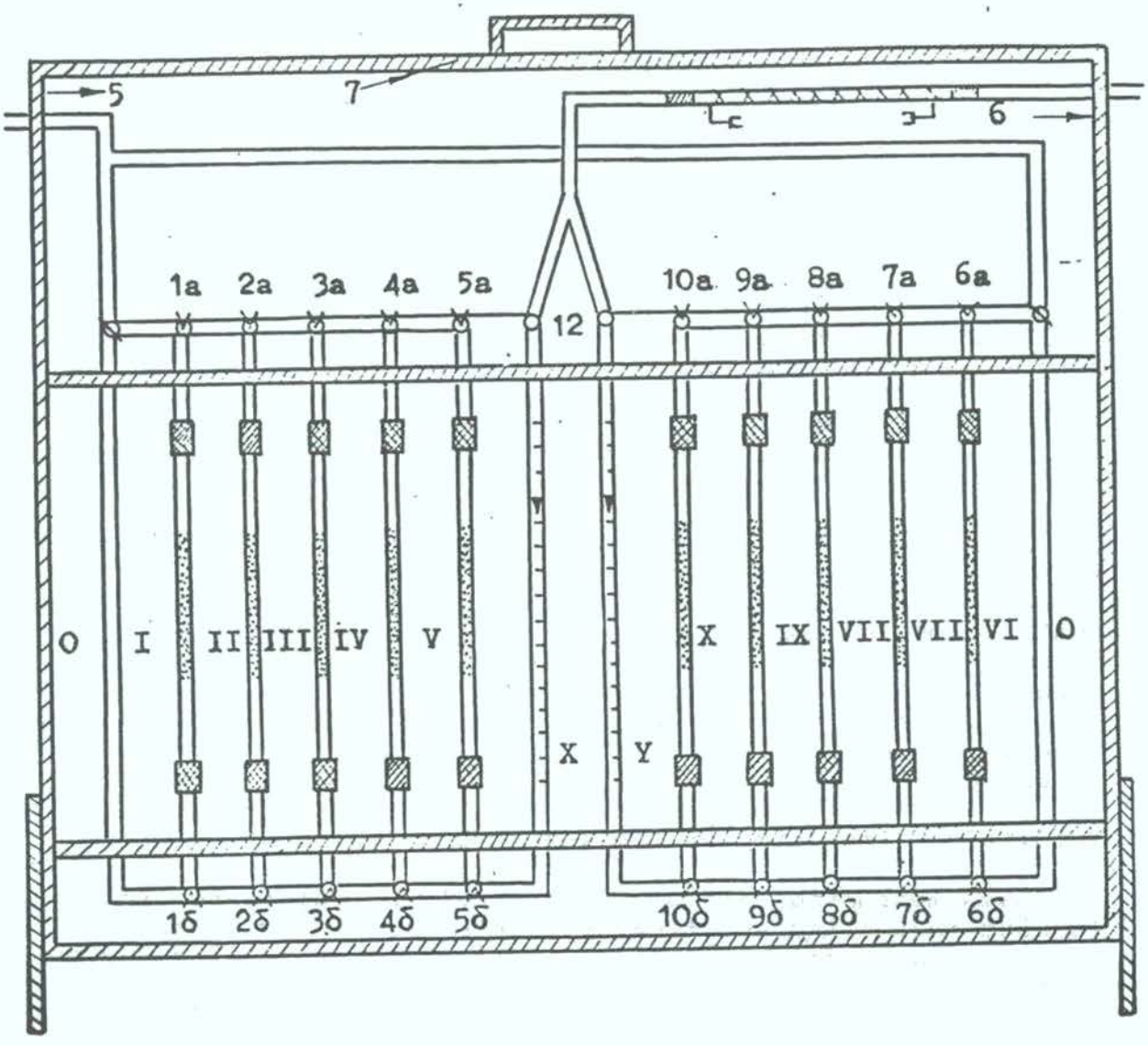

Figure 11. Sampling device for mercury determination in the ambient air

1a - 10b - Chaco taps;
I - X - sampling amalgamators;
1,2 - volume air-flow control taps;
X,Y - rheometers;
O - O -by-passes;
5 - air inlet;
6 - air outlet;
7 - framework

are equalized using taps 1 and 2. In this case one pump and one gas meter are used. Bypasses provide for a series connection of 2 amalgamators (e.g., to check mercury skips).

Measurement. To determine the amount of mercury, a sampling amalgamator is connected to a measuring amalgamator with the help of a silicone hose. Then the silver sampling amalgamator is inserted into the tube furnace assembly heated to 300 degrees C, and the released mercury is transferred to the measuring amalgamator by the nitrogen flow (0.5L/min) within 5 minutes. Figure 12 presents a scheme of the transfer unit. When mercury is transferred to the measuring amalgamator, the latter is to be connected to the analyzer using silicone hoses (Figure 13) and inserted into the furnace heated to 500 degrees C. Then the maximum signal is read from the instrument. Mercury content in the sample is determined by the calibration plot.

In the case of gold amalgamators, mercury is transferred from the sampling amalgamator to the measuring one in the tube furnace at 500 degrees within 1 minute. Then the measuring amalgamator is connected to the analyzer and heated to 500 degrees C. At a nitrogen flow rate of 0.7 L/minute, mercury enters the AAS cell at the 21st second. Simultaneously the recorder draws sharp peaks whose height is proportional to the amount of mercury, provided the analytical conditions are observed.

7.10.1.7 Calibration of the Instrument (Calibration Plot)

New measuring amalgamators should be calcinated in the tube furnace in a nitrogen flow (0.5 L/min) at 700 degrees C for 2 hours. Each measuring amalgamator is calibrated by syringe injection of mercury vapor doses. Injection of mercury doses into the measuring amalgamator is shown in a flow chart (Figure 14).

The calibration requires saturated mercury vapor which is in equilibrium with metallic mercury in a closed vessel at a fixed temperature. A 1 L polyethylene bottle with a polyethylene screw stopper is filled with 20-30 g of metallic mercury. A 2 mm hole is made in the stopper. The hole is filled with a vacuum rubber gasket and the stopper is screwed on the bottle neck. The bottle is allowed to stand in a thermostat or at constant room temperature for a few hours. The temperature is measured by a thermometer with the least division of 0.1 degree C. The needle of the medical syringe is inserted into the bottle through the rubber gasket in the stopper hole to collect various samples of mercury-saturated air. Mercury doses are injected into the amalgamator together with the air passing through the hose by puncturing the amalgamator with the syringe needle and gradual depression of the piston (Figure 14).

Table 10 presents the atmospheric concentrations of saturated mercury vapor for temperatures between 12 and 30 degrees C,

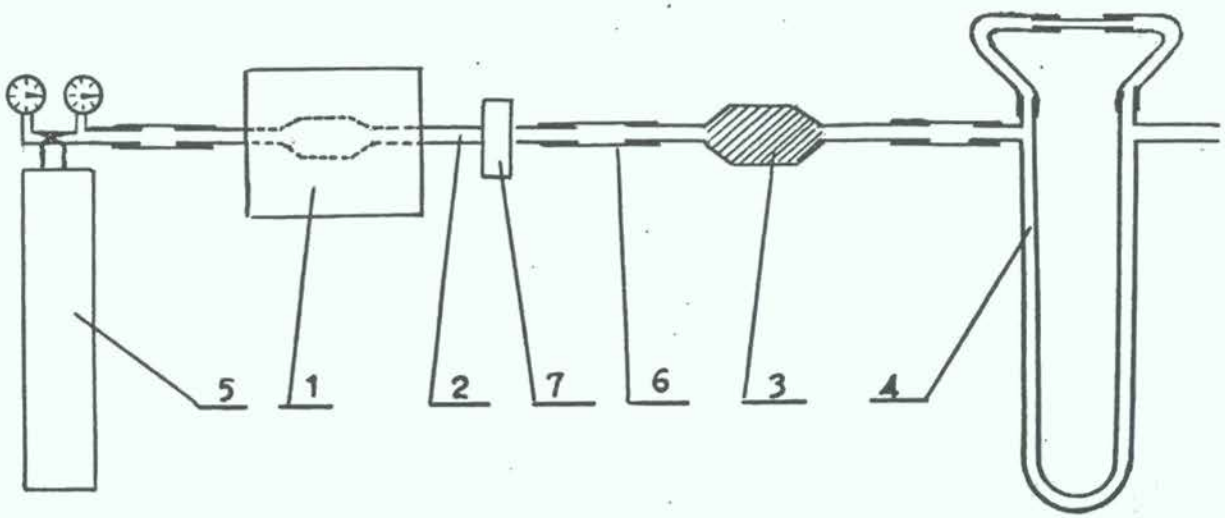

Figure 12. Scheme of the device for sample transfer from sampling to measuring amalgamator

1 - tube furnace;
2 - sampling amalgamator;
3 - measuring amalgamator;
4 - rheometer;
5 - nitrogen cylinder;
6 - silicone hose;
7 - trap with magnesium perchlorate for drying

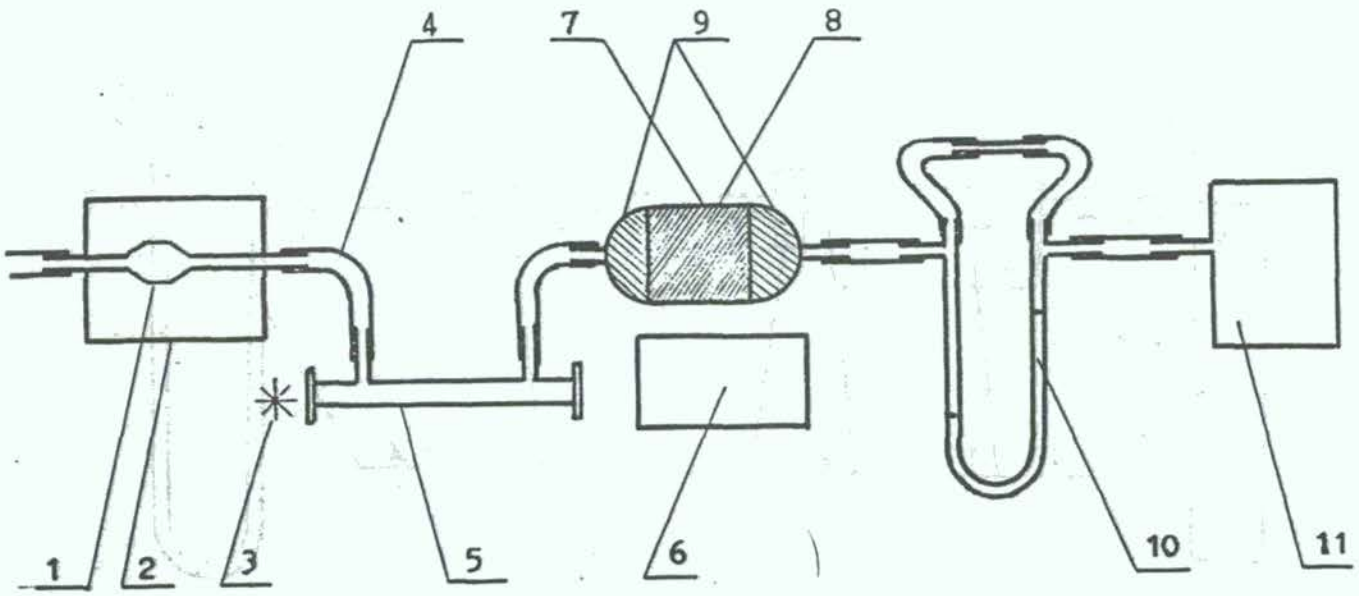

Figure 13. Calibration and analysis installation

1 - measuring amalgamator;
2 - tube furnace;
3 - mercury discharge lamp;
4 - silicone hose;
5 - atomic absorption spectrophotometer cell;
6 - monochromator and measurement unit of the spectrophotometer;
7 - absorption chuck;
8 - activated carbon layer;
9 - glass wool layer;
10 - rheometer;
11 - microcompressor

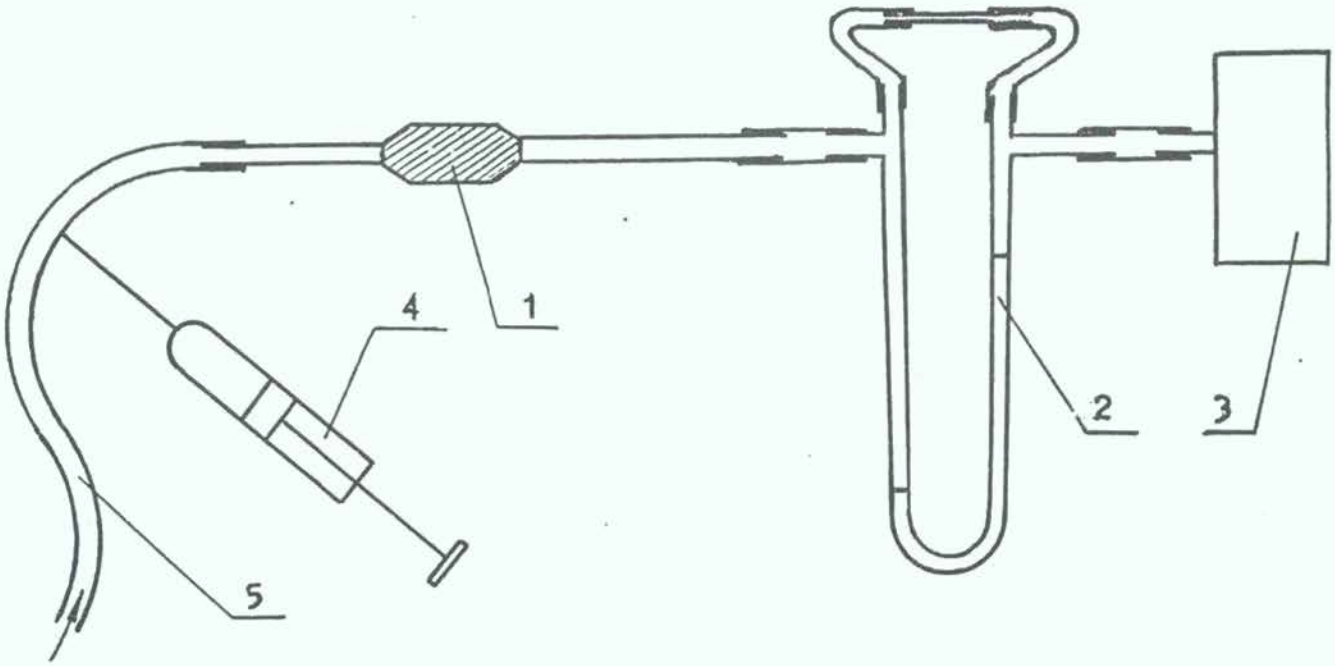

Figure 14. Scheme of mercury-dose introduction into the measuring amalgamator

1 - measuring amalgamator;
2 - rheometer;
3 - microcompressor;
4 - medicinal syringe;
5 - vinylic hose

calculated using a Clapeyron-Mendeleev's equation and reference tables for saturated mercury vapor pressures at various temperatures. The concentration of saturated mercury vapor can also be calculated by the following equations (a modified Smith-Menzies equation):

$$\lg P(\text{mm Hg}) = 9.957094 - \frac{3283.92}{T} - 0.66524 \lg T \qquad (15)$$

$$Q\ (\text{mg Hg/m}^3) = 3.2404 \times 10^6 \frac{P}{T} \qquad (16)$$

The concentrations of saturated mercury vapor for intermediate temperatures are calculated by linear interpolation.

Table 10. Atmospheric concentrations of saturated mercury vapor at various temperatures

Degrees C	12	13	14	15	16	17	18	19	20	21	22
ng/ml	6.75	7.36	8.05	8.8	9.6	10.5	11.3	12.3	13.4	14.5	15.8
Degrees C	23	24	25	26	27	28	29	30			
ng/ml	17.1	18.5	20.1	21.8	23.5	25.5	27.5	29.7			

To carry out the calibration and analysis the measuring amalgamator is to be connected to the spectrophotometer cell, and an absorbing chuck with activated carbon is installed at the cell outlet to prevent mercury vapor release into the ambient air. Figure 13 presents a scheme of the calibrating and analyzing unit. The whole system is initially purged with nitrogen at room temperature then the tube furnace heated up to 500 degrees C is opened and closed again after insertion of the measuring amalgamator. When heated, mercury releases from the amalgamator and enters the spectrophotometer cell. The instruments reading increases rapidly to the maximum and then starts falling to zero. Concentrations are calculated from the maximum reading. Nitrogen flow rate is 0.5 L/min.

The calibration of the instrument and sample analysis should be carried out at equal furnace temperatures and nitrogen flow rates since these parameters essentially affect the shape of the pulse and instrument's maximum reading. The plot is constructed against the peak height and mercury concentration. The calibration should be carried out for mercury amounts within 1-50 ng.

It is necessary to perform daily monitoring of the calibration curve and blank sample measurement.

7.10.1.8 Calculation

Mercury amount in the sample (ng) is determined by the results of atomic absorption spectrophotometry:

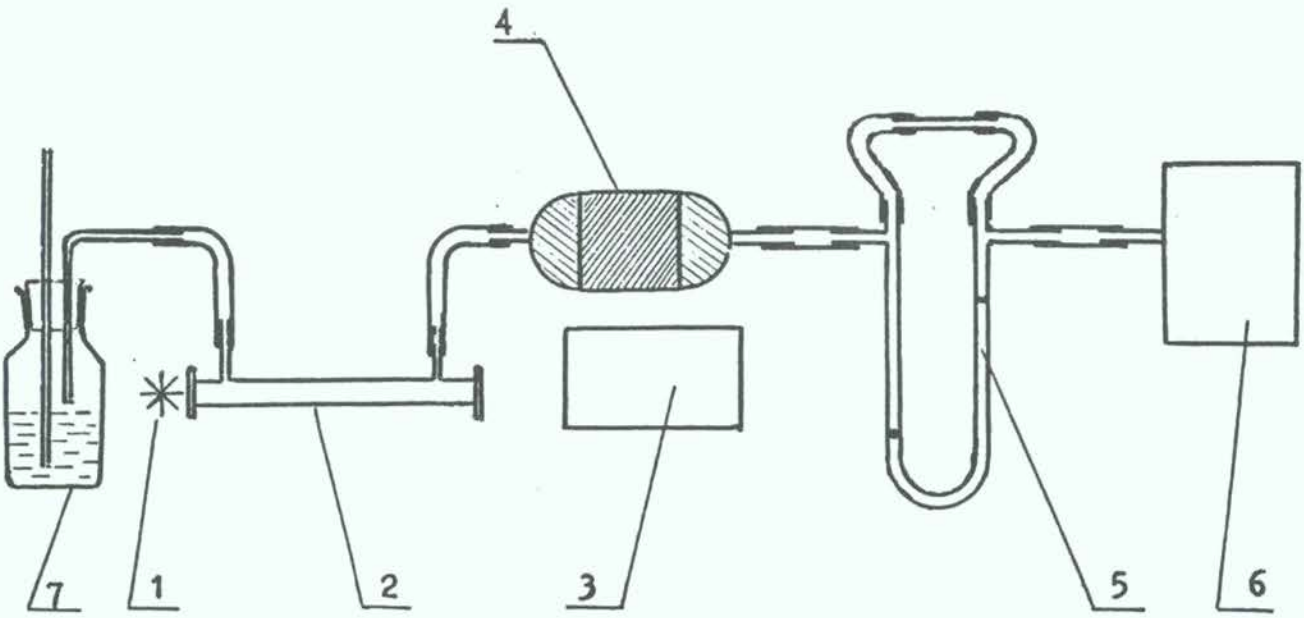

Figure 15. Installation for mercury determination in atmospheric precipitation

1 - mercury discharge lamp;
2 - atomic absorption spectrophotometer cell;
3 - monochromator and measuring unit of the spectrophotometer;
4 - absorption chuck;
5 - rheometer;
6 - microcompressor;
7 - bubbler

$$C = \frac{q}{V_o} \quad ng/m^3 \qquad (17)$$

where C - mercury concentration in the ambient air, ng/m^3;
q - mercury amount in the sample, ng;
V_o - air volume reduced to normal conditions, m^3.

7.10.2 Atmospheric Precipitation

7.10.2.1 Principles of the Method

Water samples undergo a chemical treatment for the mineralization of organic mercury compounds. Then a sample aliquot is transferred into the bubbler where bivalent mercury is reduced to the elemental state using tin chloride. Mercury vapor is purged into the atomic absorption spectrophotometer cell by a nitrogen flow at a rate of 0.5 L/ min.

7.10.2.2 Specifications of the Method

Detection limit is 0.05 ug/L; relative error does not exceed 10 percent.

7.10.2.3 Interferences

Organic mercury compounds that cannot be measured directly should be decomposed at room temperature by a mixture of mineral acids (sulfuric and nitric), potassium permanganate and potassium persulfate. Interferences can also result from water vapor condensation on the cell walls. To eliminate them, the sample should be cooled to a temperature below the laboratory one, or the cell must be heated.

7.10.2.4 Instruments, Equipment and Materials.

Dual beam atomic absorption spectrophotometer with a hollow-cathode mercury lamp (or specialized MAS-50 analyzer for mercury determination.
Unit for mercury determination (Figure 15) consisting of an air blower or microcompressor, magnetic stirrer, bubbler with a nitrogen purge nozzle, rotameter or rheometer with the measurement range of 0-1 L/min., cell and sorption tube with activated carbon connected by silicone hoses. The cell must have the maximum possible length of the optical base and the minimum possible volume. Cells of 15 cm length and 0.75 cm internal diameter can be used for the majority of atomic absorption spectrophotometers.
Filter unit
Glass filter funnels or membrane filters
Micropipettes with replaceable tips
Sorption tubes for magnesium perchlorate
Glass wool

Activated carbon
Colored silica gel indicator
Silicone hoses (i.d. 6 mm)
Measuring flasks (50, 100, 500 ml)
Pipettes (0.1, 0.2, 1, 5, 10 ml)
Measuring cylinders (25, 50, 100, 500, and 1000 ml)
Glass bottles (0.5 and 2 L)
Paper filters

7.10.2.5 Reagents and Solutions

Chemically pure concentrated and 50 percent (by volume) sulfuric acid
Superpure concentrated and 5 percent (by volume) nitric acid
Superpure concentrated 5 N hydrochloric acid
Magnesium perchlorate
Chemically pure potassium persulfate, 5 percent solution
Chemically pure potassium bichromate
Chemically pure hydroxylamine hydrochloride; 2 percent solution is prepared by dissolving 2 g of NH_2 CH x HCl in 1-2 N hydrochloric acid
N-octyl alcohol
Tin chloride, 10 percebnt solution 11.3 g of $SnCl_2 \times 2\ H_2O$ are dissolved in 10 ml of hot concentrated hydrochloric acid and the resultant volume is diluted to 100 ml with bidistilled water (Long-term storage results in a gradual oxidation of Sn^{2+} to Sn^{4+} due to atmospheric oxygen. Such solutions produce precipitates and suspensions due to hydroxide formation and are not applicable)
Superpure carbon tetrachloride
Chemically pure dithizone
Chemically pure mercury (II) chloride

Basic standard mercury solution, 1000 mg/L. 1.352 g of $HgCl_2$ dissolved in 1 L of 5 percent HNO_3 or 1.080 g of HgO in 20 ml of 5 N HCl should be diluted to 1L with distilled water. The solution can be stored for a year.

Working standard mercury solutions within a concentration range of 0.1-10 mg/L are prepared by relevant dilution of the basic standard solution with distilled water acidified with nitric acid.

All reagents should be tested for the absence of mercury. All reagents and standard solutions are to be prepared with the help of bidistilled water.

Reagent cleanup. Acids are rectified in a quartz or siliciboride still. Before the application,the tin chloride solution is purged with nitrogen prefiltered through sorption tubes with activated carbon. The working hydroxylamine solution is purified by extraction with a few batches of 0.05 percent dithizone solution in superpure carbon tetrachloride. Potassium permanganate is recrystallized when necessary.

All chemical utensils are sequentially washed in a 2% solution of potassium permanganate, nitric acid (1:1) and then in distilled water.

7.10.2.6 Sample Preservation

Immediately after collection a sample is filtered through a membrane or glass filter. The first portion of filtrate (about 0.1 L) is discarded, the next portion (about 0.1 L) is to be taken into a polyethylene bottle and preserved in 5 percent HNO_3 and 0.02 g of $K_2Cr_2O_7$.

7.10.2.7 Analytical Procedure

Prior to mercury determination in water, all organo-mercuric compounds are mineralized. To this end, a 0.1 L sample is treated with 1 ml of 50% H_2SO_4 and 1 ml of 1% $KMnO_4$ one day before the analysis, or 30 ml of the sample are diluted with 4 ml of mixed acids (2:1 mixture of concentrated sulfuric and nitric acids), 200 ul of a 5 percent solution of potassium permanganate, and 500 ul of a 5 percent solution of potassium persulfate and thoroughly mixed. In 48 hours, excess oxidants should be reduced by 500 ul of a 2 percent solution of hydroxylamine hydrochloride.

The measurement scale of the instrument (gain) is set depending on the anticipated concentration level (x 10 for concentrations with 0.01-1 ug/L; x 2 for concentrations within 0.1-3 ug/L.

Prior to the analysis, a 2 percent solution of hydroxylamine is added to the samples drop by drop till decoloration, i.e., disappearance of the pink color and dissolution of a possible precipitate. The sample is placed into the bubbler (Figure 15), treated with 2-3 ml of 10 percent solution of tin chloride, and the vaporous mercury reduced to the elemental state is transferred into the atomic absorption spectrophotometer cell by nitrogen flow at a rate of 0.5 L/minute. The maximum signal is recorded. The blank test and each sample measurement are always repeated. Mean blank values are deducted from mean sample values.

When the content of mercury in water is low, it is concentrated on the silver measuring amalgamator by the absorption of mercury vapor released from the bubbler. Then the amalgamator is heated at 500 degrees C, and mercury is transferred into the spectrophotometric cell by the nitrogen flow.

7.10.2.8 Calibration Plot

A set of standard solutions is prepared with concentrations of 0, 0.02, 0.05, 0.07, 0.1 ug of Hg^{2+} per 100 ml of bidistilled water which contain 1 ml of 50% sulfuric acid and 1 ml of 1% solution of potassium permanganate, or 0.5 ml of nitric acid can

be added to the aforementioned working solutions and the resultant volume is diluted to 100 ml with distilled water. All solutions should be fresh.

The calibration curve is based on the working standard solutions pretreated like the samples (7.10.2.7). Three parallel measurements are carried out for each concentration, and the calibration curve is plotted by mean measured values against the absorption value and the amount of mercury (ug) in a 100 ml solution.

7.10.2.9 Estimation

Mercury concentration in water is determined by the following equation: $C = 10 \cdot q$ ug/L (17)

where q - mercury amount in a 100 ml sample determined from the calibration curve, ug;
10 - conversion factor.

7.11 Organochlorine Pesticides and Polychlorobiphenyls

The application of organochlorine pesticides (OCPs) in agriculture, forestry and public health service has been increasing steadily over the last decades. It is well-known that new pest generations eventually get used to a particular pesticide which requires dose increment or replacement by another pesticide. During the application from aircraft, a significant fraction of pesticides (up to 30 percent and over) remain in the atmosphere and spread over long distances. Pesticides that settle down on the earth's surface are partly evaporated and re-enter the atmosphere. Global propagation of DDT has been fully recognized since it has been discovered in environmental objects at very long distances from its source area. Almost the same global propagatic pattern is characteristic for polychlorinated biphenyls (PCBs) widely used in industry. It should be noted that background environmental pollution by PCBs is less studied than that by OCPs. As a rule, PCB and OCP concentrations in background areas are about equal. The highest amounts of OCPs and PCBs are accumulated in organisms which are the end links of various food chains. Thus these pollutants enter the human organism. The background concentration range of most persistent and widespread OCPs is given in Section 4.

7.11.1 Determination in the Atmosphere and Precipitation

7.11.1.1 Principles of the Method

The determination of OCPs and PCBs is based on organic solvent extraction of these substances from environmental samples, followed by the extract cleanup and concentration, separation of OCPs and PCBs and measurement by electron capture detection gas-liquid chromatography.

7.11.1.2 Specification of the Method

Detection limits for the most abundant OCPs and PCBs are as follows: in air, DDT - 0.03; HCCH - 0.005; PCBs - 0.6 ng/m^3 (air sample volume of 150 m^3); in precipitation, DDT - 2; HCCH 0.5; PCBs - 40 ng/L (sample volume of 1L). The error is 10-15%.

The relative error of parallel measurements of OCPs and PCBs in extracts does not exceed 15%.

7.11.1.3 Interferences

PCBs contained in a sample interfere with the determination of comparable amounts of OCPs and vice versa. To eliminate the mutual interference, OCPs and PCBs are separated. PCB and OCP determination is also affected by organic sulfur compounds (OSC).

7.11.1.4 Instruments, Equipment and Materials

Gas chromatograph with electron capture detector
Glass columns: length 1-2 m, i.d. 0.2-0.4 mm
Microsyringes (5-10 ul)
S.p. compressed nitrogen cylinder with reducer
Sample shaker
Rotational evaporator
Stopwatch
Centrifuge
Drying oven
Muffle furnace
Water-jet or backing pump
Microsection solvent still
Soxhlet apparatus
Microsection mercury thermometers (0-100 degrees C)
Water bath
Ultrasonic apparatus
Magnetic stirrer
Bidistilled water generator
Covered coil electric heaters
Analytical balance
Disiccator
Micropipettes (0.1, 0.2 and 1.0 ml)
Separating funnels (25, 50, 100, 250, 1000, and 2000 ml)
Measuring cylinders (10, 50, 100, 250, 500 ml)
Cone flasks with ground stoppers (50, 100, 250 ml)
Chemical funnels (4-15 mm)
Porcelain cups
Porcelain mortar with a pestle
Test tubes with ground stoppers (5 and 10 ml)
Graduated pipettes (2,5 and 10 ml)
Glass columns (length 25 cm, 3-3.5 cm)
Tweezers
Scalpel

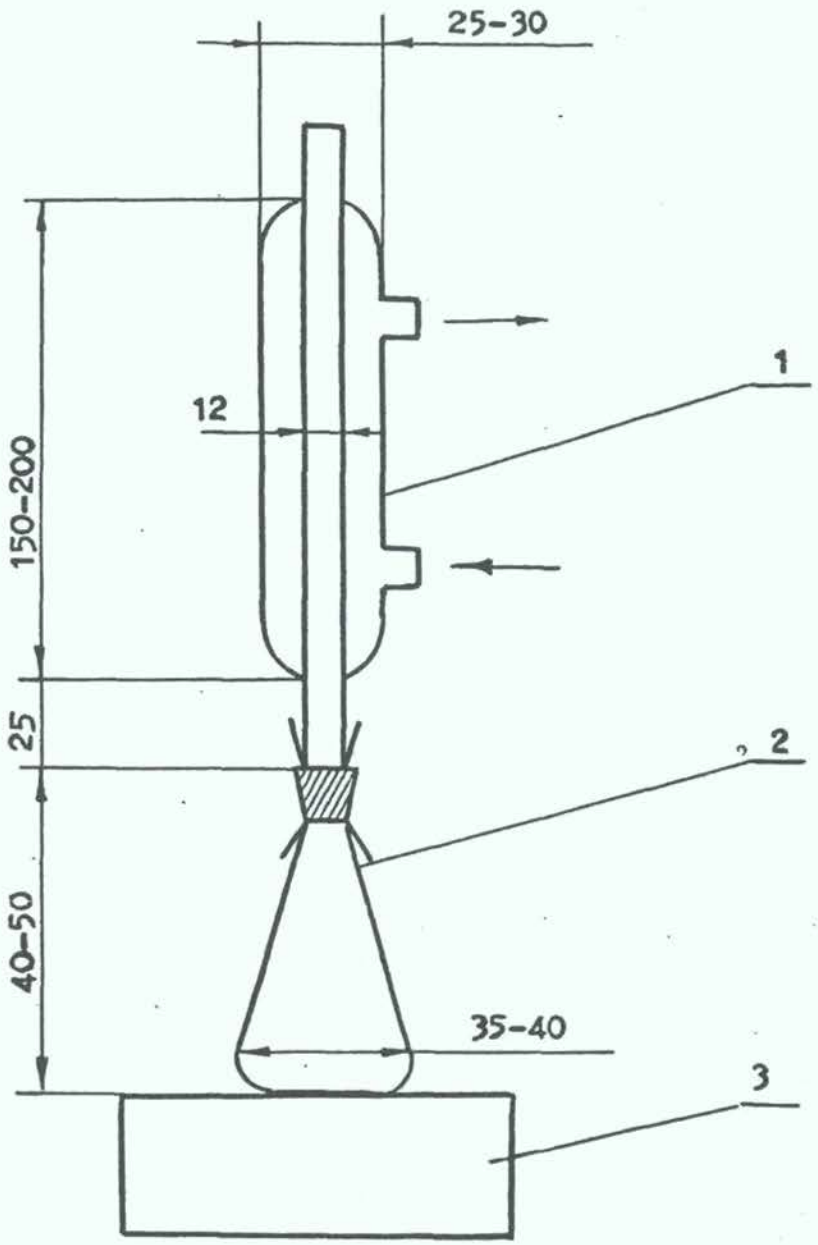

Figure 16. Alkali dehydrochlorination device (mm)

1 - reverse glass cooler;
2 - 50 ml cone bulb;
3 - magnetic mixer

"Blue ribbon" filters (18 cm)
Universal paper indicator
Filter paper
Degreased wool
Dehydrochlorinator (Figure 16)

7.11.1.5 Reagents and Solutions

Chemically pure or pure twice-distilled n-hexane
Chemically pure twice-distilled acetone
Analytically or chemically pure anhydrous sodium sulfate
Analytically or chemically pure sodium bicarbonate
Analytically or chemically pure sodium chloride
Chemically pure ammonium chloride
Analytically pure anhydrous sodium sulfite
Chemically pure tetrabutyl ammonium sulfate. 15% solution is prepared first by dissolving 1.7 g of tetrabutyl ammonium sulfate in 50 ml of distilled water, and then adding 12.5 g of sodium sulfite. 11.3 ml of the above solution are diluted with 38.7 ml of distilled water. The resultant solution is purified by a 3-fold n-hexane extraction in a 100 ml separating funnel (Each time 20ml of the solution are taken). The 15 p.c. solution of tetrabutyl ammonium sulfate (TBA) and sodium sulfite are prepared on the cleanup day.
Chemically pure potassium hydroxide
Ethyl alcohol (rectified)
Chemically pure diethyl ether
Petroleum ether, a fraction (t_{boil} = 40-56 degrees C)
Chemically pure isopropyl alcohol
Chemically or analytically pure concentrated sulfuric acid
Chemically pure oleum
Chromatographic column packings:
Cellite - 545
5 p.c. SE - 30 on chromaton N - AW - DMCS (grain size 0.125 - 0.160 or 0.160 - 0.200 mm);
5 p.c. XE - 60 on chromaton N - AW - DMCS (grain size 0.125 - 0.160 or 0.160-0.200 mm);
mixed phase; 2.5 p.c. QF-1 + 1 p.c. OV-II + 0.5 p.c. XE-60 on chromosorb W/HP (grain size 0.125-0.149 mm);
mixed phase; 1 p.c. QF-1 + 0.5 p.c. OV-17 + 0.5 p.c. XE-60 on varaport (grain size 0.125-0.149 mm);
mixed phase: 1.5 p.c. QF-1+1 p.c. OV-1 + 0.5 p.c. XE-60 on chromosorb W/HP (grain size 0.125-0.149 mm);
mixed phase: 1.5 p.c. QF-1 + 1 p.c. OV-1 on chromosorb G/HP (grain size 0.149-0.177 mm);
mixed phase: 1 p.c. QF-1 + 1 p.c. OV-17 + 1 p.c. XE-60 on chromosorb W/HP (grain size 0.149-0.177 mm).
Purified bidistilled water. Bidistilled water is purified via a double extraction with twice-distilled n-hexane (100 ml of extractant per 1000 ml of water). To remove n-hexane traces water is to be boiled for an hour.
Standard substances: -HCCH, -HCCH, heptachlorine, aldrine, heptachloroepoxide, dieldrine, p, p'-DDE, p,p'DDD, O, p'-DDT, p,p'-DDT, PCBs: arochlor 1221, 1242, 1254, 1260 or their

analoges, chlorophenes, sovols, canechlors, etc. Standard solutions with pesticide concentrations of 100 ug/ml (solutions "A") are prepared in the following way: 10 mg of each pesticide are weighed on the analytical balance, transferred into 100 ml measuring flasks (each compound has its individual flask) and diluted to the containing mark by n-hexane.

Standard solutions with pesticide concentrations of 1 ug/ml (solutions "B") are prepared by diluting solutions "A" by n-hexane (1:99 ratio).

The working standard solution of a pesticide mixture (solution "B") is prepared by mixing prescribed volumes of standard solutions "B" in a 100 ml measuring flask, and diluting the resultant volume to the containing mark with n-hexane.

Standard solutions of PCBs are prepared like those of OCPs. PCB concentrations in the working standard solutions should be 5-10 ug/ml; the standard solution of the PCB mixutre is not prepared.

All standard solutions are stored in a refrigerator in chemical glassware with ground glass stoppers: solutions "A" and "B" for a year, working solution "B" for a month.

7.11.1.6 Sampling

Sampling of ambient air and precipitation is carried out as described in Section 6.

7.11.1.7 Analytical Procedure

Concentrations of OCPs and PCBs are determined at three consecutive stages: extraction, extractant cleanup and gas chromatographic analysis. If present simultaneously in a sample, OCPs and PCBs are separated by alkaline dehydrochlorination.

7.11.1.7.1 Extraction

Ambient air. Atmospheric organochlorine compounds (OCCs) sampled on a filter and solid sorbent are extracted with twice-distilled n-hexane. To this end, the sorbent and filter are inserted into separate 250 ml cone flasks with ground glass stoppers, flushed with 50 ml of n-hexane and subjected to a cold extraction in the shaker. Then the extracts are drained into bulb flasks from the rotationary vacuum evaporator kit. The adsorbent and filter are again flushed with 50 ml of n-hexane for the second extraction. There should be at least three hour-long extractions. All the extracts are combined (separately for the adsorbent and filter) and evaporated at the rotation evaporator to 0.5-2 ml.

Atmospheric precipitation. A water sample (1 L) is transferred into a 2 L separating funnel. Rinse the sampling bottle

with 50 ml of twice-distilled n-hexane and add it to the sample. Shake contents of the funnel for 15 minutes.

After the extraction, the lower water layer is returned to the bottle and the upper hexane layer is transferred into a cone flask through anhydrous sodium sulfate placed into a chemical funnel with degreased wool substrate pretreated with 2-3 ml of n-hexane. Sodium sulfate is rinsed with 3-5 ml of n-hexane and pressed out using the glass stopper. The extraction procedure is repeated two more times (10 minutes each). The second and third extractions require 50 ml of n-hexane each. All hexane extracts are filtered through sodium sulfate. The combined hexane extract is evaporated in the rotationary vacuum evaporator to 0.5-2 ml.

7.11.1.7.2 Extract Cleaning

Usually air sample extracts do not require any cleaning. Water sample extracts should be cleaned from coextracted impurities.

Evaporated hexane extracts are cleaned by re-extraction of impurities with concentrated sulfuric acid in a 25 ml separating funnel (5-7 ml of the acid per 2-4 ml of the extract). The contents of the funnel should be carefully shaken 5-10 times and allowed to stay until the phases separate. The spent acid is drained. The cleanup procedure is repeated several times until colorless sulfuric acid is formed. The purified extract is neutralized with 0.5 N solution of sodium bicarbonate, rinsed with purified distilled water to bring it to neutral rinsing water reaction,and dried by filtration through anhydrous sodium sulfate. Sodium sulfate is thoroughly rinsed with 3-7 ml of n-hexane. The dry extract is evaporated in the rotation vacuum evaporator.

Concentrated sulfuric acid can be replaced with oleum applied on cellite-545. Oleum fills a glass column and the extract evaporated to 2-4 ml is passed through the column. Then the column is to be rinsed several times with n-hexane (total volume 150 ml). The eluates are combined and evaporated in the rotation evaporator to 2-4 ml.

The presence of organic sulfur compounds (OSCs) may distort the results when measuring substances with a retention time similar to that of HCCH. OSCs are removed in this way: transfer 2-3 ml of the extract into a 25 ml separating funnel, treat with 1 ml of isopropyl alcohol, 1 ml of 15% TBA solution and sodium sulfite. If sodium sulfite does not precipitate, it is added in about 100 mg portions until precipitate formation. Then 5 ml of distilled water should be added into the separating funnel, the solution shaken and separated. The hexane phase is filtered through a funnel containing 3-5 g of anhydrous sodium sulfate and drained into a flask for subsequent evaporation in the rotation evaporator. The aqueous phase is to be returned into the separating funnel and extracted for the second time with 5 ml of

n-hexane. The extracts should be dehydrated and combined; the separating funnel and sodium sulfate rinsed with 3-5 ml of n-hexane. The rinsing liquid is added to the extracts and evaporated to 0.5-1 ml.

7.11.1.7.3 Dehydrochlorination

To separate OCPs and PCBs, alkaline dehydrochlorination is used. To do, concentrated and purified extracts are divided in halves. One half is analyzed by gas chromatography, the other undergoes alkaline dehydrochlorination in an apparatus shown in Figure 16.

A 15-25 ml cone bulb is filled with the extract, 2 ml of ethyl alcohol and 0.4-0.5 g of melted potassium hydroxide (4-5 pills). The bulb is connected to a return cooler and placed on the magnetic stirrer. Then heating is turned on. At 50-55 degrees C dehydrochlorination takes place within 30 minutes. Time is counted from the moment of potassium hydroxide pill dissolution. The bulb is cooled, the cooler disconnected and the contents quantitatively transferred into a 25 ml separating funnel. After adding 4-5 ml of distilled water the liquid is carefully mixed by up-and-down movements. The organic and aqueous phases are then separated. The aqueous/alcohol phase undergoes a second extraction with 2-3 ml of n-hexane. The organic phases are combined in another separating funnel, neutralized with 2 ml of 1 p.c. sulfuric acid and rinsed with distilled water (2-3 ml batches) to neutral rinsing liquid reaction. The obtained hexane extract is dehydrated by filtration through anhydrous sodium sulfate (3-6 g) and evaporated.

7.11.1.7.4 Gas Chromatographic Analysis of Purified Extracts

Gas chromatographic analysis of the extracts is carried out using an organochlorine selective gas chromatograph with an electron capture detector. Table 11 describes conditions for organochlorine compound separation on various chromatographic columns.

The selected chromatographic column is preconditioned in a carrier-gas flow (50 ml/min) with a gradual temperature increase from 100 degrees C to 200-250 degrees C (depending on the stationary phase heat resistance). The same sample is analyzed in a prescribed regime (see Table 11) at least twice.

7.11.1.8 Instrument Calibration.

The chromatograph is daily calibrated by analyzing standard OCP and PCB solutions (solutions "B") in the working regime used for sample extract analysis. The linear character of readings should hold within the following concentration ranges: 0.005-1 ug/ml for HCCH isomers; 0.01-2 ug/ml for DDT, DDD, and DDE, 0.2-50 ug/ml for PCBs.

Table 11 Conditions of OCP and PCB chromatographic separation

Parameter	Chromatographic regime					
Column length, dimensions i.d.	100 cm 4 mm	180 cm 2 mm	140 cm 2 mm	200 cm 3 mm	180 cm 3 mm	100 cm 3 mm
Liquid phase	mixed:	mixed:	mixed:		mixed:	mixed:
	1 p.c. QF-1	2.5 p.c.GF-1	1.5p.c.GF-1	5p.c.SE-30	1p.c.XE-60	1p.c.OV-1
	0.5p.c.OV-17	1p.c.OV-11	1p.c.OV-1		1p.c.OF-1	1.5p.c.GF-1
	0.5p.c.XE-60	0.5p.c.XE-60	0.5p.c.XE-60		1p.c.OV-17	
Solid substrate	Varaport 0.125-0.149mm	Chromosorb W/HP 0.125-0.149mm	Chromosorb W/HP 0.125-0.149mm	Chromaton N-AW-DMCS 0.125-0.160mm	Chromosorb W/HP 0.149-0.177 mm	Chromosorb G/HP 0.149-0.177 mm
Temperature: column	180°C	190°C	180°C	180°C	190-200°C	175°C
Evaporator	225°C	225°C	225°C	220°C	250°C	200°C
Detector	250°C	250°C	250°C	240°C	280°C	240°C
Carrier-gas flow rate, ml/min	26	26	28	50	15	50

7.11.1.9 Calculation

OCP and PCB are determined by the outer standard method. The calculation is based on mean peak heights of substances analyzed. Proceeding from chromatographic analysis data, the amount of the i-th component in a sample (q_i) is calculated by the following formula:

$$Q_i = \frac{V_{st} \cdot C_i^{st} \cdot h_i^{s} \cdot R_i^{s} \cdot V_{ex}}{V_s \cdot h_i^{st} \cdot R_i^{st}} \quad ng \qquad (18)$$

where V_{st}, V_s – volumes of the standard solution applied and evaporated extract, respectively, ul;

C_i^{st} – concentration of the i-th component in the standard solution, ng/ul;

V_{ex} – volume of the evaporated extract, ul;

h_i^{st}, h_i^{s} – peak heights of the i-th component measured when analyzing the standad solution and sample, respectively, mm;

R_i^{st}, R_i^{s} – scale of the i-th component peak recording when analyzing the standard solution and sample, respectively.

The concentration in ammbient air samples, C_i, is calculated by the following formula (wth allowance for blank tests);

Aerosol component $$C_i^{a} = \frac{q_i^{f} - q_i^{f}\ bl}{V_o \cdot K_i} \quad ng/m^3 \qquad (19)$$

Gaseous component $$C_i^{g} = \frac{q_i^{ads} - q_i^{ads}\ bl}{V_o \cdot K_i} \quad ng/m^3$$

where q_i^{f}, q_i^{ads}, – amounts of the i-th component calculated by formula (18) for filter and adsorbent extracts

q_i^{f} bl, q_i^{ads} bl – when analyzing samples under study and blank samples, ng;

K_i – detection factor for the i-th component (see Table 12);

V_o – air sample volume reduced to normal conditions, m^3.

The concentration in water samples, C_i, is calculated by the following formula:

$$C_i = \frac{q_i - q_i\ bl}{V \cdot K_i} \quad ng/L \qquad (20)$$

where V – volume ofthe water sample analyzed, l;

q_i, q_i bl – amounts of the i-th component calculated by formula (18) when analyzing samples under study and blank samples, ng;

K_i – detection factor for the i-th component (see Table 12).

Total PCB concentration in a sample is determined as a sum of concentrations of typical PCB components calculated by formulae (19-20). When OCP and PCB are simultaneously present in the sample, the purified extract is divided into halves and analyzed at the chromatograph before and after dehydrochlorination. OCPs are calculated by the difference between peak heights:

$$C_i = \frac{C_i^{st} (h_i^1 \cdot V_1 - h_i^2 \cdot V_2) R_i^s \cdot V_{st} \cdot 2}{R_i^{st} \cdot h_i^{st} \times V_s \times K_i \cdot V} \quad ng/m^3; ng/l \quad (21)$$

where C_i - concentration if the i-th pesticide in a sample, ng/m^3; ng/l

C_i^{st} - concentration of the i-th pesticide in the standard solution, ng/ul;

V_1, V_2 - volumes of evaporated extracts before (V_1) and after (V_2) alkaline dehydrochlorination, respectively

V_{st}, Vs - volumes of the standard solution applied and sample, respectively, ul;

h_i^{st} - i-th pesticide peak height in the standard solution chromatogramme, mm;

h_i^1, h_i^2 - heights of respective i-th pesticide peaks in extract chromatogrammes before (h_i^1) and after (h_i^2) alkaline dehydrochlorination, mm;

K_i - detection factor (see Table 12);

V - volume of the sample analyzed, m^3, l;

R_i^{st}, R_i^s - scale of the i-th component peak recording when analyzing the standard solution and sample, respectively.

p,p'-DDE concentration in a sample is determined in the following way: the total amount of p,p'-DDE and the PCB component is calculated by formula (18) using the chromatogramme peak height for extract 1 with p,p'-DDE retention time. Then the amount of the PCB component in the sample is calculated by formulat (18) based on the chromatogramme peak height for extract 2 that follows p,p'-DDE. Taking into account the ratio between the concentrations of PCB components in their standard solution, the content of the PCB component in the sample is calculated, whose peaktime coincides with that of p,p'-DDE. The obtained value is deducted from the calculated total amount and divided by the mass of the sample analyzed. The total PCB concentration in the sample is calculated by the sum of characteristic peak heights of PCB, whose retention times in the extract 2 chromatogramme do not coincide with the retention time of OCP decomposition products resulting from the alkaline dehydrochlorination.

$$C_{PCB} = \frac{C_{PCB}^{st} \cdot R_{PCB}^s \quad h_i^s \cdot V_2 \cdot V_{st}}{R_{PCB}^{st} \quad h_i^{st} \cdot V_s \cdot K_i \cdot V} \cdot 2 \ ng/m^3, \ ng/l \quad (22)$$

where h_i^{st}, h_i^s - the sum of characteristic peak heights in

the chromatogrammes of the PCB standard solution and extract 2, respectively;

C_{PCB}^{st} - total PCB concentration in the standard solution, ng/ul.

Other designations are as in formula (21).

The factor of 2 in formulae (21) and (22) is accounted for by initial extract division into two equal parts.

OCP and PCB concentrations in blank samples are determined by formulae (21) and (22) in a similar way and the obtained values are deducted from respective concentrations of samples analyzed.

Organochlorine compound losses in the process sample cleaning from organic sulfur compounds are accounted for at the expense of the factors 0.9 (for DDT, DDE, and DDD) and 0.8 (for PCB and HCCH). The concentrations calculated for formulae (18-22) should be divided by these factors.

Table 12. Detection Factors

Environmental objects	α-HCCH	γ-HCCH	hepta-chlorine	p,p'-DDE	p,p'-DDD	p,p'-DDT	PCBs
Air	0.8	0.8	0.8	0.9	0.9	0.9	0.8
Precipitation Water	0.6	0.6	0.6	0.7	0.7	0.7	0.7

7.12 Polycyclic Aromatic Hydrocarbons (3,4-Benzo-a-pyrene)

Environmental objects contain a mixture of polycyclic aromatic hydrocarbons (PAH). The most abundant among them are 3,4-benzo-a-pyrene, 1, 12-benzpyrelene, fluorene, phenathrene, fluoranthene, pyrene, tetraphene, chryzene, pyrelene, etc. Modern analytical techniques provide for simultaneous multicomponent PAH determination. This guidance, however, describes the method for determination of 3,4-benzo-a-pyrene only - a most toxic PAH possessing highest carcinogenic and mutagenic activity. The bulk of environmental 3,4-benzo-a-pyrene is of anthropogenic origin though there is some evidence for the existence of natural sources as well. The range of background environmental concentrations of 3,4 benzo-a-pyrene is given in Section 4. Different laboratories use different methods and instruments for 3,4 benzo-a-pyrene determination. Low-temperature thin-layer spectrofluorimetry is a sensitive technique, however, it is more complicated than fluorescence detection liquid chromatography. The present manual describes the latter technique, since it has been most widely used in various laboratories for environmental mass analysis.

7.12.1 Determination in the Atmosphere and Precipitation

7.12.1.1 Principles of the Method

The method for 3,4 benzo-a-pyrene determination in environmental samples is based on organic solvent extraction, chromatographic cleanup of the extracts, and concentration measurement by high performance liquid chromatography with fluorescence detection. 3,4 benzo-a-pyrene is measured at an absorption maximum wavelength of 292 nm.

7.12.1.2 Specification of the Method

3,4 benzo-a-pyrene detection limit is 0.001 ng/m^3 in air sample of 500 m^3, and 0.5 ng/l in liquid samples at a sample volume of 1 L. The error is 10%.

7.12.1.3 Interferences

The major interference in 3,4 benzo-a-pyrene determination in environmental samples is from high molecular compounds absorbing the measurement wavelength light (e.g., humic substances, fats, phenols, oxygen-bearing compounds). To eliminate interferences the obtained extracts are to be cleaned from coextracted impurities using thin-layer chromatography on a loose aluminum oxide layer or column chromatography.

7.12.1.4 Sampling

Air and precipitation are to be sampled as described in Section 6. Air sampling rate for fibre filters is 80-100 m^3/hr.

7.12.1.5 Instruments, Equipment and Materials

High pressure liquid chromatograph with a fluorescence detector and separation column, an acid resistant 250 mm long steel tube 4 mm i.d. filled with CHROMSil-RPC 18 reverse phase (grain size 10 um) containing octadecyl functional group.
SEP-PAK C18 adsorption column
Chromatographic column: a convergent glass tube (40 x 5 mm) filled with Brockman reactivity II aluminum oxide and rinsed with 10 ml of n-hexane.
UV lamp
Ultrasonic apparatus
Rotation evaporator
Analytical balance
Electric heater
Sneider apparatus
Soxhlet apparatus
Atmospheric pressure organic solvent still
Chromatographic glass plates
Test tubes with ground glass stoppers (10 ml)
Microsyringe (10, 50 ul)

Measuring bulbs (25, 100 ml)
Flat bottom bulbs (100, 250 ml)
Beakers (50, 100 ml)
Pipettes (1,2 ml)
Wide-neck vessels with ground glass stoppers
Superpure compressed nitrogen cylinder with reducer.

7.12.1.6 Reagents and solutions

Chemically pure distilled n-hexane
Chemically pure distilled benzene
Chemically pure distilled acetone]
Chemically or analytically pure methanol
Chemically pure chloroform
Chemically pure dichloromethane
Chemically pure cyclonexane
Chemically pure pyridine
Chemically pure toluene
Silica gel
Kiesel gel 6
Anhydrous aluminum oxide, Brockman reactivity 11
Acetyl cellulose
Analytically pure anhydrous sodium sulfate
Chemically pure 3,4 benzo-a-pyrene

A 3,4 benzo-a-pyrene basic standard solution with the total concentration of 200 ug/ml is prepared in cyclohexane. Working standard solutions with concentrations of 1, 2, 5, 10, 20, and 50 ng/ml are prepared by diluting step-by-step basic standard solution aliquots using methynol as a solvent.

7.12.1.7 Analytical Procedure

Ambient air. Aerosol PAH is extracted in the ultrasonic apparatus using a 19:1 mixture of benzene and acetone. Complete extraction takes 30 minutes.

Benzene/acetone extract is evaporated in a vacuum to 1-2 ml and then applied as a strip on a 1 mm-thick plate with silica gel. The plate is inserted into the chromatographic chamber. The 19:1 benzene/acetone mixture is a mobile phase, so chromatography should cover the whole plate length.

PAHs located near the front glow blue and blue-violet in UV light. Strips with this glow are marked and transferred to the chromatographic column where PAH is eluted with 150 ml of the benzene/acetone mixture. The eluate is evaporated in a vacuum to dryness.

After the evaporation the residue is dissolved in 0.5-1 ml of the solvent mixture and subjected to chromatographic analysis on a thin layer (0.25 mm) of 40% acetylated cellulose (mobile phase - 5:10:2:3 mixture of acetone, methanol, pyridine and water) to a height of 17 cm. The obtained wet chromatogram is

placed under the UV lamp to mark different colored fluorescent strips with a sharp needle. The violet fluorescent strip is scraped off into a separate chromatographic column and 3,4 benzo-a-pyrene is eluted with 100 ml of benzene. The eluate is evaporated to dryness in a vacuum, the residue washed off with 5-8 ml of methanol into a 10 ml test tube with ground stopper. The methanol solution should be evaporated once more. The analysis is carried out using the high pressure liquid chromatograph: 10 ul of the solution injected with a microsyringe into the column with CHROMSil-RPC18. Methanol is used as the eluate.

Atmospheric precipitation. A 2 L water sample is pumped through the SEP-PAK C18 column at a rate of 100 ml/min. 0.5 ml of tetrahydrofuran should by syringed in, and the eluate collected. Syringe 0.5 ml of tetrahydrofuran a second time and collect the eluate.

Tetrahydrofuran eluates are combined and evaporated almost to dryness by bubbling with nitrogen. The residue is dissolved in 1 ml of n-hexane and injected into the column with aluminum oxide. After pumping 10 ml of hexane, the solution is eluted with 10 ml of toluene and 3 ml of dichloromethane. The toluene and dichloromethane eluates should be collected and evaporated almost to dryness in the Sneider microevaporator. The residue is dissolved in 1 ml of methanol. 20 ul of the solution should be injected into the column with CHROMSil-18 using a loop-type liquid chromatograph batcher. The separation is performed with a 80:20 methanol/water mixture at 1 ml/min flow rate under room temperature.

7.12.1.8 Instrument Calibration

The high-pressure liquid chromatograph is calibrated by measuring 3,4 benzo-a-pyrene standard solutions under prescribed working conditions. Calibration curves are plotted against peak height and standard solution concentration.

7.12.1.9 Calculation

3,4 benzo-a-pyrene concentration in the eluate, C_e (ng/ml), is determined by 3,4 benzo-a-pyrene peak height in the eluate chromatogram using the calibration plot.

3,4 benzo-a-pyrene concentration in the sample is calculated by the following formula:

$$C = \frac{C_e \cdot V_1}{V_o} \quad ng/m^3,\ ng/l \qquad (23)$$

where V_1 - volume of the evaporated eluate, ml;
V_o - air sample volume reduced to normal conditions, m^3, or water sample volume, l.

7.13 Multielemental analytical techniques

Water, soil, vegetation, and forest litter samples are analyzed for a number of trace elements by multielemental analytical techniques such as spark source emission spectroscopy and inductively coupled plasma emission. The procedures differ slightly for each media and are briefly described below.

7.13.1 Soil

After collection in the field, soil samples are returned to the laboratory for elemental analysis. The procedure requires that a fairly homogeneous soil sample be extracted in concentrated nitric acid. Screening the soil sample is the preferred method from our work for helping achieve a relatively homogeneous sample for analysis. Care is taken to properly clean the screens between each sample to prevent cross contamination.

The specific procedure is as follows. Ten grams of an air dried soil sample are placed in a 500 ml round bottomed flask. Next 36 ml of concentrated nitric acid are added. The soil/acid mixture is swirled and after any foaming has subsided, the mixture is refluxed for sixteen hours. After this extraction procedure, the flask and its contents are cooled by adding 20 ml of deionized water. When cooling is complete the mixture is filtered and the filtrate collected in a 100 ml volumetric flask. The filtrate is then brought up to 100 ml volume by adding deionized water. This sample is then ready to be sent for analysis by inductively coupled plasma emission spectroscopy. This procedure gives simultaneous results for the following elements:

Calcium
Aluminum
Iron
Magnesium
Barium
Zinc
Strontium
Vanadium
Lead
Molybdenum
Chromium
Copper
Nickel
Boron
Tin
Cobalt
Silver
Cadmium

7.13.2 Water

Water samples are analyzed by inductively coupled plasma emission spectroscopy without any additional preparation to what they received in the field. This includes filtered and unfiltered samples. All samples are acidified to pH 2.0 with ultrex nitric acid. Elements analyzed are the same as for soil.

7.13.3 Vegetation and forest litter samples

Vegetation and forest litter samples are analyzed for trace elements in a similar fashion. The method of choice is spark source emission spectroscopy. Samples are collected in the field as previously described. Once in the laboratory the sample is transferred from the clean bag to an unused paper bag by a technician using a pair of disposable plastic gloves. New gloves are used for each sample. The paper bags are then placed in a drying oven and are dried at approximately 50 degrees centigrade for approximately 24 hours. After drying, the samples are removed from the drying oven and using the disposable plastic gloves are transferred to unused 150 ml plastic vials. A pair of teflon balls are placed inside the plastic vial, and then the vial is fixed inside of a Spex mill - a kind of shaking mill. The sample is then shaken with the teflon balls inside until the sample is uniformly powdered. This usually takes from 2 to 7 minutes, depending on the type of sample. After this, the sample is ready for direct analysis by spark source emission spectroscopy. A sub-sample is always sent to the analytical laboratory in a clean scintillation vial. The remainder of the sample is archived. See the quality assurance section of this report for results of an experiment to test this procedure for cross contamination. Also note that Table 11 shows the elements detected and their detection limits.

7.14 Chlorinated hydrocarbon analyses

7.14.1 Soil water and forest litter

Normally samples collected in the U.S. pilot programs were not analyzed for chlorinated hydrocarbons because of the costs involved. However on infrequent occasions, samples were analyzed for chlorinated hydrocarbons. These analyses were conducted by the University of Iowa at Iowa City, Iowa. What follows is basically a description of their analytical procedures.

7.14.1.1 Equipment

The gas chromatograph used is a Tracor, Model 222, modified to a four column capacity and equipped with a ^{63}Ni electron capture detector and a flame photometric detector operated in a phosphorus mode. The columns used are 6 feet Pyrex U-tubes which are 6 mm o.d., 4 mm i.d. The instrument is operated in the constant voltage mode and the carrier gas is high purity dry nitrogen.

7.14.1.2 Materials

Standards. The pesticide and PCB standards are provided by the Pesticide Standards Laboratory of the Environmental Protection Agency at Research Triangle Park. The standard solutions are prepared by dissolving a weighed amount of the solid standard in the appropriate volume of hexane or iso-octane and making the necessary dilutions with the same solvent.

Solvents. All solvents are Pesticide quality purchased from Matheson, Colemen and Bell.

Reagents. Both the activated Florosil (Scientific Products) and the anhydrous sodium sulfate ("Baker Analyzed" Reagent) are stored in an oven at 115 degrees C.

Chromatographic Supplies. The gas chromatograph columns are packed with either 1.5% OV17/1.95% OV210 on Chromosorb W HP, or 4% SE 30/6% OV 210 on Chomosorb W HP. Both column packings and septum are obtained from Supelco, Inc.

7.14.2 Method of Analysis for Organochlorine and Organophosphorus Pesticides.

Place 10.0 grams undried soil (mix sample well before weighing) in a 250 ml glass stoppered Erlenmeyer flask. Add 14 mls 0.2M NH_4Cl solution and let stand 15 minutes. Add 100 ml 1:1 hexane:acetone mixture and stopper tightly. Shake for 12 hours.Pour off slurry into a Buchner funnel with filter and remove liquid with suction. Rinse the Erlenmeyer and soil in funnel with 25 ml 1:1 hexane:acetone. Save the filtrate, and place the soil and filter paper back into the 250 ml Erlenmeyer. Add 14 ml 0.02 M HN_4Cl solution and let stand 15 minutes. Add 100 ml 1:1 hexane:acetone mixture and stopper tightly. Shake for four hours. Pour off slurry into a Buchner funnel with filter and remove liquid with suction. Rinse the Erlenmeyer with 25 ml of 1:1 hexane:acetone. Save the filtrate and discard to soil. Using a transfer pipette, remove the aqueous layer from the vacuum flask.

Using a rotary evaporator and a water bath at 50 degrees C (max), evaporate solution to 20 to 30 ml. Transfer the concentrate onto a prepared Florosil column (10 cm x 10 mm i.d., topped with 3 cm Na_2SO_4). Rinse column with 20 ml of 1:1 hexane:acetone. Transfer the eluate to a 1 liter separatory funnel.

To the separatory funnel add 200 ml distilled H_2O and mix for 30 seconds. Drain and save the aqueous phase including any emulsion. Drain the organic phase into a 250 ml Erlenmeyer with a stopper. Replace the aqueous phase into a separatory funnel and extract with the 50 ml of hexane in the 1 L separatory funnel. Wash the combined extracts twice with 100 ml H_2O (gently).

Dry the hexane extracts with 25-30 grams Na_2SO_4 added to the separatory funnel. Shake vigorously. Draw off dried hexane, rinse separatory funnel and remaining Na_2SO_4 with 10 to 20 ml hexane and collect the dried hexane extract in a 500 ml evaporation flask. Concentrate to 30-40 ml on a rotary evaporator with a water bath at 50 degrees C (maximum).

Prepare a second Florosil column (10 cm x 10 mm i.d., topped with 3 cm Na_2SO_4). Prewet column with 10 ml petroleum ether. Transfer hexane extract to column. Elute with 100 ml 15% diethyl ether in petroleum ether (use 20 ml of eluting mixture to rinse the evaporation flask). Collect eluent in another evaporation flask. Concentrate eluent to 10.0 ml on a rotary evaporator. Transfer to a 15 ml graduated centrifuge tube. Record final sample volume at the time the sample is injected on the gas chromatograph.

Use the organochlorine and organophosphorus standards to calibrate the gas chromatograph.

Calculations:

$$\frac{\text{sample attenuation}}{\text{standard attenuation}} \times \frac{\text{standard injection volume}}{\text{sample injection volume}} \times$$

$$\frac{\text{final sample volume}}{\text{original sample weight}} \times \frac{\text{sample peak height}}{\text{standard peak height}} \times$$

dilution factor x standard solution concentration (ppb) =

concentration in sample (ppb)

7.14.3 Method of Analysis for Organochlorine and Organophosphorus Pesticides and Phenoxy Herbicides in Water.

Measure volumetricly 200 ml of the H_2O sample. Extract in a separatory funnel with 100 ml ethyl ether, collect ethyl ether extract in an Erlenmeyer flask. Re-extract H_2O samples with 100 ml more of ethyl ether, and add extracted ethyl ether to the Erlenmeyer flask. Add 5.0 gm of acid-washed anhydrous Na_2SO_4. Allow the extract to remain in contact with the Na_2SO_4 for at least two hours.

Concentrate extract to 10 ml. Transfer extract to a 15 ml graduated centrifuge tube. Adjust volume to exactly 10 ml. Remove 5.0 ml to another centrifuge tube and concentrate to 1.0 ml. To the remaining 5.0 ml, add 1.0 ml diazomethane in a glovebox. Let stand for 15 minutes. Bubble off excess derivatizing reagent, then raise needle above the surface and concentrate to 1.0 ml.

Analyze the underivatized 1.0 ml extract for organochlorine and organophosphorus pesticides. Analyze the derivatized extract

for phenoxy herbicides.

Calculation is performed the same as listed previously.

7.14.3.1 Preparation of Reagents for Phenoxy Herbicide Analysis

In a 100 ml separatory funnel add 1,000 ml of tap distilled water. Add 0.2 ml concentration H_2SO_4 and shake for a few seconds. The pH should be below 3.0 at this point. Add 100 ml hexane and extract water vigorously for about two minutes. Allow layers to separate and dispense water layer into a 1,000 ml rinse bottle for use.

Weigh 3.0 g hexane-extracted glass wool into a 1 quart wide mouth jar. Add 0.1 ml concentration H_2SO_4 directly to the glass wool and then add 350 ml ethyl ether (containing 2% ETOH). Slurry the glass wool for several minutes using a glass rod. Place the glass wool and ethyl ether onto a Buchner funnel and vacuum off the ethyl ether for several minutes. After filtering, place the glass wool on a piece of aluminum foil and air dry for 15 minutes followed by oven drying for ten minutes. Store glass wool in a clean one quart wide-mouth jar.

To a 250 ml stoppered Erlenmeyer flask add 56.5 ml hexane-extracted distilled water. Then add 43.5 g KOH pellets (85% assay) mixing the solution periodically. After the solution has cooled, transfer to a screw-cap bottle and store until use.

To a 100 ml graduated cylinder add 74 ml hexane-extracted distilled water. Then slowly and carefully, add 26 ml concentrated H_2SO_4 with a Pasteur pipette. After solution has cooled, carefully transfer the solution to a stoppered 100 ml reagent bottle and store in a refrigerator until use.

In a 1 quart wide-mouth jar weigh out 500 g of hexane extracted Na_2SO_4 for several minutes using a glass rod. Place the Na_2SO_4 and ethyl ether onto a Buchner funnel and vacuum off the ethyl ether for about ten minutes. After filtering, place the Na_2SO_4 onto a piece of aluminum foil and air dry for 30 minutes. Then transfer the Na_2SO_4 into a clean one quart wide-mouth jar, cover jar with aluminum foil, punch several small holes in the foil and store in oven at about 130 degrees C until use.

7.14.3.2 Method of Analysis for Phenoxy Herbicides.

Weigh 75 g soil (5-25% moisture) into a 500 ml glass-stoppered Erlenmeyer flask. Add 150 ml ethyl ether to the jar, close the lid tightly, and shake the jar on a reciprocating shaker for two hours.

After two hours of shaking, open the jar and quickly add 40 ml acid water to the flask. Close the lid tightly, and shake an additional two hours.

After the second shaking, allow the soil to settle in the jar for 15 minutes. Pour off a 50 ml aliquot of ethyl ether extract into a graduated cylinder.

Transfer the 50 ml ethyl ether extract to a 250 ml Erlenmeyer with a 24/40 joint. Rinse the graduated cylinder with an additional 25 ml ethyl ether, and combine the rinse with the original 50 ml extract.

To the 250 Erlenmeyer, add 2 ml of 37% KOH followed by 15 ml of hexane-extracted distilled water. Add several small boiling beads, fit the flask with a 3-ball Snyder column, and place the flask in a water bath (90-100 degrees C) for a total of 1 hour and 15 minutes.

After cooling, transfer the concentrate to a 60 ml separatory funnel. Extract the basic solution two times with 20 ml of petroleum ether and discard the petroleum ether layers. Then extract the basic solution once with 20 ml ethyl and discard the ethyl ether layer.

Acidify the contents of the separatory funnel by adding 2 ml of cold (4 degrees C) 25% H_2SO_4. Extract the acidic solution once with 20 ml ethyl ether and twice with 10 ml ethyl ether. Collect the ethyl extracts in a 125 ml Erlenmeyer containing 0.5 g of acid-washed Na_2SO_4. Allow the extract to remain in contact with the Na_2SO_4 for at least two hours. NOTE: Overnight contact with Na_2SO_4 will not adversely affect recoveries.

After drying over Na_2SO_4, transfer the ethyl ether extract, through a funnel plugged with acid-washed glass wool, into a 250 ml round-bottom flask. Rinse the 125 ml Erlenmeyer with two 25 ml portions of ethyl ether and add the rinses to the round-bottom flask. Break up any clumps of Na_2SO_4 with a glass stirring rod during the transfer.

Concentrate the extract to approximately 5 ml on a rotary evaporator. Transfer to a 15 ml centrifuge tube, rinsing the flask with 2-3 ml ethyl ether and adding the rinse to the tube. Concentrate the extract to 4-5 ml under N_2 steam.

Using a glove box, add 1 ml diazomethane. Let it stand for 15 minutes. Bubble nitrogen through for 10 minutes to remove excess derivatizing reagent, then raise the needle above the surface and concentrate to 0.3 ml.

Add 2 ml hexane, mix, and continue evaporating the hexane solution to 0.3 ml. Prepare a 50 ml Kontes #7 column by plugging with glass wool and adding 1.5 cm Florisil (which has been kept at 100 degrees C overnight) topped with 2 cm Ma_2SO_4. Transfer

soil extract quantitatively to a column using 2 ml benzene. As soon as the extract reaches Na_2SO_4, add 40 ml benzene. Concentrate the eluate to 5 ml.

Use 2,4-D and 2,4,5-T standards to calibrate the gas chromatograph.

Calculation:

$$\frac{\text{sample attenuation}}{\text{standard attenuation}} \times \frac{\text{standard injection volume}}{\text{sample injection volume}} \times$$

$$\frac{\text{final sample volume}}{\text{original sample weight}} \times \frac{\text{sample peak height}}{\text{standard peak height}} \times$$

dilution factor x standard solution concentration (ppb) = concentration in sample (ppb)

Limits of Detection

Hexachlorobenzene	1 ppb
Lindane	1 ppb
γ-BHC	7 ppb
Heptachlor	1 ppb
Aldrin	1 ppb
Heptachlor Epoxide	2 ppb
P,P' DDE	3 ppb
Dieldrin	3 ppb
O,P' DDT	10 ppb
P,P' DDD	4 ppb
P,P' DDT	10 ppb
Aroclor 1254	200 ppb
Diazinon	80 ppb
Methyl Parathion	290 ppb
Malathion	220 ppb
Ethyl Parathion	160 ppb
Ethion	270 ppb
2,4-D	2 ppb
2,4,5-T	1 ppb

8.0 QUALITY ASSURANCE AND DATA ANALYSIS

8.1 Quality Assurance

Elements of a complete quality assurance program are:

1. Organization and personnel
2. Facilities and equipment

3. Analytical methodology
4. Sampling and sample handling procedures
5. Quality control
6. Data handling

This manual covers many of these elements in other sections such as sampling and sample handling, and analytical methodology. This section primarily deals with the aspects of quality control.

Quality assurance of observational and sample analysis data is one of the most important tasks facing the global IBM network. The task can be difficult and requires continuous attention throughout the operation of the stations and regional laboratories.

There are many error sources througout the whole technological procedure of the acquisition of information for single measurements and measurement series. Let us consider the.basic ones.

Error sources in measurements carried out directly at IGBM stations:

a) inadequately qualified personnel;
b) power supply failures;
c) collection of nonrepresentative samples;
d) secondary contamination of samples;
e) errors in observations and sample analysis carried out directly at background stations;
f) errors made by observers in sample labeling;
g) observation errors occurring in documentation (e.g., when filling in tables sent to the regional laboratory).

Inadequate qualification of personnel can lead to various errors in final information. The principle way to overcome the difficulty is to select people with required qualifications, to train them in operational techniques and methods and to exercise regular control. The importance of the station activity and the necessity for a strict observance of measurement and observation instruction should always be explained.

Power supply failures which can occur in remote areas, where the stations are sited, affect sampling and measurement regimes (atmospheric observations are most vulnerable in this respect). Major preventive measures include a regular checkup of the voltage and detection of any deviation. Instruments used (primarily continuous monitors) should allow for current fluctuations. In case of a complete power break, which can occur at any time of the day, monitors should be equipped with an automatic device that would switch on as soon as the instrument is powered again, and with a cyclic storage for the actual amount of air pumped through.

Collection of nonrepresentative samples can be attributed to various causes. Most frequently air samples are affected by local nearby settlements. The presence and activity of the station personnel is another possible reason. To prevent such errors it is essential to provide the optimum location of observation sites. (If primary selection is not very lucky, the site should be transferred to some other point. Decision-making is to be based on the analysis of the obtained observation series when all other error sources are excluded.) The personnel activity must be organized to eliminate any impact on information obtained. To reveal nonrepresentative atmospheric measurements and air samples, all anomalous observation cycles should be correlated with meteorological conditions over the given period.

Secondary contamination of samples presents a constant danger of measurement distortion. Instructions on sample collection, treatment, storage and transportation should be carefully observed, as well as cleanliness of materials and chemical utensils used (both before and after sampling). The working room where these activities are carried out should be cleaned on a regular basis.

Other error sources can be eliminated only with strict adherence to instructions by the station personnel under supervision from the regional laboratory.

A convenient way to reveal random errors is to analyze observation series and sample measurements obtained at a given background station. The analysis should be carried out at a regional laboratory. Its efficiency increases if parallel samples are taken (or their aliquots are analyzed) and stored for a possible second analysis. Some types of observations (e.g., atmospheric dust, ozone, sulfur dioxide, nitrogen oxides) cannot be repeated, even if necessary. Such observations require particular attention to all the procedures.

Measurements Carried out at Regional Laboratories.

The principle source of systematic errors is the application of unsatisfactory or low-quality standards. These errors are most difficult to reveal since they involve observation series from a whole group of background stations under a given regional laboratory. In this case statistical or meteorological analysis of an observation series does not give the desired effect. The principle way to prevent such errors is interlaboratory comparison (intercalibration) of standard and sample measurements.

8.2 Laboratory and Interlaboratory Control (Intercalibration)

Laboratory control should be carried out both at a background station and the regional laboratory. It includes a number of activities.

The first activity is the systematic checkup of the observance of all the prescribed procedures related to carrying out observations and measurements, keeping of records, and the filling in of tables. This work is to be done on a continuous basis. Duplication of all types of measurements (except rather simple ones, such as exposed filter weighing) would be requisite to exclude random errors, primarily in the initial observation period. To this end, it would be sufficient to divide collected air and precipitation samples into two (if possible, equal) parts and analyze them separately. The difference between parallel analyses should be within the error of the given method.

To monitor the cleanliness of materials and chemical utensils, as well as the purity of reagents used at stations, they should be periodically sent to a quality control laboratory for a checkup. Analyses performed at background stations must be systematically checked using "blank tests". All activities included in the laboratory control are aimed primarily at preventing and eliminating random errors.

Elimination and prevention of systematic errors requires interlaboratory control (intercalibration). Two levels of interlaboratory control should be provided for in the global IGBM network.

The first level involves background stations under a given regional laboratory. In this case, the regional laboratory must ensure a regular checkup of the fulfillment of observation and measurement procedures at each background station, cleanliness of materials and chemical utensils used, and purity of reagents, as well as representivity of data sent to the regional laboratory, i.e., it should undertake all measures to eliminate random errors. To eliminate systematic errors the regional laboratory should check all measurements and observations carried out at background stations, such as air flow rate measurement when sampling gases and aerosols, gas analyzer calibration, and standard solutions. To assure high data quality it is essential that all stations in a given region be equipped with similar instruments, materials, chemical utensils, reagents, and standards.

The second level involves different regional laboratories within the global IGBM network. In this case, the responsibility for data quality should be with the central quality control laboratory. Data quality assurance by this laboratory consists mainly of checking standards used in regional laboratories and providing recommendations on the application of various monitoring techniques. The quality control laboratory should always carry out the intercomparison and intercalibration of methods and instruments used at the stations and in regional laboratories. To this end, the regional laboratories should carry out periodic comparative measurements of standards and aliquots of specially prepared environmental samples from background regions.

International experiments with participation of highly qualified experts could be very helpful in data quality assurance and representivity assessment. The experimental program must be based on the IGBM program and implemented at the background station site.

One of the most important prerequisites for obtaining high quality data is a supply of standards, especially environmental matrix standards.

At present various countries produce standard samples and standard solutions which could be successfully used within the global IGBM network. Table 13 gives information on some standards.

Table 13. Characteristics of some standards

Standard sample, matrix	Units of measurement	Standardized components, the error is given for 95% confidence
1	2	3
Solution, GSORM-1	mg/l	Hg, Cd, Mn: 1.00 ± 0.01; Pb, Zn: 2.00 ± 0.02
Solution, GSORM-2	mg/l	Cu, Co, Ni, Sr, Cr: 1.00 ± 0.01; Fe: 1.00 ± 0.05
Solution, GSORM-3	mg/l	V, Sb, Mo, Bi: 1.00 ± 0.01; Ti, Sn: 2.00 ± 0.02
Solution, GSORM-4	mg/l	Ca, Al, Mg, Fe: 5.00 ± 0.05
Soil*. Light brown Caspian region	ug/g	Sn:4.9±1; Co:14±1; Pb:16±3; Cu:30±1; Ni:56±4; Zn: 73±2; V:110±10; Cr:140±10
Soil*Kursk chernozem	ug/g	Sn:3.9±0.5; Co:10±1; Pb:16±3; Cu:22±1; Ni:33±3; Zn:52±2; V:77±8; Cr:82±8
Soil* Sodly-podzolic, Moscow region	ug/g	Sn:2.8±0.3; Co:10±1; Pb:14±1; Cu:17±1; Ni:25±2; Zn:45±6; V:64±7; Cr:84±8
Bottom sediments* Terrigenous clay (SDO-1)	ug/l	Co:38±4; Cr:62±15; V:120±20; Cu:160±20; Ni: 190±20; Zn:260±20
Bottom sediments* Volcanous terroge-	ug/g	Co:45±2; Zn: 130±10; Ni:150±10; Cu:180±10; V:190±10; Cr:240±20

genous sludge (SDO-2)

Vegetation* Wheat grain (SBMPO-01)	ug/g	Sn:0.032±0.005; Co:0.06±0.02; V: 0.11±0.04; Pb: 0.19±0.02; Cr:0.31±0.05; Ni:0.7±0.1; Cu:4.8±0.1; Zn: 31±1
Vegetation* Mixed grass crop(SBMT-01)	ug/g	Co:0.06±0.02; Sn:0.15±0.02; V:0.4±0.1; Ni:0.7±0.1; Cr:0.8±0.1 Pb:1.3±0.1; Ni:1.3±0.2; Cu:13.2±0.3; Zn:34±1
Vegetation* Potato tubers (SBMK-01)	ug/g	Co:0.1±0.02; pb: 0.2±0.04; V:0.33±0.04; Sn:0.35±0.07; Cr:0.8±0.1; Ni:1.3±0.2; Cu:12.3±0.3; Zn:23±1
Coal Fly Ash (US NBS)*	%	Ca 1.11±.01; Fe 9.4±0.1; K 1.88±.06; Mg 0.455 ± .01; Na 0.17±.01; S:22.8±0.8;
	(ug/g)	Ag 145±15; Cd 1.0±1.5; Cr:196±6 Cu 118±3; Hg 0.16±.01; N:127±4; Pb 72.4±0.4; Ru 131±2; Se:10.3±.6 Sr 830±30; Th:24.7±3; Th 5.7±.2 U 10.2±0.2; U 10.2±0.1; Zn 220±10
Water (USNBS)*	(ng/g)	As 49; Ba 44±2; Be 19±2; Bi 11; B 94; Cd 20±1; Cr 18.6±0.4; Co 26±1; Cu 21.9±4; Fe 99±8 Pb 23.7±0.7; Mn 28±2; Mo 85±3; Ni 49±3; Se 9.7±0.5; Ag 9.8±0.8; Sr 227±6; Th 8.0±.2; Va 45.2 ±0.4; Zn 66±2
Tomato Leaves	(%)	K 4.46±.03; Ca 3.00±.03; P 0.34±.02
	(ug/g)	Fe 690±25; Mn 238±7; Zn 62±6; Sr 44.9±3; Ru 16.5 ±.1; Cu 11±1 Pb 6.3±0.3; Cr 4.5±.5; As 0.77±.05; Th 0.17±.03; U 0.061±.003
	(%)	N 5.0; Mg 0.7; Al 0.12
	(ug/g)	B 30; Br 26; Cd 3; Ce 1.6; La 0.9; Co 0.6; Sc 0.13; Hg 0.1; Th 0.05 Ev .04
Pine Needles	(%)	Ca 0.41 ±.02; K 0.37±.02; P 0.12±.02; N 1.2
	(ug/g)	Mn 675±15; Al 545±30; Fr 200±10 Ru 11.7±0.1; Pb 10.8±.5; Sr 4.8±.2 Cu 3.0±.3; Cr 2.6±.2; As 0.21±.04; Hg 0.15±.05; Th 0.037±.003; U 0.02±.004; Br 9; N 3.5; Ce .4; Cd <0.5; Sb 0.2; La 0.2; Co 0.1; Th .05; Sc .03 Eu .006

* Material predried at 105 degrees C. The substances given are standardized trace elements included in the IGBM program (basic and optional.
** United States National Bureau of Standards

All samples submitted for analysis must have quality control samples submitted with them. This usually includes a known or spiked sample, a replicated sample, a blank sample for both water and acids as necessary. Known samples wherever possible in the U.S. program were traceable to or directly received from the U.S. National Bureau of Standards (NBS). These standards included the NBS orchard leaves, pine needles, tomato leaves, water, and river sediment. Generally, a set of standards is included with every 10 field samples submitted to the laboratory.

Specifically for vegetation and forest litter samples, every ten samples is accompanied by one NBS vegetation and one replicated sample. Every ten soil sample extracts are accompanied by a spiked sample containing a wide range of the elements to be analyzed for, an acid blank and a distilled water blank. Every ten water samples are accompanied by a known NBS water standard and a distilled water blank.

Prior to submitting the samples, appropriate accept/reject criteria are formulated and used in evaluating the data. Table 14 is an example of such criteria. It also shows the detection limits and elements detected using spark source emission spectroscopy.

Table 14. Precision limits for spark source emission spectroscopy

Elements	Maximum allowable percent deviation from a known value
K, Ca, Mg, Cu, Mn, B, Sr, Ba, Al	20%
Zn, Fe, Cr, Ag, Ti, V	40%
Li, Pb	50%

Detection limits by element:

Element	ppm	Element	ppm	Element	ppm
P	50.0	B	1.0	Sr	0.2
Na	1.0	Al	1.0	Ba	0.2
K	150.0	Si	1.0	Li	0.3
Ca	1.0	Ti	0.5	Ag	0.1
Mg	50.0	V	1.0	Sn	0.3
Zn	5.0	Co	1.5	Pb	1.0
Cu	0.2	Ni	0.5	Be	0.2
Fe	0.6	Mo	0.2	Cd	3.0
Mn	0.1	Cr	0.2	As	1.0

Quality assurance also deals with possible routes of contamination from sample handling procedures. As described under field sampling, a number of precautions were instituted in the field to help miminize contamination. However, we were concerned about our sample handling procedures in the laboratory. Therefore, an experimental design was set up to test if we were adding contamination to our samples in the laboratory and is described below.

When collecting vegetation and litter samples in remote areas, a real concern is to be certain that no contamination is added to the samples during sampling. In order to determine whether or not our sample handling preparation procedures in the laboratory are potentially contaminating our samples with trace elements, a test was devised using a surrogate substance. The surrogate substance chosen was pure glycene supplied by Cal Biochem, Lot #309692.

The standard sample handling procedure is as follows:

Samples are collected in the field in new unused polyethylene bags. These bags have minimum dust contamination and very low potential for trace metal contamination. After collection, the samples are placed in these bags and held under refrigeration until sample preparation. When ready for processing, a sample is removed from the clean bag and placed in a new unused brown paper bag. The brown paper bag is then placed in an oven and the sample is dried at approximately 50 degrees C for 24 hours. The samples are then removed from the oven and a pair of unused non-powdered plastic gloves are used to transfer the vegetation sample or the litter sample from the paper bag to a 100 ml snap cap plastic vial. Two teflon balls are placed inside that vial. The vial is placed inside a spex mill and shaken for 1-10 minutes. The resulting sample is ready to be sent for analysis by spark source emission spectroscopy. Part of the sample is held as an archive. No further processing is needed.

Based upon this system, we felt that the potential areas in sample handling for contamination could be from the clean bag, from the paper bag, or from the spex mill operation, i.e., the plastic vial and/or the teflon balls. Therefore, we designed a four treatment one-way analysis of variance experiment to determine if contamination was entering our samples at any of these points. The null hypothesis was that there was no difference among treatments. The treatments were as follows:

1. Treatment One: Glycene is placed in a clean bag, held under refrigerated conditions for four weeks, then taken out, placed in one of our standard paper bags, put in the oven for the prescribed period of time, taken out, and ground with teflon balls in the spex mill.

2. Treatment Two: Glycene ground in a spex mill only.

3. Treatment Three: Glycene samples that had been placed in brown paper bags, gone through the oven drying procedure, and then ground in a spex mill.

4. Treatment Four: Control of glycene only.

Each level had 10 samples. Each sample was analyzed three times. The glycene was analyzed for 25 trace elements using the spark source emission spectroscopy; the same analytical procedure we use for our samples of vegetation and litter. Table 15 lists the elements and the lower limit of detection. Of these 25 elements, 15 were below the instrument detection limit; therefore, for these elements, we can say that none of our laboratory procedures added contamination to our samples at a level which can be detected with our current instrumentation. An additional 6 elements had average concentrations above the detection limits of our analytical procedure, but the analysis of variance indicated that there was no significant difference between the four treatments, therefore we accepted the null hypothesis.

This leaves four elements in which there appear to be a significant difference in the four levels of our test. The first of these was titanium. In this situation, the analysis of variance indicated that the glycene control in the spex mill and paper bag treatments had significantly higher amounts of titanium than the spex mill only and the clean bag-spex mill-paper bag treatment. However, a closer look at this data indicates that the average values for each of these levels ranges from 0.2 ppm titanium to 0.7 ppm titanium bracket. The detection limit of the instrument is 0.5 ppm, therefore these results are too close to the detection limit to be valid.

The second element that showed a significant difference between the four levels and also was within the detection limits (barely) was strontium. In this case, treatment one, the total treatment, appeared to be significantly higher than the glycene control, as did treatment two, which is the spex mill only.

Treatment three, which was the spex mill and the paper bag, but not the control, indicated no difference between that and the control. These results are not consistent considering the design of the experiment. If the spec mill was adding contamination, it should have shown up in treatment two and three, but it did not. Again, the average concentrations of strontium for these four levels of test bracketed the detection limit. We are probably not warranted in including the values that average below the detection limit in the analysis variance. Therefore, we believe that these results also are not valid.

The third element that showed a significant difference was lithium. Here we had the same situation as we had in titanium, where the test indicated that the total processing actually was significantly less than the glycene control. Again, we are operating at very close to the detection limit, and we believe that these results probably are not valid.

The final element is iron. In the case of iron, it appears that the total treatment category plus the spex mill only category are significantly higher than the control, and the paper bag and spex mill treatment. But again, one would expect that if the results were consistent, that the spex mill treatment would show up on both treatments two and three,and it only shows up on treatment two. Again on iron, we are relatively close to the detection limit. Furthermore, the amount that was apparently added is relatively very small compared to the amounts of iron that we normally detect in our field samples.

Based upon this series of tests, we concluded that sample collection and preparation procedures in the laboratory were not significantly adding contamination to our field samples, with the possible exception of iron, but that should be considered along with caveats listed above.

Table 15. Summary of Analysis of Variance Results for Glycene Test

Element	F	Significant	Mean Range	Detec. Limit	Valid
Mn	0.34	No	.03 to .06	0.1	No
B	1.59	No	.02 to .06	1.0	No
Al	0.90	No	2.7	1.0	Yes
Si	1.10	No	1.8 to 3.1	1.0	Yes
Ti	31.40	Yes	0.2 to 0.7	.5	Yes
V	1.96	No	.1 to .8	1.0	No
Co	2.60	No	.05 to .5	1.5	No
Ni	1.75	No	0.1 to 0.4	0.5	No
Mo	0.69	No	0.1 to 0.6	.2	No
Cr	1.89	No	0.2 to .1	.2	No
Be	0.38	No	<1.00-3.0	.2	No
Cd	23.40	Yes	0.25-.009	.3	No
As	.38	No	<.003	1.0	No
P	2.87	Yes	0 to 4	50.0	No
Na	1.26	No	1.4 to 4.2	1.0	Yes
Ca	1.01	No	.04 to .1	1.0	No
Mg	2.40	No	.8 to 2	50.0	No
Sr	23.60	Yes	.03 to .5	.2	Yes
Ba	.90	No	.17 to .26	.2	Yes
Li	8.40	Yes	.4 to 1.2	.3	Yes
Ag	5.19	Yes	.01 to .05	1.0	No
Sn	3.80	Yes	.05 to .2	.3	No
Pb	0.80	No	5.5 to 3.7	1.0	No
Cu	2.55	No	0	0.2	Yes
Fe	12.55	Yes	0 to 3	0.6	Yes

8.3 Statistical Processing of Monitoring Data

Statistical processing serves various purposes. In the case of parallel measurements, the arithmetic mean is calculated using common rules:

$$C_m = \frac{\sum C_i}{n} \qquad (24)$$

where C_i - individual measurements, n - number of measurements.

The arithmetic mean of an average daily concentration of ozone, for example, can also be calculated from 24 measurements with an hourly instrumental averaging.

To obtain an averaged concentration of atmospheric substances under study over a month and/or season, or any other period, the distribution law should be taken into account. As shown in

Izrael et al. (1984), pollutant concentrations in the background atmosphere have a lognormal distribution, so to obtain precise characteristics of a given time interval the median concentration is calculated on the basis of the mean daily values.

However, to simplify the calculations in practice it is quite enough to estimate the geometric mean for a given time interval (month, season, etc) which essentially does not differ numerically from the median value. To this end, the following formula can be used:

$$Ci = \sqrt[n]{C^1_i \times C^2_i \ldots C^n_i} \qquad (25)$$

where C^1_i, C^2_i ... C^n_i - mean daily concentrations.

To obtain mean monthly and/or mean seasonal concentrations of a given substance in precipitation, a weighted average concentration is to be calculated by the usual formula:

$$C_i = \frac{C^1_i \cdot h^1 + C^2_i \times h^2 + \ldots + C^n_i \cdot h^n}{h^1 + h + \ldots + h^n} \qquad (26)$$

where C^1_i, $C^2_i \ldots C^n_i$ - concentrations in weekly precipitation samples

h^1, $h^2 \ldots h^n$ - precipitation amount over the sampling period, mm.

The comparability of the interlaboratory analyses of standard samples and/or unified natural samples is evaluated by the relative standard deviation (σ) from standard sample ratings from mean concentrations in unified natural samples. The standard deviation is calculated as:

$$S = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \qquad (27)$$

where x_i - substance concentration in the sample analyzed as determined at the i-th laboratory;

$\bar{x}$ - mean of rated concentration;

n - number of laboratories participating in the comparison.

The value of σ is calculated by the following formula:

$$\sigma = \frac{S \times 100}{\bar{x}} \ \% \qquad (28)$$

The comparability of simultaneous parallel measurements of atmospheric pollutant concentrations is evaluated on the basis of calculating t-statistics and correlation factor r.

For a sufficiently long parallel measurement series t-statistics is estimated as:

$$t = \frac{(\bar{x} - \bar{y})\sqrt{n}}{\sqrt{S^2_x + S^2_y}} \qquad (29)$$

where x and y - selected means of the series analyzed;

S^2_x and S^2_y - sampling variances;

n - number of parallel observations.

The correlation factor is calculated by the formula

$$r_{x,y} = \frac{\sum_1^n (x_i - x)(y_i - y)}{\sqrt{\sum_1^n (x_i - \bar{x})^2 \sum_1^n (y_i - \bar{y})^2}} \qquad (30)$$

The significance of discrepancies between parallel measurements and degree of their interrelation are determined by comparing calculated and tabular values of the cited statistics.

9.0 PREPARATION AND PUBLICATION OF INTEGRATED MONITORING DATA

The ultimate goal of the IGBM network is the publication of observational data so that they could be used (together with other data) to assess and predict the background state of the environment. The preparation of data publication consists of 3 stages according to the hierarchical structure of the IGBM system.

The 1st stage. Every month, IGBM stations should send to the regional laboratories observation materials for the previous month and accompanying data, including meteorological and other information. A suggested tabular form is given in Appendix 1. BAPMoN data should be compiled in accordance with the WMO instruction (WMO, 1978).

The 2nd stage. Two to four times a year, regional laboratories should send to the IGBM center data summaries from all background stations of the region. At this stage, data quality should be checked and nonrepresentative data must be discarded. It is advisable, for example, to reduce published air and precipitation measurements to calculated mean monthly values. Suggested tabular forms are given in Appendices II and III.

Data base accumulated in regional laboratories should be used for statistical, meteorological and other analyses, for revealing local and regional climatic and other patterns. The

results of these investigations must also be sent to the IGBM center for further publication.

The 3rd stage. Once a year, the IGBM center publishes a summarized volume for each preceding year. The publication includes both tables of background indicators for each IGBM station and results of observational data analysis and pattern definition. It is necessary to establish spatial and temporal patterns of background environmental pollution on a global scale.

The summarized volume of observational data and assessments of global background environmental pollution are circulated among WMO members and other international organizations concerned.

TABLE OF ATMOSPHERIC OBSERVATIONS AND
MEASUREMENTS - IGBM PROGRAM

IGBM Station (name, country, coordinates, altitude above sea level)

Year, month

Day of the month	Dust ug/m³	SO_2 ug/m³	SO^{2-}_4 ug/m³	NO_2 ug/m³	O_3 ug/m³	Meteorological data (mean daily values)						Notes
						Temp-erature	Pres-sure	Rel. humi-dity,%	Wind direc-tion	Wind speed	Atmos-pheric phenomena*	
1												
2												
3												
.												
.												
.												
31												
mean monthly												

* in a code form

Appendix I

TABLE OF ATMOSPHERIC IGBM PROGRAM

egional Laboratory (name, country)

GBM Station (name, country, coordinates, altitude above sea level)

ear

lonth	Dust ug/m3	SO2 ug/m3	SO4 ug/m3	NO2 ug/m3	O3 ug/m3	Pb ng/m3	Hg ng/m3	Cd ng/m3	As ng/m3	3,4 benzo-a-pyrene ng/m3	DDT ng/m3	HCCH ng/m3	PCBs ng/m3	NOTES
lanuary														
ebruary														
larch														
ecember														

Appendix II

TABLE OF PRECIPITATION MEASUREMENTS - IGBM PROGRAM

Regional Laboratory (name, country)

IGBM Station (name, country, coordinates, altitude above sea level)

Year

Month	Precip. Amount	Pb ug/l	Hg ug/l	Cd ug/l	As ug/l	3,4 benzo-a-pyrene ng/l	DDT ng/l	HCCH ng/l	PCB ng/l	pH	Na+	K+	NH+	Ca2+	Mg2+	SO_4^{2-}	NO_3^-	Cl-	Acidity	Conductivity	Notes
												mg⁺/l	mg³/l	mg/l	mg/l	mg⁻²/l	mg³/l	mg/l			
January																					
February																					
March																					
.																					
.																					
.																					
December																					

Appendix III

10.0 REFERENCES

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