ENVIRONMENTAL POLLUTION ANALYSIS

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Fisheries and Environment,
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FOREWORD

The object of this series of monographs is the timely dissemination of essential information about topics of current interest in science. Interdisciplinary aspects are given fullest attention. The series aims at the presentation of new techniques, ideas and applications in sufficient detail to enable those who are not specialists in a particular subject to appreciate the applicability of the subject matter to their own work, and the bibliographies included in each monograph will guide readers in extending their knowledge of the subject to any desired depth. The depth of treatment, of course, makes them compact definitive books for the specialist as well. The series will from time to time include more general reviews of selected areas of scientific advancement, for which a somewhat wider readership is envisaged.

The topics and the depth of treatment should suit both the student and the research worker, academic or industrial. The range of topics in this series will eventually span the whole extent of scientific interests and the authorship will reflect the international nature of the subject matter.

The widespread realization of the importance of monitoring the environment, to ensure that man's activities do not result in an unacceptable deterioration in its quality, clearly indicated that a book on this subject should be included among the early titles in this series. The present volume is the result: it considers sampling methods for pollutants in air, soil and water; analytical techniques for metals, inorganic non-metals, radionuclides, organic compounds and micro-organisms; and concludes with a discussion of continuous monitoring techniques.

The description of the chemical and instrumental techniques used in the identification and determination of environmental pollutants is sufficiently detailed to enable newcomers to the field to carry out routine analyses. The extensive bibliographies provide the necessary guidance for the extension of background knowledge to any desired depth and, as a result, this volume will be of value to all who are interested or involved in the monitoring or control of environmental pollution.

L. C. Thomas

PREFACE

Pollutants in the environment are of concern to people working in a number of diverse fields. Biologists are concerned with the effects on plant and animal life of the materials in the water, air and soil; physicians are concerned with the effect on health of the materials that are in the food we eat, the water we drink and the air we breathe; engineers are concerned with the effect of chemicals and suspended material in the water and air used for domestic and industrial processes. The legislators must decide what levels of pollutants in our environment we are willing to accept in order to enjoy the benefits of modern technology. In these decisions scientists are called upon for advice as to what are 'safe' levels that industries may discharge. Regulatory bodies are concerned with the implementation of the legislation so that these 'safe' levels are not exceeded.

In the early days of environmental concern, analytical methods were not very sensitive and many pollutants could not be detected in air and in natural water a short distance from the emission source. Under these conditions the desirable levels were often defined as 'zero' levels, meaning in fact levels that could not be detected by the available analytical techniques. In recent years great advances have been made in analytical methodology: for example, it is now possible to determine levels of the metallic elements at fractions of a part per 10^9 (parts per billion) and to identify and measure organic materials at levels of one part per 10^{12} (parts per trillion).

The development of these specialized techniques for environmental analysis has tended to make the field an esoteric one. The analyst naturally has an understanding of the methods, their capabilities and their limitations. However, other workers in the field who are concerned with setting up sampling and control programmes, and making decisions from the data produced, do not necessarily have the same detailed knowledge and understanding. As a result the right questions may not be asked at the beginning of a programme, and the data obtained may not be collected in the most efficient way. This monograph has been written with the intention of providing a means whereby non-analytical

specialists may become more familiar with how environmental samples are collected and analysed and at what levels particular pollutants may be determined.

Burlington, Ontario
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P. D. Goulden

INTRODUCTION

A work on Environmental Pollution Analysis should properly begin with a definition of 'pollutant'. This term has been defined as any substance which changes the natural composition of the environment. However, the environment has been changing since the world began, and its natural composition is difficult to identify. Man has played, and continues to play, a major part in bringing about changes and for the purpose of this discussion the term pollutant means a material that enters the environment primarily as a result of man's activities.

Most of the pollutants enter the environment as emissions to the atmosphere or as discharges to water bodies. These may be either in concentrated point sources, such as from factory smoke stacks and sewage discharges, or in a diffuse form such as from automobiles' exhaust and run-off from agricultural land. Most of the material emitted to the atmosphere eventually returns to the earth as particulate fall-out or with rain and snow. Where these materials return over land they may be absorbed by the soil and eventually by the vegetation or they may be washed into the waterways.

The materials discharged to the rivers and streams flow via larger rivers and lakes to the oceans. On the way they may become incorporated into the sediment. Alternatively they may be metabolized by the plant and animal life in the water and thus enter into the food chain. Hence, wherever in the environment the samples are collected, they represent the same process of pollution although occurring in different time spans. Air samples and water discharge samples give a measure of the pollution occurring on a day-to-day, or minute-to-minute, basis. Soil, vegetation, sediment, lake water samples, etc., can give a measure of the pollutants released over a longer time period, often representing in fact an integration of the pollution that has occurred over previous months or years.

In the past it has often been the practice to consider the measurement of air pollution as being a distinct area from, for example, the measurement of water pollution. However, as analytical techniques have become more sophisticated

(and analytical equipment has become more expensive), in many cases the final measurement process for a particular pollutant is the same, whether the original sample was of air, water or sediment. The difference in the methods used for the analysis of the various types of sample lies in the sampling technique and in the pretreatment given to the sample to convert it to a form amenable to analysis. Hence the format chosen for this work is to organize the description of the measuring techniques by specific pollutants and, where necessary, to describe how the various types of environmental samples are processed to use this measuring technique.

CONTENTS

CHAPTER 1

SAMPLING METHODS

When a decision is made to determine the level of a particular material in part of the environment, the first step is to formulate clearly why the information is required and how the analytical results will be used. Typical objectives may range from the desire for general information on a number of parameters, for the purpose of obtaining baseline data, to a legal requirement to establish the loadings or emissions of a specific pollutant. As will be seen in the later discussion, at many stages of the sampling-analysis process there are decisions to be made as to the specifics of the procedure to be followed. These decisions can best be made if there is a clear understanding of the rationale for the analyses being carried out.

To determine levels in a river, in the air, etc., at a specific location, it is necessary to take samples. The location of the sampling points, the frequency of sampling, the size of the samples and the analytical procedures used are all dependent on the objectives of the analytical programme. The samples should be as representative as possible of the area being sampled. This is important, not only at the time they are taken but also when they have been transported to the laboratory for analysis. Most often this entails that some preservation technique be used. In a programme looking at levels of pollutants in the environment perhaps the most important part is ensuring that valid sample preservation techniques are used and confirming that the analytical results obtained in the laboratory do represent the levels in the samples as taken. Montgomery and Hart[1] have given an excellent discussion of the design of sampling programmes for rivers and effluents which also has application to sampling programmes in any area of the environment. Complete details of the methods by which the various types of environmental samples are taken can be found in the literature references given. Below is given a brief description of these methods for the environmental samples most commonly taken. Also described in general terms are the procedures by which the samples are converted to a form in which they can be analysed.

WATER

For sampling a river or lake from, for example, a bridge, dock or small boat, a bottle of polyethylene or glass of one- or two-litre capacity is used. After determining the depth of the water the bottle is placed in a metal holder attached to a string and thrown into the water. By regulating the rate at which the bottle is lowered to the bottom it is possible to obtain a sample that approximates an integrated sample of the water between the surface and the bottom. However, the bottle should not be allowed to touch the bottom in the sampling to avoid stirring up the sediment. To take a sample at a specific depth the simplest procedure is to immerse the stoppered bottle to the required depth with some arrangement for the removal of the stopper by pulling another string.

There are a number of samplers which were primarily designed for oceanographic sampling, such as the Knudson bottle and the Van Dorn bottle. These are attached to wires hanging in the water and, by a 'messenger' system, allow samples of water to be taken at particular depths. Other similarly suspended samples allow an integrated sample to be collected over a specific range of depths. A description of water samplers is to be found in the ASTM Standards.[2]

Many waters as sampled contain suspended material. If it is desired to include this material in the analysis and to determine the 'total' composition, an appropriate preservative is added to the sample as taken. If only the soluble portion of the water sample is to be determined, the sample is filtered when it is taken and before the preservatives are added. By general definition the 'soluble' portion of a water sample is that which passes through a 0.45 μm membrane filter.

In any natural water sample, chemical and biological processes are occurring when the sample is taken, and these will continue in the sample bottle. In addition, there may be interaction with the bottle, such as adsorption of ions on the bottle wall. To stop, or at least to slow down, these reactions, preservatives are added to the sample. There is no universal preservative available, the most common technique that is effective for many systems being to bring the sample to a pH below 2, and to refrigerate the sample at 4 °C. The low pH stops much of the biological action and retards the adsorption of many cations on the container wall. Some parameters require a special preservative system, for example:

Mercury: per 100 ml sample, 1 ml H_2SO_4 and 1 ml of a 5% solution of $K_2Cr_2O_7$ are added;
Phenol: per 100 ml sample, H_3PO_4 to bring the sample to a pH of 4 or less and 0.1 g of $CuSO_4 \cdot 5H_2O$ are added;
Cyanide: NaOH is added to bring the pH to 12.

For many parameters, such as orthophosphate, sulfite, etc., a satisfactory chemical preservative is not available and the best that can be done is to refrigerate the samples at 4 °C and to analyse them as promptly as possible.

Hence, when sampling, it may be necessary to collect several bottles of water at each sampling point, depending on the parameters to be determined. The specific preservatives required are given in the descriptions of the analytical procedures used. In the case of the determination of microorganisms, it is desired to keep them alive. Hence sodium thiosulfate is added to destroy available chlorine and heavy metals are complexed with EDTA (ethylene diamine tetra-acetic acid).

SEDIMENT

To obtain a sample from the bed of a river, or a lake, a variety of grabs are available. These consist essentially of a bucket having jaws which are either spring-loaded or weight-loaded open. The sampler is lowered to the bottom on a rope and the jaws snap shut to take a sample. The trigger for the jaws to shut may be the weight of the sampler resting on the bottom or a 'messenger' weight dropped down the rope.

There are a variety of designs suitable for use from a small row-boat, such as the 'Ekman' or the 'Ponar' grab. These take samples of about one to two litres in volume and are available from scientific supply houses. To take samples that retain the layer structure of the sediment a core sampler is used. This is a tube which is dropped to the bottom and penetrates to take a cylindrical sample. A valving arrangement at the top of the tube stops the sample from falling out as the sampler is brought to the surface. If the sample is for bacteriological studies a sampler used by Van Donsel and Geldreich[3] is recommended because of the difficulties in maintaining aseptic conditions in the field with other samplers.

There are a number of grab samplers designed to be used from a large vessel, such as the Franklin–Anderson, the Peterson and the Shipek samplers. These take a much larger sample from the lake bed and with these the top ten centimetres or so of the structure is retained. Samplers used for sampling sediment in the Great Lakes have been discussed by Sly.[4] No chemical preservatives are added to the sediment sample; immediately it is taken it is placed in a plastic bag and refrigerated or stored in an ice-chest. If the sample is not to be analysed on the day it is taken, it is immediately deep-frozen.

To carry out an analysis the sample, as taken, or the thawed-out sample if it has been frozen to preserve it, is passed through a 10-mesh screen to remove large pieces of foreign matter such as twigs or stones. If necessary the sample can be pressed through the screen with a rubber stopper. The sample is then treated in a blender (such as a 'Waring' blender) set at high speed, to homogenize it. Portions of this homogenized sample are taken for the various analyses desired.

Since the most unambiguous basis for reporting results is on a dry basis, a portion of the wet homogenized sample is oven dried at 105 °C. The loss in weight in this drying provides a conversion factor by which the analysis carried out on the other portions of the sample can be converted to a dry-weight basis.

In the determination of the inorganic constituents of the sediment there are two ways to look upon the analysis. If the concern is to determine the materials which are adsorbed on the mineral particles, then the analysis is carried out upon a solution made by extracting the sediment with, for example, an acid. This does not dissolve the mineral particles but is believed to solubilize the metal ions that are adsorbed upon them. The rationale for this approach is that the concern is for those pollutants which have been deposited in the sediment and which might be available for biological processes at the sediment–water interface, rather than for the geochemical composition of the minerals on the lake bed.

Hence a variety of dilute mineral acids are used to extract the anions such as nitrate, sulfate, and phosphate which are adsorbed on the sediment. A mixture of concentrated nitric acid and hydrogen peroxide is used to extract the metals. Materials which are volatile, such as ammonia, phenol, and cyanide (as HCN), are separated from the sediment by distillation. To determine organic materials, herbicides, pesticides, etc., the sediment is extracted with organic solvents.

If the concern is for a 'total' analysis, i.e. the chemical constitution of the total sediment, it is necessary either to employ an analytical technique that uses solid samples, or to solubilize all the minerals completely. Classically this solubilization has been done by a fusion with a variety of inorganic salts, but the most convenient way now is to use a 'Parr' bomb. This is a 'Teflon'® capsule enclosed in a steel shell which allows solubilization of the sediment with hydrogen fluoride under pressure. The technique was described by Bernas[5] and has been used for a variety of environmental samples besides sediments.

FISH

Fish when caught are classified by species, size and estimated age. The fish are cooled in ice or refrigerated as soon as possible after they are caught. If the whole fish is to be analysed it may be preserved by being deep-frozen immediately. If certain parts of the fish, such as the liver or muscle tissue, are to be analysed, the separated organs can be preserved by being deep-frozen.

The fish, or part of the fish, is homogenized in a blender. Portions of this homogenate are then weighed for the analysis. For the determination of organic pollutants the fish tissues are ground and extracted with organic solvents. The treatment and clean-up procedures used on these extracts are discussed in the chapter on the analysis of organic pollutants (Chapter 6).

To analyse for inorganic material by methods using a sample in solution, the sample is ashed and the inorganic residue solubilized. There is a choice in ashing procedure between dry-ashing and wet-ashing. In dry-ashing, the sample is heated to 400–600 °C in an open dish and oxidized by the ambient air. In wet-ashing the sample is treated with a variety of oxidizing systems such as nitric–sulfuric acid, perchloric–nitric–sulfuric acid, sulfuric acid–potassium permanganate, and hydrogen peroxide.[6] Dry-ashing has the advantage that the minimum amount of chemicals are added and hence the reagent blank for trace metals is

reduced. However, some of the metals may combine with the vessel in which ashing is carried out and volatile elements such as arsenic, selenium and mercury may be lost.

Rather than combustion in an open dish, the sample may be burnt in an oxygen combustion flask. The sample is dehydrated by being stored over phosphorous pentoxide and then ignited in a flask filled with oxygen. Since it is a closed system the volatile materials are retained. Procedures for the determination of selenium[7] and mercury[8] using this technique have been described.

Another option for dry-ashing is plasma-oxidation where the organic sample is treated with an oxygen-bearing plasma.[9] In this case the oxidation proceeds at temperatures of around 100 °C so that the loss of volatile materials is minimized.

A discussion of ashing procedures is given in the texts on atomic absorption spectroscopy (see Chapter 2). The preparation of biological samples for multi-element analysis is discussed by Hamilton *et al.*[10]

AIR

There are three methods of sampling air: a static sensor; taking a whole-air sample; and separating the pollutants at the sampling site.

A static sensor is the simplest form of air sampler. This uses the natural movement of air past it to present the sample. One example of this is the dustfall jar, which consists of a container that is used to collect particulate matter that falls freely into it. Another example is the 'candle' or plate used to measure the sulfur-containing gases. These consist of a matrix containing lead peroxide which combines with these gases to form lead sulfate. After being exposed to the air for a time the candle is taken to the laboratory, the matrix is dissolved and the amount of sulfate produced is measured. Another type of static sensor is the CDE Toxic Hazard Monitor.[11] This consists of a small holder containing an adsorber, such as a piece of charcoal cloth, covered with a semipermeable membrane. The pollutant vapour diffuses through the membrane, is adsorbed by the charcoal and is later eluted for measurement. The sensor may be used for atmospheric sampling or, attached to clothing, it may be used as a personal exposure monitor by people working in a contaminated work area. Determinations of air pollution may also be made by exposing indicator paper to the air and comparing the colour produced after a certain time with a standard chart.

For a whole-air sample, air is taken in a container for later analysis in the laboratory. This air may be collected in a previously evacuated vessel by merely opening a valving device to the atmosphere being sampled. In the flasks described in ASTM Standards[2] a glass flask (of up to about 500 ml volume) is evacuated and the end of the connecting tube is sealed with a flame. To take the sample the end of the tube is broken to admit the air sample; after sampling, the end is closed with a rubber cap or wax-filled cartridge. Alternatively the sample may be

drawn into a container by a rubber aspirator bulb, a vacuum pump, or by water displacement. With the aspirator bottles samples of up to five litres are normally collected. Plastic bags can also be used to collect the sample; the bag is purged and filled with a rubber squeeze bulb or other pumping device.

Whole-air sampling has the advantage that very little equipment is needed in the field in order to take the sample. It is often a convenient way to take a sample for an organic pollutant where there is no well-established adsorbent available and where the sensitive detection techniques of gas chromatography can be used to overcome the limitation of the sample size. There are possible problems of sample preservation since reactive gases such as hydrogen sulfide, oxides of nitrogen, sulfur dioxide, etc., will react with dust particles, moisture and perhaps the container material itself.

Separation of the pollutants at the sampling site is the most usual way of sampling. The pollutants are separated from a known volume of air and analysed later in the laboratory (or in the field). For the collection of particulate matter a number of sampler types are available. The particulates may be separated by drawing air at a known rate through a filter medium. They may also be collected with an impingement device. The air is blown at a surface and because of their inertia the particles collect on this surface. A microscope slide as the collector surface is often used. This facilitates later examination of the particles. The surface may be dry, in which case the apparatus may be called an impactor, or the impingement surface may be covered by a liquid. The particulates may also be collected by electrostatic precipitation or by thermal precipitation.

The particulates may be collected for three reasons: to determine their total amount, to determine their particle size distribution and/or to determine their chemical composition. The particle size distribution may be determined by physical examination of the collected particulates, or the different sizes may be separated by the collector itself, e.g. a series of impactors in cascade. To collect particulates for chemical analysis, typically a filter in a high-volume sampler is used.

For elemental analysis where a solution is required, such as the determination of the metal content by atomic absorption, the particulates are dissolved in acid. A more complete solution can be made by digesting with hydrogen fluoride in a 'Parr' bomb. This also has the advantage that refractory materials such as silica in the particulates can be determined.[1,2] Organic materials are recovered by extraction with solvents. For analysis where solid samples can be used, such as in X-ray fluorescence, pieces of the filter are used directly.

Collection of gases and vapours is usually by absorption in a liquid. The air sampled is first cleaned from particulates by passing it through a filter. This air is then passed through an absorber containing a liquid which extracts the pollutant of interest. Various absorbers are described in the ASTM Standards.[2]

For gases which are readily soluble distilled water may be used in the absorber. Often a reagent which will react chemically with the pollutant is used because this solution may be used later in the analytical procedure.

Adsorption of the gases and vapours on to solid materials is another method of collection. Such adsorbents as activated carbon, silica gel, or activated alumina are used. Sometimes the adsorbent is made more specific for a pollutant by impregnating the solid with an appropriate chemical. After exposure to the air stream the pollutant is recovered from the adsorbent by heat or by chemical treatment. A discussion of adsorbents and techniques is given in the ASTM Standards.[2] Separation of gases and vapours may be made by condensation where the gas is passed through a trap at low temperature. This may be combined with adsorption to separate a whole range of pollutants.

For measurements in the field, indicator tubes can be used. The air is drawn through a tube containing reagents that react with the pollutant to form a colour, the amount of colour produced being compared with colour standards. Indicator tubes are available for over a hundred pollutants; these are listed by Saltzmann.[13]

Many of the 'standard' pollutants such as nitrogen oxides, sulfur dioxide, ozone, etc., which in the past were measured by absorption into a reagent solution and determination of the resulting colour, can now be more conveniently measured by direct reading instruments. Particularly, the application of chemiluminescent methods[14] to the measurement of air pollution is resulting in the use of the direct reading instruments for some pollutants being preferable to the taking of an air sample and analysis by wet chemistry. These methods are discussed in the chapter on continuous monitoring.

A comprehensive list and description of air-sampling instruments is given in a publication by the American Conference of Governmental Industrial Hygienists.[15]

VEGETATION

When sampling vegetation such as leaves from trees, it is important that the samples be carefully identified with respect to the species of the plant, the age or maturity of the foliage and the age of the plant. This ensures that the data obtained can be related to data from other sampling sites. Samples of foliage from trees are taken by cutting the outside growth from ground level up to about 20 ft or more in height and collecting all the leaves. A useful sample size is 500–1000 g. If a particular source of air pollution is being investigated, it is preferable to sample the sides of trees that face this source. When sampling field crops or grass, leaves or blades are cut at regular intervals in a network across the field. Flower heads and stalks are not included in the sample, nor is root material. Any areas of very local contamination such as those receiving roadside dust should preferably not be sampled, unless of course it is this type of contamination that is being studied.

The samples are collected in perforated polyethylene bags and placed in refrigerated storage or an ice-chest as soon as possible. They can be safely stored in a refrigerator for a few days.