Methods for Assessing the Effects of Mixtures of Chemicals
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2 Environmental Transport*

2.1 INTRODUCTION

This section deals with what happens to chemicals or mixtures of chemicals between the time they are released to the environment and their arrival at a receptor. It contains some discussion not only of transport and transformation, but also of procedures for assessing them—modelling and monitoring. These subjects are closely related to each other and to the collection of data through sampling and analysis. Given the inclusion of this subject matter, this section is divided into four parts: transformation, modelling, monitoring, and sampling. One of the chief purposes of these activities is to provide qualitative and quantitative information about exposures.

2.2 TRANSFORMATION OF SINGLE CHEMICALS AND MIXTURES DURING TRANSPORT

2.2.1 Abiotic Transformations

After emission, a single chemical may be converted to a mixture of chemicals before reaching the target organism. Under environmental conditions, the complete conversion of one compound into another is extremely rare. A mixture of only two components, the parent compound and one conversion product, may occasionally be formed; the formation of multicomponent mixtures is much more frequent. For example, by irradiation of its aqueous solution, the herbicide 2,4,5-T is converted into at least five new products (Crosby and Wong, 1973). These mixtures, as well as the mixtures originally emitted (such as polychlorinated biphenyls (PCBs), insecticides such as toxaphene and technical hexachlorocyclohexane, and industrial wastes), are further altered by various environmental mechanisms.

Physical processes that occur during transport may change the composition of the mixture by partial fractionation of its components. The most relevant processes are volatilization from water or soil, adsorption and desorption

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(including the transfer from water to sediment), migration within soil, and run-off and transport through soil into groundwater. An example of a separation of the components of a mixture by migration through soil are those that result from the conversion of the insecticide aldrin. They consist of the parent compound aldrin, its epoxide dieldrin, its photoconversion product photodieldrin, and the ring cleavage product dihydrochlordene dicarboxylic acid, but only the last compound is found in the leachate since it is highly hydrophilic due to its two carboxylic groups (Klein *et al.*, 1973; Moza *et al.*, 1972). However, it should be pointed out that a chemical reaches the groundwater zone in an unconfined aquifer after passing through a soil column only if it is stable enough to resist degradation during passage. Thus, the compositions of chemical mixtures in leachates reflect both the mobility and environmental persistence of their components. The results of soil column experiments must be applied to field situations with caution because of the complexity of the processes operating to produce the concentration profiles—biotic and abiotic transformations as well as physical transport.

Abiotic *chemical* changes may occur in air, water, and soil, and include hydrolytic and photolytic reactions, auto-oxidation, and reduction or reductive dechlorination by redox systems found in anaerobic environments. For several important classes of organic chemicals, linear free energy relationships have been developed that make it possible to estimate reaction rate constants for conversion of chemicals by different reaction mechanisms in different solvents (Hammett, 1937, 1970; Taft, 1952a,b, 1953, 1956). These relationships are empirical and are applicable over a limited range of conditions. Attempts to use molecular orbital theory to estimate reaction rate constants have also proved to be only partially successful (Dewar, 1969). In this approach, a particular reaction pathway is chosen. Then the chemical reactivity of different molecular structures can be calculated either by *ab initio* techniques (Richards and Horsley, 1970), or by semiempirical methods (Pople and Beveridge, 1970) that use spectroscopic and other experimental data to define more precisely the set of functions used to approximate the wave functions of the ground-state energy levels of the reactants and products.

For aqueous phase reactions that would occur in rivers, lakes and groundwaters, the application of both the free energy approach and the molecular orbital approaches could provide a very useful method of estimating the products of chemical transformation under environmental conditions. These techniques have been applied to homogeneous aqueous phase reactions, but methods should be developed to extend this procedure to heterogeneous chemical and biologically mediated reactions of single chemicals and mixtures of chemicals. Methods should also be developed to examine the full range of molecular interactions (Morokuma, 1977). These interactions include the many processes that change the electrical properties of molecules in mixtures and can affect the reactivities of components of a chemical mixture.

Chemical reactions in the atmosphere are almost exclusively abiotic; chemical reactions in water or soil are both abiotic and biotic. In all alterations of chemical mixtures, non-persistent components are lost by total degradation and new, more stable, components appear. Molecular changes of single components are often affected by other components; in photochemistry, the phenomena of photosensitization, quenching, photonucleophilic displacements in the presence of hydroxyl ions, or catalysis by hydrogen peroxide may be cited as examples (Bedding *et al.*, 1983).

The chemical reaction between two emitted pollutants to form a new compound is rare in the environment since both the concentration and chemical reactivity of components are generally too low; however, in polluted air or in waste water such interactions do occur. In a few cases chemical reactions between components of a mixture, forming a new compound, have been reported in agricultural soils or in stored grain. It has been shown that the fumigant sodium *N*-methyldithiocarbamate may be esterified in soil by halogenated hydrocarbons used as nematocides (Miller and Lukens, 1966). Ethylene oxide is sometimes used as a sterilant to destroy microbial populations on stored grain. If the grain is fumigated at the same time or before with methyl bromide or ethylene dibromide, then the ethylene oxide may react and form ethylene bromohydrin (Heuser and Scudamore, 1969).

2.2.2 Biotic Transformations

Biotic alterations of chemicals can be important, even when only a small amount of conversion product is formed. This is the case when metabolites are formed that are highly toxic to organisms and undergo biomagnification in food chains. The biological formation of methyl mercury in aquatic organisms is an example (Wood, 1974). Biotic processes may also transform a single chemical into a mixture or alter the composition of mixtures. The biotic processes of interest occur primarily in water, sediments, soil, and stored food products such as grain. They include selective uptake by biota as well as biological conversion and degradation, which depend on the ability of organisms to alter the chemicals. The uptake of chemicals from water by aquatic organisms or from soil by terrestrial plants is often different for a chemical in a mixture than for an isolated chemical due to mutual interactions and influences, for example, on water solubility. Thus, the uptake of mercury by aquatic organisms (Jernelöv, 1972) or the uptake of non-nutritive elements from soil by corn is significantly higher when the pH of water or soil is low (Lutz *et al.*, 1972).

Biological conversion and degradation of chemicals are affected by other components in the mixture, mostly by their effect on the microorganisms responsible for biodegradation. These effects may result in either a decrease or increase in persistence. Decrease in persistence due to effects on microorganisms has been reported for several pesticides such as substituted benzoic acids, phenoxyacetic acids or phenols (Kaufman, 1972). Increase in persistence may be due either to the inhibition of proliferation of microorganisms, or to the inhibition of enzymes, either by direct inactivation or by competition for active sites. Numerous examples of increased persistence have been reported for pesticides of various chemical classes such as carbamates, organophosphates, phenyl ureas, azides, and organochlorine compounds (Scheunert *et al.*, this volume). The inhibition of conversion and degradation of an anionic detergent in soil by the herbicide atrazine has also been reported (Scheunert *et al.*, 1983).

The formation of new compounds by reaction between two components of a mixture may also be mediated by enzymes in the microorganisms of the soil. Thus, one-electron oxidation of anilines in soil, mediated by peroxidases, may produce a mixture of azobenzenes from anilines derived from different acylanilide or phenyl urea herbicides (Bartha, 1969; Kearney *et al.*, 1969).

Thus it is not sufficient to study the environmental behaviour of individual chemicals in isolation; it is also necessary to consider and evaluate interactions between the various chemicals in a released mixture as well as between the chemicals and the environment. Particular attention should be given to the characteristics of the microbial populations present in each soil horizon. Different microorganisms can produce different degradation products from the same chemical, and environmental conditions such as humidity, temperature, moisture content, pH, etc., also affect degradation. The role of the molecular structure of the components of a mixture on the rates and products of degradation should be examined.

2.3 MODELS FOR ESTIMATING THE ENVIRONMENTAL BEHAVIOUR OF CHEMICAL MIXTURES

Environmental models can be used to estimate mathematically how a chemical mixture would behave in the environment, i.e. routes of transfer, degradation, persistence, exposure. These models are used to organize the available information concerning the rates of various processes (e.g. sorption, photolysis, microbial degradation) occurring in different environmental compartments such as air, water, soil, etc. The rates of these processes are dependent upon both environmental factors and the physical and chemical properties of the mixture of chemicals. It is essential to derive a model in a rigorous manner starting from fundamental principles based on the transport of energy and mass among all components of the mixture, where available. Without attention to detail in the initial stages of development, including documented reasons for discarding terms of negligible importance, the model will have only limited utility.

Advances in computer technology have provided the capability to construct complex models that describe a multitude of chemical processes. An increase in complexity is, however, not necessarily accompanied by an increase in accuracy of description or prediction. The numerical procedures needed to solve the more complex problems can introduce inaccuracies that are traceable to the mathematics of the solution algorithm. In many cases, additional complexity and mathematical sophistication are not required. Many simple models that depict the environment as a system of a few compartments may be well suited to some situations. To avoid inappropriate applications of models and to establish conditions when simple models are appropriate surrogates for complex phenomena, the scientists constructing the models should work closely with field scientists. The models constructed in this way should become an integral part of the environmental programme.

When simple models include the important processes describing transport and transformation of single chemicals or mixtures they can indicate the most important variables and transfer coefficients that determine the environmental behaviour of the chemicals. Examples of the use of simple models to explain complicated processes that occur in mixtures of air pollutants are given in the paper by Piver (this volume) and for chemicals in groundwaters by Piver and Lindstrom (1984).

2.3.1 Modelling the Environmental Behaviour of Single Chemicals

Before discussing models for mixtures of chemicals there is much to be learned from experience with models for single chemicals; in fact, under certain conditions single chemical models can be used as surrogates for determining concentration profiles for mixtures. In models developed for single chemicals the precise details of how variables and transfer coefficients that characterize transport and transformation vary in space and time are not known and must be estimated from empirical relationships. However, even if the precise nature of these details were known, it is not at all certain that this would add significantly to the understanding of variations of chemical concentrations in space and time. A legitimate concern of modelling efforts for both single chemicals and mixtures is, therefore, to formulate testable hypotheses to determine the spatial variability of the coefficients that characterize the dynamic behaviour of chemicals in the environment.

Models that incorporate the most important transfer and degradation processes should be used to predict where in the environment the most effective sampling stations should be sited for monitoring networks, and to estimate concentrations of chemicals at different distances from the point of entry as well as concentrations in different environmental compartments. Implicit in model development is the collection of data required to describe the many processes actively participating in the dynamics of the system. For this reason, models can be useful in directing the collection of data in laboratory–field studies.

The output of models for single chemicals is strongly influenced by the method of solving the transport and degradation equations that define the models. Because particular situations may demand models of great complexity, numerical, as opposed to analytical, methods are most often used to compute concentration profiles. This is true regardless of the final form of the model (deterministic, stochastic, or compartmental). As the complexity of the model increases, the likelihood of introducing serious errors in the computation routine increases rapidly. An example is the simulation of transport of single chemicals in soil above the water table using finite difference approximations for the set of equations describing transport of water and chemicals in soils (Bresler, 1975). Because important transfer coefficients such as dispersion coefficients and water conductivities are functions of position in the soil and its moisture content, which is due not only to variations in soil type but also to changes of porosity in non-homogeneous soils (Baker and Bouma, 1976), inadequate attention to these conditions can easily introduce computational errors that make estimated values of concentration meaningless. Descriptions of methods to reduce the impact of computational errors in mathematical models, scattered throughout the literature, should be collected and analysed. Since these methods have been set up for specific cases, it would be most useful to develop from them general procedures that would be applicable to a wider variety of chemicals and environmental conditions. If models are to gain widespread credibility, criteria must be established for minimizing computational errors in the estimation of concentrations. In addition, it would be most useful to identify the situations in which analytical mathematical solutions would adequately describe the transport and transformation of single chemicals.

2.3.2 Extension of Models of Single Chemicals to Mixtures

Establishing models describing the transport and transformation of mixtures is a complex task because solutions must be found for the multicomponent equations for the simultaneous transport of heat, mass, and momentum in time and three-dimensional space. It is important that methods be developed for the simplification of these models without sacrificing essential details about molecular interactions.

There are many examples of this approach in which an indicator or surrogate chemical has been used to predict the concentration ranges for mixtures. Ozone is frequently used in photochemical smog (Friedlander and Seinfeld, 1969) and unreactive chemicals such as PCBs have been used to examine the movement of refractory chemicals from subsurface burial sites into groundwater (Piver and Lindstrom, 1985). However, each case is site-specific, and before applying a model to a new situation one must be assured that the model matches the environmental setting.

2.3.3 Modelling of the Behaviour of Mixtures

Four approaches have been employed in modelling the environmental behaviour of complex mixtures. In none of these approaches, however, has any attempt been made to incorporate, or to account for, interactions between chemicals in the mixture. The incorporation of the chemical kinetics of these interactions into environmental models requires adequate information about the chemicals present and their reactions with each other. The four approaches are summarized below.

(1) The 'chemical by chemical' approach to the modelling of exposure to mixtures is the most commonly used approach. Ideally, each constituent in the mixture is identified and quantified, and its rate of transformation determined. Common sense indicates that this may not be a very practical approach because it does not allow for chemical interactions and treats chemicals as if they existed in an isolated state. Exhaustive analytical characterization of a mixture may be very expensive. This poses a dilemma because constituents that are not looked for will not be detected. Another problem is that the composition of the mixture may change rapidly with time.

(2) The approach through 'bulk properties' has been suggested as a means of reducing the analytical effort and cost of the 'chemical by chemical' approach. In this approach, the mixture is considered as having its own physicochemical properties (such as water solubility, octanol–water partition coefficient and vapour pressure) and degradation processes (e.g. hydrolysis, biodegradation, and photolysis). The obvious problem with this approach is that the determinations of process rates in the laboratory will probably reflect only those compounds that are most volatile, sorptive, and degradable, and that the remaining mixture may differ greatly in composition and properties.

(3) The 'representative chemical class' approach may be especially useful where one or more components of the mixture can be identified as being of biological significance and where chemical data exist, or can be obtained, on these components. Frequently, however, chemicals have been selected to represent a class simply because some data existed or because they were easy to analyse, and not because they were really representative of a class or mixture. If this approach is used, its limitations should be fully appreciated.

(4) The 'chemical fractionation' approach may be applicable especially to waste effluents from synthetic fuel production facilities. The mixture is divided into several fractions, each containing chemicals of increasing similarity (Parkhurst, 1982). Each fraction is further analysed to determine chemical fate and transfer properties to be used in modelling. This is conceptually very similar to the 'representative chemical class' approach although there may be greater similarity between chemicals within a fraction than between chemicals in a designated class. A variation of this approach is to evaluate the toxicity of each fraction of the mixture with further analysis restricted to the fraction(s) having the highest toxicity (Noordsij *et al.*, 1983).

Examination of these approaches (Kinerson, this volume) suggests that:

(1) Many transport and transformation processes may be influenced by the presence of other chemicals in the mixture.

(2) Modelling of chemical interactions in a mixture has to await the development of a better scientific understanding.

(3) Attempts to model the fate and exposure of complex mixtures using the 'bulk properties' approach or the 'representative chemical class' approach will increase the uncertainty of prediction while providing few compensating benefits (short-term economy).

2.4 MONITORING

Monitoring may be defined as a series of measurements of a defined variable for a predetermined purpose according to an established schedule in time. The terms 'defined variable' and 'predetermined purpose' are emphasized because far too often monitoring programmes are implemented without sufficient attention being given to the real purpose of the programme or to the use of data. Monitoring can be carried out at several points along the pathways of chemical substances from the source to the target (Holdgate, 1979).

Any monitoring system is an expensive exercise, and the larger the number of variables or chemicals monitored the greater is the cost. Clear and concise problem definition and understanding are thus prerequisites for choosing the most appropriate variables to be monitored. Models can provide useful guidance in designing a monitoring programme. Even so, the design of monitoring networks is not a trivial activity, and without careful attention to the characteristics of the chemicals being monitored and the environmental setting in which they are being measured the concentrations that are measured can be meaningless.

2.4.1 Emission or Source Monitoring

The main objective of emission or source monitoring is to determine the output of mixtures of hazardous compounds related to specific processes or process variables. The source from which the mixture enters the environment may be associated with industry, energy conversion, agriculture or domestic and municipal activities. When setting up this type of monitoring system it is important to determine total emissions as well as concentrations of different chemicals within the emissions.

Two subgroups, external and internal monitoring, may be distinguished; one refers to point sources at the external boundary of an emission generator whereas the other refers to internal point sources. External monitoring is concerned with regulations, standards, and other legal requirements relating to external environmental conditions, plant process control, and emission source data for modelling. Internal monitoring is concerned with regulations, standards, and other legal requirements relating to internal pollution sources (in the working environment and other indoor environments), plant process control, internal emission data for modelling, and control measures for workers' health protection.

2.4.2 Environmental Monitoring

Environmental monitoring can be considered under two subheadings: work environment and outdoor environment.

Monitoring of the work environment provides data required for checking compliance with regulations relating to workers' exposure to hazardous substances and for estimation of occupational exposure to mixtures of chemicals; this may provide information for the establishment of revised limits for single or combined exposures.

Outdoor environment (air, water, soil) monitoring is carried out to:

(1) determine changes in environmental conditions with time;
(2) determine the effectiveness of regulations pertaining to the protection of human health and the environment;
(3) determine compliance with regulations;
(4) obtain additional data on specific environmental problems so as to provide a sound basis for the development of appropriate legislation and other environmental management tools;
(5) validate and refine models;
(6) determine transport and transformation of contaminants in time and space; and
(7) obtain data for human exposure estimation and assessment.

A network of fixed sites for environmental monitoring of mixtures of chemicals is difficult to design. The environment receives emissions from a large number of different sources and all sources are not recorded. The various flows mix and emissions are diluted, and in some cases the pollutants may interact chemically to produce new pollutants. Some airborne pollutants settle on soil, are trapped by foliage or are washed down with rain. Aqueous pollutants may be taken up by water, plants, and animals, or be bound either chemically or physically to sediments.

In addition to monitoring levels in ambient air, water, soil, plants, and animals, environmental monitoring may be defined to include samples of food and drinks, cosmetics, and other consumer products. Monitoring of food and feedstuff is carried out to ensure that food and feedstuff meet health standards, to construct and test food-chain models, and to provide data for estimation of exposure through ingestion of food and drinks. Collection and analysis of samples of cosmetics and other consumer products provide information on possible additional exposure to chemicals contained in these products.

Exposure monitoring at the external surface of the target (receptor) is more difficult to carry out. An example of exposure monitoring is individual surface monitoring of workers exposed to mixtures of hazardous chemicals at the workplace. Very often, however, the samples at the surface of the target are assumed to be similar to samples in the bulk of the medium (air, water); this may not be true, but the sampling is simpler. This simplification may introduce large errors in exposure estimates.

2.4.3 Biological Monitoring

This type of monitoring can be divided into two subcategories depending on the nature and location of the exposed target. These targets may be human populations (including workers), plants, or domestic or wild animal populations. The procedure generally involves one or a combination of several of the following measurements: chemical analysis of biological specimens such as blood, urine, or tissue samples to determine the concentration of different pollutants or their metabolites, and measurement of biological alterations in an organism or population resulting from exposure.

Biological monitoring of workers and of members of the general population is carried out to ensure that the exposure to chemicals is within predetermined limits, and to provide information on exposure for epidemiological studies. Biological monitoring of plants and animals aims at determining levels of environmental pollution and at assessing the effects of pollutants on plants and animals that may or may not be used as biological indicators of contamination.

Methods of biological monitoring are discussed in more detail in section 3 of the Joint Report. Table 2.1 summarizes in a matrix form the various purposes for designing and implementing monitoring programmes.

2.5 ANALYSIS OF ENVIRONMENTAL SAMPLES

2.5.1 Sampling

Sampling is a critical step in the monitoring of environmental pollutants; samples should be representative of the medium that is being sampled. Obtaining representative samples of environmental pollutants requires considerable care in the planning and implementation of sampling. This includes such considerations as sampling methods, choice of sampling sites, way of sampling, and the use of samples.

Some sampling procedures involve continuous measurement of pollutants. In one approach, a sample is continuously extracted from a source or from the environment, prepared if necessary, and transmitted to an appropriate detector (Homolya, 1974). More recently, methods for *in situ* monitoring of pollutants have been developed. These measurements avoid any extraction of the sample; the effluent stream or the ambient compartment itself is used as a chamber for

Table 2.1 Matrix relating type and purpose of monitoring programmes

	Purpose of monitoring											
	Control and technological research					Human health assessment					Evaluation of ecosystem conditions	
Type of monitoring	Development of criteria and standards	Development of regulations	Development of control technology	Modelling	In-plant process control	Workers	General public	Water supplies	Food and feedstuff	Air	Flora	Fauna
EMISSION/SOURCE												
External emissions	×	×	×	×	×		×	×		×	×	×
Internal emissions	×	×	×	×	×	×				×		
ENVIRONMENTAL												
Working environment	×	×	×	×	×	×				×		
Outdoor environment (air, water, soil)	×	×	×	×			×	×		×	×	×
Food				×			×		×			
BIOLOGICAL												
Workers	×	×	×	×	×	×				×		
General human populations	×	×		×			×	×	×	×		
Plants and animals	×			×			×	×	×	×	×	×

analysis (Pitts, 1983). By this method it is customary to measure only one chemical and so this method is mainly useful for measuring the components of a mixture.

The sampling frequency or the interval between sample collections must take into account the rates of removal or degradation processes (e.g. chemical reaction, adsorption, deposition). Many chemicals have a residence half-life of the order of hours to days; other chemicals have half-lives that range from months to years. The rates of removal can often be estimated from the molecular structure of the chemicals using empirical relationships (Kinerson, this volume).

Different sampling techniques, analytical procedures and reporting methods are usually employed in different laboratories. These differences reduce the possibility of obtaining reliable, reproducible and comparable data bases. It is more difficult to obtain reproducible results when using mixtures because the proportions of components in the mixture may change during sampling or storage of the sample. Several national and international organizations have proposed standardized sampling and analysis programmes for air, water, and soil pollutants (Munn, 1973). It may sometimes be desirable to store samples for additional analysis at a later time so as to provide an historical record of environmental contamination; however, this approach may be costly. For further discussion of environmental 'specimen banking' see, for example, Lewis *et al.* (1984).

2.5.1.1 Air Sampling

In order to decide on the most appropriate sampling technique(s) to provide reliable information on concentration, it is necessary to consider a number of factors. Among these are air movements on a meso- and macroscale, and the dispersion of chemicals in these systems, along with the choice of sampling techniques available to deal with these, including the height of the sampling device above ground level. When techniques are not available they must be developed.

Concerning mixtures of chemicals, air sampling techniques that should be given high priority for development are techniques to:

(1) identify, and determine the rate constants for formation of the reactive free radicals that participate in the atmospheric reactions of photochemical smog; and
(2) reduce the interference of other substances with the measurement of the concentration of each compound of interest.

An air sampler may consist of an apparatus or filter to separate ambient particles into several size fractions, and an absorber to sample gaseous components. Since the gases of interest have a wide range of vapour pressures and breakthrough volumes, no one single sorbent can simultaneously collect all of them. Gaseous pollutants may also be collected by the freezing out of each gas at low temperatures (cryogenic techniques).

2.5.1.2 Water Sampling

Adsorption sampling techniques for mixtures of chemicals have also been widely used for ambient water samples. A direct method is to pass the water to be sampled through a series of suitable columns where the components of interest are removed from the water stream (Dressler, 1979; Jolley, 1981). An indirect method is to strip the water sample of its volatile components by bubbling an inert gas through the water sample. The gas stream is then passed through a column containing a suitable sorbent. The subsequent removal of adsorbed compounds is achieved by thermal description or by solvent extraction (Bellar and Lichtenberg, 1974).

2.5.1.3 Soil Sampling

The boundaries of a groundwater aquifer are difficult to determine, and the size and extent of the contaminant plume are not easy to define. Soils are very complex mixtures and the transport of chemical mixtures through this matrix will separate the chemicals due to the differential adsorptivities of components of the mixture to components of the soil (Hamaker and Thompson, 1972; Helfferich and Klein, 1970; Hsieh *et al.*, 1977; Rhee and Amundson, 1982). There is considerable lateral and vertical variability in samples of field soils. Data published on nitrogen distribution in the field apply, in principle, to other chemicals as well (Nielsen and MacDonald, 1978). In the aerobic zone of the soil, pH and organic matter content can strongly influence the solubilization and transport of elements (Ball *et al.*, 1979; Cataldo and Wildung, 1978). Measurements of concentration profiles in saturated and unsaturated soils require much attention to detail (Barber *et al.*, 1981; Cherry *et al.*, 1983).

The development of more sensitive techniques to sample groundwater for both organic and inorganic pollutants and their transformation products is a high priority. The research of Cataldo and Wildung (1978) indicates a strong need to develop analytical procedures for the determination of the chemical characteristics of metal complexes in soil solutions. Because of the nature of these metal complexes, careful attention must be given to the separation procedures used to isolate them. The formation of these complexes is mediated by microorganisms, and during sample preparation artifacts may be introduced into the sample forming complexes different from the ones present in the soil.

2.5.1.4 Sampling of Biota

Biotic samples are particularly useful in the study of mixtures of chemicals in the environment because they may accumulate a variety of chemicals released at different times and, if the organism is mobile, different places. The interaction and transformation of chemicals may be enhanced through metabolism, and organisms not only can be used to monitor exposure, but also may be used to determine the biological effects of the mixture. The quantity of chemicals in the organisms is an index of both the concentration of chemicals and their bioavailability. Another advantage of biotic samples, common to the monitoring of both mixtures and single chemicals, is the accumulation of chemicals in the biota in concentrations greater than that found in the environment. This is especially valuable for chemicals that are present in concentrations too low to be readily detected by traditional means, such as methyl mercury in water.

Most of the biota monitoring programmes operate in aquatic environments and are concerned with such compounds as PCBs, radionuclides, or heavy metals. The biotic species used for these programmes are normally fish, mussels, oysters, and algae (Phillips, 1977, 1978). For air monitoring, a common technique is to analyse mosses and lichens (Carlberg *et al.*, 1983).

There are problems in the interpretation of biotic sampling results which must be kept in mind. One important limitation is that the relative proportions of chemicals in a mixture that are concentrated in the biota are not the same as they occur in the environment. The accumulation of a chemical in an organism is meaningless unless the characteristics of the entire ecosystem of which that organism is a part are considered. Because of species variability, and the differences in mechanisms of tolerance to chemicals, metabolic pathways, and other pharmacokinetic properties of different members of an ecosystem, the singling out of a specific organism as an indicator of the fate of chemicals in the environment is erroneous. This concept needs to be expanded, and studies should be conducted on the range of variability in the tolerance and toxicity of different species to mixtures of chemicals (see section 7). Methods should also be developed to examine the comparative effects on entire communities, e.g. what level of stress will cause the complete collapse of a community*. The use of indicator organisms is a useful tool, but if it is to be an effective method to monitor the transport and transformation of chemicals in the environment, a much broader variety of organisms must be sacrificed.

2.5.2 Sample Preparation and Analysis

There exist a great number of analytical approaches for quantitative determination of chemicals in a given environmental sample.

The selection of a single chemical as representative of a complex mixture may often be sufficient to identify a source of pollution, measure changes in pollution levels, or indicate the presence of a particular class of pollutants (Becher and

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* For more detail, the reader should consult Dr Ronald Mount, Environmental Research Lab-EPA, 6201 Congdon Blvd, Duluth, MN 55804, USA.

Bjørseth, this volume). For instance, sulphur dioxide is often used as an indicator of the reducing type, and ozone is used as an indicator of the oxidizing type, of air pollution in larger environmental pollution monitoring programmes (Munn, 1973). The major disadvantage of using single chemicals is that no information is obtained about the qualitative composition of the mixture.

Detailed characterization of the chemical components in environmental samples requires analytical techniques that are specific enough to quantitatively distinguish a large number of compounds of differing chemical properties. Very often crude separation procedures are used as a first step (Becher and Bjørseth, this volume). Selective extraction, especially solvent extraction, is widely used. Recently, chromatography has proved to be a very useful tool for the isolation of compound classes from mixtures.

Predetermined analysis is aimed at the identification of specific compounds such as those on a priority pollutant list. This list affects the selection of the method, as sample processing and measurement techniques may be optimized for a particular pollutant. Detailed chemical and instrumental procedures are sometimes used to isolate pollutants from mixtures, minimize known interferences, concentrate components of the mixture, and measure the quantities present with general or selective detectors. These procedures have been applied, for example, to the analyses of polycyclic aromatic hydrocarbons (Bjørseth, 1977), PCBs (Ofstad *et al.*, 1978) and polychlorinated dibenzodioxins (Rappe, 1984).

A preliminary approach to the analysis of compounds in environmental samples should not be restricted to identifying a predetermined list of compounds. Rather the idea is to identify the broad spectrum of chemicals present. Sample preparation should be designed to preclude losses of significant components, and to minimize the possibility of sample contamination. Frequently, the sample is divided into classes of compounds (fractionated) and general purpose chromatographic methods are applied for the separation of individual compounds in each group (Kveseth, 1981). The biological activity of a particular compound is highly dependent on its molecular structure. Sometimes chemical characterization of the fractions of the whole mixture is replaced by direct toxicological screening (Alfheim *et al.*, 1984) followed by chemical characterization of those fractions in which significant toxicity was observed.

2.6 CONCLUSIONS

(1) Free energy and molecular orbital approaches could provide useful methods of examining rates of chemical transformations. Photolysis and biodegradation are the major routes of chemical transformation; volatilization and sorption are physical processes altering the composition of chemical mixtures during transport.

(2) In some cases the techniques for modelling the transport and transformation of single chemicals can be useful for developing models for mixtures as well. Environmental models can be used for designing monitoring programmes and determining the kind of data to be acquired, and can aid in the interpretation of data.

(3) Modelling the fate of, and exposure to, complex mixtures using the 'bulk properties' approach or 'representative chemical class' approach may achieve short-term economies but they increase the uncertainties of prediction. Effective modelling of chemical interactions is currently not possible.

(4) Any programme for monitoring mixtures in the environment should have a clearly defined purpose related to estimating exposure or the accumulation of chemicals in environmental compartments. There are three basic types of monitoring: source, environmental, and biological.

(5) It is difficult to obtain reproducible results in studies of mixtures because many different sampling techniques and analytical procedures are available and are employed in various laboratories. Also, the components of a mixture will change with time.

(6) Monitoring a single chemical can often be used to identify a source of pollution, measure changes in pollution levels, or indicate the presence of a class of pollutants; however, no information is obtained about the composition of the mixture. Detailed characterization of the individual components of a mixture is necessary to identify the most biologically active constituents.

2.7 RECOMMENDATIONS

(1) Laboratory tests, field studies, and modelling programmes should be coordinated to establish the conditions under which models for single chemicals can be used to describe the transport and transformation of mixtures of chemicals.

(2) Before reliable models for the behaviour of mixtures can be developed, the molecular interactions among components of mixtures must be examined. Special attention must be given to those changes that influence chemical and biological reactivities.

(3) It is necessary to estimate transfer coefficients that describe chemical transport due to large-scale (e.g. rainfall) and small-scale (e.g. molecular behaviour) variables. It is also necessary to determine the kinetics of processes that remove or retain chemicals. These processes include chemical reactions, biological transformations, adsorption/desorption and volatility.

(4) Exposures of human individuals and populations and of non-human biota should be estimated not only in terms of chemicals originally present in the mixture but also in terms of products of chemical interactions.

(5) When environmental monitoring is carried out for the purpose of human exposure estimation or for epidemiological studies, the analysis of samples to

identify and measure the components of mixtures should be as complete as feasible.

(6) A high priority should be given to research to improve methods for biological monitoring of mixtures, and to correlate environmental exposure estimates with the results of biological sample analysis and biological indicators of exposure.

(7) Sampling procedures for mixtures of chemicals in soils must also include measurements of moisture content, rain infiltration, groundwater flow, soil composition, and other important hydraulic and dispersive properties of soils that affect chemical transport.

(8) Before studies of mixtures can be made, studies should be made to elucidate the nature of heterogeneous chemical and biological reactions. These should include theoretical and laboratory explorations of molecular properties and reactivity.

(9) The use of indicator organisms to measure environmental contamination should be expanded to organisms that display a wider range of tolerance to toxic chemicals.

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