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Environmental Fate of Mixtures as a Background for Human Exposure Monitoring

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ABSTRACT

Numerous compounds are continuously released into the environment during their production and use. The resulting mixtures contaminate the environment and can be a potential threat to organisms including man. Monitoring programmes are designed to assess levels of individual compounds and mixtures in various compartments of the environment. Such levels depend on the release rate and the environmental fate, which in turn is strongly influenced by physicochemical properties and stability. Monitoring can be carried out by chemical, mainly instrumental, analysis (chemical monitoring), analysis of humans and other biological organisms which are representative of exposure (biological monitoring), and observation of biological effects (toxicological monitoring).

1 INTRODUCTION

In the last century, the industrial production of chemicals expanded very fast. The number of compounds of commercial interest grew to over 50 000, production volumes increased considerably, and more than one million tons of several compounds are now produced per year. Approximately 50 substances are produced in amounts of more than 100 000 tons/year, and a few hundred over 10 000 tons/year (SRI, 1980). This enormous chemical production and its continuous growth require regulation and control of the production, use, and environmental release of potential pollutants.

Chemical monitoring is part of these regulatory procedures. Other measures are the setting up and standardization of pre-production environmental screening tests for new chemicals (OECD, 1981).

During the last decade, scientists as well as governments in most technically developed countries became more interested in monitoring programmes for chemicals. Pollution problems on the one hand and accumulating scientific knowledge of environmental processes and toxicological effects on the other were largely responsible for the progress in the regulatory monitoring of production. Monitoring of chemicals can be divided into two different areas: (a) biological/toxicological monitoring, and (b) chemical monitoring.

In chemical monitoring the basic objective is the registration of concentration changes in time and variations with geographical location. In toxicological monitoring the effects of the concentrations are observed, as they vary in time as well as in geographic distribution. Chemical monitoring of environmental contaminants may be done for a number of reasons (Holden, 1975): (1) to indicate changes in contamination levels with time; (2) to indicate biological transformations of the pollutant in time; (3) to enable comparison of contamination levels between different areas; (4) to identify highly contaminated areas which can lead to the identification of the pollutant source; (5) to indicate the potential environmental risk to species and ecosystems, especially when used in conjunction with biological (toxicological) monitoring; (6) to indicate the quality of human food, drinking water and air; and (7) to indicate the effectiveness of the control measures used for protection of the environment.

The parallel between the sequence of chemical cycles of compounds produced and the sequence of environmental safety testing and control, of which monitoring is one part, is illustrated in Figure 1.

2 EXPOSURE

From the perspective of environmental health chemistry, humans can be exposed to chemicals by different routes (Hutzinger, 1980). Exposure of individuals is, in



Figure 1 Chemical production and environmental safety testing and control

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Occupational exposure



many cases, primarily determined by their behaviour patterns (Figure 2). Persons working in paint factories, for instance, will be exposed to higher concentrations of organic solvents in air than will others. Similarly, differences in food habits are responsible for disparities of polychlorinated biphenyl (PCB) uptake between fish-eating persons and vegetarians.

In addition to human behaviour, differences between properties of chemicals determine the importance of specific routes to the total human exposure. For example, PCB uptake by air is not important in contrast to the respiratory uptake of carbon monoxide. This means that assessment of environmental and human safety must be influenced by the fate and properties of chemicals. As stated above, at least five types of chemical monitoring programmes can exist: monitoring of (1) occupational exposure concentrations in workrooms; (2) direct exposure concentrations such as food, drinking water, drugs, etc.; (3) pollution sources such as waste water or smoke stacks; (4) environmental concentrations; and (5) environmental fate.

The first three types of monitoring programmes have existed for years in many countries (SRI, 1981). Government laboratories, for example, have been involved in analysis and quality control of foods for decades to ascertain absence of harmful levels of potentially toxic compounds from materials used for human consumption. At the moment the most advanced monitoring programmes function in this area, for example in drinking water quality control. Source monitoring has been part of the production process control by many industries for years. Originally many plants themselves monitored their waste output into the environment. Recently regulatory agencies started more frequent monitoring programmes in the environs of plants and factories which could release potentially harmful pollutants.

Workroom monitoring for certain industries is regulated by law in many countries. Increasingly stringent requirements for worker safety, as expressed in the lowering of maximum acceptable concentration (MAC) values (TLV), will demand more and better planned monitoring of actual concentrations in the workplace.

The only type of monitoring that is not used in practice on a large scale is environmental fate monitoring. In addition, knowledge of environmental fate processes has rarely been used in the other monitoring types in the past. The present efforts in environmental fate monitoring have evolved from traditional types of programmes. Expansions of the programmes often resulted in useful monitoring networks. For example, some sulphur dioxide, PCB, DDT, and other pollutant programmes are of high quality and give useful information about the environmental distribution of these pollutants. Although these recent developments are of interest, they are only the beginning of more fundamental fate monitoring which is of importance for human exposure. This is particularly true for human exposure to mixtures of chemicals.

In principle man can be exposed to three types of chemical mixtures, which, theoretically, can originate from (a) one production process, (b) coincidental presence of components in a sample, and (c) similar chemical and physico-chemical properties.

- (1) The first type of mixture is formed at a certain time and place, and has a certain composition. These mixtures may result from chemical factories or from incineration processes and are not necessarily composed of compounds having comparable chemical structures or properties. For many well-controlled processes these mixtures may have relatively stable compositions, e.g. cosmetics or artificial food additives. However, many minor composition changes may occur which can be very important toxicologically. When the production process varies in time the created mixture can be different, which makes comparison difficult.
- (2) The second type of mixture to which biota can be exposed is the coincidental mixture. These mixtures are composed of compounds that occur by coincidence, at the time and place of sampling in the environment. No similarity need exist between the single compounds of the mixture. This coincidental presence may be typical of the mixture over long periods or it may result from a single release.
- (3) The third type of mixture consists of compounds with similar physical and chemical properties. Because of the similarity in their physicochemical behaviour, many compounds will be present in the same environmental sample. Because of the various distribution and transformation processes of individual compounds, as well as the continuous variation of release, the composition of the mixture changes in the environment.

The first two types of mixtures are found not only in environmental samples, but also in source, occupational exposure, and direct exposure monitoring. Although the latter types are typical results of fate processes, they are also of interest in food and drinking water monitoring.

3 ENVIRONMENTAL FATE PROCESSES

The environmental behaviour of single compounds or mixtures is a combination of transformation and distribution processes. These processes determine not only the places where compounds will be present, but also the amounts and the composition of mixtures which are crucial for monitoring (Figure 3).

Variation of the chemical composition of mixtures after production and environmental release is a continuous process. Many distribution processes that influence those changes in composition are governed by the physicochemical properties of the substances. Hydrophobicity, volatility, solubility in water, presence of polar groups, and other properties are of interest for the distribution behaviour. Final disposition of chemicals is also influenced by transformations for which, for example, biochemical and thermal stability are important properties (Hutzinger and Veerkamp, 1981).

Although some of these fate processes are properly understood at the laboratory level, most of the relations between environmental behaviour and chemical structure variables are oversimplified. Scientific knowledge is increasing rapidly in this area, and in many cases it is sufficient to use it as a background for environmental fate monitoring programmes (Hueck-van der Plas and Hueck, 1979).

3.1 Environmental Simulation Models and Monitoring

Simulation models of transformation and distribution processes in nature at different levels are available. Some of them are concerned with only small parts of the total environment (microlevel), for example at certain small ponds or rivers. Others focus on the global environment (macrolevel). Proper simulation at the mesolevel (e.g. Rhine River in combination with North Sea) does not exist at the moment.

The potential of simulation models in the creation of monitoring programmes is at present restricted. For the macrolevel environment, quasithermodynamic equilibrium assumptions are made most of the time (Haque and Freed, 1974; Mackay, 1979). This includes assumptions that global mixing is sufficient by



Figure 3 Environmental fate of chemicals

conventional long-distance transport systems, and that transitions between environmental phases are well described in terms of mass-flow relationships. To some extent transformation processes can be incorporated in these models (Mackay, 1979). The central problem in these models results from the fact that equilibrium or steady-state levels for many environmental compartments can be calculated, but they will never be reached. This is partly due to the insufficient descriptions of transition processes used in the models. Another fundamental problem is the description of the kinetic rates of most processes. Although both of the above problems will restrict the use of models to set up monitoring programmes, these fate models will provide an important background to the monitoring of global pollutants which include persistent chlorinated aromatic compounds such as PCBs, sulphur dioxide, nitrogen oxides, and some heavy metals. At the environmental microlevel, quasithermodynamic fate models are of little value for monitoring for at least two reasons. First of all, the environmental microsystem in question is not isolated and is strongly influenced by its surrounding systems. These interactions between microsystems are intensive, which means that variations in neighbouring systems directly influence the behaviour of compounds in the system under investigation. Expansion of the proposed monitoring programme to a larger area is not possible because the modelling problems at the mesolevel are even more complex. The second type of problem at the microlevel is the dependence of the usefulness of a model on the type of pollutant source. In global monitoring the source type is not relevant, but at the microlevel this is of major importance for the type of monitoring that must be used. For example, the release of lead or nitrogen oxides from automobile fuel is very dispersed at microlevels whereas the release of effluent from a chemical plant into a pond is geographically concentrated. Both these extremes need different types of fate monitoring. Although many problems arise at the macroas well as the microlevel, there are existing models which can be used for monitoring at these levels. At the mesolevel even more complex problems arise. A quasithermodynamic description cannot be used for several reasons and, in addition, interactions between different types of pollutant sources create other problems.

3.1.1 Some Problems of Models and Chemical Monitoring at the Mesolevel. An Example: Monitoring of Pollutants in the Aquatic Environment

Transformation and distribution processes of pollutants in the aquatic environment and in other natural compartments are largely determined by the structural properties of the compounds. Also, the composition of that particular aquatic area is of importance to the behaviour of the substances. For example, the persistence of compounds capable of undergoing hydrolysis will be determined by the pH of the water, and rate of degradation by microorganisms of the compounds will be influenced by the water temperature and other factors. One of the crucial processes in the aquatic environment is adsorption of pollutants on sediments or particulates. Adsorption/desorption processes are generally described by the adsorption isotherm given by Langmuir or Freundlich.

For the majority of non-ionized organic compounds of current industrial and environmental interest, the adsorption process is strongly influenced by the organic matter content of the adsorbent. This means that after the release of a certain amount of pollutant the percentage adsorbed will depend on the composition of the adsorbent. Thus, the release of chlorobenzenes in a sandy area will result in a different environmental distribution than release into a peaty area.

Adsorption is not only of interest in itself but it also determines, to a large extent, other processes. The mobility of chemicals is strongly reduced after adsorption. Particulates in the hydrosphere, like rivers, are transported many times more slowly than the streaming water and dissolved compounds. Even between particulates, differences in transport rates exist; the lighter particulates move faster and the heavier move very slowly because of rapid sedimentation. All these aspects are of interest for the environmental behaviour of the pollutants. No adsorption means transportation is as fast as the streaming of the water. Adsorption to heavy particulates means rapid sedimentation at the dumping place. Besides the total adsorption potential, which is described by the Langmuir and Freundlich isotherms, the rates of adsorption and desorption are also important for the determination of fate. Rapid adsorption means fast removal of the pollutant from the major transport system. On the other hand, slow desorption from the sediment results in a continuous release of pollutants into the environment. This can result in a persisting pollution concentration long after industrial production and release have been stopped (Figure 4).

Adsorption is closely related to other fate processes in the aquatic environment. Bioaccumulation of hydrophobic chemicals by fish, for example, is much faster by direct uptake from water than by internal uptake from the intestinal tract. Rapid adsorption in this case means reduction of the bioavailability of the compounds. The reverse can be true for organisms that live in the sediment; because of the sedimentation of heavy particulates, pollutants will be available for filter feeders (mussels, etc.) if the adsorption is a reversible partition process. Also, in volatilization, biodegradation, and other transformation and distribution processes, adsorption plays a major role. This knowledge ideally should influence the set-up of the aquatic monitoring programmes, for example a separation of the sample into dissolved compounds and particulates. Partition of the pollutant in the different sample fractions gives information about the potential transport rate, the mean residence time, availability to biota, and other environmental processes (Figure 5).

In addition to fish and other biota, sediment and water have to be analysed as well. The particulates fraction, in particular the size and weight distribution, is important in assessing the mean transport rates and the potential bioavailability

Dumping of three compounds



- 11 Slow adsorption, rapid desorption
- III No adsorption



Figure 4 Dumping of three compounds. Compound I: rapid adsorption, slow resorption. Compound II: slow adsorption, rapid desorption. Compound III: no adsorption, Dumping time $= t_0$. Because of the rapid adsorption of I, this compound creates a local, highly concentrated pollution at position A, which is not significantly available to biota. Dumping of compound II results in a long-lasting pollution of low concentration at all positions A-D, which is more bioavailable. Compound III gives rise to a short, intense exposure of biota at all positions



Figure 5 Fate processes in aquatic environments

of adsorbed pollutants. Analysis of sampled waters without separating the particulate fraction can mean that the detected amount of pollutant was adsorbed to floating particulates. The potential reduction of bioavailability after adsorption probably says nothing about the potential environmental risk. This is of interest not only for biota living in water that will be used for human consumption (fish), but also for the use of this water as a source of drinking water (Figure 6) (Miveos, 1982).

4 MONITORING OF MIXTURES

Aside from the intensive interrelation between released chemicals and natural environment, disposition of mixtures creates another dimension of complex problems for monitoring. These problems have, to some extent, a toxicological/biological background. As mentioned above, mixtures in the environment can be divided into at least three different types; often combinations of chemicals cause potentially higher risks for biological damage to organisms of ecosystems than occurs with single compounds (Figure 7). This is a result of the potential synergistic toxicological action of the combined exposure. Of course the reverse (antagonistic effects) can also take place. This new uncertainty is an inherent problem with mixtures. Interpretation of monitoring results is for this reason a totally different task than for single compounds. Many interactions of substances are known at the moment. Also, interrelations between chemicals and particulates, fog, or other natural conditions are often described. These



Figure 6 Important compartments of the aquatic environment that should be analysed in an environmental fate monitoring programme together with the relevant fate processes



Figure 7 Joint action of two chemicals A and B

interrelations resulting from the environmental behaviour of substances and mixtures must be used in chemical monitoring. Monitoring of nitrogen oxides and related smog compounds, for example, must be intensified on sunny days in heavy traffic areas because the potential pollution load on these days is greater.

Because many distribution and transformation processes influence the environmental behaviour of the single compounds of a mixture, the mixture composition is changing continuously. After release from a mixture based on the production process, the unstable and degradable compounds may disappear after some time. The more stable components of the mixtures persist. The persisting compounds may have different distributional behaviours which result in further separation of the original mixture. For example, from an industrial PCB mixture the lower chlorinated biphenyls are degraded by microorganisms, but the higher chlorinated compounds persist. Depending on the differences in hydrophobicity, molecular configuration, and potential to metabolize, these compounds will adsorb to sediment or accumulate in organisms. As an overall result, the composition of PCB mixtures in organisms and sediments is completely different from that of the PCB mixtures originally released.

This means that the analytical composition of the recovered mixture depends on the amount of sampling and the location in which the mixture is sampled. Interpreting the relation of the analysed composition to the original mixture composition at the time of release is generally impossible.

Aside from the transformations and distributions that are of importance for released mixtures, fate processes also determine the disposition of other

pollutants. This results in the creation of new mixtures in environmental samples with components from different origins. Many mixture combinations are a result of the similarity of physical and chemical properties of the constituent compounds. Combinations of PCBs, DDT, toxaphenes, and other persistent organic chemicals are examples of these newly created mixtures. Also, totally different pollutant compounds can be present in environmental samples as, for example, mercury and PCBs in fish. In this instance coincidental occurrence is not based on comparable fate behaviour.

The potential risks from the environmental health safety point of view cannot be estimated in most of these cases. Toxicological interrelations of different types of compounds are scarcely known, and even the biological availability of individual compounds in the presence of others can vary. Due to the continuous variation of the chemical compositions of mixtures, standardization of sampling, preparation, and final analysis are problematic.

4.1 Chemical Monitoring with Biota

When studying the environmental fate of chemicals or pollutants, or assessing the exposure of organisms or man to pollutants, biological information can support the physicochemical method of pollution monitoring. In many cases, organisms are used as indicators of the presence of pollution. The biological or toxicological impact of single compounds and mixtures cannot be adequately estimated by chemical analysis alone, even if the analysis is straightforward.

Alternatively, measuring only biological responses or changes in ecosystem characteristics, without knowing pollutant concentrations, is also insufficient in environmental fate monitoring. Therefore, adequate information of dose–response curves must include an array of information about (a) the concentration of the chemicals or other pollutants being tested, (b) ecosystem quality and exposure conditions, and (c) the observed species. Biological evidence, however, can find useful applications in correlating exposure concentrations and biological response to estimate the potential health risk for humans exposed to environmental pollutants.

Active use of biota in monitoring can be divided into two types: (a) active toxicological monitoring, and (b) active biological monitoring. The first type of monitoring with biota is used to prevent release of high levels of harmful contaminants. Many indicator species of ecosystems can be used to warn against too high pollution levels. This use of biota for toxicological monitoring is possible in many different situations (Cairns and Van der Schalie, 1980) and can vary from early warning systems with fish in waste effluents, to damage of trees due to acid rain. The other potential use of biota in monitoring has no toxicological implications. The organisms act solely as a pollutant indicator by means of the pollution content which is assumed to be an index of the average

availability of pollutants to biota at the collection site and its close surroundings (Phillips, 1978).

Most of the developed biota monitoring programmes are conducted in the aquatic environment and are based on or concerned with, for example, the environmental fate of organochlorine compounds such as PCBs, radionuclides, or heavy metals. The species used for these programmes are normally fish, mussels, oysters and algae.

The major advantages of the use of biological indicators over the usual physicochemical methods for monitoring are: (1) direct measurement of the biologically available amount of the total pollutant, which cannot be determined from studies of water or sediment; (2) time integration of the ambient pollution concentration at the site of a collection, which can only be elucidated from water analysis by the study of a large number of samples; (3) the high concentrations of pollutants obtained in comparison with the surrounding environment which can reduce detection problems; (4) the relatively low cost; and (5) the possibility to monitor a large variety of pollutants at one time.

However, the net uptake of pollutants such as heavy metals or organochlorine compounds by indicator organisms is subject to a variety of biological, physical, and physiological variables. The effects of natural or sampling variables may interfere with the correct interpretation of results from indicator surveys for pollutants. Variables that must be considered in indicator surveys are: (1) the choice of the indicator organism; (2) body lipid content; (3) physiological factors such as age, size, weight, sexual cycle, reproduction, shell deposition, etc.; (4) effects of season; (5) salinity; (6) temperature; (7) geophysical differences (at various collection sites); (8) interactions between individual chemicals; and (9) toxicity of chemical compounds. Indicator surveys provide valuable methods for monitoring the exposure to chemical mixtures in specific environmental compartments. This is due to their ability to accumulate various substances at certain places during a certain period. These typical biota properties make biological monitoring a very useful support to physicochemical detection methods of pollutants in the environment.

5 CONCLUSIONS

To develop more sophisticated monitoring programmes to assess and control exposure of man to mixtures of chemicals, some modifications in the approaches of many programmes are needed. In exposure monitoring in the workplace, present intake models for man are generally sufficient. These models, in combination with monitoring data, result in useful estimates for the average exposure in those situations. In food, water, and other types of direct exposure monitoring, the same developments exist and can be used in practice at the moment. Traditionally 'source monitoring' programmes had defined approaches. Monitoring the environmental fate of single compounds and mixtures

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to monitor the exposure of man requires totally different philosophies; the pathways and nature of the contaminants must have a central place. The continuous variation of absolute concentrations of compound mixtures and also the composition changes make the modelling of potential exposure very difficult.

This is of interest not only for the design of monitoring programmes and for the installation of data collection network, but also for simulation models to interpret these data. Further developments in environmental fate monitoring must be influenced by knowledge of transformation and distribution processes. Although at the moment knowledge of typical fate problems is not always sufficient, neglecting them may result in inefficient monitoring programmes and a waste of money and scientific manpower. Biologically active forms of the contaminants present must also be considered. The same is true for the potential transition from one chemical form to another, and for the transfer from one environmental compartment to another.

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