Appraisal of Tests to Predict the Environmental Behaviour of Chemicals
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CHAPTER 1
The Role and Nature of Environmental Testing Methods

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1.1 INTRODUCTION

The major concern of ecotoxicologists is the recognition and prediction of hazards from the large and ever-increasing array of chemicals released into the environment. Hazard refers to the potential for deleterious impacts of a chemical on specific organisms or on the ecosystem as a whole, when exposed at toxic concentrations. The ecotoxicologist encounters a multifaceted problem that can be conceptualized as containing three aspects: (1) the detection, quantification and prediction of the environmental behaviour of chemicals, (2) the estimation of exposure, (3) the diagnosis of toxic effects and the estimation of their magnitude.

An accurate assessment of the environmental behaviour of chemicals is essential to the identification of high risk zones of exposure in the environment and hence to the prediction of subsequent effects on the biota. The objective of this presentation is to define some of the problems encountered in characterizing the environmental behaviour of chemicals and in particular, to evaulate relevant testing methodologies. Such a critical evaluation is a necessary step to integrate the hazard assessments by ecotoxicologists into appropriate management strategies. The complex problems encountered in estimating exposure and toxic effects have been and are currently being addressed elsewhere by national and international scientific organizations (e.g. Butler, 1978; NAS, 1981; Sheehan *et al.*, 1983; Vouk, in preparation).

1.2 DESCRIPTION OF THE PROBLEM

Since Rachel Carson's *Silent Spring* warned of the dangers of synthetic chemicals accumulation in the environment and the subsequent increased incidence of toxicity to biota, more and more attention has been directed toward the elucidation of the environmental behaviour of pesticides, drugs, industrial organic compounds and certain heavy metals. However, the number of chemicals for which transport, abiotic and biotic transformation, as well as accumulation patterns have been described is minuscule in comparison to the approximately 50 000 synthetic and potentially toxic compounds which are still untested.

The public demand for increased environmental protection has placed pressure on regulatory agencies and consequently on the scientific community to assess or predict the hazard of potentially toxic chemicals as quickly as possible. The assessment problem is made more difficult by the lack of reliable data on production and use of many synthetic compounds, a disturbing lack of information on effluent composition, and the amounts and sites of releases. Many of the newer synthetic compounds also represent classes of molecules with which environmental chemists, biochemists and toxicologists have had little previous experience upon which predictions could be based. Many are toxic and others can be converted into hazardous substances in nature. The problem is particularly acute as the persistence and fate of these compounds depend as much on environmental factors as on the properties of the chemicals themselves.

Although synthetic organic chemicals by virtue of their numbers, unfamiliar properties and potential for persistence, constitute the bulk of the ecotoxicological testing burden, other organic and inorganic compounds are serious toxic pollutants and must be considered in any testing program. Certainly emphasis must be placed on evaluating the behaviour of new synthetic compounds prior to their use and release. However, the goal of any testing program in as much as possible must be to incorporate experimental methods applicable to evaluating all chemicals.

The term environmental behaviour, itself, encompasses a variety of complex and interacting processes which ultimately define the concentration and distribution of the chemical in the ecosystem. These processes include (1) inter- and intra-media transport, (2) abiotic and biotic transformation and degradation (including mineralization) and (3) partitioning and bioaccumulation. The partitioning of a chemical within an ecosystem is related to its affinity to various components within the system. When the appropriate information is available on input, transformation and degradation rates, the expected distribution can be described with mathematical equations (Mackay, 1979; Neely, 1979). Problems involved in modelling chemicals transport were discussed by Miller (1978) and a variety of physical transport models for air and water pollutants have been developed (e.g. Knox, 1974; Wagenet *et al*., 1978). Many of the abiotic processes contributing to chemical change and movement in natural systems were reviewed by Korte (1978). He emphasized the significance of abiotic degradation of organic compounds under atmospheric conditions. The importance of biotransformation of synthetic chemicals in terrestrial and aquatic systems has been consistently stated. The general types of metabolic reactions producing structural changes in environmental chemicals have been recently reviewed and will remain an important ongoing research interest (Klein and Scheunert, 1978; Alexander, 1981). Although there is a basic conceptual understanding of many of the abiotic and biotic processes affecting the environmental behaviour of chemicals, the identification of individual reactions and the quantification of these processes remains the primary goal of environmental testing and a necessary step towards improving the prediction of behaviour of chemicals released into the environment.

The obvious need for a systematic approach to the assessment of chemical behaviour in ecosystems has been extensively discussed (e.g. NAS, 1975). The *laissez-faire* experimental approach has lacked the efficiency to cope with the expanding assessment problem. Results obtained from such procedures were often dependent upon specific characteristics of the test systems and therefore, of little use in providing predictions of environmental behaviour in other situations or in establishing general behaviour patterns for various chemical types (NRCC, 1981). These approaches have also hampered the interlaboratory comparison of data essential to the comprehensive evaluation of individual experimental programs (Korte and Rohleder, 1981).

Inevitably, many policy decisions regarding chemical hazards will, for the most part, be based on extrapolations of environmental behaviour from knowledge of the physical and chemical properties of these substances and short-term small-scale laboratory experiments and field simulations. The selection of appropriate experimental methods is thus critical to the relevance and utility of any testing program.

Much of the past scientific effort to develop methodologies in this area has been applied to few selected groups of chemicals. These 'model' chemicals, often initially studied because of immediate public concern rather than systematically chosen to evaluate some aspect of environmental behaviour, have now achieved the status of 'bench-mark' compounds. Their well-studied properties are being used to indicate the probable behaviour of similar less well characterized chemicals. Organochlorine pesticides, for example, have become the model for bioaccumulation and persistence, synthetic detergents for biodegradation, SO_2 for atmospheric transport, radionuclides for total distribution and global transport and heavy metals together with fertilizers for analysis of soil adsorption and plant–soil interactions. The question of the applicability of these chemical models needs to be critically examined. Certainly, some of the chemicals chosen as models are not generally representative of typical environmental behaviour nor are they necessarily the most hazardous. For instance, extensive evaluations have been done for DDT and its metabolites, including numerous bioaccumulation studies with mammals, although there is little evidence of toxicity in mammals that is attributable to this accumulation. Mercury has received a disproportionate research effort among heavy metals, but because of its methylation by biota, it is not necessarily representative of this group of elements. Extensive public pressure on the detergent industry has prompted it to carry out extensive work on biodegradation, yet their model compounds often differ greatly from more persistent synthetic industrial compounds.

Therefore many data on specific processes come essentially from a limited group of compounds, and the applicability of these models and of the testing procedures developed specifically for their examination to other chemical groups is not well established. The use of bench-mark chemicals is essential to hazard screening programs but the choice of the appropriate chemical model must be systematic and should be based on criteria such as those discussed by Roberts *et al*. (NRCC, 1981).

1.3 ENVIRONMENTAL FACTORS

The specific abiotic properties of the natural system and the composition of the biotic community have dramatic effects on the behaviour of environmentally released chemicals. For this reason one would not expect the same processes to dominate in the atmosphere and also in soil and water. Consequently the focus of experimentation must necessarily be specific to the environmental compartment in which the chemical occurs.

Atmosphere

Abiotic processes are virtually the only ones operating in the atmosphere making it unique among environmental compartments. Assessment of abiotic fate should concentrate on photochemical decomposition under simulated atmospheric conditions. Although photochemistry is a well developed science, simulating atmospheric conditions is extremely difficult. A major problem has always been to describe properly the chemistry of the atmosphere. Theoretically, $OH^{\cdot}$ and other reactive species are formed from solar irradiation in the atmosphere and these react with other atmospheric chemicals. This has been shown by the irradiation of water vapour but quantification of these processes in the atmosphere is lacking in most cases.

Little is known of the half-life time of free molecules and radicals (see Perner, Section 2.2) in this dynamic medium. The important area of abiotic stability on aerosol surfaces is also poorly investigated. Nevertheless, the atmosphere is believed to be an important sink for many chemicals. Thus, effective methodologies for describing chemical behaviour in the atmosphere are essential.

At present there are four main approaches to the developing of testing procedures to predict the stability and fate of chemicals in the atmosphere. These include examination of processes in the gas (see Barnes and Zabel, Section 2.3), liquid and adsorbed phases (see Parlar and Kotzias, Section 2.4) and in smog chamber systems.

Aquatic Ecosystems

In recent years with the increasing evidence of pollution in aquatic systems, attempts have been made to develop specific methodologies for the assessment of the environmental behaviour of chemicals in water. Both abiotic and biotic processes have been demonstrated to be important. Attempts have been made to standardize tests for microbial degradation of chemicals in sewage and in surface waters. The US Environmental Protection Agency has proposed a test for primary photodegradation (see Hulpke and Wilmes, Section 3.1). Although the laboratory and field procedures for determining the presence and the half-lives of chemicals in aquatic systems have received general acceptance, the complexity of natural aquatic systems has made exact quantification and prediction of behaviour from laboratory experiments extremely difficult. The chemical characteristics of water itself are difficult to define due to the many natural and introduced impurities in all waters. In additional, the reactions and transport processes of chemicals in aquatic systems are highly dependent upon suspended particles, bottom sediments, living and dead organic materials (see Scheunert, Section 3.2). Natural variations in chemical composition of water and sediments, in ambient temperature and in biotic components frustrate estimations of average pollutant concentrations. Therefore, simulation studies of a 'natural' aquatic system can only be expected to yield information approximating behaviour in that type of aquatic system and the validity of further extrapolation of results to other systems remains to be demonstrated.

The importance of the physico-chemical properties of a chemical in determining its mobility and accumulation within aquatic systems has been emphasized by Hulpke and Wilmes (Section 3.1). In addition to depending on the properties of the compound, biodegradation is controlled by the number and nature of organisms at the corresponding site (see Cabridenc, Section 4.2).

Processes such as the methylation of mercury are of great importance in the mobilization, bioaccumulation and toxicity of certain compounds. Aquatic animals, unlike their terrestrial counterparts, are exposed to chemicals both through the medium they inhabit and through their food. The role of bioaccumulation in the transport and compartmentalization of toxic compounds is especially critical to those species, such as man, high in the food web (see Ernst, Section 4.4).

Terrestrial Ecosystems

Terrestrial ecosystems constitute by far the most complex environmental compartment in which chemical compounds are deposited, transported, transformed, and accumulated. Because of the complexity and variability of the soil system, chemical behaviour is extremely difficult to quantify. Investigations of chemical behaviour in terrestrial systems can rarely be reduced to a single factor, the significance of which can be identified. The development of methodologies for examining chemical behaviour in terrestrial systems has necessarily been pragmatic although the importance of protecting agricultural soils has evoked much scientific effort. Winteringham (Section 3.3) has emphasized the need to examine the plant–soil system and to develop models quantifying inputs as well as abiotic and biotic factors affecting disappearance. Laboratory soil columns and the field lysimeter are valuable techniques for the terrestrial system. Equilibrium partitioning, volatility and microbiological degradation methods are similar to those applied to aquatic systems.

Major gaps in the understanding of environmental pathways in terrestrial systems are evident. Many critical transformation pathways initiated by microbes remain either unknown or unquantified (see discussion in Klein and Scheunert, Section 4.1). Identification of key organisms in transport pathways also remains a major gap in understanding. Food is the major source of pollutant uptake for many terrestrial animals although prediction of body burden is normally difficult (see Roberts, Section 4.3 and Moriarty, Section 4.5).

1.4 TESTING METHODOLOGIES

Although the complexities of chemical reactions in the environment make the identification and quantification of such processes difficult, numerous testing methodologies have been proposed to elucidate environmental behaviour. It is realized that no simulation of natural conditions can be perfect, so that predictions of behaviour from tests will require judgement. The practical methodological problem facing ecotoxicologists is not so much a lack of techniques (except in certain areas) but that of selecting from the large number of potential tests reported in the literature. It is a question of which tests best answer specific questions on the environmental behaviour of chemicals for a given situation. These test methods need to be critically evaluated as to their practicality, utility, predictiveness and limitations. Simple, inexpensive tests usually yield only limited information but they may be useful if their limits are clearly understood and if conclusions are not drawn on issues for which the test was not designed to provide answers. More complex test systems and experimental designs are generally better at approximating conditions of the natural environment; however, simple tests may in fact be preferable to complex long term experiments if these do not yield information in reasonable proportion to the amount of effort expended.

The choice of a test is dependent upon the kind of information desired. There are essentially two types of information necessary to predict the various aspects of chemical behaviour:

1. *Relative* information allowing comparison of chemicals tested under similar conditions.
2. *Specific* information identifying processes and metabolites, quantifying their exchange rates and estimating concentrations in environmental compartments under natural conditions.

To obtain relative data, standardized experimental conditions and procedures are indispensable to provide reproducible and comparable results. To maintain standard laboratory conditions usually requires significant deviation from natural environmental conditions. Tests for relative information include determination of physico-chemical properties and the simpler qualitative laboratory tests indicating transport, transformation, accumulation and persistence of chemicals. Specific quantitative information generally requires more complex laboratory tests under simulated environmental conditions or direct assessment of chemical behaviour under field conditions. Results of these more sophisticated tests are representative of behaviour in the natural environment but are confirmatory of the behaviour of the test chemical only under the specific environmental conditions simulated. Since a multitude of environmental variables affect experimental results, extrapolations of chemical behaviour should be undertaken with caution.

To assess the ability of a test to predict the environmental behaviour of a chemical, comparison of results with those obtained from environmental monitoring programs is indispensable. Such comparisons are essential to evaluate results from both laboratory and field testing programs.

The largest proportion of testing of environmental chemicals can be classified as screening. These tests, as the name signifies, are intended to provide preliminary data for separating chemicals for further examination based on certain relative properties such as ready biodegradability, bioaccumulation potential or persistence in the environment (OECD, 1979; Kawasaki, 1980; NRCC, 1981). Screening tests are designed to provide comparative information on a large number of compounds with a minimum of data and experimental effort. This is not meant to infer that all screening procedures are simple. In actuality screens for various aspects of chemical behaviour are found at several layers of the testing hierarchy with generally increasing complexity and cost as the specificity of the test objective increases and the number of compounds tested necessarily decreases. The importance of screening tests is emphasized by the number of integrated screening strategies recently proposed. For example, Mill (1981) suggests a hazard ranking system for synthetic chemicals based on minimum information and the intelligent application of structure–activity relationships for properties, transformations, and effects. The US Environmental Protection Agency recommends for screening purposes the estimation of environmental concentrations of a chemical using material balance, equilibrium partitioning and behaviour assessment methodologies (Wood, 1981). The key data elements include:

1. Information on production, use and disposal.
2. Equilibrium constants for distribution of the chemical in air, water, soil and biota.
3. Kinetic constants for transformation processes.

A more complex screening format is the ecotoxicologic profile analysis proposed by Korte *et al*. in 1978. This method defines certain processes that govern the behaviour of chemicals in ecological systems, and designs a set of standard laboratory tests to assess these parameters. The processes included in the profile analysis are mammalian metabolism, bioaccumulation, atmospheric breakdown, fate in sewage, waste incineration and waste composting. Individual data are relative estimates of overall environmental behaviour. They need to be compared with known information or to a reference chemical in order to predict comparable environmental behaviour.

Although screening methods are normally designed to be quick, easy and often standardized, a good understanding of the basic principles involved in individual behaviour processes is essential to the utility of an appropriate screen. The appropriate level of complexity and specificity of the test model should be in line with the intended use. Appropriate bench-mark chemicals are necessary to maximize interpretative value. The overall reliability of screening techniques is governed by the individual components composing the screen. Priority lists developed from screening tests are only a means to a further end; they are intended as a basis for more detailed investigation (Egan, 1980).

Methodologies designed to provide specific data on exchange, or transformation rates in simulated and natural systems are essential to predicting the behaviour of those priority compounds identified as persistent, bioaccumulated and toxic. These test systems are generally complex. Although this complexity of the test system often enhances the ecological realism and may improve one's confidence in extrapolated results, such tests are difficult to replicate (see papers in Giesy, 1980) and exceedingly difficult to integrate as part of a standardized testing scheme (see Schmidt-Bleek, Chapter 6).

Field-scale tests are an essential part of any ecological testing scheme. These methodologies take into account interactions such as food web transport and transformation which may not be observable in the laboratory. Although the need for large-scale studies is well recognized and has played a significant role in describing the chemodynamics of pesticide components, results can be complicated by the large number of unmeasurable relationships.

1.5 ORGANIZATION

This book is intended to provide an integrated evaluation of laboratory and field techniques to predict the behaviour of chemicals in nature. The initial chapters of the report discuss the chemodynamic concepts and specific methodologies utilized to assess the contribution of abiotic processes on the transport, transformation and compartmentalization of chemicals in the atmosphere (Chapter 2) and in water, sediment and soil (Chapter 3). The next section (Chapter 4) appraises methods quantifying biotransformation, biodegradation and bioaccumulation of pollutant chemicals. In Chapter 5 methodologies for predicting the intercompartmental movement of chemicals are examined with emphasis on those processes integrating the abiotic and biotic components. Those features of tests, requisite to meeting regulatory requirements, are discussed in Chapter 6. The final chapter presents a critical summary of conclusions as to the utility of commonly used methods and the potential utility of techniques in the developmental stage. Specific recommendations are made for facilitating the process of predicting chemical fate.

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