CHAPTER 7
Conclusions and Recommendations

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The objective of this report is to appraise the utility and limitations of laboratory and field tests used to predict the behaviour of chemicals in the environment. Such an appraisal must include evaluations of technical aspects of proposed tests as well as the ecological relevance of their results.

The list of processes necessary to describe the behaviour of chemicals in the environment is relatively well characterized and not extensive. Key processes include:

(1) Abiotic and biotic degradation (rates, extent of breakdown).
(2) Biotic transformations (potential for production of toxic forms).
(3) Bioaccumulation or biomagnification.
(4) Environmental partitioning.
(5) Transport.

Although the list of processes is well developed, the relative importance of individual processes is more difficult to determine and this is the crux of the problem of accurately predicting exposure for man or the ecosystem. The relative importance of a specific process is dependent on the structure of the compound as well as the environmental compartment into which it is released and eventually dispersed.

There are a wide variety of tests available to qualitatively and quantitatively predict various aspects of chemical behaviour. The choice of appropriate test(s) is dependent upon the types of information desired

(relative or specific), the level of resolution required, and the specific circumstances prompting the test, i.e., is the objective an initial screening of compounds or the determination of eventual fate of a persistent toxic substance; is the chemical likely to be sequestered in atmospheric, terrestrial or aquatic environments; are biotic or abiotic processes likely to be dominant? There are also obvious trade-offs in the comparative value and ecological relevance of data from the standardized test versus that from more complex and less easily replicated microcosm and field studies. Therefore, few unqualified generalizations can be made on the choice of appropriate tests.

There are certain basic criteria upon which the utility and limitations of methods should be appraised:

(1) Predictive power/ecological significance.
(2) Reproducibility.
(3) Generalizability.
(4) Potential for validation under appropriate environmental conditions.
(5) Ease of performance/cost.
(6) Standardization/harmonization.
(7) Utility in hazard assessment schemes.

Care must be taken to recognize environmental effects which cannot be qualitatively mimicked in laboratory tests. The need for and importance of demonstrating that laboratory results parallel those that occur under natural environmental conditions cannot be overstressed. The validation procedure includes demonstrating that the processes do, indeed, occur in the field, that the relative importance of individual processes agrees with laboratory predictions, and that the disappearance rates of the chemical are convergent. The cost limitations on large-scale field studies and on detailed testing accentuate the importance of identifying a set of proper reference compounds (benchmarks), representative of the range of physico-chemical properties and reactive types to be encountered in chemical testing. Parallelism within classes of benchmarks must be demonstrated.

The multiplicity of chemicals for which testing is required, as well as the effort that must be expended with more complex procedures, suggests the increasingly important role that structure–activity correlations must have in forecasting environmental hazard.

This report has not attempted to give equal emphasis to the presentation of background material, nor to the appraisal of tests used for the various environmental compartments. In this respect, far greater emphasis has been placed on the review of individual chemical reactions in the atmosphere, than on equivalent processes in soil and water. This reflects the historically greater emphasis given this medium, undoubtedly due to the public's concern with

air pollution as well as the conceptually greater ease in designing studies to mimic homogeneous rather than heterogeneous systems (such as soil).

Atmospheric processes are almost entirely abiotic. A number of important reactions have been described and reaction kinetics evaluated under both uncontaminated and polluted atmospheric conditions. A major question to be resolved is the relative importance of different reaction pathways in the degradation of chemicals under varying atmospheric conditions. The presently accepted approach using homogeneous gas-phase reactions is probably adequate to qualitatively predict chemical degradation in the 'background' atmosphere during daylight when OH is the prime interactive component. The accuracy of estimations based solely on the half-life of the OH pathway have been questioned. The importance of examining additional reactive species such as O^3P atoms and other excited oxygen species as well as heterogeneous reactions when predicting degradation in polluted air is stressed. Heterogeneous transformations increase in importance and can become rate limiting when high levels of complex organic contaminants are present in the atmosphere. Quantum yield data will be essential for photostability comparisons. Except in those cases where a known reaction pathway is dominant, classical rate determinations are not considered appropriate. Aerosols are seen as an important atmospheric sink for chemicals and provide active surfaces for degradation processes. There is a pressing need to quantify the relative rate of processes associated with aerosols.

Although there are a number of levels of complexity in tests of atmospheric degradation, from standardized photodegradation methods to environmental chamber experiments, all results must currently be considered only as qualitative indications of environmental behaviour.

There is an expressed need for a single simple test which will demonstrate that degradation does or does not occur and which is unhampered by the problem of boundary effects or specific properties of the test chemical. This is probably an unrealistic goal considering the complexity of the problem. Two standard laboratory tests for atmospheric photodegradation are described (GSF, Fujiki) neither of which totally meet these criteria. The GSF test is based on chemicals adsorbed on silica gel. Test results can be concentration dependent, and interpretation is hampered by the problem of potential spectral shifts due to adsorption. The Fujiki test is limited to gaseous chemicals or those which readily volatilize. Its utility, as that of the GSF test, is hampered by the problems of boundary effects. The further development and refinement of simple tests of comparative atmospheric degradation under conditions of sunlight, which are not hampered by the restrictions mentioned, is a recommended priority.

The use of environmental test chambers has been productive in two areas:

(1) To obtain time–concentration profiles which are important to the generation of computer-assisted kinetic models; and
(2) to detect reaction intermediates and provide mechanistic information for air pollutant mixtures.

Chamber experiments are limited in their simulation of the atmosphere and are hampered by 'chamber effects' such as unknown sources and sinks for chain carriers.

The additional heterogeneity and variability in terrestrial and aquatic systems, and the need to consider biotic processes, necessitates significantly different methodological approaches to the prediction of the behaviour of chemicals released into and sequestered in soil or water.

In water, the important abiotic pathways of chemical degradation are hydrolysis, direct photodegradation, and oxidation. Hydrolysis can be assessed with standard laboratory techniques, normally carried out in buffered solutions at a constant pH. Additions of buffers and miscible solvents have a marked effect on the rate of hydrolysis, and should be minimized to approximate ionic strength conditions of freshwater. The role of natural catalysts in hydrolysis needs to be further clarified.

Comparative photodegradation data can be obtained for soluble compounds with the EPA procedure. These results can be grossly extrapolated to natural aquatic systems and they are currently considered a more useful estimate of degradation than are data produced from microcosm studies. The role of humic and fulvic compounds in sensitized photolysis is considered to be important and requires further elucidation. Triplet processes are thought not to play a major role in photodegradation, but processes including the adsorption of the chemical on the sensitizer have not been sufficiently investigated. Singlet oxygen is an important reactive species in water. A screening test has been proposed for assessing the reactivity of test substances with singlet oxygen. There is a need to define the pattern and level of oxidants in aquatic systems in order to improve predictions of the relative contribution of radical reaction to chemical degradation.

Sediments are an important sink for chemicals and provide a reactive surface for degradation reactions. Although various methods are available to estimate the particulate binding of chemicals, the heterogeneous nature of sediments has frustrated attempts at comparisons. Artificial adsorbents could provide a means of obtaining comparative data. The quantitative importance of sediment-surface-catalysed degradation needs further assessment.

The relevance of laboratory data to the prediction of chemical behaviour in the aquatic environment is best examined in terms of the total available information on transport and degradation processes. Synthesis can be accomplished through mathematical integration of experimental and/or calculated degradation and transport rates, or through an assessment scheme

such as the ecotoxicological profile analysis based on laboratory data and structure–activity correlations with comparisons to reference compounds.

The terrestrial ecosystem is the most complex environmental medium and hence the most difficult to analyse. It is important to examine chemical behaviour in this compartment in the context of the plant–soil system, due to the intimate linkage. Because of the complexity and heterogeneity of the plant–soil system, the majority of investigations have been limited to the determination of gross overall rates of disappearance of the test compounds. This approach contrasts with the single factor studies used to predict aquatic and, in particular, atmospheric behaviour. Tests are available to assess volatilization, photodegradation, erosion, leaching, abiotic inactivation, and biotic transformation and accumulation. There is a lack of understanding of the behaviour of sorptive processes. Chemical–biotic interactions are important in soils; however, the degree to which microbes contribute to degradation in natural systems is difficult to determine. The relative importance of different microbial populations to the degradation process is unknown. A simple soil test characterizing soil biomass, composition and activity is needed to make possible adequate predictions regarding the contribution of natural microbial communities.

The spatial and temporal variability in soil properties causes a great deal of difficulty in evaluating comparative data and in making general predictions. Further development of standardized procedures with 'synthetic' soil is recommended. The value of comparative testing with well-known reference compounds is also stressed. Laboratory tests are presently considered most effective in the evaluation of comparative properties. More complex test systems (microcosms) should be used only with chemicals assigned sufficient priority and only when a high degree of resolution in extrapolations to a particular plant–soil system is required. The use of radiolabelled compounds is particularly important in the quantification of mineralization, the detection of bound residues, and for 'mass balance' studies.

Synthesis of chemical transport and degradation in terrestrial systems can be accomplished with mathematical integration of the inputs and disappearances in continuous exposure or discontinuous total exposure models.

Biotic transformation of chemicals in aquatic and terrestrial systems cannot be predicted from structure–activity relationships. Transformations can be qualitatively predicted with laboratory test results. Laboratory data are most effective in comparisons of the degree of transformation of chemicals. Mass balance experiments can be conducted under controlled but not under field conditions and the value of such studies is enhanced by the use of labelled compounds.

In vitro techniques provide a rapid screen for transformations, eliminate the influences of other animals, and yield mechanistic information. These

techniques do not, however, take into account transport processes in the organisms and the interference from competitive reactions. *In vivo* methodologies overcome some of these difficulties. Results from *in vivo* tests are of the greatest predictive value when the animal or component microcosm is representative of the natural system, when appropriate environmental conditions are maintained, and when the experimental period is appropriate to the time-dependent kinetics of the transformation.

A necessary step towards improved assessment of biological conversion and degradation rates is more extensive comparisons of laboratory data with reliable environmental data which will aid in clarifying the problems of scaling in laboratory tests. More of both representative (for specific conditions) and generally applicable procedures (for a variety of chemicals) are needed for estimating biodegradability. Prior to the development of such tests there is a requirement for more detailed information on natural factors controlling the rates of biodegradation.

The uptake of chemicals by organisms has received much attention. Models of bioaccumulation have two levels of resolution: (1) empirical correlations to develop first estimates, and (2) simple pharmacokinetics. Neither type of model can mimic complex exposure scenarios, therefore the value of bioaccumulation models is in the prediction of the importance of various vectors and in screening for gross accumulation.

Structure–activity correlation should play an increasingly important role in predicting transport, partitioning and bioaccumulation in aquatic systems. Bioaccumulation data bases for fish and mussels are well developed but such is not the case for other aquatic organisms. The validity of predictions regarding accumulation in other species, based on these indicators, remains unconfirmed. The limitations of water/octanol or solubility–BCF correlations for fish and mussels are still undefined due to the small number of compounds which, for as yet unexplained reasons, are outside the general pattern. There is an obvious need for the development of a good base of bioaccumulation data for ecologically important zooplankton and insect grazers, and key predators in freshwater systems. It is necessary also to standardize laboratory procedures and to place more emphasis on verification of rates in the natural environment.

For terrestrial animals, food is the principal source of bioaccumulation of chemical contaminants. Concentration factors for terrestrial species have been difficult to interpret and the emphasis on trophic position as a determinant of pollution concentration seems to be overemphasized. Physiological status and biochemical function of the individual animal are paramount factors. To predict the likelihood of bioaccumulation, information on the percentage assimilation and the degree of persistence is required. To predict the magnitude of accumulation, knowledge of the environmental

behaviour of the chemicals and laboratory measurements of assimilation and loss are required.

Predictions on the movement of chemicals between environmental compartments are largely dependent upon physico-chemical characteristics. Validation of transport phenomena in the field is generally lacking and is critically needed.

A general concern expressed throughout this report is the need to systematically integrate available and proposed tests into an effective and comprehensive testing scheme. This is generally of greater priority than the improvement of tests in specific areas of degradation and transport assessment. The understanding of structure–activity relationship needs also to be improved in order to increase their utility in screening for hazardous chemicals. In general, available laboratory tests provide, at best, data for comparative evaluation. Improvement in the ability to extrapolate from laboratory test results to accurately and quantitatively predict degradation, transformation, accumulation, and transport in the field is critical to hazard assessment. The optimizing of microcosm and field test designs is an essential priority.