

Paper presented at the Nordic Seminar.
To be published in Ambio
(Royal Swedish Society Journal).

**TEST SYSTEMS AND EXPOSURE
IN THE AQUATIC ENVIRONMENT**

by

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NWRI Contribution No. 87-97

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Abstract

The article is an introductory paper for the session on "Testing the Fate of Chemicals in Aquatic Systems" held at the Nordic Seminar on Evaluation of Test Systems for Chemicals in the Aquatic Environment, Smygehamm, in southern Sweden from October 6 - 8, 1987. It discusses the topic of exposure as it relates to the hazard assessment of chemicals in the aquatic environment. Multi-compartment approaches to developing an integrated expression for the concentration levels of environmental chemicals are noted as alternatives to meso-/microcosm methods of describing their fates. Much of the focus of the session is on such test ecosystems and this paper discusses the role of modeling and monitoring as well as presenting information on the approach being used to evaluate hazard and exposure of chemicals in the North American Great Lakes ecosystem.

Résumé

Cet article sert d'introduction à la session sur la détermination du sort des produits chimiques dans les réseaux aquatiques nord dans le cadre du Nordic Seminar on Evaluation of Test Systems for Chemicals in the Aquatic Environment, qui s'est tenu à Smygehamm, au sud de la Suède du 6 au 8 octobre 1987. On y traite des liens qui existent entre l'exposition et l'évaluation des dangers des produits chimiques dans le milieu aquatique. On fait observer que des approches pour une expression intégrée de la concentration des produits chimiques dans l'environnement faisant appel à plusieurs compartiments pourraient remplacer les méthodes méso-/microcosmiques utilisées pour déterminer le sort de ces produits chimiques dans l'environnement. La plus grande partie de la session porte sur de tels écosystèmes témoins, et cet article traite du rôle des modèles et de la surveillance ainsi que de la présentation des données sur l'approche utilisée pour évaluer les risques de l'exposition aux produits chimiques dans l'écosystème des Grands Lacs en Amérique du nord.

Introduction

The modern-day world is full of chemicals! It is also full of people who have been sensitized to a concern over their personal and collective exposures to hazardous chemicals. They are particularly concerned about those chemicals that are introduced into their environment by Man. Chemicals over which they exercise a degree of control, such as cigarette related ones, may be accepted or not as the individual decides. People are not prepared, however, to accept those that are toxic and "foisted" upon them through the actions of others.

Governments, in an effort to respond to this genuine concern, have instituted various programs aimed at evaluating whether a chemical represents a hazard to humans or to the environment and if so under what conditions. Programs that address new chemicals were the subject of an OECD (Organization for Economic Co-operation and Development) Chemicals Testing Program which produced the "Guidelines for the Testing of Chemicals" (OECD, 1987) and the reports for the OECD Hazard Assessment Project (OECD, 1982). Both of these activities were intended to address the problem of assessing chemicals before they reached the market or the environment but did not focus upon chemicals already "existing" in commerce, some of which were already present in the environment. A subsequent project of the OECD attempted to establish some of the principles that would be applicable for assessing the latter and dividing the work load implied by the world's chemical inventory or even the identified environmental chemicals.

The National Swedish Environment Protection Board undertook, in

1982, to develop "Systems for Testing and Hazard Evaluation of Chemicals in the Aquatic Environment" (ESTHER) (Landner et al., 1982). The recent meeting of the ESTHER project, which took place in Smygehamn in southern Sweden, was the final one and was called to review the project's accomplishments. Many of the presentations at this Nordic Seminar have been supported under this program. These researchers and others will discuss the significance of different types of test systems, each of which is intended to serve similar but not identical purposes. The authors will no doubt identify these purposes and also others for which the systems might find application. The objective in this brief presentation is to generalize concerning the methods of describing the fates of environmental chemicals and, in particular, to note approaches other than the use of test ecosystems or mesocosms. It is further noted that the terms exposure and fate, in this paper, will often be used interchangeably although fate is more customarily used when discussing the degradation aspects of exposure; movement among and within ecosystem compartments, including bioaccumulation, are also part of exposure.

Hazard Assessment and Exposure

Most hazard assessments of a chemical take place either to determine whether to regulate and concurrently monitor for compliance and effectiveness, or, for general scientific understanding of their behaviour in the environment. Different agencies and researchers may apply different emphases within the assessment process but it should be apparent that the evaluation of the hazard of the chemical to Man or to the Environment must include a comparison between the effect

levels and the exposures to be expected or already realized. As such, the two "terms" must be expressed in similar units. Effects are generally developed as concentrations for aquatic organisms or doses for mammals; it follows that environmental exposure must also.

There is a range of approaches to developing a concentration expression for a chemical in the aquatic environment. On the one extreme, there are actual field measurements of the compound, usually taken in a single compartment but for which, properly done, there is a high level of confidence in the stated concentration level. The results apply, of course, to the particular system in which they were observed but their relevance in other locations and at other times must be qualitative and determined by scientific judgement about the similarities and differences between the systems. Such considerations should require detailed knowledge of the physical, chemical and biological dimensions of the systems and of the masses of the chemical being released to them.

On the other extreme, modeling may also give an expression for exposure. There will be less confidence in the specific numerical estimates of concentrations than for those obtained in a direct analytical determination but there may be more generic utility for the various systems which can be simulated by the model. Several of the "new" chemical assessment processes use this approach (Landner, 1984) -- necessarily so since there can be, or should be, no environmental data. This approach depends on the development of high quality physical-chemical property data for the chemicals and also on the adoption of realistic compartmental size descriptions for whichever scenario(s) are considered relevant to the purposes of the assessor.

The Ecosystem Approach

It is more than just fashionable to state that in all considerations of assessment -- for both regulatory/monitoring purposes and scientific understanding -- ecosystem relations should be taken into account. A schematic representing some of the more important processes determining the movement of persistent toxic chemicals in a water related ecosystem is presented in Figure 1. This represents an overwhelming amount of data development if it is taken to mean that any assessment must first have all possible pieces of data pertaining to the fate of a chemical in such a system, simple as it is, where only the parts of the environment directly interacting with the water column are shown.

This is obviously a major simplification of the real world but it is one which contains the compartments necessary to describe the exposure of a persistent chemical. There are no transformations indicated and biota have not been designated because, aside from degradation, they have little impact on the distribution of the chemical in the indicated compartments. The representation may be less than necessary, even for persistent compounds, since it has little to describe the role of the terrestrial environment in the movement of chemicals. The components in the figure would have to be expanded to include degradation processes in the case of non-persistent compounds but the present figure serves as a starting point for the development of an exposure expression.

The Monitoring Approach to Exposure

One method of integrating monitoring data is to attempt a mass balance of the chemical for the system under investigation. Such mass balance (or accounting) of a chemical may be accomplished through the consideration of fluxes between the compartments of the ecosystem. The approach can also incorporate degradation processes occurring within the several compartments and then it becomes like the dynamic models (Fugacity level III (Mackay et al., 1983), EXAMS (Lassiter et al., 1979) and others) which have been developed but for which there always seems to be insufficient data to provide the needed validation.

A mass accounting scheme used for estimating the relative importance of toxic chemical fluxes to lakes is shown in Figure 2. Contributions from rivers are divided into tributaries and connecting channels, a feature particularly relevant to the North American Great Lakes where much of the toxic substance loadings takes place. It is apparent that much data on concentrations are needed and that there is also a requirement for fundamental information related to atmospheric and aquatic particulate matter. In the Great Lakes, where there have been intensive efforts on monitoring for selected toxic chemicals for 15 or more years, there is still an insufficiency of the necessary data. This arises in part from the concern about Man's health and the resultant focus on food-stuffs and biota and partly from analytical convenience because of the accumulation phenomenon relevant for many of the substances. If the need is to determine exposure, there will need to be an improved emphasis on abiotic components of the system. The tools to undertake this are available now which was not the case when toxic chemical monitoring first began in the region. Such

determinations should be basic to the hazard assessment process.

In mass balance type of approach, the parameters relevant to the system are already provided for since the concentration data are from the field. As such, there might appear to be little further to do other than assess the data quality when developing an exposure statement. There is great concern, however, over whether the concentrations selected are seasonally or geographically (in the case of the large lakes) representative of current conditions in or over the waterbody. There is also concern whether other required parameters are known with sufficient accuracy and precision to permit even an order-of-magnitude of estimate of the fate of the chemical. A need exists as well to determine some of the basic data pertaining to particulate matter in both the atmosphere and the water column and also information on the Henry's Law constant and the mass transfer coefficient for the chemical itself.

The Modeling Approach to Exposure

For the most part, the models of interest are those which attempt to describe the distribution of chemicals through the use of physical-chemical and rate data in addition to size parameters for the "scenario(s)" of interest. Processes are allowed for which affect the levels of the chemical in the modeled compartments of the ecosystem and empirical procedures are provided for many missing data elements. These computerized models are linear combinations of differential equations most of which assume that the processes so described are first order, i.e. dependent only upon the concentration of the

chemical. The "systems" that they describe are theoretical, the dimensions of which are adjustable parameters in the models. Several of these were discussed in the earlier OECD exercise on Hazard Assessment and while there have been subsequent versions, the principles remain the same.

A major difficulty in applying these models is the paucity of existing data available to validate them. Since, for the most part, these models do not purport to provide realistic concentration estimates for actual systems, it is through their relative levels in the several compartments that such validation can be achieved. The results of the models, however, are presented as concentrations and the temptation is always there to use them as exposure estimates in hazard assessments. Their greatest utility, however, lies in directing pre-assessment activity -- research for basic rate and system parameterization as well as cost-efficient monitoring of the appropriate compartments.

The Great Lakes Experience

The Great Lakes region of North America, shared jointly between Canada and the United States, is an area of considerable chemical pollution. Some 362 man-made chemicals from among a list of approximately 1000 reported compounds have been positively established as being present (CCACGLE, 1987); they must be evaluated as to their significant hazard to humans and/or the environment. There is an umbrella agreement (the Great Lakes Water Quality Agreement: 1978) which, among other things, provides a mechanism for jointly undertaking assessments of chemicals present in the system. Many

discussions have taken place, including a workshop (Strachan et al., 1986), on how to approach the evaluation of these chemicals.

A general protocol for performing the hazard assessment of environmental chemicals and determining the related control actions has been identified as well as most details which are amenable to detailed description; the overall process is indicated in Figure 3. The experience has been that the first and major step to be taken in a process evaluating with a large number of compounds is the "preliminary assessment" process. In this, an identified chemical is examined for some minimum data base and a judgement made as to whether it appears to represent a hazard. The chemical must meet identification data quality criteria and, subsequently, "all" existing data in the literature is compiled. The essential data set is obtained from the literature or developed separately and the whole evaluated together with any Great Lakes exposure data (some of which resulted in its "identification"). The minimum data elements so identified are presented in the Table.

The precise details of how these data elements will be combined to give collective expressions of exposure and effects is not decided at this time but several principles have been accepted that will determine this. First, it is accepted that there will be no removal of a chemical from the process -- or progress along the decision track -- without some description of both exposure and effects nor without a complete essential data set. Also, those elements that are labelled "important" are to be weighted equally with the essential data set whenever they are available. Each element is designated as of

high, medium or low concern and it is the comparison of the exposure and effects combinations of these which will constitute the screening and be used to assign priorities for further activity. It is planned that there will be comparisons to be made between the predictions of this preliminary screening process and conclusions already reached for proven problem chemicals.

The "in-depth" assessment(s) do not lend themselves as well to a formula description. They are to be conducted by specific panels set up for each chemical which passes the screen of the preliminary assessment. Each stage will have access to all of the data and will be expected to produce a report on whether the chemical poses a hazard and if so, what the nature of that hazard is. The report will also include either what type detail) of controls appear to be indicated or, if they cannot come to that decision, what information is required to do so. Feedback information from monitoring for compliance and effectiveness of the controls may result in altered conclusions and controls.

This is the approach to assessing hazard of environmental chemicals which has been selected to deal with the large number of potentially toxic chemicals found in the Great Lakes. It is still somewhat vague but an important principle that is present in all statements about the mechanism is that "expert, scientific judgement" will be required at all stages of evaluating the chemicals. This is interpreted to mean that there will be no "formula" or fixed expression, either from the monitoring or modeling extremes.

Mesocosms and Microcosms

Many of the activities under ESTHER and of the papers presented at this seminar are focussed somewhere between the two extremes of modeling and monitoring. The use of micro- and mesocosms can give much information on the rates of various processes likely to occur in the real world. They can serve, as do some of the models, as a mechanism to provide relative fate estimations among the chemicals which are tested and they can provide a higher degree of confidence than can most models. Great care must be taken, however, to ensure that the various abiotic and biological components in the systems are sufficiently representative of the ecosystems that they are intended to mimic and that these components are, at the time of measurement, in equilibrium or steady-state with respect to the chemical and each other.

The meso- and microcosm approach is particularly useful in describing the biodegradation and bioaccumulation aspects of exposure; indeed, these systems are essential for this purpose unless one is 'fortunate' enough to be in a position of taking advantage of an environmental accident and to follow these two processes in a real system. It is this author's opinion, however, that deliberate introduction of a persistent toxic chemical into the open environment should not be undertaken; even for those which are non-persistent, such discharges should be considered only under the most pressing of circumstances.

Since a number of the papers to be presented in this session are by authors reporting on aspects of biodegradation and bioaccumulation

in such laboratory systems, they will not be discussed at length here. One principle which should be followed when considering the development of such systems, however, is that of restricting their complexity to the minimum necessary to provide the description of exposure -- or effects -- needed. There are two opposing considerations in selecting the components of a system -- the desire to mimic a real life situation where complexity provides some resiliency and protection, and, the need to provide a reproducible and therefore simpler and controllable system. If the system is too complex, the results are interesting but perhaps not so universally applicable in situations other than the specific mesocosm in which the study was conducted; they are also difficult to maintain and long periods are needed to achieve steady-state or equilibrium. On the other hand, if the system is too simple, the study leaves too many questions unanswered not the least of which is the impact of the system on the chemical (as opposed to the impact of the chemical on the system). It should therefore be incumbent on the developers of these system to state what system they are attempting to simulate and what questions they hope to be able to answer with their particular mesocosm. The balance of this session will address many of these concerns.

Acknowledgments

The author wishes to thank the Swedish National Environmental Protection Board (SNV) and the personnel of its Research Directorate for the opportunity to participate in the ESTHER program. He would also like to thank the many colleagues who, through argument and example, have added greatly to his sense of the assessment process. Appreciation is also expressed to Steve Eisenreich with whom he has enjoyed collaborating over the mass balance accounting of toxic chemicals in the Great Lakes.

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Table: Essential and Important Data Elements
for a Preliminary Assessment

<u>Data Element</u>	<u>High</u>	<u>Medium</u>	<u>Low</u>	<u>Data Category</u>
<u>ESSENTIAL</u>				
Mammal LD50 (mg.kg ⁻¹) ¹	<5	5-500	>500	Effects (Toxicity)
Aquatic LC50 (mg.L ⁻¹)	<10	10-100	>100	
Mutagenicity (cell lines) ²	two or more positive	one positive	none positive	
PK _{ow} (log units) ³	>5	3.5-5	<3.5	
				Exposure (Predicted)
<u>IMPORTANT⁴</u>				
Environmental Release	dispersive and high production	dispersive or high production	non-dispersive and low production	Exposure (Actual)
Environmental Concentrations	high and ubiquitous	high or ubiquitous	neither high nor ubiquitous	

1 - Values based on acute lethality in a limit test are not presented but could be developed.

2 - At least one cell line should be mammalian

3 - Other partitioning parameters should be considered if the potential hazard warrants it; this is particularly so for vapour pressure which may be used to develop the air-water partition coefficient.

4 - Specific values cannot be assigned without reference to effect levels of the chemical. Expert opinion must be relied upon in these instances.

Figure Captions

Fig. 1: Distribution of Toxic Chemicals in an Aquatic Ecosystem

Fig. 2: Framework for Fluxes of Chemicals in an Aquatic Ecosystem

Data Requirements:

C's	- concentrations in rain, air (vapour plus particulate), water (dissolved), suspended solids, tributaries (total) and connecting channels (total)	(mole.m ⁻³)
f _v	- fraction of atmospheric contaminant present as vapour	
f _s	- fraction of lake area with significant deposition	
H	- Henry's Law constant	(atm.m ³ .mole ⁻¹)
K	- bulk (or net) mass transfer coefficient	(m.yr ⁻¹)
P	- precipitation to lake surface	(m.yr ⁻¹)
Q's	- flows in tributaries and connecting channels	(m ³ .yr ⁻¹)
R	- gas constant	(atm.m ³ .mole ⁻¹ .°K ⁻¹)
SA	- surface area of the lake	(m ²)
T	- surface air temperature	(°K)
V _d	- particulate deposition velocity	(m.yr ⁻¹)
W _{acc}	- average sediment accumulation rate (deposition zones)	(m.yr ⁻¹)

Note: (1) F_s should be more precisely described by two terms — suspended solid settling and sediment resuspension.

$$F_{ss} = C_{ss} \cdot W_{ss} \cdot f_s \cdot SA \quad \text{where } W_{ss} = \text{settling velocity}$$

$$F_{sr} = C_s \cdot W_{rs} \cdot f_s \cdot SA \quad \begin{matrix} C_s = \text{sediment concentration} \\ W_{rs} = \text{resuspension velocity} \end{matrix}$$

(2) F_v, F_d could be expressed in terms of actual concentrations in the vapour and adsorbed states, if these data were available.

$$F_v = K \cdot (C_w - C_v \cdot \frac{R \cdot T}{H}) \cdot SA$$

$$F_d = C_d \cdot V_d \cdot SA$$

(3) No allowance is made for degradation in the compartments. For "persistent" chemicals, this should not introduce a major error.

Fig. 3: Assessment and Control of Chemicals: The Great Lakes Approach





