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Prioritization of Chemicals According to the Degree of Hazard in the Aquatic Environment

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Chemicals designated as "priority pollutants" or "toxics" have received special attention recently because the discharge of these compounds into public water is to be restricted to the maximum possible with little regard to water quality or economics. The selection of many of the 129 priority cemicals was not based on an objective scientific assessment of the exposure and effect data. In fact, for some compounds, including acenaphthene and 4-chlorophenyl-phenyl ether, the necessary data for listing were non-existent.

As an alternative to arbitrarily listing or delisting chemicals for the purpose of prioity control, this paper suggests a promising scientific approach to selecting priority chemicals based on the principles of hazard assessment for chemicals in the aquatic environment. According o the hypothesis, the highest priority chemicals are those with the least margin of safety, defined as the gap between the no-observable-effect concentrations and the ambient exposure concentrations.

The no-observable-effect concenrations are based on the results of chronic or sensitive life stage tests with aquatic organisms and the acceptable daily intake rate for fish eates. The ambient exposure concentrations are levels either measured in fish and water, or roughly estimated from a simple nomogram that requires only two of the following three factors: environmental release rate, ratio of dissipation to bioconcentration potential, or ambient residues in fish.

The chemicals studied to illustrate this approach to prioritizing chemicals based on hazard assessment are: polychlorinated biphenyls, di-2-ethylhexyl phthalate, linear alkylbenzene sulfonate, and pentachlorophenol.

Introduction

The principles of hazard assessment used in this paper are those developed at a recent workshop in Pellston, Michigan (*1*). At this workshop, representatives of government, industries, and universities reached a consensus that hazard in water could be assessed only after both effect and exposure of the chemical substance had been taken into account. Figure 1 illustrates the relationship. In general, the margin between the no-effect concentration and the expected exposure concentration in water is the statement of hazard or margin of safety. Estimates of these two concentrations are made in a sequential fashion, and the error limits on these two estimates narrow as the amount of information about biological effects and exposures increases. It is important to recognize that the essential environmental information can be estimated even from preliminary screening studies but the error limits on these estimates are usually quite large. To illustrate the use of hazard assessment techniques in prescreening priority chemicals, no emphasis on error limits was made.

This concept of hazard assessment is fairly new in the field of aquatic toxicology. Another new concept in our field is regulation of those specific chemicals which represent the greatest cause for concern for pollution in the aquatic environment. The 1977 amendments to the Clean Water Act contained a list of 65 categories of substances, which was later defined in terms of 129 specific priority chemicals (*2*). These chemicals are to receive the maximum possible discharge control in effluents. This paper suggests combining these two concepts into an objective selection criterion for prescreening priority pollutants. Such selection criteria are needed, since Congress provided a process for adding and sub-

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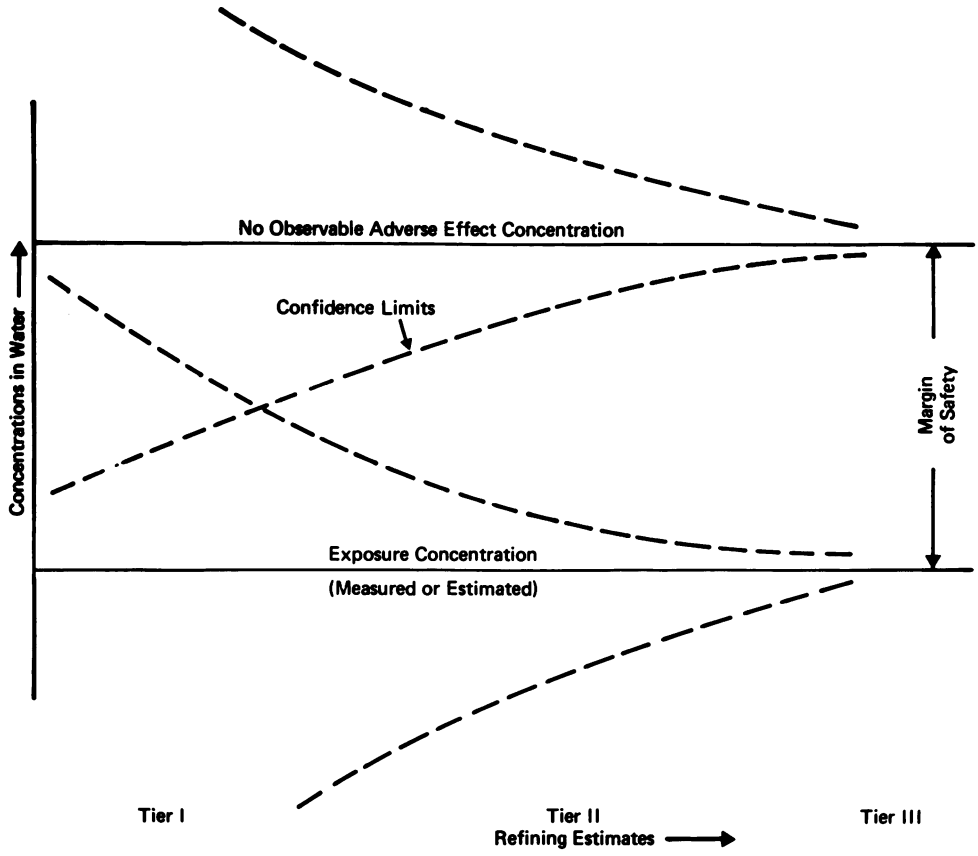

FIGURE 1. Principle of sequential hazard assessment of chemicals in the aquatic environment. Large gaps between the no observable adverse effect concentration and the exposure concentration indicate a low degree of potential hazard and vice versa.

tracting chemicals from the list of priority chemicals. If the hypothesis is correct that principles of hazard assessment can be employed as a prescreen for selecting priority chemicals, then it may be possible to distinguish between priority chemicals and those chemicals whiih more appropriately should be classified as chemicals with less potential to cause harm to man or the environment. The discharge of chemicals that might be removed from the list will also be regulated but to the extent that water quality is protected rather than to the maximum possible extent with little regard to economics.

Case Study Chemicals

Four chemicals were selected to illustrate the principles of hazard assessment—two with fairly high environmental release rates, di-2-ethylhexyl phthalate (DEHP) and linear alkylbenzene sulfonate (LAS), and two other chemicals with moderately high environmental release rates, polychlorinated biphenyls (PCB), and pentachlorophenol (PCP).

The environmental release rate, according to a National Science Foundation (NSF) workshop (*3*), is the maximum amount of material which may enter public receiving water and is calculated from the amount produced minus the amount consumed, destroyed, or contained. The estimates of environmental release rates in the NSF workshop were based on 1972 production records. For DEHP and LAS, the maximum environmental release rate in 1972 was 100 million to 500 million lb/yr, and for PCB and PCP 10 million to 50 million lb/yr. The distinction between production rates and environmental release rates is important, because rarely is all of the chemical produced released to the aquatic environment.

In order to assess the hazard of chemicals in the aquatic environment, certain environmental values must be measured or estimated. Table 1 shows the environmental information for the case study chemicals. This information includes the maximum concentrations of the case study chemicals which should not cause an observed adverse effect to fish-eaters, including man, i.e., acceptable daily intake (ADI) values combined with fish residue data. The ADI values were derived from long-term feeding studies

Table 1. Essential information for assessing the hazard of chemicals in the aquatic environment.

Chemical	Hazard to fish			Hazard to fish eaters		
	Ambient exposure concentration in water, mg/l. (ppm)[a]	NOEC mg/l. (ppm)[b]	Safety margin[c]	Ambient concentration in fish, μg/g (ppm)[a]	ADI residues for fish eaters[d]	Safety margins[c]
LAS	<0.05	0.5	>10	<0.5	750	1500
PCP	<0.000033	~0.005	150	0.01	9	900
DEHP	~0.0025	0.003	~1.2	~10	180	18
PCB	0.000010	0.005	500	>5	<5	<1

[a]Samples from areas outside the mixing zone of an effluent; large lakes, rivers, and estuaries; concentration of chemical in true solution.
[b]NOEC = no observable adverse effect concentration in chronic or sensitive life-stage tests.
[c]Safety margin = no observable adverse effect concentration/ambient exposure concentration.
[d]Fish residue = acceptable daily intake (ADI) μg/g/day × 60 kg fish eater/0.2 kg fish eaten per day.

in rodents and assumed a safety factor of 100. For the case study chemicals, the following ADI values were used: DEHP, 0.6 mg/kg-day (*4*); LAS, ~2.5 mg/kg-day (*5*); PCB, ~0.016 mg/kg-day (*6*); PCP, 0.03 mg/kg-day (*7*). It is appropriate to use long-term exposure data since the hazard assessment of the case study chemicals was based on ambient concentrations of the chemicals.

If all the information in Table 1 is available, hazard assessment is an easy task, involving merely dividing the no-effect concentration by the exposure concentration, but rarely, if ever, is all the information available to everyone's satisfaction. Typically, the data least available or reliable are the ambient exposure concentrations. As an alternative to direct measurements of the exposure concentration, it seemed reasonable that rough estimates of exposure could be made for the purpose of prioritizing chemicals, by examining the quantities released to the aquatic environment, the resulting residues in fish, the bioconcentration potential, and the degradation potential.

Correlation Between Release Rates, Persistence/Accumulation, and Fish Residues

It was assumed in reviewing the available information for this paper that in the future more and better data will be available on the ambient concentrations of chemicals in fish tissue. It was further assumed that these concentrations were a direct function of the persistence/accumulation properties and environmental release rates.

The PCB residues in Table 1 of 5 ppm were for the years 1972 and 1975 and were increasing with time (*6*). The linear alkylbenzene sulfonate residues in fish are estimated to be less than 0.5 ppm based on limited measurements of the concentrations in water and bioconcentration factors of approximately ten (*8*). Pentachlorophenol measurements are about 0.01 ppm and declining (D. Stallings, personal communication, 1979). The DEHP residues are not well documented. Characteristically, they are measured as by GC-MS *M/e* 149, which is the common mass ion for all phthalate esters. The limited monitoring data which are available suggest that the ambient levels in fish tissue of DEHP are at least 10 ppm (*9*).

The third part of this correlation deals with the persistence/accumulation. A composite of these properties was represented as a ratio of dissipation and bioconcentration potential; ratio DIS/BCF. Dissipation was assumed to be the sum of both the evaporative loss of the chemical from water and the rate of photochemical, hydrolytical, or biological degradation (Table 2). Since quantitative measurements of the rate of degradation were either not readily available or comparable, relative rates were assigned, where 100 was the maximum rate and a minimum rate of 1 was chosen for substances like metal ions which generally do not degrade or evaporate from water. For LAS, a relative degradation rate of 100 was assigned based on the first-order rate constant for CO_2 evolution, 0.10/day as reported by Larson (*10*). For PCP, a relative degradation rate of 50 was assigned based on 100% disappearance in various soils after 4 hr to 30 days (*11*). For DEHP, a relative rate of 10 was assigned based on 50% of the parent compound remaining in a hydrosoil test after 14 days (*12*). For PCP, a relative degradation rate of 1 was assigned based on the second-order rate constant for $^{14}CO_2$ evolution from ^{14}C-[2,5,2′-trichlorobiphenyl] in activated sludge, 0.009 g/g-hr (*13*). In the future, rate constants should replace these arbitrarily assigned relative rates.

The bioconcentration factors used to calculate the ratio of dissipation to bioconcentration potential were all measured values (Table 3) and relative dissipation rates were obtained from Table 2. What can be seen by this ratio of dissipation to bioconcentration potential is that the greater the dissipation and

Table 2. Dissipation of chemicals from water.

Chemical	Water solubility, mg/l.[a]	Evaporation $1/k \times 100$	Degradation biol/photo (relative rate)[b]	Relative dissipation rate (DIS)
LAS	>10,000	<0.1	100	100
PCP	8,000	<0.1	50	50
DEHP	6	1	10	11
PCB[c]	0.00025	4	1	5

[a]pH 7.5
[b]100 is maximum value combining both evaporation and degradation rates. Metal ion dissipation has minimum value of 1.
[c]Representative PCB isomer; 2,5,2′-trichlorobiphenyl (*13*).

Table 3. Ratio of dissipation to bioconcentration potential of chemicals in aquatic environment.

Chemical	Relative Dissipation (DIS)[a]	Factor (BCF)	Ratio DIS/BCF
LAS	100	10[b]	10
PCP	50	200[c]	0.25
DEHP	11	800[d]	0.014
PCB	5	50,000[e]	0.0001

[a]100 is maximum value combining both evaporation and degradation rates. Metal ion dissipation was a minimum value of 1.
[b]Data of Comotto et al. (*8*).
[c]Data of Dow Chemical Co. (*11*).
[d]Data of Branson (*15*).
[e]Data of Nisbet (*6*).

the lower the bioconcentration potential, the larger the value of the ratio. Chemicals like LAS receive a large number, DIS/BCF = 10, because of high degradation and low bioconcentration potential; chemicals like PCB's with high bioconcentration factors and low dissipation potential receive very small numbers, DIS/BCF = 0.0002. The nomogram for predicting the unknown ambient exposures (Fig. 2) illustrates an empirical relationship between fish residues, environmental release rates, and the ratio of dissipation to bioconcentration potential. Recognizing that the straight lines plotted on this graph are only made from two points each, the absolute position of the line is tentative at best. It seems reasonable, however, to assume that higher environmental release rates would result in a parallel line higher on this graph and lower release rates would result in a lower line. The graph does serve to illustrate the hypothesis that if any two of the three pieces of information are known, the third piece can be estimated. For example, if the DIS/BCF ratio for a chemical is 0.001 and its release rate is about 10^7 lb/yr, then the predicted ambient residues in fish are about 1 ppm, but if the environmental release rate is about 10^8 lb/yr then the ambient residues in fish would be about 100 ppm. Also, given that fish residue data (C_f) are available, measured or estimated from Figure 2, the ambient exposure concentration in water (C_w) can be estimated by dividing by the bioconcentration factor: $C_w = C_f/\text{BCF}$. The shaded

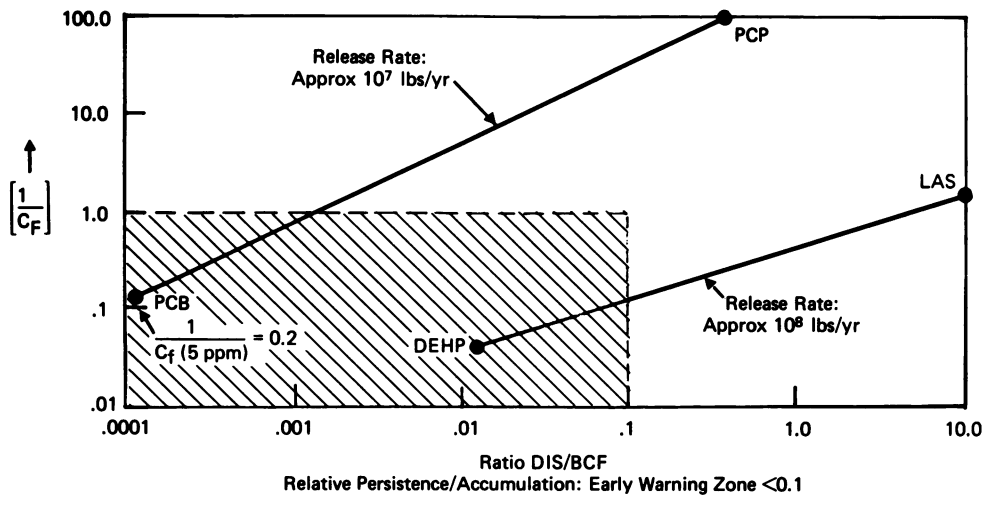

FIGURE 2. Preliminary nomogram for predicting the unknown ambient exposures. The ambient concentration of a chemical in water, C_w, can be roughly estimated from the ambient concentration in fish, C_f, and the bioconcentration factor at steady state, BCF, i.e., $C_w = C_f/\text{BCF}$.

area illustrates qualitatively that chemicals with high environmental release rates and/or persistence/accumulation properties will end up in this zone. Most of the chemicals, on the other hand, will end up outside this zone, since these curves were drawn with chemicals with known fish residues and fairly high environmental release rates.

Correlations of environmental properties of chemicals derived from large data bases confirm that most of the chemicals are outside this zone of concern. Vieth and Konasewich (personal communications, 1979) have shown that only about two-thirds of the 2,100 chemicals manufactured or used around the Great Lakes have octanol-water partition coefficients suggestive of low concern for fish residues. Also Bailey (personal communications, 1979), indicated approximately two-thirds of 600 chemicals screened for biodegradability in a simple biochemical oxygen demand test yielded 30% or more BOD in 20 days, indicating a low degree of persistence in the aquatic environment. Both of these properties, accumulation and persistence, appear to be related to low water solubility (Table 2). In general, the environmental fate of the majority of chemicals currently manufactured and used by society is characterized by a low degree of persistence and accumulation and will, therefore, be of low hazard because the ambient exposure concentrations are low.

Hazard Assessment

Figure 3 compares the margin between the no effect concentrations and the ambient exposure concentrations for the case study chemicals. A reciprocal of hazard was used to show hazard by the height of the bar graph, i.e., narrow margins of safety yield tall bar graphs and vice versa. The PCB example illustrates a case in which residues in fish would cause concern to fish eaters but the ambient levels of PCBs in water would cause little or no concern to aquatic life. On the other hand, DEHP illustrates a case in which the aquatic organisms could be at risk but not the fish eaters. Both of these materials fall across an arbitrary line where the margin between effect and exposure is equal to or less than five. A safety margin of five appears to be a reasonable criterion for distinguishing between chemicals that should and should not be classified as "priority." Neither LAS nor PCP appears to be reasonably classified as a priority chemical.

The safety margin concept was also employed by Klapow and Lewis (*14*) in selecting water quality standards in the marine environment. More importantly, the safety margin of the typical standard was less than a factor of five above the ambient exposure concentration, e.g., for copper, ambient 0.002 mg/l., standard 0.005 mg/l., margin of safety 2.5; and for

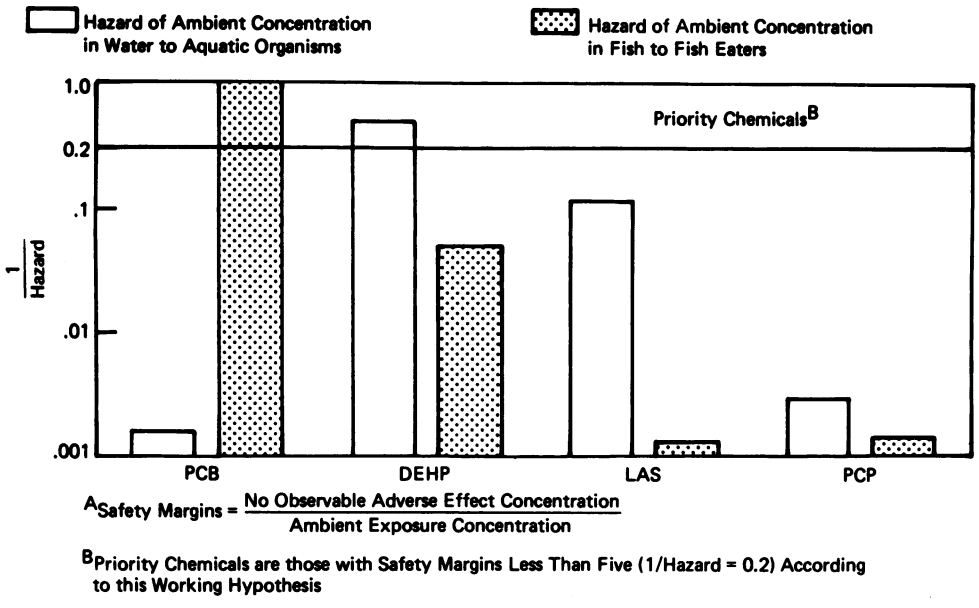

FIGURE 3. Safety margins of chemicals in the aquatic environment. The numerical values associated with each chemical are only meant to illustrate the concept of prioritization of chemicals according to safety margins, i.e., degree of hazard. Confidence limits and difference in geographical sites for ambient measurements should be considered before using these values for more than illustrating the concept.

zinc, ambient 0.008 mg/l., standard 0.02 mg/l., margin of safety 1.5. Therefore the margin of safety factor of five used here to select priority chemicals is conservative.

Research Needs

The basic premise for suggesting areas of research to improve hazard assessments of any chemical in the aquatic environment for any decision-making values is that exposure and effect concentrations must be available for both and that the biggest research need is estimating exposure concentrations. The following areas of research are very important.

It is necessary to develop and validate test methods for measuring rates of degradation, evaporation, and bioconcentration of chemicals in water. These test methods must accommodate chemicals with low water solubility (less than 1 ppm), and the results should be reported as measured rate constants. With more experience in generating rate constant data, it is hoped that some preliminary estimates of their value can be based on structure through various regression correlations.

The lack of reliable information on the amount of chemicals released to the environment is the single largest source of error in environmental hazard assessment (Baughman, personal communications, 1978). The approach used by the 1975 NSF Workshop seems promising and should be updated. It takes the use patterns of industrial chemicals into account.

There is a glaring lack of field studies to show that laboratory data correctly forecast the fate and effects of chemicals in the real world. Predictive models need to be validated for several different aquatic environments based on time-concentration data with adequate material balance accountability.

It would be valuable to add more data points (case study chemicals) to Figure 2, as data are generated from more and better analysis of fish and water samples, DIS/BCF, ratios and environmental release rates. These data should be used in prioritizing and deprioritizing chemicals.

Conclusions

Principles of hazard assessment can be used as a prescreen in selecting priority chemicals. These principles involve estimates or measurements of both the exposure and the no effect concentrations. In addition to narrow safety margins, chemicals should not be classified as priority chemicals unless there is evidence of (a) potential to cause significant human toxicity including carcinogenicity, mutagenicity and teratogenicity; or (b) analytical detection at toxicologically significant concentrations in five or more controllable point sources.

Rough estimates of ambient exposure concentrations can be made if environmental release rate and the ratio of dissipation (DIS) to bioconcentration potential (BCF) are known. Also, the ratio DIS/BCF can be used as an early warning index for chemicals or used for predicting fish residues or environmental release rates.

Under the principles of environmental hazard assessment, both PCB and DEHP would be candidates for a list of priority chemicals. Neither LAS or PCP would be priority chemicals.

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