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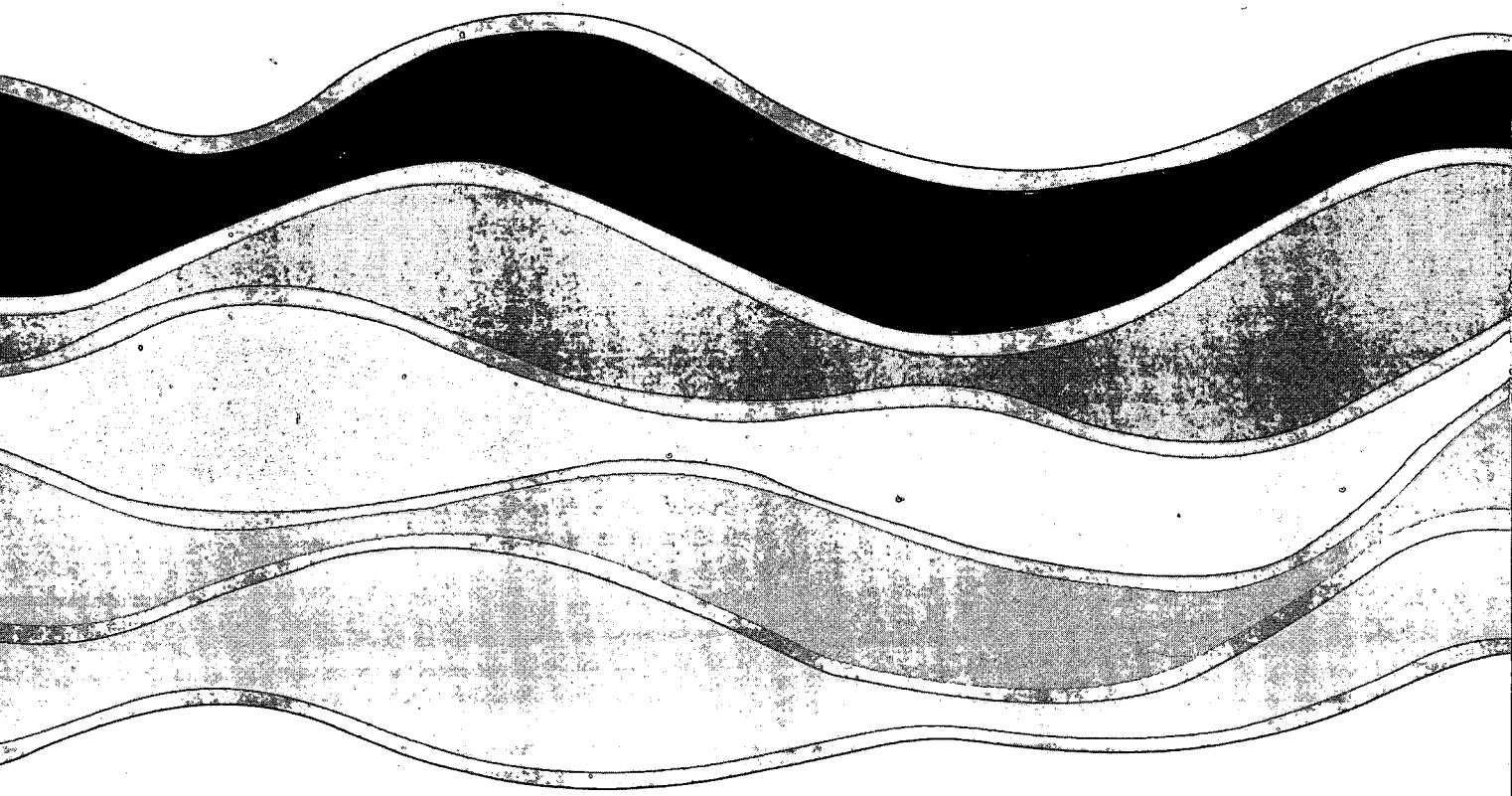

ASSESSMENT OF THE ENVIRONMENTAL HAZARDS OF PESTICIDES TO AQUATIC BIOTA

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EXECUTIVE SUMMARY

The assessment of the environmental risk of pesticide contamination of aquatic ecosystems requires the integration of information by experts on the toxicity of such chemicals to aquatic biota along with an estimation of the extent of environmental exposure. This information comes from a variety of sources including laboratory and field studies to determine the physicochemical characteristics and transformation kinetics of the pesticide itself as well as toxicity tests using single-species of organisms and groups of organisms (microcosms) in the laboratory. Field studies in replicated enclosures (mesocosms), replicated stream channels or whole-pond studies under simulated field conditions are used less often but provide important information on the direct and indirect effects of toxicity. This paper briefly reviews the information obtained from these studies as they pertain to pesticides and outlines some of the advantages and disadvantages of their use in the evaluation of risk to surface waters. In addition, data requirements and gaps for the setting of Canadian water quality guidelines for ambient concentrations of pesticide residues are discussed.

PERSPECTIVE DE LA DIRECTION

L'évaluation du risque pour l'environnement de la contamination par des pesticides des écosystèmes aquatiques exige l'intégration d'informations provenant de spécialistes de la toxicité de ces produits chimiques pour le biote aquatique ainsi qu'une estimation de l'ampleur de l'exposition ambiante. Ces informations proviennent de sources diverses notamment d'études en laboratoire et sur le terrain afin d'établir les propriétés physico-chimiques et la cinétique de la transformation du pesticide lui-même et d'essais de toxicité effectués en laboratoire au moyen d'organismes monospécifiques et de groupes d'organismes (microcosmes). Des études sur le terrain dans des enceintes multiples (mésocosmes), des canaux d'essais multiples ou des études portant sur des étangs entiers dans des conditions pratiques simulées sont utilisées moins souvent, mais fournissent des informations importantes sur les effets directs et indirects de la toxicité. Le présent document analyse brièvement les données tirées de ces études parce qu'elles concernent des pesticides et souligne certains avantages et inconvénients de leur utilisation pour l'évaluation des risques pour les eaux superficielles. De plus, on étudie également les données requises et les écarts en vue de la formulation de recommandations pour la qualité des eaux au Canada relativement aux concentrations de fond des résidus de pesticides.

ABSTRACT

The assessment of the environmental risk of pesticide contamination of aquatic ecosystems requires the integration of information by experts on the toxicity of such chemicals to aquatic biota along with an estimation of the extent of environmental exposure. This information comes from a variety of sources including laboratory and field studies to determine the physicochemical characteristics and transformation kinetics of the pesticide itself as well as toxicity tests using single-species of organisms and groups of organisms (microcosms) in the laboratory. Field studies in replicated enclosures (mesocosms), replicated stream channels or whole-pond studies under simulated field conditions are used less often but provide important information on the direct and indirect effects of toxicity. This paper briefly reviews the information obtained from these studies as they pertain to pesticides and outlines some of the advantages and disadvantages of their use in the evaluation of risk to surface waters. In addition, data requirements and gaps for the setting of Canadian water quality guidelines for ambient concentrations of pesticide residues are discussed.

RÉSUMÉ

L'évaluation du risque pour l'environnement de la contamination par des pesticides des écosystèmes aquatiques exige l'intégration d'informations provenant de spécialistes de la toxicité de ces produits chimiques pour le biote aquatique ainsi qu'une estimation de l'ampleur de l'exposition ambiante. Ces informations proviennent de sources diverses notamment d'études en laboratoire et sur le terrain afin d'établir les propriétés physico-chimiques et la cinétique de la transformation du pesticide lui-même et d'essais de toxicité effectués en laboratoire au moyen d'organismes monospécifiques et de groupes d'organismes (microcosmes). Des études sur le terrain dans des enceintes multiples (mésocosmes), des canaux d'essais multiples ou des études portant sur des étangs entiers dans des conditions pratiques simulées sont utilisées moins souvent, mais fournissent des informations importantes sur les effets directs et indirects de la toxicité. Le présent document analyse brièvement les données tirées de ces études parce qu'elles concernent des pesticides et souligne certains avantages et inconvénients de leur utilisation pour l'évaluation des risques pour les eaux superficielles. De plus, on étudie également les données requises et les écarts en vue de la formulation de recommandations pour la qualité des eaux au Canada relativement aux concentrations de fond des résidus de pesticides.

INTRODUCTION

In 1986, over 32,000 metric tonnes of 224 pesticide active ingredients were sold in Canada as 2350 different pest control products (Environment Canada/Agriculture Canada, 1987). Herbicides made up the majority of sales (83.4%) while insecticides and fungicides constituted approximately 8.8% and 7.8% respectively of the total volume (Pierce and Wong, 1988). The extensive use of pesticides may result in such chemicals entering aquatic ecosystems in a number of different ways i.e., pesticides may enter water directly through overspray, aerial drift, careless handling, accidental spills, improper disposal and/or actual treatment of basins for chemical control of pests. In addition, pesticides applied to foliage and soil may enter water via surface runoff resulting from rainfall or snowmelt as well as via leaching through the soil to the water table.

The transport of any particular pesticide from the site of application to aquatic ecosystems is a complex function of the physicochemical properties of the chemical itself and its formulation as well as the time interval between pesticide application and rainfall, duration of precipitation, rates of application, soil texture, condition and topography and the type and amount of ground cover (Wauchope, 1978; Willis and McDowell, 1982; other papers in this symposium).

The ecological risk assessment of the environmental hazards presented by pesticides to natural aquatic ecosystems in Canada is presently determined by experts who analyze the available scientific information on toxicity to non-target aquatic organisms and compare this toxicity with the expected environmental concentration (EEC) of a pesticide to determine the extent of exposure of aquatic organisms. In the case of new pesticide products or pesticides on the re-evaluation list (Trade Memorandum R-1-226), a judgement is made

regarding the acceptability of this exposure by officials of the Departments of the Environment and Fisheries and Oceans and the information is relayed to Agriculture Canada where a decision is made (along with other considerations of mammalian toxicology, etc.) under the Pest Control Products Act as to whether the chemical will be registered (in the case of new chemicals), restricted in its use or removed from the market. In addition, water quality guidelines under the auspices of the federal Department of the Environment in cooperation with the provinces may be set for the protection of all forms of aquatic life for priority in-use pesticides (CCME, 1990).

This paper will review the current methods for estimating the toxicological hazards of pesticides to non-target aquatic biota and for determining environmental exposure. A brief discussion of the data gaps which need to be filled for more accurate assessment of hazard is also included.

Estimating toxicological hazard

Historically, the main source of information on the toxicity of pesticides to aquatic organisms has been through laboratory bioassays on single-species of vertebrates (mainly fish), invertebrates, algae (some) and microorganisms.

In an acute test, organisms are exposed to a pesticide for a relatively short period of time under controlled laboratory conditions, typically 24-96 h, and the end point measured is either death or a non-lethal effect expressed as either an LC50 or EC50 (i.e., concentrations of substances estimated to kill or have an effect on half of a group of organisms under a specified duration of exposure). The advantages of acute toxicity tests

include the availability of acceptable and standardized methodologies, scientific and legal defensibility, simplicity, replicability, reproducibility, cost-efficiency, ability to rank chemicals for their relative toxicity and comparison of relative toxicities to organisms representing different trophic levels (La Point et al., 1989).

Table I gives ranges of the acute toxicities (48-96 h LC or EC50s) for several classes of pesticides for three trophic levels - algae, invertebates and fish. In general, the organophosphate insecticides and synthetic pyrethroids are the most toxic chemicals to aquatic biota with animal life more sensitive than plant life. However, there are certain instances where a pesticide, especially a herbicide, may be very toxic to primary producers e.g., a concentration of 1.0 μg atrazine/L to certain species of algae. Table I also indicates that toxicity levels can vary widely between species within any given trophic level.

TABLE I

Ranges of acute toxicities (48-96 h LC or EC50s) in μg/L for algae, invertebrates and fish for several pesticides[a].

	Algae	Invertebrates	Fish
Herbicides			
Atrazine	1.0 - >100,000	360-30,000	220 -> 100,000
2,4-D	100 - > 100,000	2600 - > 100,000	3700 - > 100,000
Glyphosate	-	> 100,000	> 100,000
Triallate	-	880 - 2300	600 - 9600
Insecticides			
Carbaryl	100 - 5000	2.7 - 13	250 - 39,000
Chlorpyrifos	1 - 200	0.8 - 50	15 - 550
Permethrin	1600 - > 100,000	0.2 - 8.8	0.04 - 40
Fonofos	-	2 - 330	45 - 109
Fungicides			
Thiram	1000	170 - 270	220 - 330

[a] compiled from Stratton & Corke (1982), Van Leeuwen et al. (1985), Smith & Stratton (1986), Mayer & Ellersieck (1986), Mayer (1987), Eisler (1989), Swanson (1989), Buhl & Faerber (1989)

A most comprehensive listing of the acute toxicities of selected pesticides to aquatic animals is that of Mayer and Ellerseick (1986) who collated and evaluated for good laboratory practice, toxicity data developed by the Columbia National Fisheries Research Laboratory of the U.S. Fish and Wildlife Service since 1965 (i.e., 4901 tests with 410 chemicals [mainly pesticides] and 66 vertebrate and invertebrate species). Amongst 82 chemicals tested with 6 or more species, the highest toxicity values within a chemical averaged 256X the lowest and values ranged from 2.6 to 166,000X, demonstrating great interspecific variability. Similar results have been demonstrated for plant species by Blanck et al. (1984) who tested 18 pesticides with 13 green algae and showed that differences in sensitivity among species within a chemical may be as high as a factor of 2000.

The data by Mayer and Ellersieck (1986) were also analyzed by various statistical approaches to make taxonomic comparisons and to assess the degree to which various factors affect toxicity. Insects, particularly mayflies and stoneflies, were the most sensitive group, followed by crustaceans, fish, and amphibians. Among the four most commonly tested forms, daphnids were the most sensitive 58% of the time, followed by rainbow trout, *Salmo gairdneri* (35%), bluegills, *Lepomis macrochirus* (5%) and fathead minnows, *Pimephales promelas* (2%). Factors which were shown to have a modifying effect on the toxicity include pH, dissolved oxygen, temperature, pesticide formulation, nutritional status, source of organisms, life stage and size of animals, etc. (Mayer and Ellersieck, 1986; Sprague, 1990).

Users of acute toxicity data for hazard evaluation must be aware that the LC50 or EC50 generally measures only one biological response, a lethal one, and from the results, a toxicologist can only recommend maximum concentrations for the well-being of aquatic

organisms at one point in time. Acute toxicity tests provide no information about the long-term impacts of contamination (La Point et al., 1989).

The estimation of longer-term, chronic effects of pesticides is generally determined by exposing a group of organisms to a particular chemical over an extended period of time in the laboratory (typically 30-60 days which may include whole life-cycles, partial life-cycles or early life stage testing) (Pickering and Gilliam, 1982; Jarvinen et al., 1988). The effects measured may be lethal or sublethal and can include changes in survival, growth, reproduction, biochemistry, physiology or behavior. Table II provides an example of a comparison of acute to chronic toxicity levels for fathead minnow larvae (*Pimephales promelas*) exposed to three insecticides - chlorpyrifos, fenvalerate, and endrin - for either 96-h or 30-d continuous dosing. Chlorpyrifos was not as acutely toxic as endrin or fenvalerate in short-term acute toxicity tests but under conditions of continuous exposure, organisms were much more sensitive to this chemical.

TABLE II

Comparison of acute to chronic toxicity levels for fathead minnow larvae (*Pimephales promelas*) exposed to three insecticides (after Jarvinen et al., 1988).

	96-h LC50	30-d continuous exposure
Chlorpyrifos	122 µg/L	2.1[a] µg/L 7.1[b] µg/L
Endrin	0.70 µg/L	0.38[c] µg/L 0.73[c] µg/L
Fenvalerate	0.85 µg/L	0.36[bc] µg/L

[a]increased deformities [b]decreased growth [c]decreased survival

Single-species chronic toxicity tests can be very useful in measuring time-independent toxicity relations, sensitivities of different species and life stages and bioconcentration potential. These estimates can later be used in establishing threshold concentrations below which a tested population could be expected to persist indefinitely (the no-observable-effects-concentrations (NOEC)). However, such tests, especially with vertebrates, are time-consuming, expensive, species-dependent and sometimes toxicant-dependent and may be unfeasible for routine use in many laboratory situations (La Point et al., 1989).

An alternative approach to whole organism tests is within-organism studies i.e., biochemical and physiological indices used to predict and monitor the effects of pesticides on the growth and development of aquatic organisms. For example, the inhibition of acetylcholinesterase activity has been used successfully in combination with other measurements e.g., behavior and/or toxic response, as a tool in diagnosing organophosphate poisoning in fish and benthic invertebrates (Jarvinen et al., 1983; Day and Scott, 1990). Exposure to organophosphate pesticides has been shown to alter the biochemical composition and mechanical properties of fish bone and result in vertebral abnormalities, lordosis and scoliosis (McCann and Jasper, 1972; Cleveland and Hamilton, 1983). Although biochemical measurements have been shown to provide a sensitive indication of sublethal toxicity in laboratory studies in some instances, it is unknown if these aberations occur in the field and whether the multiplicity of field variables will potentiate or mitigate contaminant influences on these responses (La Point et al., 1989). In addition, Sprague (1990) suggests that concentrations of toxicants causing meaningful within-organism changes are no lower than, and are often much higher than, those that cause sublethal whole-organism effects.

The assessment of chemical toxicity to aquatic organisms using single-species toxicity tests has considerable value when used to determine toxicological effects on survival, growth, reproduction, physiology and behavior. For this reason, these tests are the mainstay of hazard assessments and are usually found in the early stages of most hierarchical hazard assessment programs. At present, acute and chronic laboratory bioassays are still most often used to assess the effects of pesticides in aquatic ecosystems and to obtain basic information for legislation on environmental protection (Ravera, 1989). For example, Canadian Water Quality Guidelines for priority in-use pesticides are currently being developed by Environment Canada for the protection of aquatic life (CCME, 1990). The goal of the guidelines is to protect all forms of aquatic life and all aspects of aquatic life cycles. For this purpose, the minimum aquatic toxicological data requirements for freshwater are:

Fish - at least three studies on 3 or more freshwater species resident in North America, including at least 1 coldwater species (e.g., trout) and 1 warm water species (e.g., fathead minnow); of the above studies, at least 2 must be chronic (partial or full lifecycle) studies.

Invertebrates - at least 2 chronic (partial or full lifecycle) studies on two or more invertebrate species from different classes, 1 of which includes a planktonic species resident in North America (e.g., daphnid)

Plants - at least 1 study on a freshwater vascular plant or freshwater algal species resident in North America; for highly phytotoxic variables, the requirements increase to include 4 acute and/or chronic studies on non-target freshwater plant or algal species.

In cases where data are available but limited, interim guidelines are set which are deemed preferable to no guidelines.

The guidelines are preferentially derived from the lowest-observable-effects level (LOEL) from a chronic study using a non-lethal endpoint for the most sensitive life stage of the most sensitive aquatic species investigated. The LOEL is then multiplied by a safety factor of 0.1 to arrive at the guideline value. This safety factor is chosen to account for differences in sensitivity to a chemical variable due to differences in species, laboratory vs. field conditions, and test endpoints. When this type of data is unavailable, guidelines can be derived from acute studies by converting short-term medium lethal or medium effective concentration data (LC50 or EC50) to long-term no-effects concentrations using acute/chronic ratios (ACR). An ACR is calculated by dividing a LC50 or EC50 by the NOEL from a chronic exposure test for the same species. It is important to note that an ACR should only be used from studies which were designed for this purpose in order to avoid complications arising from different test conditions or different test populations. In the event that acute/chronic ratios are not available, the alternative method of choice is to derive a guideline value from an acute study i.e., to multiply the LC50 or EC50 value by a universal application factor. The application factor for non-persistent variables (half-life in water < 8 weeks) is 0.05 and for persistent variables the application factor is 0.01.

Two pivotal assumptions upon which single-species toxicity tests are based are 1. that, by using the most sensitive species results and ensuring that these species are protected in natural systems, all other species will inevitablity be protected and 2. as a consequence, it is not possible that malfunctions at higher levels of biological organization will occur (Cairns, 1989). Several investigators have criticized the extrapolation of results from single-species toxicity tests to predict adverse ecological effects in the natural environment (Cairns, 1983; Slooff, 1985; Lynch et al., 1985). For example, such tests may fail to predict indirect effects of pesticides on aquatic ecosystems i.e., changes in predation, competition, succession and nutrient cycling, which may ultimately affect the fate and effect of toxicants in aquatic environments (National Research Council, 1981). In addition, changes in water quality may mediate toxicity, the responses of other life history stages of the test species are not included in the test, interactions with other chemicals might make the biological response additive, synergistic or antagonistic, etc. Cairns (1989) also suggests that the use of application factors or ACRs ensures that the estimated 'safe' concentration is exceeding low and that the cost of meeting the environmental concentration of the chemical is frequently prohibitive.

Based on these criticisms, it becomes highly desirable to validate single-species laboratory toxicity tests by studying effects in a functioning community. One approach is to use 'artificial ecosystems' variously described as "multispecies toxicity tests", "laboratory streams", "microcosms" or "mesocosms" depending on design (Sprague, 1990).

There are many current attempts to develop standard laboratory microcosms (i.e., aquaria of $\leq 1\ m^3$ volume that contain a known medium, biota, and toxicant concentrations) for testing toxicants especially pesticides (Sheehan et al., 1986; Giddings, 1986; de Zwaart

and Langstraat, 1988; Yount and Shannon, 1988). The two approaches which have received the most attention and have well-developed protocols are mixed flask cultures (MFC) (Leffler, 1981) and standardized aquatic microcosms (SAM) (Taub and Read, 1982). These systems attempt to reproduce community- and ecosystem-level processes in a controlled manner representative of some portion of a natural environment (Shannon et al., 1986). The SAM protocol calls for the development of a defined community from pure stock cultures of algae and other small aquatic animals in a defined medium in glass jars. The species assemblage does not simulate a specific community but serves as a generalized model aquatic ecosystem that includes species at the primary and secondary trophic levels as well as decomposers. Changes in population densities, nutrient cycling and ecosystem-level variables are monitored to evaluate toxic effects. The MFC approach allows a community of organisms to develop from a variety of natural sources over time - a so-called "co-adapted" species assemblage. Evaluation of toxicity involves monitoring only ecosystem level changes (e.g., community production and respiration). Species population dynamics are ignored on the assumption that system-level variables are species-independent. The method is considerably less labour-intensive but not nearly so "data-rich" as the SAM procedure and may not present a complete picture of toxic effects. Some criticisms of these systems include concerns about the cost and the fact that artificial communities may not be representative of "natural, co-adapted species assemblages" and are therefore not reliable for studies of ecosystem-level properties. There are also problems with the development of variable communities which results in problems of repeatability.

Microcosms will never replace single-species toxicity tests in hazard assessments but should be considered as a means of providing supplementary information about effects on

complex living systems and to verify single-species toxicity tests. Microcosms can also be used for the refinement and confirmation of chemical and mathematical models.

An example of results from a microcosm study is that of Stay et al. (1985), who examined community level responses (i.e., primary productivity, community respiration, primary production efficiency and P/R ratios) in SAM microcosms exposed to several concentrations of atrazine (60, 100, 200, 500, 1000, and 5000 μg/L). All variables measured in the high treatment levels (i.e., 500, 1000 and 5000 μg/L) declined immediately in response to added atrazine and remained suppressed throughout the experiment with little or no recovery. Lower treatment levels (60, 100 and 200 μg/L) had variable effects on the parameters measured. The ^{14}C-uptake/chl *a* ratio, which is an index which measures the effectiveness of the algal photosynthetic system, was the most sensitive measure of the effect of atrazine. This ratio normalizes the rate of carbon fixed over the large range of chlorophyll *a* concentrations and ^{14}C-uptake rates found in these microcosms. Data developed with this ratio in this study suggest that primary priductivity in the 60 to 200 μg/L treatments was reduced and although photosynthesis eventually recovered to control levels, the effectiveness of the photosynthetic system remained impaired. Community respiration was the least sensitive measure of the effects of atrazine and differences were not significant at treatment levels of less than 200 μg/L atrazine.

Recirculating or continuous flow laboratory streams have also been used to test small but complete communities of microorganisms i.e., algae, invertebrates and fish (Lynch et al., 1986; Hamala and Kollig, 1985). Muirhead-Thomson (1987) reviewed the use of simulated streams in the laboratory to allow a more realistic approach to studying the reactions of aquatic macroinvertebrates to pesticides. Hansen and Garton (1982) assessed

the ability of a standard set of freshwater single-species toxicity tests to predict the effects of the insecticide, diflubenzuron, on complex laboratory stream communities. The effects on these stream communities were assessed at the functional group levels using biomass and diversity for the analysis. The single-species tests adequately predicted the concentrations of diflubenzuron which affected these stream communities. The most-sensitive test species (i.e., insects and crustaceans) were up to an order of magnitude more sensitive than the observed community effects. The single-species tests were less successful in predicting the exact nature of the community level effects i.e., effects resulting from direct lethality to component species were clearly predicted whereas indirect effects due to altered interspecies interactions could only be predicted with an *a priori* knowledge of the system's trophic dynamics.

Experimental ponds or mesocosms (i.e., artificial enclosures with a volume between 1-300 m^3 situated in a lake, pond or stream), if properly constructed and managed, may be regarded as the most realistic replica of larger aquatic ecosystems with nearly all the components of their natural counterparts . These experimental units have been used by a number of investigators to answer questions about the fate and effects of pesticides in aquatic ecosystems (e.g., deNoyelles and Kettle, 1982; Kaushik et al., 1985; Crossland and Bennett, 1989). The important advantages of a mesocosm or pond study are that it is possible to study effects of pesticides on populations of various species under conditions of real-world exposure, data can be obtained for species that are not easily maintained in the laboratory, direct and indirect effects may be studied (e.g., predator-prey interactions, effects on dissolved oxygen, etc.) and rates of recovery of populations from stress may be determined (Crossland and Bennett, 1989). A great deal of chemical information on the

transformation of the chemical to metabolites, its half-life and its compartmentalization can also be obtained from these types of studies (Solomon et al., 1985; Maguire et al., 1989). Some disadvantages of mesocosm studies are that they are costly, labour-intensive and some enclosures may suddenly change composition for reasons that are not always obvious (i.e., there are problems with replication).

One of the most comprehensive systems for validation of laboratory toxicity data in rivers and streams is the facility at the Montilcello Ecological Research Station, Duluth, Minnesota. This facility contains a series of parallel artificial streams of realistic sizze (1.4 m wide in riffle areas) constructed outdoors. Replicates can be used and new water water can be dosed to a constant concentration of pesticide. Eaton et al. (1985) used such a facility to study the effects of continuous and intermittent concentrations (0.12 - 0.83 μg/L and 0.94 - 7.0 μg/L, respectively) of the organophosphate insecticide chlorpyrifos. Measured system characteristics included macroinvertebrate drift and riffle benthos composition; fish survival, growth, reproduction, food habits, tissue residues and acetylcholinesterase inhibition; and system functional process indicators (P/R ratios, biodegradation, nitrate and dissolved organic carbon concentrations, bacterial growth and heterothrophic activity).

Estimating Environmental Exposure

Theoretically there exists a highest predicted environmental concentration of a pesticide in the various compartments of the aquatic environment (i.e., water, particulate organic matter, sediments, etc.) that could potentially result from the normal anticipated use of the product. An evaluation of the potential exposure of non-target aquatic organisms to such pesticide residues requires an estimation of the concentration, the bioavailability and the

duration of contact of these toxicants with biota.

Where there is little or no information on expected environmental concentration (EEC), pesticide residues in aquatic ecosystems can be estimated by approximating "worst-case" scenario by assuming direct overspray of a small pond 0.5 m in depth. For example, the EEC for a hypothetical chemical can be calculated as follows:

Maximum label rate = 3.5 kg/ha = 3500 g/10,000^2 = 0.35 g/m^2.

If this amount is applied to a surface area of 100 m^2,

then 35 g total will be applied; assuming 0.5 m depth, we have 35 g/50 m^3 = 0.70 g/m^3 which = 0.70 g/1000L or 0.70 mg/L = EEC

Information on EEC, persistence and distribution of pesticide residues in aquatic ecosystems can also be obtained from mathematical models such as PERSISTENCE (NRCC, 1981) or EXAMS (Burns et al., 1982) which integrate laboratory data on volatilization, hydrolysis, phototransformation, water solubility, octanol-water partition coefficient, leaching potential, etc. (Pierce and Wong, 1988). However, the persistence of pesticides under field conditions may be less than under laboratory conditions due to hydrological, limnological and biological interactive processes which are not always simulated in the laboratory i.e., dilution and sediment exchange; uptake, transfer and metabolism by aquatic life; sorption to dissolved and particulate organic matter, etc.

More realistic information on pesticide residues in aquatic ecosystems can be obtained from field studies using ponds or mesocosms with simulated overspray and intensive analytical sampling (Solomon et al., 1985; Maguire et al., 1989). For example, Muir et al. (1985) found that deltamethrin injected below the surfaces of two small ponds rapidly

partitioned from water into suspended solids, plants, and sediment, with a half-life of 2-4 h in water. They found half-lives of 5-14 days for total deltamethrin in sediment and observed residues up to 306 days post-treatment.

In order to determine actual concentrations of pesticides in ambient surface waters or in surface runoff from treated fields following routine use, field monitoring for pesticides residues on a seasonal and watershed basis is necessary. Limited information has been reported by Wauchope (1978), Muir and Grift (1987), Frank and Logan (1988), Wan (1989), and Frank et al. (1990a,b). Concentrations of pesticides reported are generally in the low μg/L range with residue levels in rivers and streams usually a great deal lower (Table III) than those measured in runoff events from agricultural watersheds and research plots (Table IV) (Wauchope, 1978; Willis and McDowell, 1982). Single-event runoff losses in the range of 1-2% of the total pesticide applied are not uncommon for a wide range of pesticides although wettable powder formulations, especially the triazines and other water-soluble herbicides, may be consistently higher (>5%). Maximum pesticide losses usually take place in treated fields during intense rainfall that occurs within 24 h of pesticide application (Baker et al., 1978). For example, Witt and Sanders (1988) calculated that 91%, 89% and 78% of the total seasonal losses of atrazine, cyanazine and simazine, respectively from a treated field occurred in runoff from a rainfall event that began on the day of application. They suggested that the high loss immediately after application was due to the relatively low sorption of the herbicides to organic matter and soil colloids during the short time between application and rainfall. It is also likely that herbicides originally removed from the treated fields on suspended sediment could be desorbed during transport (Spalding and Snow, 1989).

TABLE III

Concentrations of Pesticides in streams located in agricultural watersheds.

Watershed	Concentration (ng/L)
Prairies (Muir and Grift, 1987)	
Triallate	< 0.7 - 6.4
Trifluralin	< 1.3 - 22.9
Dicamba	9.7 - 48.4
2,4-D	4.5 - 227
Bromoxynil	< 0.5 - 1.63
Diclofop	1.2 - < 12.5
Ontario Streams (Frank and Logan, 1988)	
Atrazine	200 - 5400
Metolachlor	700 - 4100
Dicamba	100 - 22,000
2,4-D	10 - 300
Endofulfan	2 - 48

TABLE IV

Maximum Observed Concentrations of Pesticides in Runoff[a] in Streams Below Agricultural Fields (after Wauchope, 1978).

Pesticide	Concentration in Bulk[a]	Comments
Endosulfan	18	plots[c]; low solubility
Dicamba	4810	plots[c]; water soluble applied to foliage
Atrazine	627 - 1460	plots[c]; severe storm wettable powder
Propachlor	1702	plots[c]; wettable powder
Trifluralin	0.5 - 24	plots[c]; soil incorporated
Fonofos	5 - 60	plots[c]; severe storm soil incorporated

[a]runoff = both the water and its associated sediment lost from the surfaces of fields
[b]bulk = μg pesticide/L of water-sediment mixture
[c]plot = subsection of a field

Pesticide concentrations in runoff have been shown to vary by an order of magnitude or more during a single runoff event. In addition, pesticide concentrations in runoff decline exponentially with time on a seasonal basis due to volatilization, photolysis and other processes occuring in soil and water following field application (Leonard, 1988). Other factors which drastically reduce edge-of-field concentrations after runoff leaves the field may be added to this complexity i.e., dilution by receiving waters, sorption by stream sediments, untreated soil or vegetation surfaces, etc., and it is obvious that concentrations in aquatic ecosystems may be a highly transient property.

The lack of detectable residues of pesticides in water does not necessarily indicate that significant impacts on non-target organisms have not occurred (Wong et al., 1988). With the banning or restriction of the most persistent organochlorine insecticides, most pesticides in general use in agriculture today (e.g., organophosphate and pyrethroid insecticides) are relatively short-lived and their impacts may be localized. What this means to the exposure regime for aquatic biota (concentration vs. time profile), is that exposure will be very variable under natural conditions with significantly high levels of pesticides being present for only a short time and then rapidly declining (Jarvinen et al., 1988).

Understanding the acceptable risk

The simplest determination of risk occurs when concentrations of pesticides observed and/or estimated in the field are similar to the levels known to cause acute effects in laboratory toxicity studies; effects on aquatic organisms under field conditions will thus be anticipated. For example, Buhl and Faerber (1989) calculated maximum concentrations of

8 herbicides in bulk runoff during a projected critical runoff event as 10% of the maximum recommended application rate in runoff water 1 cm deep (Table V). In addition, they determined the acute toxicities of these herbicides and 2 surfactants to early fourth instar larvae of the midge, *Chironomus riparius*, under static conditions. A comparison between estimated maximum herbicide concentrations in runoff and results from acute tests indicated that triallate, bromoxynil, propachlor and alachlor pose the greatest direct risk to midge larvae during a storm event. However, the actual biologically available concentrations in bulk runoff depends on partitioning between sediment and water and other complex environmental factors and overall assessments must include judgements on such mitigating factors as the time and distance of impact and the abilitiy of local ecosystems to recover from temporary high concentrations of a pesticides. In addition, the exposure regime (concentrations vs. time profile) for aquatic biota in the field will be radically different from that in laboratory bioassays where aquatic organism are exposed to a constant toxicant water concentration over the exposure duration which is experimentally determined. The use of constant exposure laboratory values in toxicological hazard assessment may overestimate toxicity if expected environmental concentrations are never reached or if the exposed organisms have the ability to recover. In contrast, toxicity may be underestimated if brief exposures can, in fact, cause adverse effects. In addition, concentrations of pesticides in aquatic ecosytems are normally too dilute to produce acute toxicity but the direct and indirect effects caused by chronic exposure of aquatic organisms to low concentrations of persistent or intermittent pesticides are difficult to assess. As pointed out by Wauchope (1978), although we have a fair ability to estimate inputs of pesticides to aquatic ecosystems, we have a near complete ignorance as to what those inputs mean.

TABLE V

Comparison of projected herbicide concentrations in runoff with corresponding acute toxicity values (after Buhl and Faerber, 1989).

Herbicide	Maximum Estimated Concentration in Runoff (mg/L)	48-h EC50 to Midge Larvae (mg/L)	Ratio 48-h EC50/ Runoff Concentration
Triallate	1.68	1.23	0.73
Bromoxynil	1.12	1.90	1.70
Propochlor	6.72	2.20	0.33
Alachlor	4.48	12.5	2.79
Butylate	6.70	37	5.52
EPTC	6.70	56	8.36
Metribuzin	1.1	130	118
Glyphosate	4.5	5600	1244

[a]calculated for a 'critical' runoff event as % of the application rate lost in a given volume of runoff; a 'critical' event is defined as one in which at least 1 cm of rainfall produces a runoff volume of 50% or more within 2 weeks of application

Wong et al. (1988) ranked the 25 top selling pesticides in Canada along with some of their related chemical forms with regard to their persistence in aquatic ecosystems and their toxicity to aquatic organisms using knowledge of their physical, chemical and toxicological properties in combination with their use patterns and a variety of recognized methods (i.e., subjective ranking based on properties, weighted ranking equations, NRCC PERSISTENCE model, etc.). The input data were chosen to simulate the *in situ* dynamics of selected in-use pesticides following a midsummer single-event release at the initial concentrations expected from a direct overspray of the water body at the maximum recommended crop application rate. Three indices which incorporate progressively more measurements of toxicity, bioconcentration, expected environmental concentration and persistence were used in exploring the utility of hazard indices. The first index, the lethality index (Zitko and

McLeese (1980) is simply the ratio of the expected environmental concentrations in water to the lowest LC50 recorded for each pesticide. The EECs were obtained from runs of the PERSISTENCE model assuming no degradative losses. With this index, the most toxic pesticides were the insecticides - carbaryl, malathion, diazinon, chlorpyrifos, etc. and the fungicide, thiram. The second index, the hazard index (Burridge and Haya, 1987), was calculated simply by multiplying the lethality index by the bioconcentration factor predicted for fish by the PERSISTENCE model. The bioconcentration factor (BCF) is the ratio of the concentration of a substance in fish to the concentration in the water where it has lived. Bioconcentration has received a great deal of attention in both biomonitoring, research and technique development mainly because of the concern for the health of humans who may eat contaminated fish rather than direct toxicity to the organisms which accumulate the toxicant (Sprague, 1990). On the basis of the hazard index, chlorpyrifos, malathion, diazinon, and carbaryl were again ranked in the top five most hazardous pesticides with phorate, terbufos, lindane, thiram, etc., also ranking highly. The remaining measurement of risk, the Relative Hazard Index (RHI) of Sheehan et al. (1987), incorporates both the expected environmental concentration of a chemical as modified by its predicted persistence and its acute toxicity. The 14 most hazardous pesticides as estimated by the RHI index (assuming equilibrium in a Standard Lake or Pond system) are (in order of decreasing toxicity) carbaryl, malathion, diazinon, fenitrothion, metolachlor, atrazine, lindane, glyphosate, carbofuran, phorate, chlorpyrifos, terbufos, captan and 2,4-D BEE. Pesticides such as terbufos and phorate have much lower RHI at equilibrium than carbaryl or metolachlor even though they are more toxic because they are also much less persistent (Table VI).

TABLE VI

Ranking of the 25 most heavily used pesticides in Canada on the basis of a lethality index, a hazard index and a relative hazard index (RHI) (at equilibrium) (after Wong et al., 1988).

Lethality		Hazard		RHI	
Carbaryl	1846	Chlorpyrifos	440000	Carbaryl	8489
Malathion	1620	Malathion	92502	Malathion	3060
Diazinon	955	Diazinon	89292	Diazinon	858
Thiram	223	Phorate	45853	Fenitrothion	195
Chlorpyrifos	100	Carbaryl	34523	Metolachlor	75
Lindane	65	Terbufos	20760	Atrazine	54
Phorate	55	Lindane	16880	Lindane	30
Captan	26	Thiram	15052	Glyphosate	8
Fenitrothion	25	Fenitrothion	3722	Carbofuran	7
Terbufos	15	Fonofos	2056	Phorate	7
Chlorothalonil	13	Trifluralin	1332	Chlorpyrifos	6
Fonofos	6	Chlorothalonil	1050	Terbufos	5
Carbofuran	3	Captan	753	Captan	2
2,4-D BEE	1.4	Triallate	230	2,4-D BEE	1
2,4-D acid	1.0	2,4-D BEE	87		
Atrazine	0.45	2,4-D acid	51		
Glyphosate	0.31	Diclofop-methyl	21		
Triallate	0.28	Atrazine	19		
2,4-D amine salt	0.09	Metolachlor	7		
Metolachlor	0.08	Glyphosate	2.8		
MCPA	0.02	Bromoxynil	0.4		
Diclofop-methyl	0.01	MCPA	0.04		
Bromoxynil	0.004	2,4-D amine salt	0.03		
Difenzoquat	0.0001	Difenzoquat	0.0001		

It must be emphasized that the use of such a model requires many assumptions i.e., all processes follow simple kinetics, the settling of suspended particulates in the water column is not included, the distribution of the pesticide is assumed to be at equilibrium, good estimates of partitioning and transfer rate constants are not always available, etc. It should also be pointed out that studies on the toxicities of the various pesticides to macrophytes

and algae were not included in the toxicity data set because of the lack of consistent methodologies amongst species and pesticides.

Kent et al. (1990) reviewed the current scientific literature from the past 5 years for toxicological studies on pesticides (a total of 668 original articles) and identified a number of critical gaps for 3 out of 14 priority herbicides with regard to the aquatic toxicology and fate of these substances as follows:

1. Relatively few toxicity studies are being conducted on plants and decomposers despite their obvious importance in aquatic ecosystem food webs and energy cycles.
2. Most aquatic vertebrate toxicity studies are conducted on species of fish indicating a conspicuous lack of amphibian, reptile, bird and mammal data.
3. Toxicity studies on aquatic macrophytes are rare.
4. Approximately 2/3 of the studies sampled were acute toxicity tests with only 1/3 chronic.
5. In most tests, the medium used was only water.
6. Microcosm, enclosure and field studies were rare.

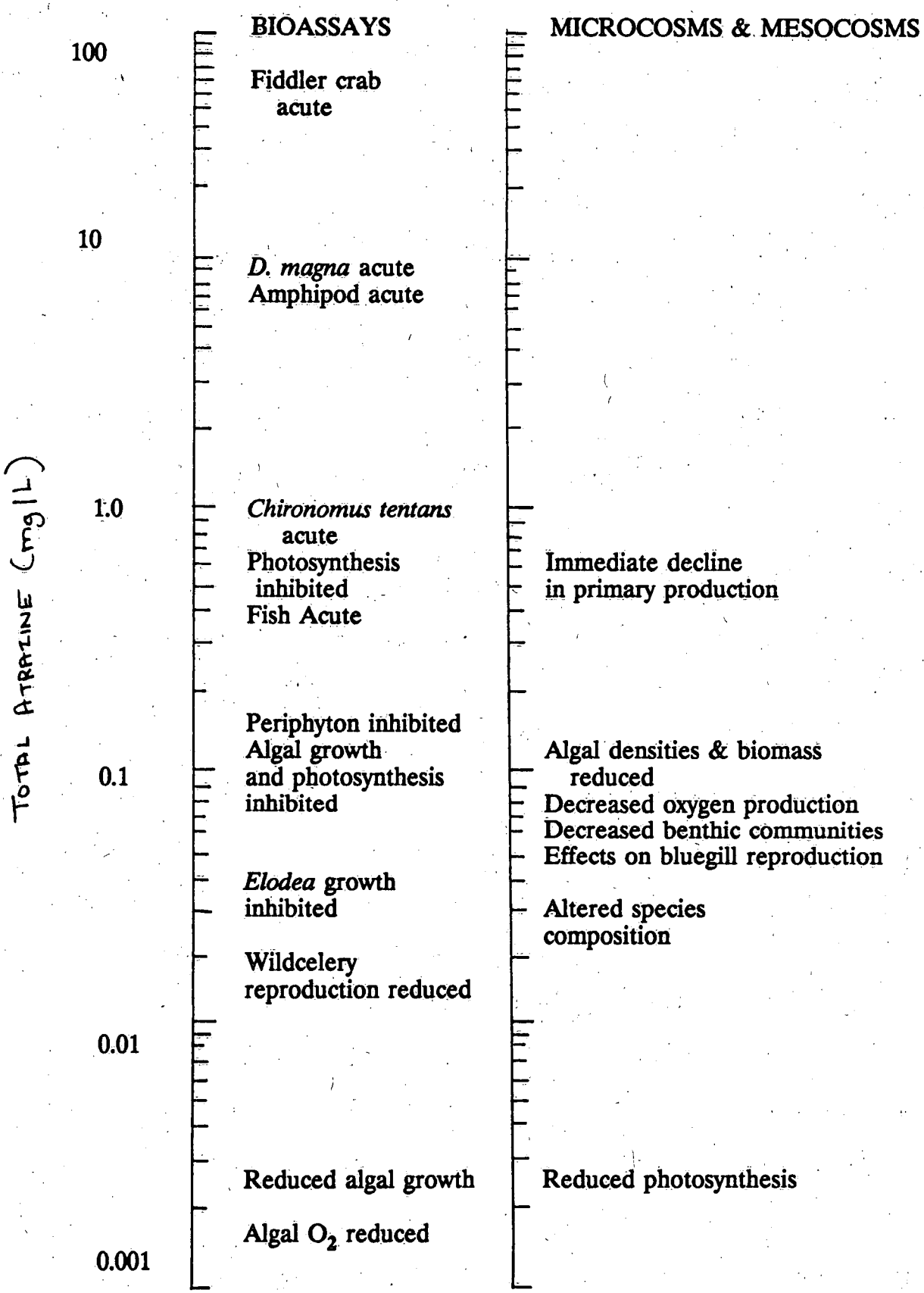
In many cases, these data gaps were severe enough to support only interim freshwater Canadian guidelines or prevent guideline development entirely.

The pesticide for which there is the most comprehensive data base for both potential adverse effects on nontarget aquatic organisms and documented presence in freshwater ecosystems is the triazine herbicide, atrazine (Eisler, 1989; Swanson, 1989; Trotter et al., 1990). Atrazine is used extensively in corn production in North America and has been

found contaminating surface and groundwater in a number of agricultural watersheds (Muir et al., 1978; Frank and Logan, 1988; Spalding and Snow, 1989; Frank et al., 1990a,b). Laboratory toxicity tests have indicated that reduced oxygen evolution and reduced growth in certain sensitive algal species can occur at concentrations of atrazine as low as 1 μg/L (Torres and O'Flaherty, 1976) (Figure 1). Mesocosms studies in pond ecosystems also indicated that photosynthesis would be reduced in sensitive species exposed to these low concentrations under field conditions (DeNoyelles et al., 1982). Concentrations as low as 20 μg/L could alter algal species succession and composition (DeNoyelles and Kettle, 1985) as well as reduce benthic invertebrate emergence (Dewey, 1982) and influence bluegill reproductive success (Kettle et al., 1987). Concentrations in the range of these levels which show direct and indirect effects i.e., 0.7 - 89 μg/L have been reported to occur albeit sporadically in streams and ponds adjacent to agricultural land where atrazine is extensively used (Table VII). On the basis of this information and the toxicity studies with algae and other aquatic vascular plants, the freshwater guideline of 2.0 μg/L was derived for the protection of freshwater aquatic life in Canada (Trotter et al., 1990).

In summary, in the hazard assessment of the effects of pesticides on freshwater biota, the ideal cost-effective approach would be to conduct a careful and comprehensive evaluation of toxicity data either from the literature or from actual laboratory toxicity tests utilizing acute and, whereever possible, chronic toxicity data for representative species of different trophic levels i.e., an alga, an invertebrate and a fish. Such data will indicate which groups of organisms are likely to be the most susceptible and therefore which should be sampled more intensively in the event of a pond or mesocosm study. Chemical information on photolysis, hydrolysis, solubility, etc. should also be consulted for estimations

FIGURE 1


BIOASSAYS
MICROCOSMS & MESOCOSMS
TOTAL ATRAZINE (mg/L)
100
10
1.0
0.1
0.01
0.001
Fiddler crab acute
D. magna acute
Amphipod acute
Chironomus tentans acute
Photosynthesis inhibited
Fish Acute
Periphyton inhibited
Algal growth and photosynthesis inhibited
Elodea growth inhibited
Wildcelery reproduction reduced
Reduced algal growth
Algal O2 reduced
Immediate decline in primary production
Algal densities & biomass reduced
Decreased oxygen production
Decreased benthic communities
Effects on bluegill reproduction
Altered species composition
Reduced photosynthesis

on persistence, solubility and transformation. These data will help in deciding whether structural and/or functional responses of organisms should be monitored. For example, in the case of chemicals that are toxic but nonpersistent, transient effects on population densities of susceptible species may be expected but populations may recover quickly in a short time. Functional responses such as growth, reproduction and productivity are often regarded as more indicative of the health and integrity of the ecosystem than structural responses and are therefore more important in the context of chronic toxicity of more persistent pesticides.

Unfortunately, the assessment of the downstream impact of pesticides in runoff from agricultural lands is confounded by factors as distance of transport, dilution, sorption processes, sedimentation, degradation and the inherent ability of any aquatic ecosystem to recover from temporary high pesticide concentrations. It has been suggested that brief exposure tests, i.e., pulses, should be incorporated into the hazard evaluation process because the effects of pesticides on aquatic organisms cannot be acurately predicted by standard toxicity tests which approximate constant exposure. Serious knowledge gaps exist in several key areas in our understanding of acceptable risk as follows (Libby and Boggess, 1989; La Point et al., 1989; Day, 1991):

1. Our ability to detect and measure chemical concentrations far exceeds our understanding of their significance
2. The effects of low-dose, extended exposure toxicities are very difficult to evaluate
3. The toxicities of mixtures of chemicals and the synergistic effects of combined chemical exposure greatly complicates evaluation of the potential effects.

4. Most studies only consider the dynamics and effects of the parent compound rather than include degradation and/or transformation products which could be more toxic.
5. Information is scarce on the cost and efficacy of alternative control strategies particularly given the site-specific nature of many contaminant problems.
6. Meaningful endpoints in tests performed at the community or ecosystem levels are difficult to determine e.g., what does the loss of a sensitive species indicate if it is replaced by a more resistant species and the role in community function is unaltered?

The challenge is to fill these knowledge gaps using cost-efficient but comprehensive toxicity tests. As pointed out by La Point et al. (1989), despite higher costs, complex test systems can remain cost-effect because multiple-species effects and chemical fate can be jointly studied in the same system. Furthermore, the information gained in ecotoxicological testing adds to the basic knowledge of ecosystem structure and function. Only when we understand more about how populations and communities respond to chemical stress will we be able to reduce their hazard potential.

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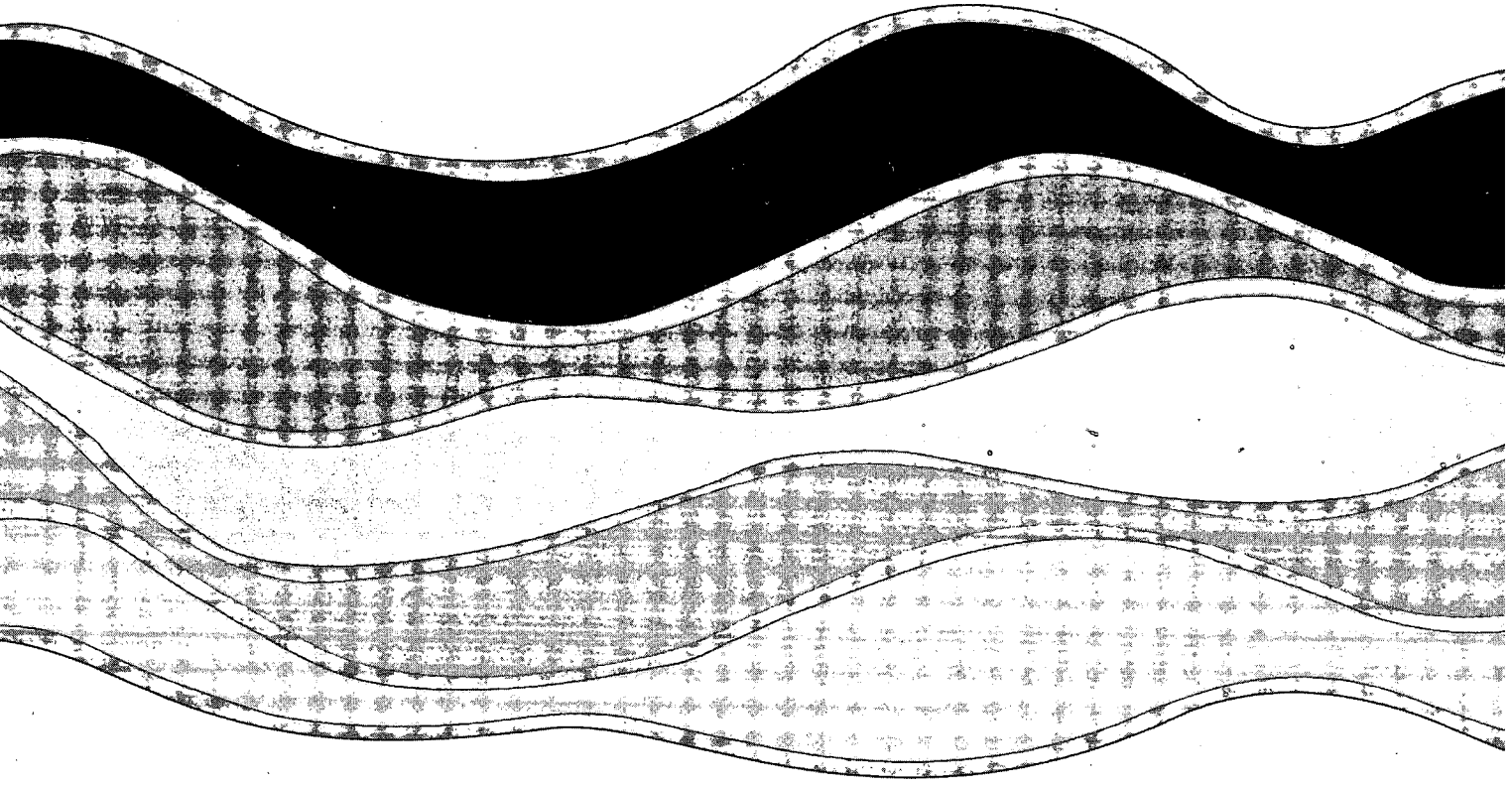

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