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Probabilistic risk assessment of agrochemicals in the environment

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Abstract

Concern for the environment has resulted in greater scrutiny of both old and new plant protection products and increased efforts have been directed to developing more rigorous but more realistic procedures for the ecotoxicological risk characterization of these agrochemicals. These techniques include probabilistic analysis of toxicity and exposure data and better understanding of the relationship between structure and function in populations of wildlife and the role of keystone species in maintaining ecosystem functioning. The ecological risk assessment method described here is centered on the use of probabilistic distribution functions that independently describe exposure concentrations and toxicological responses of organisms to the chemical of concern. The distributions are transformed to permit calculation of linear regression parameters. The regression parameters for the two distributions are then used to determine joint probabilities which interrelate the exposure and toxicology data. For ease of presentation the results are presented as an exceedence plot which depicts, based on the exposure data the percent of species likely to be affected and the percent of observations likely to cause this level of effect. In this paper, the use of the method is illustrated using data for chlorpyrifos in North American aquatic environments. These probabilistic risk assessment methods are being assessed for incorporation into assessment procedures in a number of regulatory jurisdictions.

Keywords: Pesticide; Risk assessment; Probabilistic

1. Introduction

Assessment of the potential for chemicals introduced into the aquatic environment to cause adverse effects can be determined a priori or a posteriori. Monitoring can determine actual exposures, and in some situations document effects. In other situations, even if the level of exposure can be measured, the potential for adverse effects needs to be predicted from simulations. In still other situations both the degree of exposure and response need to be predicted. Among species variation needs to be assessed, based on the same model. The most rudimentary approach to assessing the potential for adverse effects is to compare the estimate of exposure with some threshold for adverse effects. The most simple method is the calculation of a hazard quotient, where the point estimate of the measured or predicted exposure concentration is divided by the threshold or safe level determined from a dose-response relationship. An approach that uses multiple lines of evidence and information on population and community structure, exposure values, and toxicity is described and is illustrated with a pesticide that has already been introduced into the environment.

Hazard quotients are point estimates that compare an estimate of exposure to some established toxicity reference value to protect surrogate species. The hazard quotient (HQ) is the quotient of the measured or estimated environmental concentration (exposure) divided by the toxicant reference value (TRV). The simple hazard quotient method is useful only to rebut the presumption of a potential for adverse effects and belongs in the early stages or tiers of a risk assessment. If the ratio exceeds a value of 1.0 the potential of risk cannot be rebutted. However, since conservative assumptions and parameter estimates are applied in the analysis to assure that no situations where adverse effects would be expected to occur would inappropriately be declared safe, this method is very protective. However, this approach cannot be used to establish a level of risk as the quotient is based on point estimates from a concentration-response

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vector. Furthermore, the term risk implies an element of likelihood, and likelihood is reported as probabilities, which cannot be established from point estimates. We endorse the tiered assessment process suggested by ARAMDGP (SETAC, 1994) and endorsed by the US EPA (ECOFRAM, 1999), which applies increasingly complex and resource-intensive levels of assessment as needed. Some compounds that do not present a risk can be eliminated from further consideration at the lower tiers, while most insecticides that have been engineered to be toxic to at least one class of organisms generally have HQ values that exceed 1.0 in the lower tiers. This result necessitates more complex assessments. Because there is a certain amount of variation involved in the estimates, there is a degree of uncertainty in assessments of risk. For this reason, in the lower tiers, conservative assumptions and estimates of modeled parameters are generally made or safety (uncertainty) factors applied. While these estimates lead to very protective estimates, they are often extremely conservative.

The science of ecological risk assessment has been developing continually over the past 20 years. During this time, many improvements have been made in methods to estimate exposures of populations and communities to potentially hazardous materials and their responses to these exposures. Some of the improvements have been in the ability to more accurately predict exposures by use of simulation models. In addition, better methods of deriving TRVs have been developed. Still other improvements have been through the application of probabilistic approaches.

The use of probabilistic approaches to estimate risks are not new, they have been used for actuarial purposes for centuries. However, the application of these approaches to risk assessment of agrochemicals in complex ecosystems with many potential receptor organisms requires more than the minimal amount of information normally required for pesticide registration. Probabilistic risk assessments (PRAs) allow the risk assessor to include estimates of uncertainty as well as stochastic properties of both exposures and responses. The use of PRA recognizes that there are no absolutes in risk assessment; there are never any situations where there is no risk of effect and there are few situations where there is complete certainty that a given level of effect will occur. Instead, there is a continuum of potential exposure and effect situations and a range of certainty can be reported. In addition, this type of assessment allows the risk assessor to conduct the assessment independent of most value judgements. This allows the risk manager to make the decisions as to the degree of overlap between the exposure and effects function that is acceptable and the level of certainty required in a particular situation. For instance, the risk manager can suggest that 80% of the individuals of 99% of the potential species in a particular system should be protected. Based on a probabilistic risk assessment, one could predict the likelihood that such a level of protection would be attained. The assessor may require that the environmental concentration associated with this level of protection be exceeded only 5% of the time. Use patterns could then be manipulated through the application of appropriate mitigation measures to achieve the required degree of certainty that the desired level of protection would be achieved. While such analyses provide the risk assessor and risk manager with a flexible tool that provided a great deal of information, the technique cannot always be applied as the data may not be available. However, at a minimum, the application of the procedure will identify the data needs, which can thus be prioritized.

The probability of exceeding a particular concentration in the environment can be estimated directly from distributions of measured values from monitoring programs or estimated by mathematical simulations by using the appropriate distributions of input parameters (ECOFRAM, 1999). However, the range of responses in organisms is more difficult to estimate. The probability of the tolerance of an individual in a population can be estimated from the slope function of the dose-response relationship. However, the distribution of sensitivities among species requires more extensive testing. If sufficient data are available, this can be done through use of a probability distribution of species. The details for conducting such an analysis are beyond the scope of this brief article, but are given in detail elsewhere (Solomon et al., 1996; ECOFRAM, 1999; Giesy et al., 1999). These methods allow the assessor to determine the probability of finding an additional species that would be more sensitive to the effects of the toxicant of interest and are similar to those that have been used for many years by the US EPA to derive water quality criteria (Stephan et al., 1985). They do not provide an absolute measure of the most sensitive species, because, by definition, there could always be an additional species found to be more sensitive than the most sensitive species previously identified.

PRA can incorporate the ecological principles of population dynamics, community resiliency, and redundancy of ecosystem functions. This approach can recognize that some exceedences of toxic concentrations to the most sensitive species can be tolerated if the affected species can readily recover, are not critical to the function of the ecosystem (keystone species), and are not valued for some other reason such as endangered status or economic importance.

2. Methods

PRA is applicable when a range of values are available for both the exposure data and known toxicological effects. This method provides the greatest amount of

information to both the risk assessors and risk managers, but may be limited by the amount of information available. The method described below is currently being implemented by the US-EPA (USEPA, 2000a, b) and is rapidly gaining acceptance in other jurisdictions. This method provides the greatest certainty in effects prediction when the primary measure of exposure is concentrations in the ambient environment. The assessment procedure reviewed here is based on the probabilistic approach used by a number of authors (Solomon et al., 1996; Giesy et al., 1999; Cardwell et al., 1999; Hall et al., 1999, 2000). Toxicity data for all species are combined to produce an effects concentration distribution curve (Fig. 1A), where appropriate data are fitted to log-normal distributions (Burmaster and Hull, 1997), however, other models or bootstrapping models may be used (ECOFRAM, 1999). When the exposure data are plotted on the same axes as the effects data, the extent of overlap between the curves indicates the probability of exceeding an exposure concentration associated with a particular probability of effects of the substance of concern. Conceptually, there is always some degree of overlap between the two distributions. The region of overlap is between the greatest concentrations in the environment and the effects concentrations for the most sensitive species. The overlap of the distributions can more easily be conceptualized when the exposure and toxicity data are presented as cumulative frequency distribution functions (Fig. 1B). The extent of overlap between the curves is proportional to the degree of risk expected. The area under either distribution between any two points represents the probability of occurrence. Similarly, the area to the right of a point represents the probability of that point being exceeded. For instance, the probability of exceeding the concentration associated with effects on less than 5% of the individuals in 1% of the species. Once the relationships have been developed, they can be used to determine the probability of occurrence of a particular level of effect.

When characterizing distributions of environmental concentrations, it is important to retain data less than the method detection limit (MDL) in the distribution. In doing this, it is assumed that these censored values are a continuation of the uncensored values (Fig. 2) and, for the purposes of calculating plotting positions for graphical presentation, they are assigned a dummy value of zero.

The use of distribution curves for exposure and toxicity data allows the application of a joint probability method to describe the nature of risks posed by the environmental concentrations measured. In this method, the exposure and toxicity distributions are first converted to straight-line transformations of probability functions, usually by probit transformation. This results in dual probability lines with concentration of the residue being the common variable. For any level of effect an associated concentration can be determined. Similarly, for any concentration, a probability of that value being

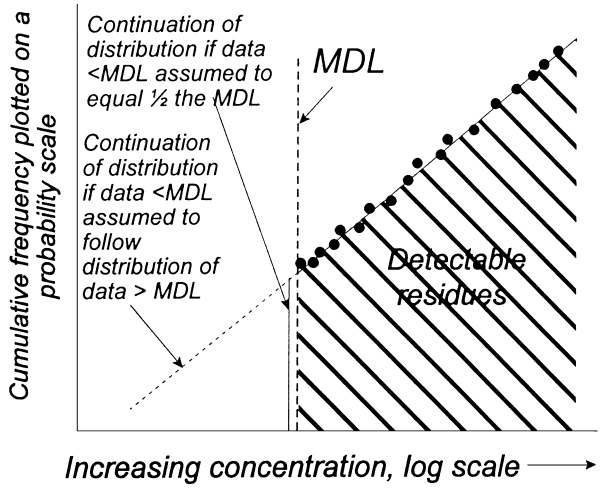

Fig. 2. Inclusion of values less than the Method Detection Limit (MDL) in probabilistic risk assessment

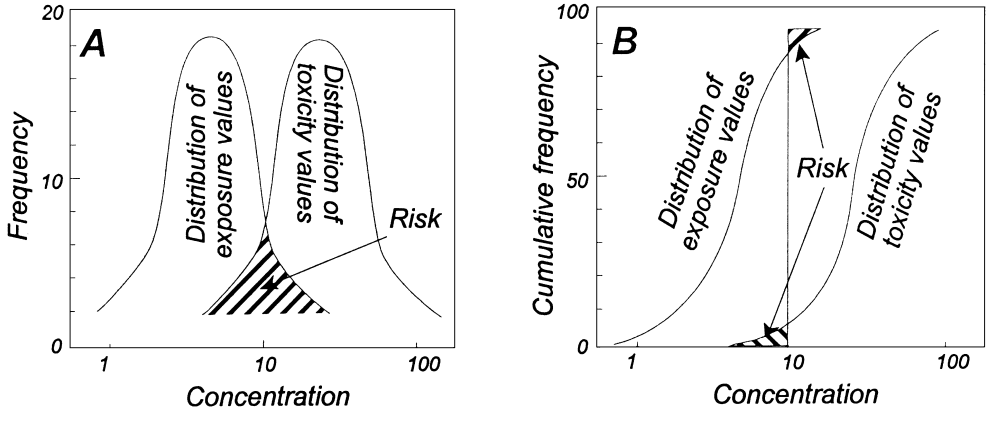

Fig. 1. Relationship between effect and exposure concentration distributions expressed as log-normal distributions (A) and cumulative log-normal distributions (B).

exceeded can be calculated (Fig. 3). In the example provided, the concentration at which 10% of species toxicity values will be exceeded is approximately 60 μg/l (Fig. 3). Approximately 95% of all exposures (water concentrations in the example) would be expected to be equal to or less than this value. Alternatively, this concentration would be expected to be exceeded approximately by 5% of the time. This is referred to as the exceedence value for exposure. It can be seen that, the smaller the concentration, the greater the degree of protection, since fewer species would be expected to be affected. Concurrently, there is a greater probability that this value will be exceeded. The level of protection can thus be selected. For instance, the probability of the concentration exceeding that below which fewer than 0.1% of species would be affected could be predicted. By selecting a toxicant reference concentration, the probability of a proportion of species being affected can be estimated. For instance, if EC5 values are plotted for each species, fewer than 5% of the individuals of that species would be affected at that concentration. It has been suggested that a LOAEL be applied rather than a NOAEL because of the difficulty in determining NOAELs (Bailer and Oris, 1997). An alternative method is to use an extrapolated EC0 which estimates the concentration predicted to affect zero percent of the individuals (Giesy and Graney, 1989).

The probabilistic model replaces species-specific effects concentrations with a distribution of effects data from numerous species. The resulting risk estimates are presented as continuous distributions and, therefore, desired levels of protection can be chosen based on the proportion of species impacted. The presentation of the continuous distribution also allows analysis of uncertainty since all of the uncertainty inherent in the analysis is "preserved" in the final distribution. For example, while a wide distribution can result from this approach, such distributions may simply reflect a wide range of environmental exposure concentrations and a wide range of species sensitivities. In this case, the distribution is reflecting natural variability in addition to uncertainty. In cases where high variability has resulted from combinations of sites and/or groups of organisms with inherently different sensitivity, site-specific contaminant measurements or limiting data to more directly relevant species could be used to improve the risk assessment.

The final step in the probabilistic approach is to generate a joint probability function of the exceedence data. This is done by solving the functions describing the probability of exceeding both an exposure and an effect concentration. This may be done with fitted regression models, from raw data sets of measured values, or from Monte Carlo modeled data (ECOFRAM, 1999). This results in a joint probability curve (JPC) or exceedence profile, which describes the probability of exceeding the concentration associated with a particular degree of effect (Fig. 4). Graphical display of the JPC also provides a means of assessing how alterations in ambient concentrations due to management efforts or natural attenuation would affect the risk assessment. The interpretation of the JPC is central to the PRA method. Each point on the curve represents both the probability that the chosen proportion of species will be affected and also the

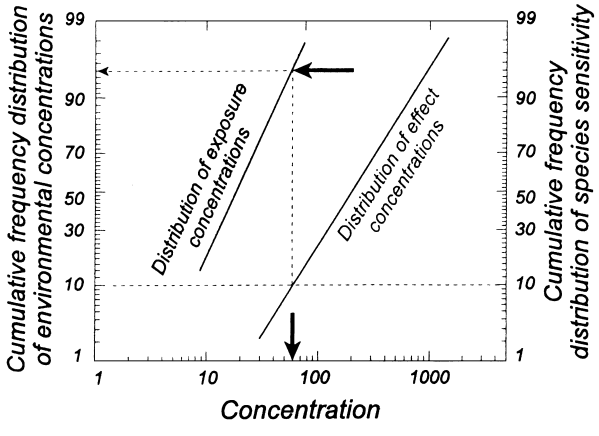

Fig. 3. Presentation of exposure and toxicology data as linearized probability distributions

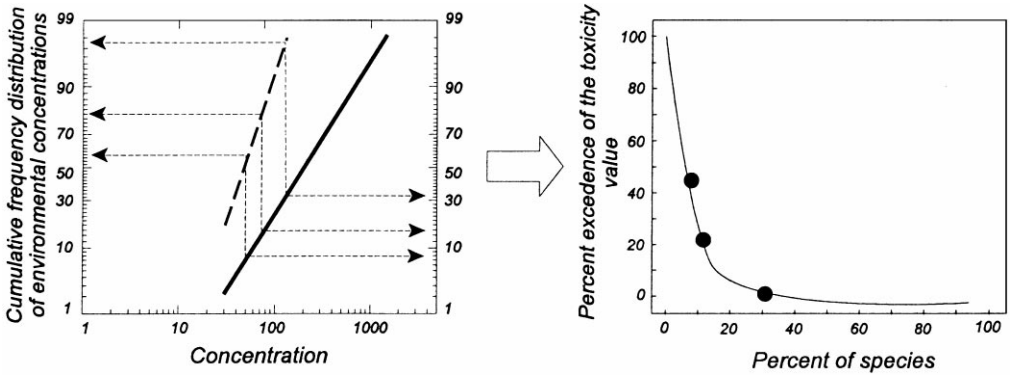

Fig. 4. Illustration of the derivation of a joint probability curve/ exceedence profile from exposure and toxicity probability functions (adapted from Giesy et al., 1999).

frequency with which that level of effect would be exceeded. These probabilities are based on the current exposure data so at each point on the line we can say "under current conditions, x% of species will be effected and that this proportion of species would be affected by y% of the current observations". Neither the probability of overlap between the two distributions nor the JPC are very useful as quantitative predictors of risk in themselves, but rather provide the risk assessor and manager with information on relative risk. Some examples for chlorpyrifos are provided below. Although it is possible to calculate the joint probability of occurrence of a particular magnitude of exposure and the proportion of taxa affected (by multiplying the two probabilities), we do not favor this approach because it is unclear what such a joint probability actually means. Instead, we favor the use of the JPC, which describes the probability of a particular set of exposure conditions occurring, relative to the number of taxa that would be expected to be affected. In this type of representation, the closer the joint probability curve is to the axes, the less probability of adverse effect (Fig. 5). The allowable exposure concentration can be adjusted until the appropriate level of protection has been achieved.

In practice, exposure and toxicity data are compiled and appropriate distribution functions fitted. This is accomplished by ranking the data and transforming the response data to probits:

$$\int(x, \mu, \sigma) = \frac{1}{\sqrt{2\pi\sigma}} e^{-(x-\mu)^1/2\sigma^1}, \quad (1)$$

where μ is the distribution mean and σ is the distribution standard deviation.

The probits are then plotted as a function of the $\log_{10}$ of the concentration. The best fit linear regression is then performed on the probit and $\log_{10}$ (concentration). The slope (m_i) and intercept (b_i) values are calculated using

$$y = xm + b, \quad (2)$$

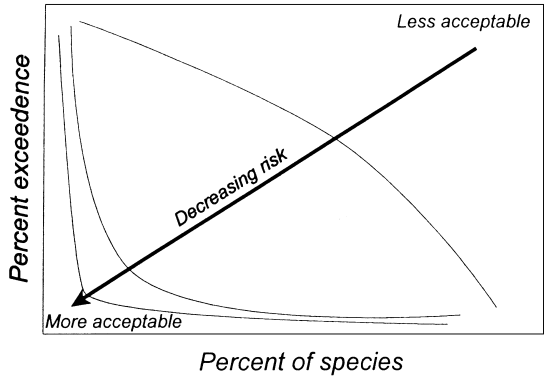

Fig. 5. Illustration of the use of the joint probability curve in decision making. (adapted from ECOFRAM, 1999).

$$m = \frac{(y - b)}{x}, \quad (2a)$$

$$b = y - (m \,.\, x), \quad (2b)$$

where y is the probit transformed toxicology or exposure data, x is the $\log_{10}$ transformed concentration data (toxicology or exposure), m is the slope of regression line and b is the intercept of regression line.

The slope and intercept of the linear regression for the two data sets can then be used to calculate the probabilities of concentrations causing adverse effects in a specified percentage of species:

concentrations effecting X% of species

$$= 10((prob(X) - b_{tox})/m_{tox} \quad (3a)$$

concentrations greater than the Xth percentile

$$= 10(prob(X) - b_{\exp}/m_{\exp}), \quad (3b)$$

where *prob(X)* is the probit value for the desired level of protection (% of species), m_{tox} is slope of the probit/log transformed regression line of the toxicology data, b_{tox} is intercept of the probit/log transformed regression line of the toxicology data, $m_{\exp}$ is the slope of the probit/log transformed regression line of the exposure data, and $b_{\exp}$ is the intercept of the probit/log transformed regression line of the exposure data. Also

prob . of conc . affecting X% of species

$$= (m_{tox} \,.\, \text{concentration}(X)) + b_{tox} \quad (4)$$

where *concentration(X)* is the the concentration effecting X% of species, from Eq. (3a), m_{tox} is the slope of the probit/log transformed regression line of the toxicology data and b_{tox} is the intercept of the probit/log transformed regression line of the toxicology data.

All the above procedures have been programmed into spreadsheets (Microsoft Excel and QuatroPro) which are available from the authors (ksolomon@tox.uoguelph.ca or jgiesy@aol.com)

The probabilistic assessment of relative sensitivities allows the assessor to identify the most sensitive types of organisms and focus the risk assessment on those taxa that are most at risk. The methodology also puts a premium on obtaining more toxicity information on the compound of interest since, if data are available on only a few species, the probability of exceedence will be artificially great. When compared to concentrations causing little or no effects in studies on communities in microcosms under field conditions, the 10th centile has proven to be a useful metric against which to compare exposure concentrations and is a conservative indicator of the threshold for effects (Solomon et al., 1996; Giesy et al., 1999; Versteeg et al., 1999). Laboratory toxicity tests are usually conducted under conditions where exposures to

the toxic substance are maximized. This is done by making exposure homogeneous; by excluding absorptive matrices such as sediment, macrophytes, or particulates that could reduce exposures; and by maintaining toxicant concentrations constant throughout the study. The differences between real and experimental exposure conditions are likely to lead to overestimation of risk. For example, when chlorpyrifos was assessed, the 10th centile of the distribution of single species LC50 values was 102 ng/l. This was only one of the metrics considered when determining a threshold for effects. For instance, a critical concentration for protecting community function of 100–200 ng/l was derived from the results of multi-species (mesocosm field studies) and a Final Acute Value of 148 ng/l was derived using the US EPA methodologies for the development of water quality criteria (USEPA, 1995; Giesy et al., 1999).

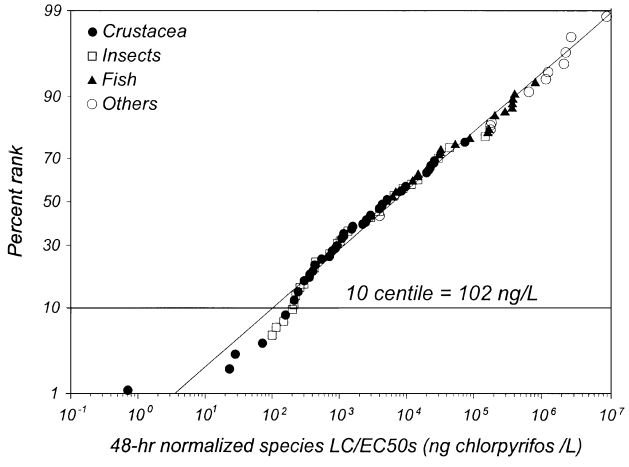

Fig. 6. Distribution of chlorpyrifos toxicity values for aquatic species. (redrawn from Giesy et al., 1999).

In conducting a PRA for chlorpyrifos (Giesy et al., 1999) the species distribution illustrated in Fig. 6 was obtained. When this distribution (and that for subsets of organisms) was compared to distributions of concentrations based on analysis of environmental samples, the JPCs illustrated in Fig. 7 were obtained. From all the sampling locations (not all shown in the Fig. 7), the probability of exceeding the critical concentration to protect community function was seldom exceeded in first order streams in the Midwestern corn belt of North America and the degree of exceedence was much less than 1% for second-order streams or higher. When a similar type of analysis was applied to California surface waters (Fig. 7) for which sufficient monitoring information was available, the probabilities of exceeding the threshold for adverse effects in all types of organisms were in the range of 3–33% in creeks drainage ditches (Turlock Irrigation Drain, Fig. 7 gave the most extreme value), but from less than 1–5% in main stems of rivers in California and similar sites in the US Midwest (San Joaquin River, CA and the Huron River, OH, Fig. 7). This indicates that there is a greater probability of exceeding the threshold in drainage ditches receiving irrigation return waters, but the probability of adverse effects on the main stems of rivers, while not zero, would be quite small. When the toxicity data for fish were considered (Fig. 7) the JPCs indicated minimal direct risks of toxicity in fish. However, in some locations, indirect effects on fish may occur through possible effects on prey species such as arthropods. The PRA was useful in prioritizing the locations based on the potential for adverse effects but is not designed to assess ecological relevance of the potential effects. The more sensitive of the organisms for which toxicity data were available (LC/EC50s < 200 ng/l) are all arthropods and most have short life-cycles and thus may recover rapidly from reductions in numbers

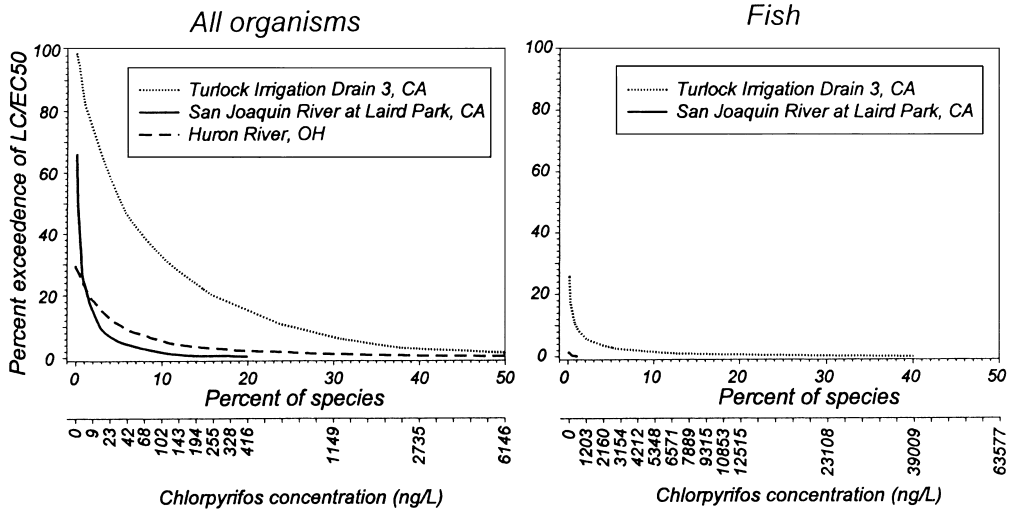

Fig. 7. JPCs for chlorpyrifos (redrawn from Giesy et al., 1999).

Table 1
LC/EC50s for chlorpyrifos in aquatic species with values below 200 ng/L (data from Giesy et al., 1999)

Organism	Genus and species	48-h LC/Ec 50 (ng/l)
Mosquito	*Aedes aegypti*	0.2
Mosquito	*various species*	0.5
Mosquito	*Culex pipiens*	22
Dragonfly	*Pseudagrim* spp.	50
Mysid	*Mysidopsis bahia*	88
Cladoceran	*Ceriodaphnia* sp.	105
Amphipod	*Gammarus pulex*	140
Cladoceran	*Ceriodaphnia dubia*	160
Cladoceran	*Daphnia* sp.	180
Brown shrimp	*Penaeus aztecus*	200

(Table 1). In addition, some other species in these groups (insects and Crustacea) were less sensitive and would be unlikely to suffer adverse effects. Thus, from an ecological perspective, sufficient redundancy of function (availability of prey species) exists that even a short-term reduction in the numbers of some arthropods because of the effects of chlorpyrifos will not have an impact on predators such as fish. This led to the conclusion that chlorpyrifos residues in surface waters of North America presented a minimal risk to environment (Giesy et al., 1999).

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