Chemical Risk Assessment based on the Framework of Basin-wide Ecological Modeling and the Ecotoxicological Index

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Abstract

This paper presents a method for estimating the ecotoxicolgical risk of toxic chemicals in terms of probability of an organism's lethality coupled with fate analysis and analysis of the dose-response relationship. The ecotoxicological index is defined as the probability of the magnitude of the exposure concentration of the chemicals in an aqueous environment being more than the organism's resistance to the chemicals. This approach is based on a second order moment approach used in statistical reliability analysis. Liner alkylbenzene sulfonates (LAS) were used as test chemicals in this study. By comparing the estimated probability and the quotient, the potential risks of the test chemicals were characterized.

1. Introduction

In hazard assessment or in screening levels of risk analysis of chemicals, the quotient method is generally employed and it provides a useful measure, although it seems to be a simplistic approach (OECD 1989). The measure is the ratio of the predicted environmental concentration (PEC) to the predicted no effect concentration (PNEC) of chemicals. If this ratio is less than 1, it only tells us that the environmental impact due to this chemical is less than the target value of the endpoint. As this value becomes large, the concern increases. In short, the quotient method is a comparison of representative values in each data set. However, the sensitivity of an organism to a chemical varies according to the dose. The concentrations of chemicals in the environment also vary in spatially and temporally. Consequently, a method that utilizes such data sets is required.

In this paper, we present as analytical framework for evaluating ecotoxicological risk in terms of the probability that takes into account the variability of the organism's resistance and the chemical concentration in the environment. The analytical framework is based on a second moment method that is used in statistical reliability analysis.

2. Probabilistic ecotoxicolgical risk assessment method

The analytical process used in this study is shown in Fig.1. First, variability in the organism's resistance to the chemicals' toxicity is calculated from the dose-response relationship. Second, assuming a lognormal probability distribution for the observed dose-response relationship, the means and standard deviations are estimated. Third, the variability in spatial and temporal distributions of environmental concentration is calculated from the mathematical fate, and the means and standard deviations are also estimated. Finally, the probability of lethality is calculated from the obtained statistical values by using a second moment method.

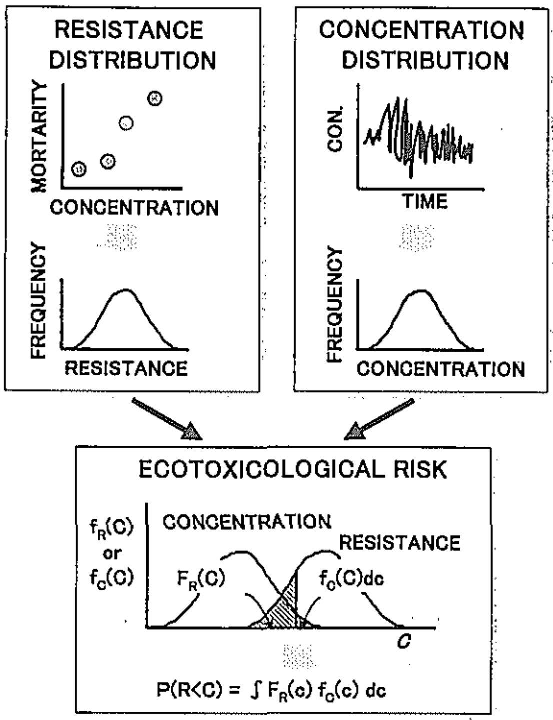


Fig.1 Diagram of Probabilistic risk assessment

2.1 *Variability in an organism's resistance to a chemicals' toxicity*

Using the results of toxicity tests, variability in resistance to a chemical is estimated by the Probit function in relation to the endpoint of acute lethality (e.g., LC_{50}). This function assumes that the distribution of individual sensitivities with respect to log dose is normal ; a probit is the normal equivalent deviate plus five. The probit function is:

$$probit(\pi i) = \frac{\log di - \mu}{\sigma} = \frac{1}{\sigma}\log di - \frac{\mu}{\sigma} \qquad (1)$$

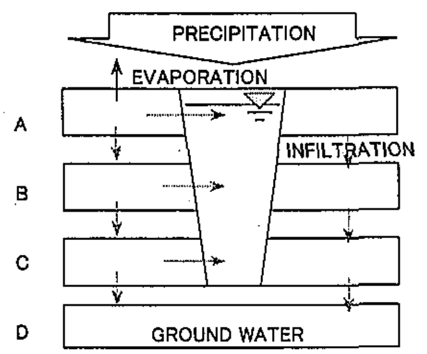
where π_i is the proportion response, *di* is dose or exposure concentration, and μ and σ are the mean and standard deviation with a normal distribution, respectively. In short, the dose-response relationship can be expressed as a linear function in relation to the logarithm of dose (*di*). Fitting to the test results and the variability is characterized as the mean and standard deviation of the probability distribution.

2.2 *Variability of contamination concentration in aqueous environments*

In estimating the environmental concentration of LAS, a mathematical model water runoff model and chemical fate model were solved simultaneously (Tokai *et al.*, 1998) is used. The concept of these models is followings.

2.2.1 Watershed model

A water runoff model is a mesh-typed model that explains vertical and horizontal water movements with the spatial resolution of 500 meters square. The concept and the governing equations are shown in Fig.2. Land is divided vertically into four layers, and horizontal and infiltration flow rates are calculated from these governing equations.



$$\frac{dS_A}{dt} = R_{ain} - Q_{AH} - Q_{AV} - EVA$$

$$\frac{dS_B}{dt} = Q_{AV} - Q_{BH} - Q_{BV}$$

$$\frac{dS_C}{dt} = Q_{BV} - Q_{CH} - Q_{CV}$$

$$\frac{dS_D}{dt} = Q_{CV} - Q_{DH}$$

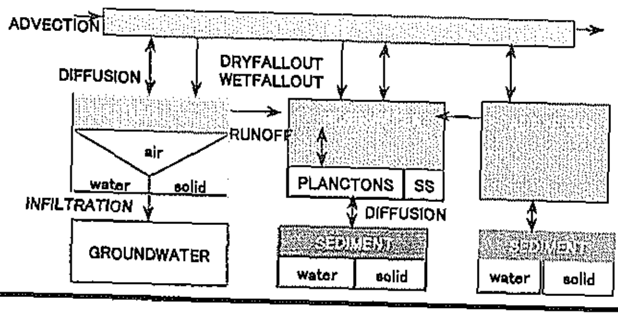
$$v = ki$$

V : flow rate
k : transmissivity
I : hydraulic gradient
S_I : water mass
Q_{IH} : horizontal flow rate in i
Q_{IV} : vertical flow rate in i
EVA: evapotranspiration from A

Fig.2 Multi-Layer runoff model

2.2.2 Chemical Fate Model

This model is constructed using the multimedia compartment model. This model consists of seven compartments (air, soil, ground water, river water, river sediment, paddy field and sediment) and incorporates a variety of transport phenomena associated with pollutant transport such as advection, diffusion, deposition and runoff. Using daily weather data, the concentration in each compartment was calculated. Fig. 3 shows a conceptual diagram of a chemical fate model.



$$\frac{dV_iC_i}{dt} = (Q_{i-in}C_{i-in} - Q_{i-out}C_i) - K_iV_iC_i - \sum_{j=1}^{N} U_{ij}A_{ij}\left(C_i - \frac{C_j}{H_{ji}}\right) + \sum_{j=1}^{N} \Omega_{ij} + S_i$$

V_i : volume of compartment i (m^3)
Q_i : volumetric flow rate to compartment i (m^3/h)
$C_{ij,n}$: concentration in volumetric flow to compartment i (mg/m^3)
$Q_{i,out}$: volumetric flow rate from compartment i (m^3/h)
C_i : concentration in compartment i (mg/m^3)
K_i : degradation coefficient (1/h)
U_{ij} : intermedia transport coefficient (m/h)
H_{ji} : partition coefficient (—)
Ω_{ij} : additional intermedia transport rate (mg/h)
S_i : emission rate(mg/h)

Fig.3 Multimedia fate model of chemicals

2.3 Approach to calculating probability of an organism's lethality

Based on statistical reliability analysis, Jacobs et al. (1991) presented an approach for estimating the probability of an organism's lethality that assumes the environmental system can resist an environmental load due to the introduction of a hazardous substance. The basic concept are followings ; the organisms will not survive the environmental contamination if its resistance is less than the contaminant concentration. Assuming that the contaminant's concentration in the environment can be modeled as a random variable *(C)* and resistance of the organism can also be modeled as a random variable *(R)*, then an organism will not survive the environmental contamination if its resistance is less than the contaminant's concentration. That is,

$$R < C \qquad (2)$$

The probability that the organism will not survive the environmental contamination is defined as the probability that the organism's resistance is less than the contaminant's concentration. Mathematically, this expressed as

$$P(R < C) = \sum_{all\ c} P(R < C \mid C = c) P(C = c) \qquad (3)$$

where $P(R<C)$ is defined as the probability that the organism will not survive. If $F_R(c)$ and $f_c(c)$ present the distribution of resistance to contamination and the distribution of contamination concentration, respectively, and R and C are independent statistical and continuous variates, the probability of the organism's lethality is defined as

$$P(R < C) = \int_0^\infty F_R(c) f_c(c) dc \qquad (4)$$

where $F_R(c)$ is the cumulative distribution of $f_R(c)$ evaluated at C. Typically, $F_R(c)$ represents the dose-response relationship.

Finally, we obtain equation (5). The details of the mathematical formulation have been explained in a previous paper (Jacobs et al, 1991). Consequently, if we obtain the mean (μ) and the variance (σ^2) of each data set, the probability of the organism's lethality can be estimated.

$$P(R < C) = 1 - \phi\left(\frac{\mu_R - \mu_C}{\sqrt{\sigma^2_R + \sigma^2_C}} \right) \qquad (5)$$

where $\Phi(\cdot)$ = the standard normal distribution function.

3. Case Study

3.1 Test chemicals and test area

The test chemicals were liner alkylbenzene sulfonates (LAS). The test watershed was Y river in A prefecture of Japan. The area of the test watershed is 120 square km. The period of model simulation was the year of 1991 with daily time step resolution. The environmental parameters of LAS and the geographical features of the test area are explained in previous papers (Hori, 1996, Masuda, 1998, and Tokai, 1997).

3.2 Test organisms

LAS is an industrial chemical that has been extensively investigated with regard to its toxicity. In this study, considering the impact of aquatic organisms, we selected the following four species: Orange killifish (*Oryzias latipes*), Carp (*Cyprinus carpio*), Ayu (*Plecoglossus altivelis*) and Minami-numaebi (*N. denticulata*). All of these are common species used as test organisms in Japan. This small number of species was considered sufficient for the purpose of this study, because each of these species has a very different level of resistance to LAS.

4. Results and Discussion

4.1 Deviation in resistance to and concentration of LAS

The results of the distribution of the organism's resistances to LAS and the calculated environmental concentrations of LAS are shown in Fig. 4. The distribution of the organism resistance was obtained from the dose-response relationship of acute toxicity test results. The spatial distribution of the LAS concentration in water was calculated using the mathematical model explained in section 2.2. Here, since we only show the results for illustrative purpose, the calculated results that correspond to the winter season are used. Because the degradation rate constant is small, a relatively higher concentration of LAS obtained. On the other hand, the range of the mortality among test organisms is different clearly. So, it showed that the sensitivity of an organism to a chemical varies according to the dose. Actually, the range of environmental concentrations is larger than the organism resistance and the probability of lethality can be calculated if the mean and variance of toxicity are introduced.

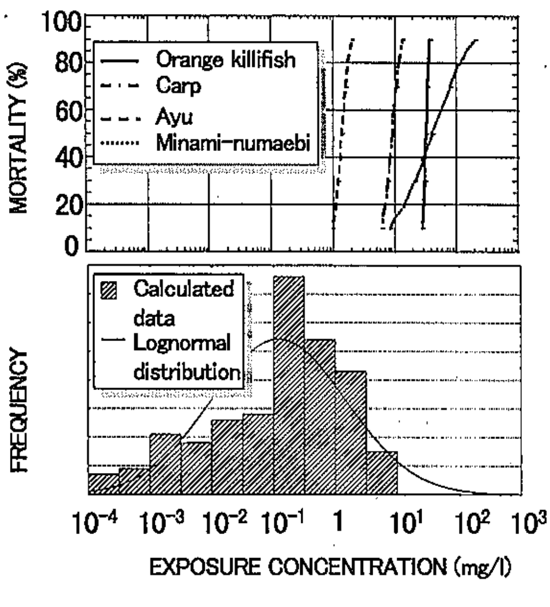


Fig.4 Distribution of the organism's resistance and the environmental concentration for LAS

4.2 The probability of lethality of the organisms due to LAS

Table 1 shows the probability of lethality and the ratio lethality of each aquatic organism to the concentration of LAS in river water in winter. Actually, the difference of probability of lethality to test organisms reflect the their resistance to LAS and the variation of environmental concentration of LAS. Comparing this value with the quotient, these evaluated results are different. Consequently, considering the variability of these data, the potential risk to test organism under the exposure of LAS was found and quantified.

Table.1 P(R<C) and μ_C/LC_{50}

	P(R<C) (-)	μ_c/LC_{50} (-)
Orange killifish	9.4×10^{-3}	5.2×10^{-3}
Ayu	1.9×10^{-1}	1.2×10^{-1}
Carp	9.3×10^{-3}	1.8×10^{-2}
Minani-numaebi	1.5×10^{-2}	4.1×10^{-3}

4.3 Spatial distribution of the probability

Fig.5 shows the spatial distribution of ecotoxicological index expressed as the value of *P(R<C)*, with special attention to parts of the watershed. There is significant variability in the susceptibilities of each target organism to LAS. Ayu was the most sensitive of organisms tested in this study. The different susceptibilities of the organisms are clearly shown. The amplification of the ecotoxicological risk from upstream to downstream corresponding to the urbanization that accompanies the increase in LAS consumption is clearly quantified. Based on this analytical framework, alternatives that reduce the risk of LAS exposure can be quantitatively evaluated in terms of the probability of lethality of organisms as a next step.

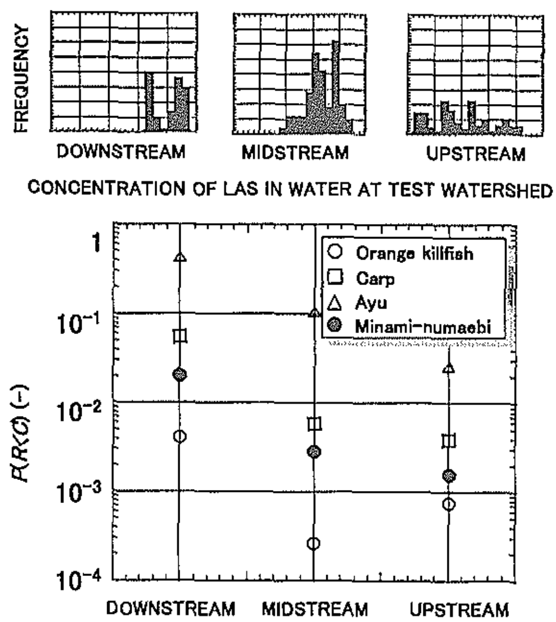


Fig.5 Amplification of *P(R<C)* from upstream to downstream for the four species

5. Acknowledgments

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