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COMPUTER-BASED ENVIRONMENTAL EXPOSURE AND RISK ASSESSMENT METHODOLOGY FOR HAZARDOUS MATERIALS

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Summary

The Chemical Migration and Risk Assessment (CMRA) methodology consists of state-of-the-art overland and surface water models and a statistical program that analyzes the simulation results. These computer models simulate the transport and fate of both dissolved and sediment-sorbed contaminants and provide the risk assessment by predicting acute and chronic impacts to aquatic biota. The CMRA methodology was applied to the Yazoo River Basin, Mississippi, and the Wolf Creek Basin, Iowa, to assess the impact on fish of the pesticides, toxaphene and Alachlor, applied to farmland in those areas. Study results indicated that toxaphene caused both lethal and sublethal damage to four species of fish studied in the Yazoo River Basin, while Alachlor did not have a measureable impact in Wolf Creek Basin. These studies demonstrated the usefulness of this methodology as both a decision-making and research tool. Partially because of the results of the Yazoo River Basin Study, the United States banned the use of toxaphene in this country.

Introduction

One of the major emerging environmental issues is the release of toxic contaminants into receiving waters (e.g., rivers, lakes, estuaries, and coastal waters) and their subsequent impact on aquatic biota. This concern is evidenced by legislation in the United States such as the Resource Conservation and Recovery Act of 1976, the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund), and the Toxic Substance Control Act of 1976.

Although considerable efforts are being made to minimize the release of toxic contaminants to receiving water bodies, the decision makers of both government and industry must have a sound basis for assessing impact. Many toxic contaminants are persistent and undergo complex interactions in the environment. Consequently, the environmental exposure and risks associated with a toxic chemical are usually difficult to determine. A mathematical model can be used to integrate many complex mechanisms controlling the transport and fate of toxic chemicals in the environment into a single framework to improve the accuracy of potential risk analysis.

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Very few mathematical models assess both the transport and associated risks of toxic chemicals [1]; however, several mathematical models assess radionuclide migration and their associated risks to humans. These models include those developed by Fletcher and Dotson [2], Bramati et al. [3], Soldat et al. [4], Watts [5], and Martin et al. [6]. However, these models were developed specifically for radionuclides and are too simplified to provide accurate contaminant exposure levels required for many toxic chemical assessments [7].

To provide a scientific basis for risk assessment and decision making, the Chemical Migration and Risk Assessment (CMRA) methodology was developed to simulate the overland and surface water transport of toxic contaminants and to predict acute and chronic impacts on aquatic biota [8]. The methodology consists of a series of state-of-the-art detailed mathematical models [7] to simulate both dissolved and sediment-sorbed (i.e., particulate) contaminants and their associated risks. In this paper, we discuss the CMRA methodology briefly and how this methodology was used to assess the potential risks of pesticides.

The CMRA methodology

By combining continuous simulation of transport of dissolved and sediment-sorbed contaminants and associated risk assessment into a single system, the CMRA methodology predicts the frequency and persistency of toxic contaminants (e.g., pesticides, heavy metals, and other hazardous materials) on land surface and in surface waters. It also predicts acute (lethal) and chronic (sublethal) damages to aquatic biota. The methodology consists of the following components: (1) overland contaminant transport modeling, (2) contaminant transport modeling in surface waters (i.e., rivers, estuaries, coastal waters and lakes), (3) statistical analysis of contaminant concentrations in surface waters, and (4) risk assessment. Figure 1 illustrates how these components are connected and what types of data are needed. A brief description of each component follows.

Overland contaminant transport modeling

The CMRA methodology uses detailed and continuous overland simulation models, such as the Agricultural Runoff Management (ARM) model [9] and CREAMS [10] for its overland modeling. For example, the ARM model predicts runoff and loadings of sediment and contaminant (both dissolved and particulate) at the edge of the receiving surface water continuously over a simulation period. For given meteorologic conditions, ARM simulates

- hydrologic response of watersheds (runoff from precipitation and snow melt)
- soil erosion
- contaminant adsorption and degradation
- contaminant migration

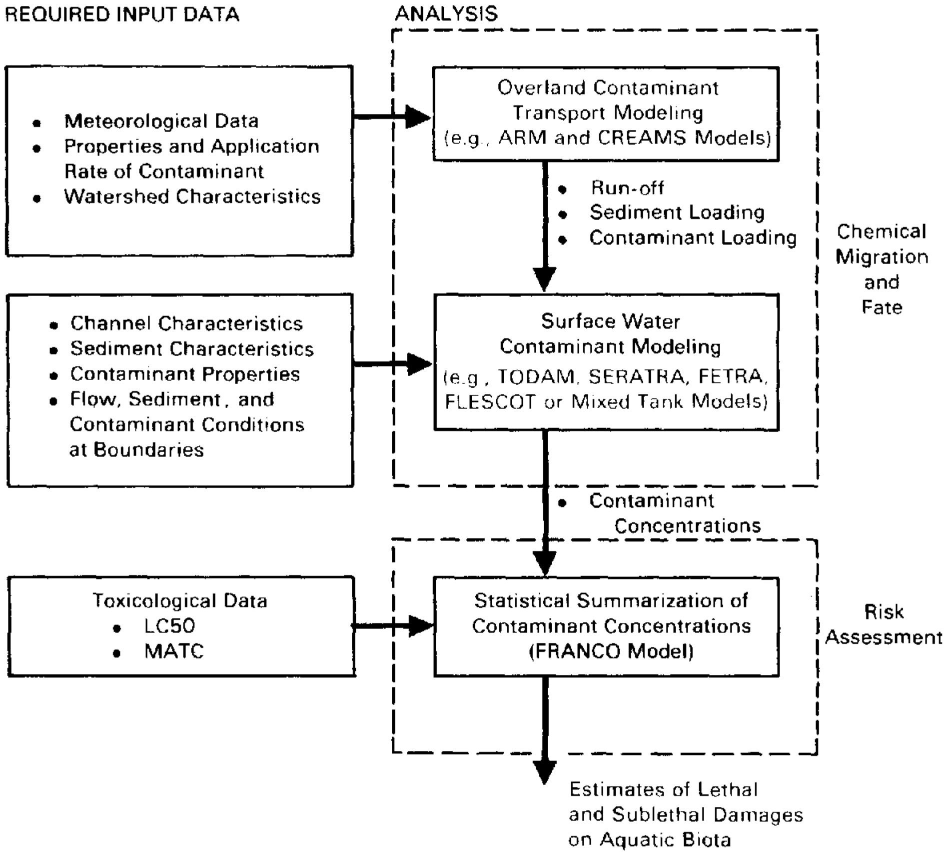

Fig. 1. Chemical Migration and Risk Assessment (CMRA) methodology.

Data requirements include meteorologic information (e.g., rainfall intensity and duration), physical and chemical properties of a contaminant (e.g., a degradation rate and adsorption amount), contaminant application rates and practice (e.g., pesticide application rate to a farm field and its timing), and watershed characteristics (e.g., length and slope of the watershed and ground cover).

Contaminant transport modeling in surface water

The CMRA methodology uses one of several unsteady, sediment/contaminant (both dissolved and sediment-sorbed) transport models that include mechanisms for sediment/contaminant interactions, such as adsorption/desorption and transport, deposition, and resuspension of sediment-sorbed contaminants. These models are the one-dimensional model, TODAM [11, 12]; the two-dimensional (longitudinal and vertical) model, SERATRA [13]; the two-dimensional (longitudinal and lateral) model, FETRA [14]; and the three-dimensional model FLESCOT [15].

All of these models have the following submodels:

- cohesive and noncohesive sediment transport
- dissolved contaminant transport and degradation
- particulate contaminant transport associated with cohesive and noncohesive sediments

They also predict the changes in bed conditions, including bed elevation changes caused by sediment erosion and/or deposition, bed sediment size distribution changes and armoring, and particulate contaminant distributions within the bed.

TODAM is a finite-element model and is applicable to rivers and estuaries. The model includes contaminant degradation processes caused by oxidation, hydrolysis, photolysis, and biological activities, individually. SERATRA is also a finite-element model and is applicable to rivers and reservoirs. Similar to TODAM, it also simulates individual chemical/biological degradation and volatilization processes. The finite-element model, FETRA, is applicable to estuaries, coastal waters, and large lakes (e.g., the Great Lakes in the United States) and includes wave actions to suspend the sediment. FLESCOT is a finite-difference model which predicts distributions of flow, turbulence, salinity, water temperature, sediment, dissolved contaminants, and particulate contaminants. All parameters are coupled. FLESCOT is thus applicable to estuaries, coastal waters, and oceans, as well as lakes and rivers. As an example of these models, formulations of SERATRA are described.

In addition, a more simplified, unsteady, one-dimensional model, the Mixed Tank Model [16], can be used to predict sediment, dissolved contaminant and particulate contaminant transport. This model divides river reaches into a series of tanks within which sediment and contaminant are completely mixed. It assumes that no particulate contaminant is deposited to the riverbed or resuspended from the bed. The model formulation will be described later.

Required input data for these models are channel characteristics (e.g., cross-sectional shapes/bathymetry), sediment characteristics (e.g., sediment diameters and fall velocities), and contaminant properties (e.g., degradation/decay rate and adsorption amount expressed by the time-dependent distribution coefficient), in addition to necessary initial and boundary conditions for sediment and contaminant transport modeling. Except for the three-dimensional hydrodynamic-transport model, FLESCOT, all other surface water models require appropriate hydrodynamic models (e.g., Refs. [17, 18]) to provide depth and velocity distribution as input data.

Because toxicological data for sediment-sorbed contaminant are usually not available, only the dissolved contaminant concentrations were analyzed further for risk assessment. However, the capability exists in the CMRA methodology to include effects of particulate contaminants adsorbed by suspended and bed sediments, which may become important for food chain analysis and/or determining long-term sources of pollutants.

Statistical analysis and risk assessment

For the risk assessment component of the CMRA methodology, the computer program, FRANCO [8], provides a statistical summarization of time-varying contaminant concentrations predicted by the surface water models discussed above for the risk assessment. FRANCO determines frequency and persistency of specified contaminant concentrations in receiving waters. Outputs for FRANCO include the number of times and the percent of time that the given concentration—duration level is exceeded, and the time these events occur.

Risk is determined by the frequency of occurrence of an event (calculated by FRANCO) and its consequential effects. The consequential effects in the CMRA methodology are expressed in terms of lethality and sublethality by using a median lethal concentration (LC50) and the maximum acceptable toxicant concentration (MATC). The LC50 with its associated duration is defined as the concentration at which 50% of an aquatic species will be killed; this represents a lethal impact to aquatic biota. The MATC range is located between the highest concentration showing no detectable harmful effects and the lowest values displaying some observable effect. Hence, MATC describes the effect/no-effect boundary for chronic toxicity. Contaminant levels between LC50 and MATC values produce sublethal damage and possible chance (less than 50%) of fish kill. By selecting specific concentration—duration levels to match LC50s and MATC values, FRANCO provides a risk assessment. FRANCO typically uses six concentration—duration pairs to define a concentration—duration curve

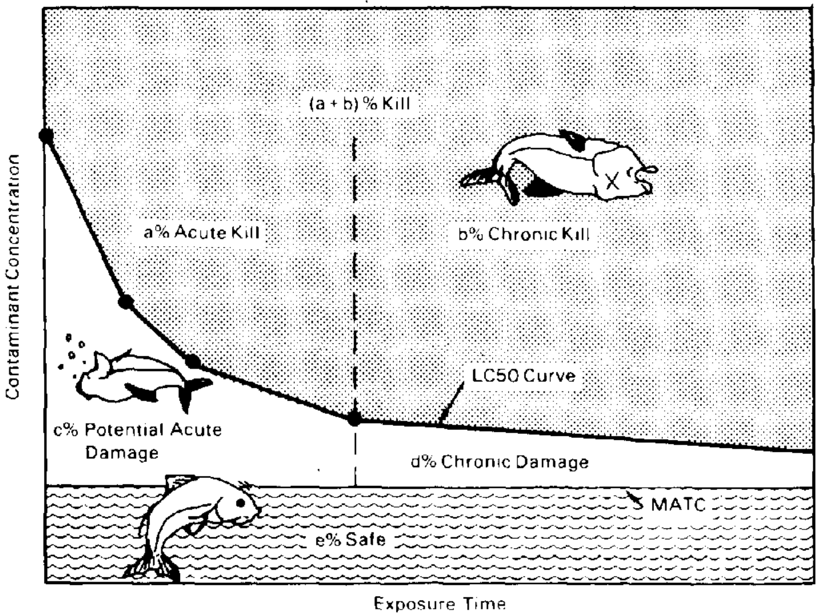

Fig. 2. Risk assessment of the CMRA methodology.

(such as an LC50 curve) to provide the number of times, duration, and frequency that this given concentration—duration curve is exceeded. As shown in Fig. 2, FRANCO can then be used to define consequential zones of acute kill, chronic kill, potential acute damage, chronic damages, and no-effect with the associated frequencies.

Because toxicological data for sorbed contaminants are lacking in general, the risk assessment is currently limited to the direct effects from dissolved chemicals. While this simplified approach is useful for comparing effects of various chemicals or determining whether concentrations exceed known toxic thresholds, values of LC50 and MATC used in FRANCO and FRANCO results must be evaluated in light of such factors as water quality, bed sediment erosion/deposition, life stage of biota, seasonal changes, local food chains, bioconcentration, and biomagnification to obtain a realistic risk assessment.

Although, as discussed above, it consists of three components, the CMRA methodology can be used in different combinations depending on the problems. For example,

- if the migration and risk assessment of a toxic contaminant are of concern only at a stream edge, FRANCO can be used to summarize ARM results
- if a toxic contaminant is directly discharged to a receiving water body, only one of the surface water models and FRANCO are required to evaluate transport and risk assessment
- depending on the types of surface water bodies and required accuracy, one of five models (TODAM, SERATRA, FETRA, FLESCOT, and the Mixed Tank models) can be used
- if continuous measurements of toxic chemical concentrations are available and only the risk assessment is needed, FRANCO alone can be used

In the following sections, the formulations of SERATRA and two applications of the CMRA methodology are discussed.

Formulation of the SERATRA model

Because SERATRA was used for one of the two CMRA methodology applications discussed, we describe the formulation of SERATRA here as an example of the surface water models. Three models (TODAM, FETRA, and FLESCOT) use formulations somewhat similar to those of SERATRA; there are, however, inherent differences among these models due to model dimensions and assumptions.

Sediment transport submodel

The movement and adsorption capacity of sediments vary significantly with sediment size. Thus, the sediment transport submodel of SERATRA solves the migration of sediment (transport, deposition, and bed scouring) for three size fractions of cohesive and noncohesive sediments.

The model includes the following mechanisms:

- advection and dispersion of sediments
- fall velocity and cohesiveness
- deposition on the riverbed
- entrainment from the riverbed (bed erosion and armoring)
- sediment contributions from tributaries and point/non-point sources into the river system and subsequent mixing.

For the sediment concentration of the j^{th} sediment size fraction (of either cohesive or noncohesive sediment), the following governing equation is used

$$\underset{\substack{\text{rate of}\\ \text{accumulation}}}{\frac{\partial}{\partial t}(C_j B l)} + \underset{\substack{\text{horizontal}\\ \text{advection}}}{(U_{\text{o}} C_j B - U_{\text{i}} C_{\text{i}j} B)} + \underset{\substack{\text{vertical}\\ \text{advection}}}{\frac{\partial}{\partial z}\left\{ C_j (W - W_{sj}) B l \right\}}$$

$$= \underset{\substack{\text{vertical}\\ \text{dispersion}}}{\frac{\partial}{\partial z}\left(\epsilon_z \frac{\partial C_j}{\partial z} B l\right)} + \underset{\substack{\text{sediment erosion}\\ \text{or deposition}}}{\frac{1}{h}(S_{\text{R}j} - S_{\text{D}j}) B l} \qquad j = 1, 2, \ldots, N \tag{1}$$

where B = river width, C_j = concentration of sediment of the j^{th} size fraction, $C_{\text{i}j}$ = sediment concentration of horizontal inflow for the j^{th} size fraction, h = water depth, l = longitudinal distance, N = number of sediment size fractions considered — currently, $N = 3$ (e.g., sand, silt, and clay), $S_{\text{D}j}$ = sediment deposition rate per unit area for the j^{th} sediment size fraction, $S_{\text{R}j}$ = sediment erosion rate per unit area for the j^{th} sediment size fraction, t = time, U_{i} = horizontal inflow velocity, U_{o} = horizontal outflow velocity, W = vertical flow velocity, W_{sj} = fall velocity of sediment particle of the j^{th} size fraction, z = vertical direction, and ϵ_z = vertical diffusion coefficient.

The SERATRA model neglects longitudinal dispersion and assumes lateral sediment concentrations to be uniform. However, the model does handle vertical variations of longitudinal velocity to cause longitudinal spread of sediment.

Boundary conditions at the water surface ($z = h$) and riverbed ($z = 0$ are

$$(W - W_{sj})\, C_j - \epsilon_z \frac{\partial C_j}{\partial z} = 0 \qquad \text{at } z = h \tag{2}$$

$$-(1 - \gamma) W_{sj} C_j - \epsilon_z \frac{\partial C_j}{\partial z} = 0 \qquad \text{at } z = 0 \tag{3}$$

where γ = coefficient (e.g., probability that a particle settling to the bed is deposited).

Sediment entrainment and deposition rates, $S_{\text{R}j}$ and $S_{\text{D}j}$, are also evaluated separately for each sediment size fraction because entrainment and deposition characteristics are significantly different for cohesive and noncohesive sediments.

Entrainment and deposition of noncohesive sediments are affected by the amount of sediment the flow is capable of carrying. For example, if the amount of sand being transported is less than the flow can carry for given hydrodynamic conditions, the river will entrain sediment from the streambed to increase the sediment transport rate. This occurs until the actual sediment transport rate becomes equal to the carrying capacity of the flow or until the available bed sediments are all suspended, whichever occurs first. Conversely, the river deposits sand if its actual sediment transport rate is above the flow's capacity to carry sediment. Sediment transport capacity of flow, Q_{T} in this model, was calculated by either the Tofaletti or the Colby formulas [19], whichever a user assigns. The computer program of the Colby method used in SERATRA was that developed by Mahmood and Ponce [20]. The sediment transport capacity of flow, Q_{T}, was then compared with the actual amount of sand, Q_{Ta}, being transported in river water. Hence

$$S_{\mathrm{R}j} = \frac{Q_{\mathrm{T}} - Q_{\mathrm{Ta}}}{A} \tag{4}$$

$$S_{\mathrm{D}j} = \frac{Q_{\mathrm{Ta}} - Q_{\mathrm{T}}}{A} \tag{5}$$

where A = the riverbed surface area. The availability of sediments in the bed for entrainment was then examined to determine the actual amount of sediment entrainment.

For sediment entrainment and deposition rates of cohesive sediments (i.e., silt and clay), the following Partheniades [21] and Krone [22] formulas, respectively, were adopted in this study:

$$S_{\mathrm{R}j} = M_j \left(\frac{\tau_{\mathrm{b}}}{\tau_{\mathrm{cR}j}} - 1\right) \tag{6}$$

$$S_{\mathrm{D}j} = W_{sj} C_j \left(1 - \frac{\tau_{\mathrm{b}}}{\tau_{\mathrm{cD}j}}\right) \tag{7}$$

where M_j = erodability coefficient for sediment of the j^{th} size fraction, τ_{b} = bed shear stress, $\tau_{\mathrm{cD}j}$ = critical shear stress for sediment deposition for the j^{th} sediment size fraction, and $\tau_{\mathrm{cR}j}$ = critical shear stress for sediment entrainment for the j^{th} sediment size fraction.

Values of M_j, $\tau_{\mathrm{cD}j}$, and $\tau_{\mathrm{cR}j}$ must be determined by field and/or laboratory tests for a particular river regime. The model then examines the availability of cohesive sediments in the riverbed to determine the actual amount of sediment to be entrained from the bed.

One of the weakest points of SERATRA, as well as of all the other cohesive-sediment transport models (e.g., Refs. [15, 23, 24]), is that, despite the importance of the fine sediment that adsorbs and transports contaminants, current knowledge on the deposition and entrainment of fine cohesive sediment is very limited.

Dissolved contaminant transport submodel

The dissolved contaminant transport submodel includes the mechanisms of

- advection and dispersion of dissolved contaminants (pesticides, radionuclides, and other toxic substances) within the river
- adsorption (uptake) of dissolved contaminants by sediments (suspended and bed sediments) or desorption from sediments into the water column
- radionuclide decay, when applicable
- degradation of dissolved contaminants caused by hydrolysis, oxidation, photolysis, and biological activities
- volatilization
- contributions of dissolved contaminants from tributaries and point/non-point sources into the river system and subsequent mixing

In SERATRA, distribution coefficients for adsorption can be assigned a value different from that of desorption. By allowing different distribution coefficients, adsorption/desorption processes which are not completely reversible can be more accurately described. Mass conservation of dissolved contaminants SERATRA may be expressed as

$$\underbrace{\frac{\partial}{\partial t}(G_{\mathrm{w}}Bl)}_{\text{rate of accumulation}} + \underbrace{(U_{\mathrm{o}}G_{\mathrm{w}}B - U_{\mathrm{i}}G_{\mathrm{wi}}B)}_{\text{horizontal advection}} + \underbrace{\frac{\partial}{\partial z}(WG_{\mathrm{w}}Bl)}_{\text{vertical advection}}$$

$$= \underbrace{\frac{\partial}{\partial z}\left(\epsilon_z \frac{\partial G_{\mathrm{w}}}{\partial z} Bl\right)}_{\text{vertical diffusion}} - \underbrace{\lambda G_{\mathrm{w}}Bl}_{\text{radionuclide decay}} - \underbrace{\sum_{i=1}^{5} K_{\mathrm{C}i}G_{\mathrm{w}}Bl}_{\text{chemical and biological degradation and volatilization}}$$

$$-\underbrace{\sum_j K_j(K_{\mathrm{d}j}C_jG_{\mathrm{w}} - G_j)Bl}_{\text{adsorption to moving sediment}} - \underbrace{\sum_j K_j'(K_{\mathrm{d}j}'C_jG_{\mathrm{w}} - G_j)Bl}_{\text{desorption from moving sediment}}$$

$$-\underbrace{\sum_j \gamma_j(1-POR)D_jK_{\mathrm{b}j}(K_{\mathrm{d}j}G_{\mathrm{w}} - G_{\mathrm{B}j})}_{\text{adsorption to sediment in bed}} - \underbrace{\sum_j \gamma_j(1-POR)D_jK_{\mathrm{b}j}'(K_{\mathrm{d}j}'G_{\mathrm{w}} - G_{\mathrm{B}j})}_{\text{desorption from sediment in bed}}$$

$$j = 1, 2, \ldots, N \qquad (8)$$

where D_j = diameter of the j^{th} sediment; $G_{\text{B}j}$ = particulate contaminant concentration per unit weight of sediment in the j^{th} sediment size fraction in the riverbed; γ_j = specific weight of the j^{th} sediment; G_{w} = dissolved contaminant concentration per unit volume of water; G_{wi} = dissolved contaminant concentration in horizontal inflow; G_j = sediment-sorbed contaminant concentration per unit volume of water; $K_{\text{C}i}$ = the first-order reaction rate of contaminant degradation resulting from hydrolysis, oxidation, photolysis, biological activities, and volatilization; $K_{\text{b}j}$, $K'_{\text{b}j}$ = transfer rates of contaminants for adsorption and desorption, respectively, with the jth nonmoving sediment size in bed; $K_{\text{d}j}$, $K'_{\text{d}j}$ = distribution coefficients of adsorption and desorption, respectively, between dissolved contaminant and sediment of the j^{th} size fraction, respectively; K_j, K'_j = transfer rates of contaminants for adsorption and desorption, respectively, with j^{th} sediment in motion (i.e., suspended and bed load sediment); and λ = decay rate of radioactive material.

It was assumed that a contaminant has the same distribution coefficient values, $K_{\text{d}j}$ or $K'_{\text{d}j}$, for the moving (suspended and bed load sediments) and nonmoving (bed sediment without any motion) jth sediment. However, these two types of sediment have two different transfer rates, K_j or K'_j and $K_{\text{b}j}$ or $K'_{\text{b}j}$, as expressed in eqn. (8).

The adsorption of contaminant by sediments or desorption from the sediments is assumed to occur toward an equilibrium condition with the transfer rate, K_j or K'_j (with the unit of the reciprocal of time), if the particulate contaminant concentration differs from its equilibrium values as expressed in eqn. (9):

$$G_j = K_{\text{d}j} C_j G_{\text{w}} \quad \text{or} \quad G_j = K'_{\text{d}j} C_j G_{\text{w}} \tag{9}$$

Contaminant adsorption/desorption with nonmoving bed sediment are treated similarly.

Longitudinal dispersion of dissolved contaminant is considered to be negligible when compared with advection. Similar to the sediment submodel, longitudinal spread of contaminants does occur due to the vertical variation of longitudinal velocity simulated in this model.

Boundary conditions at the water surface and riverbed are

$$WG_{\text{w}} - \epsilon_z \frac{\partial G_{\text{w}}}{\partial z} = 0 \qquad \text{at } z = h \tag{10}$$

$$\epsilon_z \frac{\partial G_{\text{w}}}{\partial z} = 0 \qquad \text{at } z = 0 \tag{11}$$

One of the important mechanisms affecting transport and fate of contaminants is the degradation and volatilization of contaminants in an aquatic environment. Contaminant degradation includes both chemical and biological reactions. Major mechanisms of chemical degradation are (1) hydrolysis, (2) oxidation, and (3) photolysis [25]. Because of the present lack of knowledge about degradation and volatilization of particulate contaminants [25], these degradation mechanisms were considered only for the dissolved contaminants. The degradation and volatilization rates are included in eqn. (8) as the first-order kinetic reaction rates (K_{Ci}; $i = 1, 2, 3, 4$, and 5), which are internally calculated by SERATRA.

Chemical degradation by hydrolysis

If there is a large increase in stability, a contaminant in solution will react with other species in solution and form a complex. Hydrolysis reactions are a specialized type of complex formation in which the [OH$^-$] anion acts as the ligand. They are quite sensitive to pH changes. The rate of change of dissolved contaminant concentration effected by hydrolysis is expressed by the following equation [25]:

$$\begin{aligned}
-\frac{dG_w}{dt} &= K_A[H^+]G_w + K_B[OH^-]\,G_w + K_N G_w \\
&= (K_A[H^+] + \frac{K_B K_w}{[H^+]} + K_N)G_w \\
&= (K_A \times 10^{-pH} + K_B \times 10^{pH-14} + K_N)G_w \\
&= K_{C1} G_w
\end{aligned} \tag{12}$$

where $K_{C1} = K_A \times 10^{-pH} + K_B \times 10^{pH-14} + K_N$, $K_w = [H^+]\,[OH^-] = 10^{-14}$, pH $= -\log[H^+]$, and K_A, K_B, K_N = acid, base, and neutral hydrolysis rates, respectively. Rate coefficients, K_A, K_B, and K_N, can be determined from laboratory tests [25].

Chemical degradation by oxidation

By assuming that only a small concentration of dissolved contaminants is oxidized, the rate of contaminant oxidation may be expressed by

$$\begin{aligned}
-\frac{dG_w}{dt} &= K_{ox}[RO_2\cdot]G_w \\
&= K_{C2}G_w
\end{aligned} \tag{13}$$

where K_{ox} = oxidation rate of free radical oxygen of [$RO_2\cdot$], respectively, and $RO_2\cdot$ = free radical oxygen. The rate constant K_{ox} can be obtained from laboratory tests outlined by Smith et al. [25].

Chemical degradation by photolysis

Many contaminants can be photochemically degraded by absorbing light, especially ultraviolet light. The rate of contaminant concentration change caused by photolysis reactions for each vertical computational element may be expressed by [25, 26]

$$-\frac{dG_w}{dt} = \frac{2.303}{J}\phi \sum_{\lambda} \epsilon_\lambda I_{o\lambda} \exp\left[\{-(K_1 + K_2\bar{C})(h-z)\} G_w\right]$$

$$= K_{C_3} G_w \tag{14}$$

where $\bar{C}$ = average total sediment concentration above water depth Z, $I_{o\lambda}$ = incident light intensity of wavelength λ, I_λ = light intensity of wavelength λ at water depth Z, J = conversion constant, K_i = light attenuation coefficient for water, K_2 = light attenuation coefficient resulting from suspended sediment in water, ϵ_λ = molar extinction coefficient of light with the wavelength λ, and ϕ = quantum yield.

Because each computational cell of SERATRA has a vertical finite element thickness, the above equation was averaged over the thickness of each of SERATRA's vertical elements. Various parameters and coefficients can be measured by conducting laboratory tests and/or field measurements [25, 26].

Biodegradation

A contaminant compound may be degraded by microbial activities in an aquatic environment. In this model, it is assumed that microbial degradation can be expressed by a second-order reaction [25, 27], depending on concentrations of biomass and contaminant in water, as shown below:

$$-\frac{dG_w}{dt} = K_{B_1}\ [B]\, G_w$$

$$= K_{C4}\ G_w \tag{15}$$

where [B] = biomass per unit volume and K_{B_1} = the second-order rate constant for biodegradation.

Volatilization

The volatilization of a contaminant occurs at the air—water interface. The change of contaminant concentration caused by volatilization may be expressed by the following first-order reaction [25]:

$$-\frac{dG_w}{dt} = K_{C_5} G_w \tag{16}$$

where K_{C_5} = volatilization rate of the contaminant.

Sediment-sorbed contaminant transport submodel

The transport model of contaminants attached to the j^{th} sediment includes the mechanisms

- advection and dispersion of sediment-sorbed contaminants
- adsorption of dissolved contaminants by sediments or desorption from sediments into the water column
- radionuclide decay

- deposition of sediment-sorbed contaminants to the riverbed or entrainment from the riverbed
- contributions of sediment-sorbed contaminants from tributaries and point/nonpoint sources into the river system and subsequent mixing

As in the transport of sediments and dissolved contaminants, the conservation of contaminants adsorbed by the j^{th} sediment may be expressed as

$$\underset{\substack{\text{rate of}\\ \text{accumulation}}}{\frac{\partial}{\partial t}(G_jBl)} + \underset{\substack{\text{horizontal}\\ \text{advection}}}{(U_\text{o}G_j B - U_\text{i}G_{\text{i}j} B)} + \underset{\substack{\text{vertical}\\ \text{advection}}}{\frac{\partial}{\partial z} (W - W_{\text{s}j})G_jBl}$$

$$= \underset{\substack{\text{vertical}\\ \text{dispersion}}}{\frac{\partial}{\partial z}\left(\epsilon z \frac{\partial G_j}{z} Bl\right)} - \underset{\substack{\text{radionuclide}\\ \text{decay}}}{\lambda G_j Bl} + \underset{\substack{\text{adsorption with}\\ \text{moving sediment}}}{K_j(K_{\text{d}j}C_jG_\text{w} - G_j)Bl}$$

$$+ \underset{\substack{\text{desorption from}\\ \text{moving sediment}}}{K_j'(K_{\text{d}j}'C_jG_\text{w} - G_j)Bl} + \underset{\substack{\text{entrainment and}\\ \text{deposition of}\\ \text{contaminated}\\ \text{sediment}}}{\frac{1}{h}(G_{\text{B}j}S_\text{R} - G_jS_\text{D})Bl} \quad j = 1,2,\ldots,N \tag{17}$$

where $G_{\text{i}j}$ = particulate concentration per unit volume of water associated with the j^{th} sediment size fraction in horizontal inflow.

Longitudinal dispersion of sediment-sorbed contaminant was assumed to be negligible compared with longitudinal advection. However, as noted before, the longitudinal spread of sediment-sorbed contaminant caused by nonuniform vertical distribution of longitudinal velocity is simulated in the model. It is assumed that chemical and biological degradation of sediment-sorbed contaminants can be expressed by the first-order degradation rate similar to the radionuclide decay form.

The boundary conditions at the water surface and bed are

$$G_j\,(W - W_{\text{s}j}) - \epsilon_z \frac{\partial G_j}{\partial z} = 0 \qquad \text{at } z = h \text{ and } 0 \tag{18}$$

The finite-element technique with the Galerkin weighted-residual method was used to solve the transport equations of sediments, dissolved contaminants, and sediment-sorbed contaminants [8].

Formulation of the Mixed Tank Model

The Mixed Tank Model [16] is a simplified, unsteady, one-dimensional model which predicts sediment, dissolved contaminant, and sediment-sorbed contaminant transport. This model divides river reaches into a series of tanks within which sediment and contaminant are completely mixed, as shown in Fig. 3. It assumes that (1) only suspended fine sediment adsorbs contaminant, (2) dissolved and sediment-sorbed contaminants are linearly related by a distribution coefficient, and (3) no sediment-sorbed contaminant is deposited to the riverbed nor resuspended from the bed. The mass conservation of sediment, dissolved contaminant, and sediment-sorbed contaminant in the n^{th} tank (see Fig. 3) leads to the following governing equations, respectively:

$$\left.\frac{\partial(SV)}{\partial t}\right|_n = Q_{n-1}S_{n-1} + SL_n - Q_nS_n \tag{19}$$

$$\left.\frac{\partial(CV)}{\partial t}\right|_n = Q_{n-1}C_{n-1} + CL_n - Q_nC_n - \lambda C_nV_n - S_nV_nK_1(K_dC_n - Cp_n) \tag{20}$$

$$\left.\frac{\partial(CpSV)}{\partial t}\right|_n = S_{n-1}Cp_{n-1}Q_{n-1} + CpL_n - S_nCp_nQ_n - \lambda Cp_nS_nV_n + S_nV_nK_1(K_dC_n - C_{pn}) \tag{21}$$

where C_n = dissolved contaminant concentration in the n^{th} tank, Cp_n = sediment-sorbed contaminant concentration in the n^{th} tank, CL_n = lateral influx of dissolved contaminant, CpL_n = lateral influx of sediment-sorbed contaminant, K_d = distribution coefficient of contaminant, K_1 = transfer rate at which dissolved and sediment-sorbed contaminants reach their equilibrium conditions, Q_n = flow discharge from the n^{th} tank, S_n = sediment concentration in the n^{th} tank, SL_n = lateral influx of sediment, V_n = water volume of the n^{th} tank, t = time, and λ = first-order decay rate.

The total contaminant mass balance can be obtained by adding eqns. (20) and (21). Note that

$$Cp_n = K_dC_n \tag{22}$$

under an equilibrium condition.

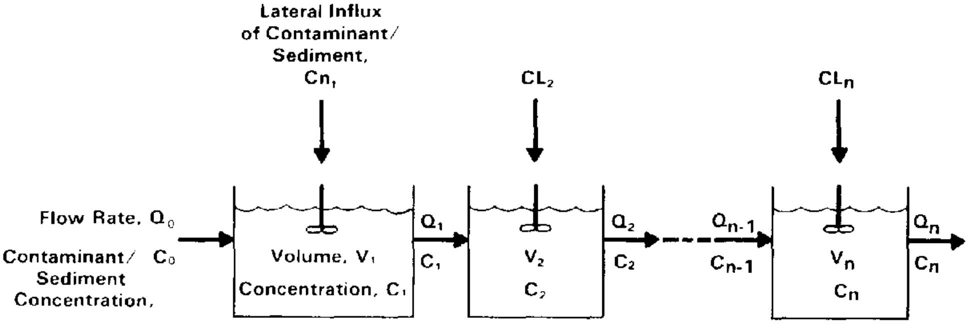

Fig. 3. Mixed Tank Model.

Rearranging the above equations leads to the following sediment and dissolved contaminant equations:

$$\frac{\partial S}{\partial t} = - S_n \left[\frac{1}{V} \left(\frac{\partial V}{\partial t} + Q \right) \right]_n + \frac{Q_{n-1} S_{n-1} + SL_n}{V_n} \tag{23}$$

$$\begin{aligned} \frac{\partial C_n}{\partial t} = \frac{1}{V_n (1 + S_n K_\mathrm{d})} & [(1 + S_{n-1} K_\mathrm{d}) \, Q_{n-1} C_{n-1} + (CL_n + C_\mathrm{p} L_n) \\ & - (1 + S_n K_\mathrm{d}) \, Q_n C_n - \lambda V_n C_n (1 + S_n K_\mathrm{d}) \\ & - C_n \frac{\partial}{\partial t} \{ V_n (1 + S_n K_\mathrm{d}) \}] \end{aligned} \tag{24}$$

Equations (23) and (24) can then be solved to obtain sediment and dissolved contaminant concentrations, S_n and C_n, in the n^{th} river reach. A sediment-sorbed contaminant concentration is then determined using eqn. (22). The total contaminant concentration, CT_n, is thus calculated by

$$CT_n = C_n + S_n \, C\mathrm{p}_n \tag{25}$$

Assessment of the pesticide toxaphene in the Yazoo River Basin

The migration and associated risk of toxaphene in the Yazoo River Basin, Mississippi, was assessed as a case study. Toxaphene, which is a persistent chlorinated insecticide for controlling pests in both food and fiber crops, was assumed to be applied to farmland in the Yazoo River Basin [7]. This study assisted the U.S. Environmental Protection Agency in deciding whether the use of toxaphene in the United States should be restricted or banned. Specifically, toxaphene migration and fate was evaluated in the Coldwater, Tallahatchie, Yazoo, and Big Sunflower Rivers (Fig. 4) and the potential impacts of toxaphene on four fish — largemouth bass (*Micropterus salmouides*), bluegill sunfish (*Lepomis macrochirus*), fathead minnow (*Pimephales promelas*), and channel catfish (*Ictalurus punctatus*) — were assessed in these rivers for the period between March 1971 and December 1975.

Transport modeling

For this study, the simple Mixed Tank Model was applied to the rivers, covering 506 river kilometers. Contaminants in these rivers are mostly adsorbed by fine sediment (e.g., silt, clay and organic matter). Fine sediment usually is transported through the river system without deposition except in very slow moving areas [7]. Thus, the Mixed Tank Model, which does not allow sediment deposition or erosion, was applicable to these relatively small and fast-moving rivers.

The suspended sediment adsorbs dissolved pesticide, resulting in a smaller dissolved concentration. Thus, for a given total pesticide concentration, the higher the suspended sediment concentration, the lower the dissolved concentration. Sediment and toxaphene loadings from farmland to each of the reaches of these rivers were calculated by the EPA, Environmental Research Laboratory, Athens, Georgia, using the ARM model. The EPA also provided toxaphene characteristics (i.e., degradation rate of 0.031 per day and the distribution coefficient of 22,600 ml/g) and toxicological data. Simons, Li and Associates, Fort Collins, Colorado, supplied the necessary input on data flow and sediment for in-stream modeling.

Toxaphene transport was mathematically simulated for four cases that differed only in how in-stream sediment concentration was handled: Cases 1, 2, and 3 did not simulate the sediment transport, but assumed sediment concentrations to be 10th, 50th and 90th percentiles of measured sediment concentrations to cover a wide range of sediment conditions affecting the amount of toxaphene sorbed by sediment; Case 4 simulated sediment

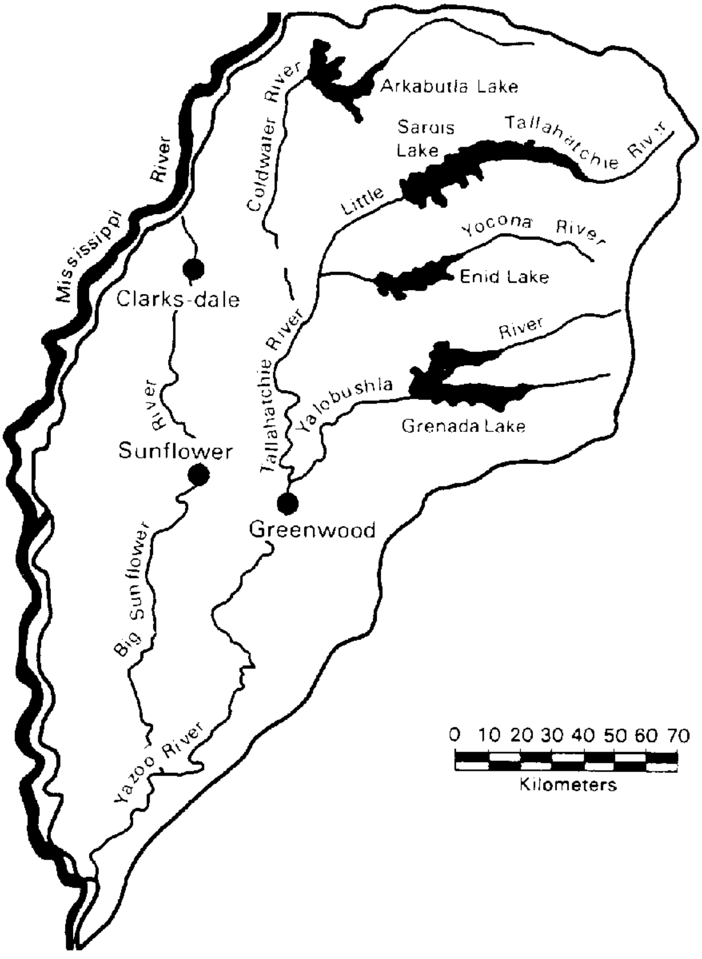

Fig. 4. Yazoo River Basin, Mississippi, the United States.

distributions in addition to toxaphene distributions based on the loadings from the farmland estimated by the ARM model.

The variation of daily river discharge (near the mouth of the Yazoo River) used for this study is shown in Fig. 5. Time variations of computed

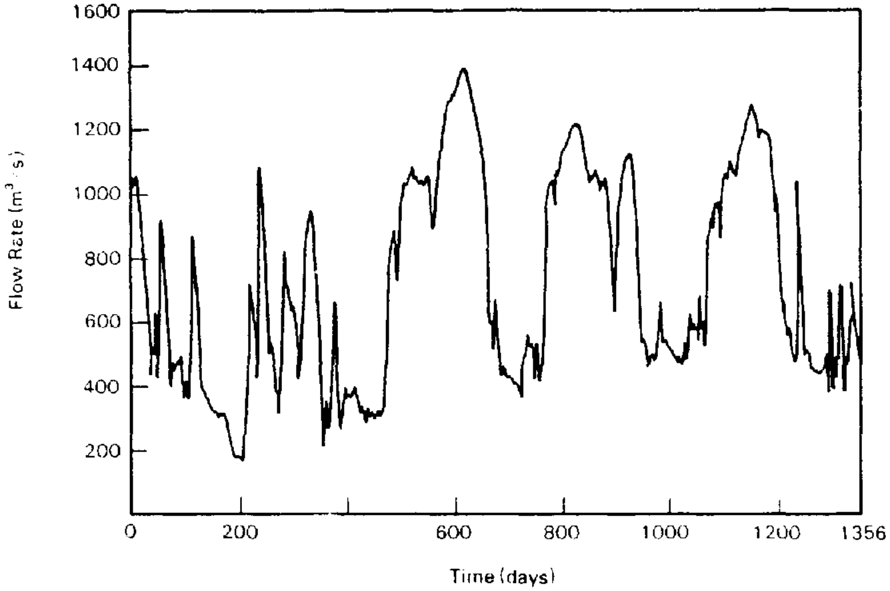

Fig. 5. Measure of daily discharge variation near the mouth of the Yazoo River.

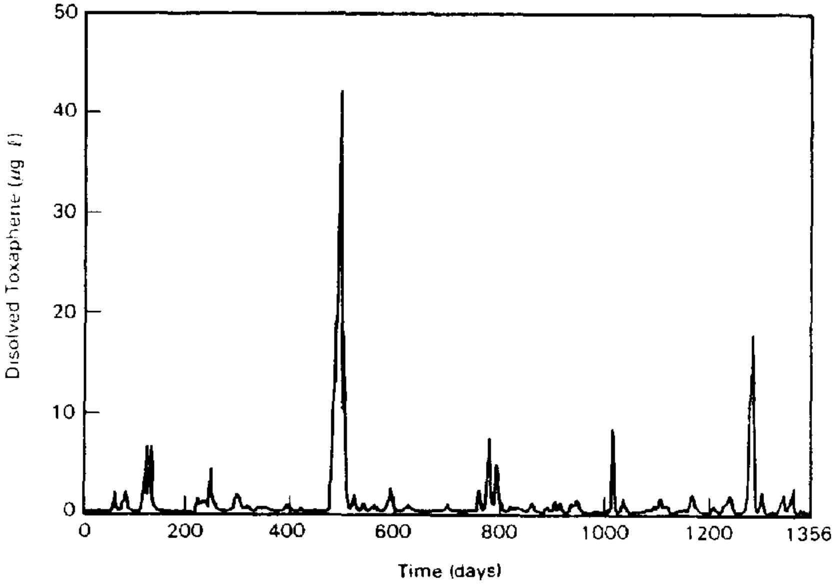

Fig. 6. Predicted dissolved toxaphene concentration near the mouth of the Yazoo River.

dissolved, particulate, and total (sum of dissolved and sediment-sorbed) toxaphene concentrations near the mouth of the Yazoo River are shown in Figs. 6, 7, and 8, respectively. Because Case 1 had the smallest sediment concentrations among the four, the predicted dissolved toxaphene concen-

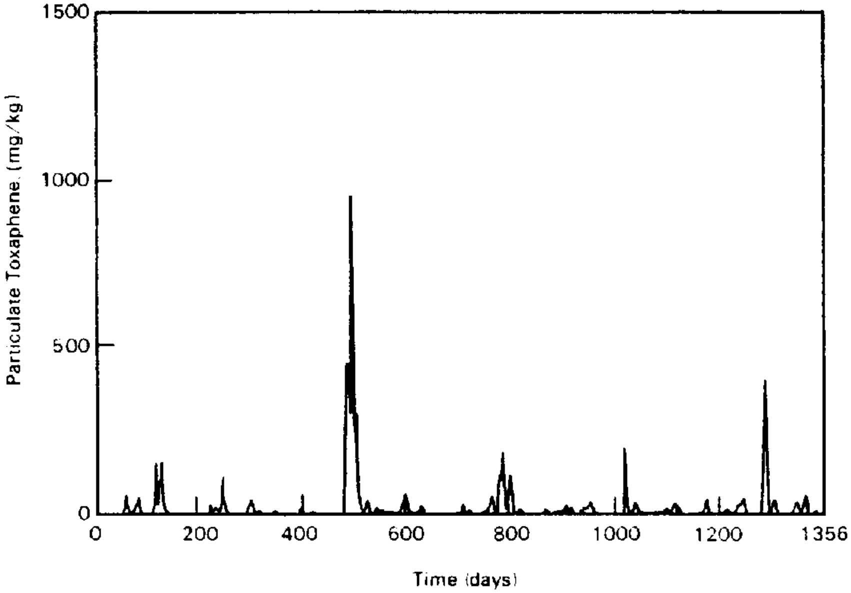

Fig. 7. Predicted particulate toxaphene concentrations near the mouth of the Yazoo River.

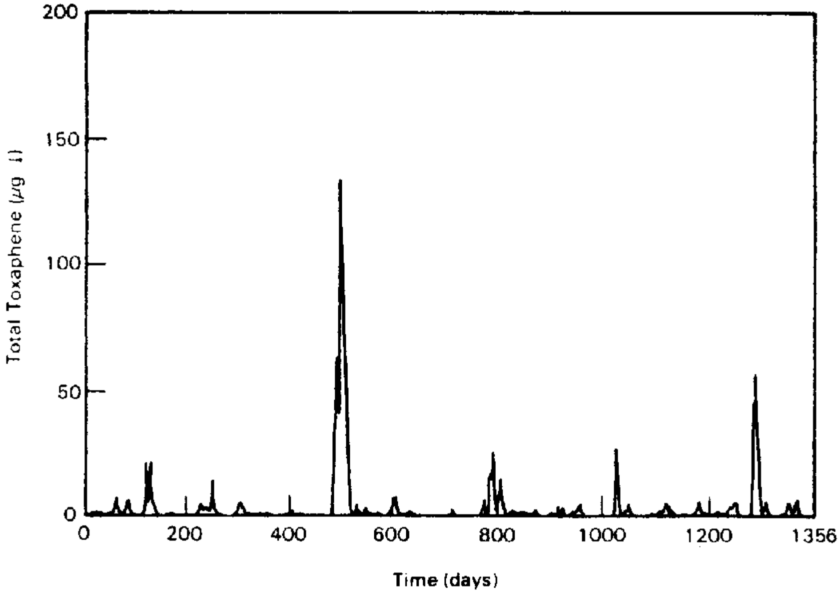

Fig. 8. Predicted total toxaphene concentrations near the Yazoo River.

trations for this case were the highest, providing the most conservative (severe) estimates of associated risk of toxaphene to the fish. These figures indicated that a number of sharp peaks occurred during the five-year simulation period. Figures 6—8 also reveal that, even though this case had the highest dissolved concentrations of the four case studied, the majority of toxaphene still moved with the fine suspended sediment and was not readily available to biota for uptake.

Risk assessment

Approximate values of LC50 and MATC for largemouth bass, bluegill sunfish, fathead minnow, and channel catfish are shown in Tables 1 and 2. Based on these values, the FRANCO program of the CMRA methodology statistically summarized the predicted dissolved toxaphene concentrations to provide risk assessment for these fish. Note that the risk assessment was somewhat hampered by a literal interpretation of the laboratory toxicology to the actual field conditions. Also, the 10-day laboratory test data were used to extend up to 117 days, most likely resulting in conservative (more fish kill) risk assessment. Figures 9 and 10 show probabilistic risk assessment results for young largemouth bass (most affected) and adult channel catfish (least affected). Figure 9 indicates that for 14.8% of the time during the five-year simulation period, the dissolved toxaphene con-

TABLE 1

Median lethal concentration (LC50) levels

	Median lethal concentration, LC50 (mg/l)				
Duration (days)	Young largemouth bass	Young bluegill sunfish	Young fathead minnow	Young channel catfish	Adult channel catfish
0.5	5.6	7.5	16	22	34
1.0	5.6	7.5	16	22	34
2.0	3.1	38	7.5	18	22.8
4.0	2.3	3.5	5.1	17.2	16.5
10.0	2.3	3.5	5.1		15.0
35.0				0.62	

TABLE 2

Median acceptable toxicant concentration (MATC) levels

	MATC (μg/l)
Largemouth bass	⩽0.072
Bluegill sunfish	0.0063~0.019
Fathead minnow	0.025 ~0.054
Channel catfish fry	0.3

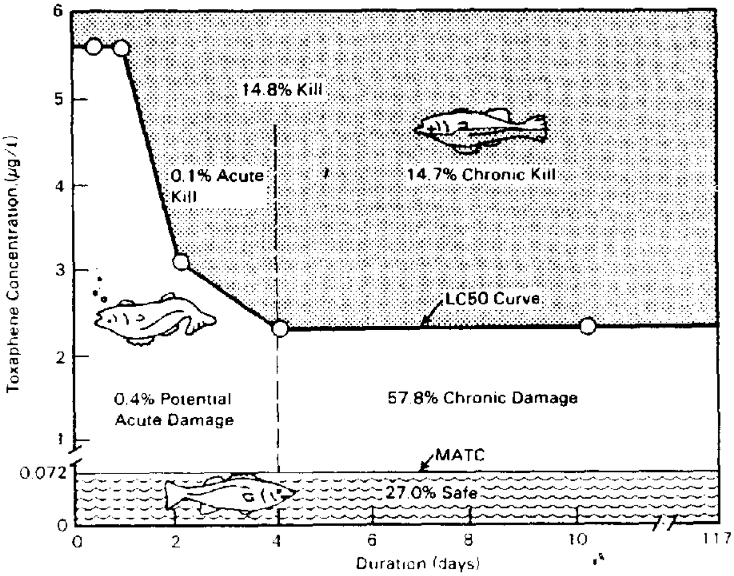

Fig. 9. Probabilistic risk assessment for young largemouth bass.

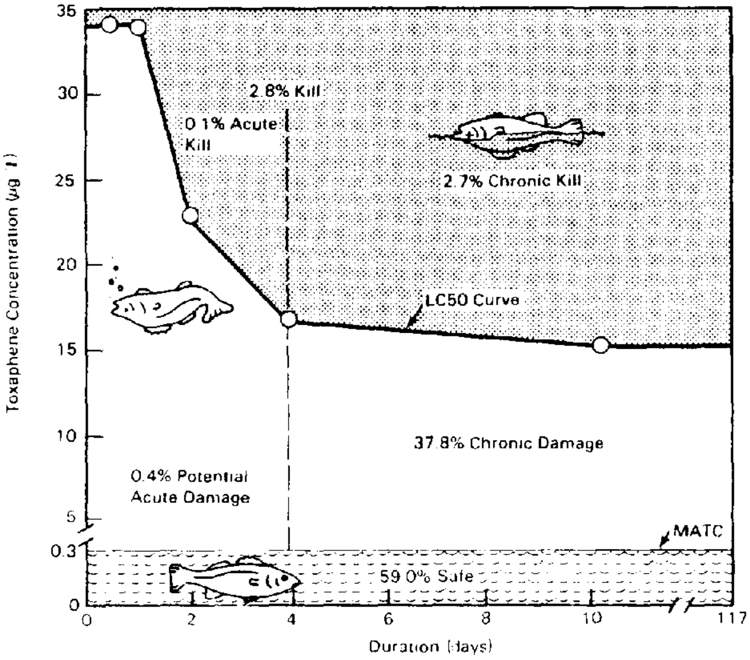

Fig. 10. Probabilistic risk assessment of adult channel catfish.

centrations were above the LC50 curve for young largemouth bass (i.e., for 14.8% of the time, over 50% of young largemouth bass would be killed). FRANCO indicated that this situation would occur 18 times, totaling 60.5 days, over the simulation duration. For 58.2% of the time (36 times, totaling 1287 days), the dissolved toxaphene fell between the LC50 curve and the MATC level of 0.072 μg/l, indicating the expectation of some lethal and sublethal damages to largemouth bass. For 57.8% of the time, dissolved toxaphene levels remained between the LC50 curve and the MATC value for longer than 4 days (96 h). This reveals that most of the impact would occur as chronic damage. However, for 27% of the simulation time, dissolved toxaphene concentration was below the MATC value of 0.072 μg/l, implying that for 27% of the time, largemouth bass would be safe from measurable effects.

Because adult channel catfish are more resistant to toxaphene than young largemouth bass, at least 50.0% of the channel catfish would die for 2.8% of the time (4 events with total of 50 days). According to FRANCO output, channel catfish would be safe from harmful levels for 59.0% of the time. For the remaining period (38.2%), some lethal and sublethal damages would be incurred, but most (37.8%) would be chronic damages. Other fish (bluegill sunfish, fathead minnow, and young channel catfish) fall between these two extreme cases (i.e., young largemouth bass and channel catfish, respectively).

Thus, the assessment results of the CMRA methodology revealed both acute and chronic damages to these fish. Partially because of these study results, the U.S. government banned the use of toxaphene in the United States.

Assessment for pesticide Alachlor in the Four Mile Creek Basin

To evaluate its applicability and limitations, the CMRA methodology was applied to a portion of the Four Mile Creek Watershed, including Four Mile and Wolf Creeks in central Iowa of the United States (Fig. 11) [8]. The study area for the in-stream modeling was a 67.6-km reach between river kilometer 19.3 in Four Mile Creek and the mouth of Wolf Creek. Four Mile Creek joins Wolf Creek at river kilometer 48.3 of Wolf Creek.

The toxic contaminant selected for the test was the pre-emergence herbicide Alachlor, a widely used pesticide in the area [28]. Alachlor is a phenylaniline with a moderate solubility and a small capacity for adsorption to sediment. It is not very persistent in soil or water, and is not known to be cumulative in its effects on aquatic biota. Pesticide migration and fate were simulated continuously for a three-year period between June 1971 and May 1974. For this test case, the two-dimensional model SERATRA was selected for the in-stream modeling to simulate transport of seven substances: sand, silt, clay, dissolved Alachlor, and particulate Alachlor sorbed by sand, silt, and clay. In this demonstration, the contribution

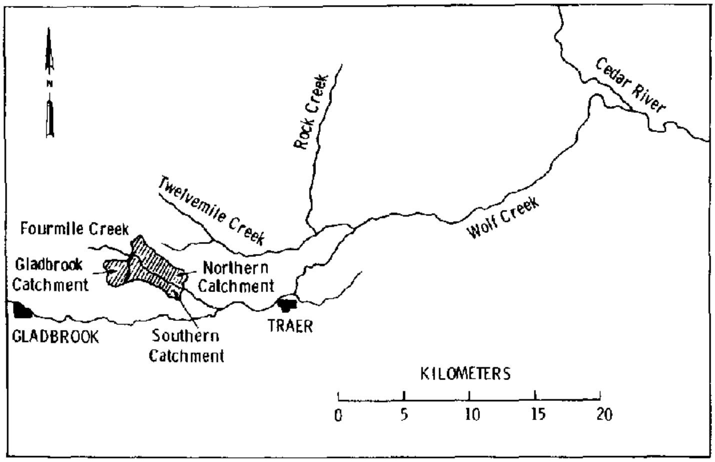

Fig. 11. Four Mile and Wolf Creeks in Iowa, the United States.

of Alachlor to Four Mile and Wolf Creeks was assumed to come from only a small portion of the Four Mile Creek watershed (three shaded catchments in Fig. 11). Therefore, this application exercise must be taken as an illustration of the methodology rather than a true assessment for the pesticide.

Transport modeling

Overland and in-stream modeling indicated that less than 2% of Alachlor applied to the land surface reached Four Mile Creek. Both overland and in-stream (Figs. 12 and 13, respectively) transport of Alachlor corresponded to seasonal pesticide application patterns (high peaks in May and June).

Figure 12 shows the predicted loading of Alachlor reaching Four Mile Creek due to runoff and soil erosion caused by rainfall, as computed by the ARM model, while Fig. 13 indicates the predicted total (sum of dissolved and particulate) Alachlor concentration near the mouth of Wolf Creek. Because Alachlor degrades very rapidly (with a half life of approximately 10 days) after application to farmland, water quality can be improved significantly by timing the application of Alachlor to allow it to degrade a significant amount before the next rainfall or through controlling and curtailing both runoff and soil erosion shortly after pesticide application.

Although Alachlor does not have a high affinity for sediment (a distribution coefficient of only 60 ml/g for bulk sediment), the high concentrations of fine sediment existing in these streams caused a significant amount of Alachlor to be sorbed by and later desorbed from sediment. Deposition to the bed and subsequent resuspension from the bed created a longer-term source of pollution.

The effect of adsorption as described above is demonstrated in Figs.

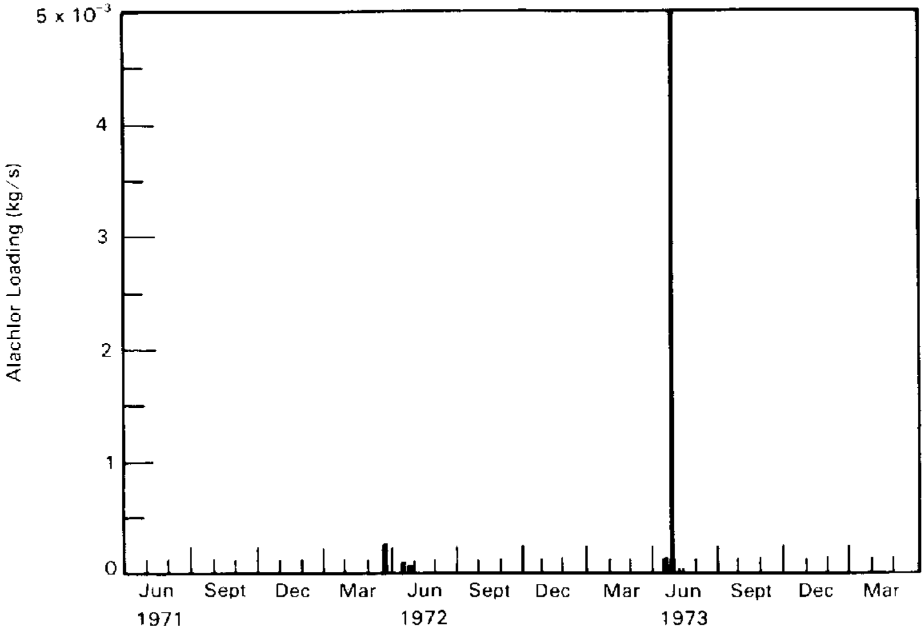

Fig. 12. Time variation of predicted total Alachlor loading to Four Mile Creek during the three-year simulation period.

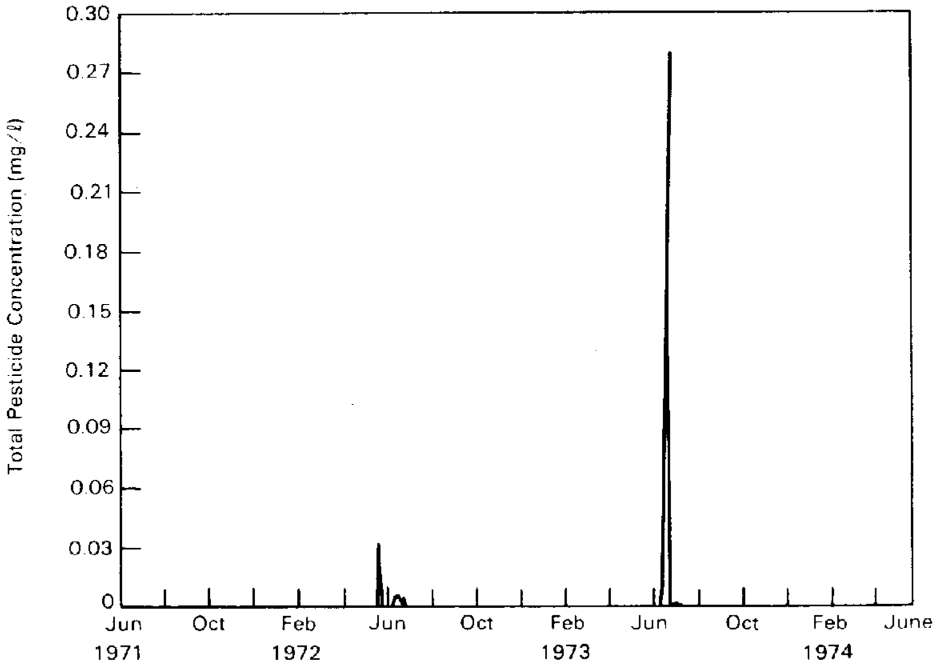

Fig. 13. Time variation of predicted total Alachlor concentration near the mouth of Wolf Creek River during the three-year simulation period.

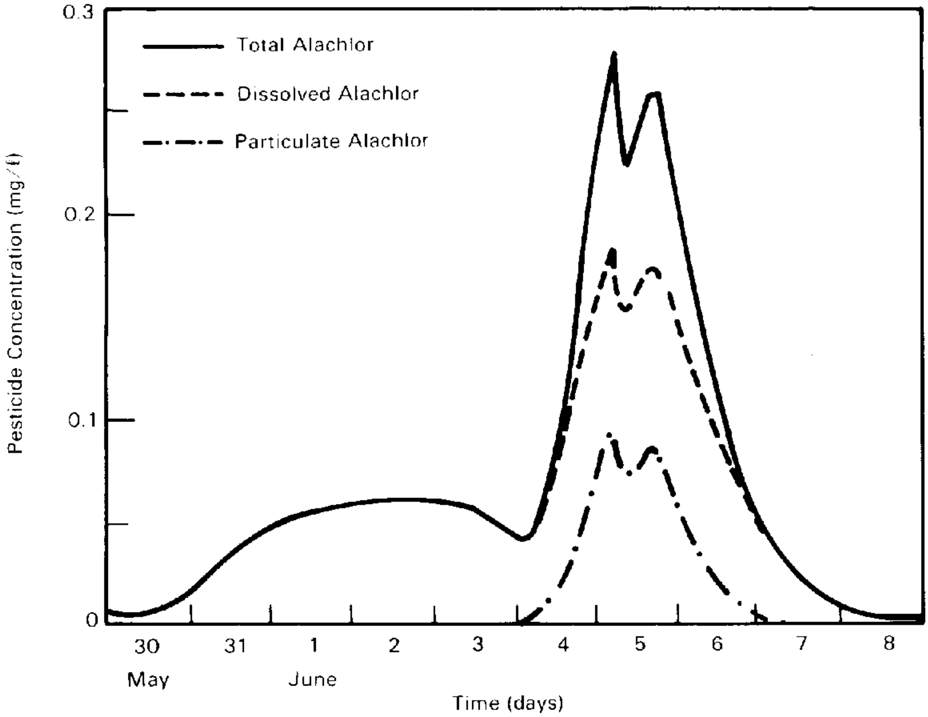

Fig. 14. Time variation of dissolved, sediment-sorbed, and total Alachlor concentration near the mouth of Wolf Creek River during the period May 30, 1973 to June 8, 1973.

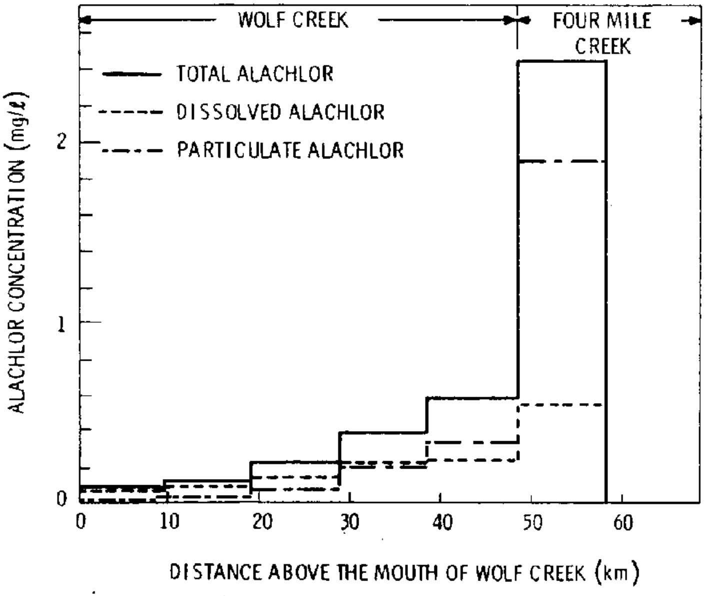

Fig. 15. Longitudinal distributions of predicted dissolved, sediment-sorbed, and total Alachlor at 12 p.m., June 5, 1973.

14 and 15. Figure 14 depicts time-varying concentrations of dissolved, sediment-sorbed and total Alachlor near the mouth of Wolf Creek during the highest pesticide concentration period (May 30 to June 8, 1973). Figure 15 presents longitudinal distributions of sediment-sorbed, dissolved, and total Alachlor on June 5, 1973. As shown in Fig. 14, when the maximum Alachlor concentration occurred near the mouth of Wolf Creek on June 5, 1973, approximately 35% of the total Alachlor was being carried by sediment, while 65% was in a dissolved form; the dissolved form is generally subject to more immediate uptake by aquatic biota. Near the

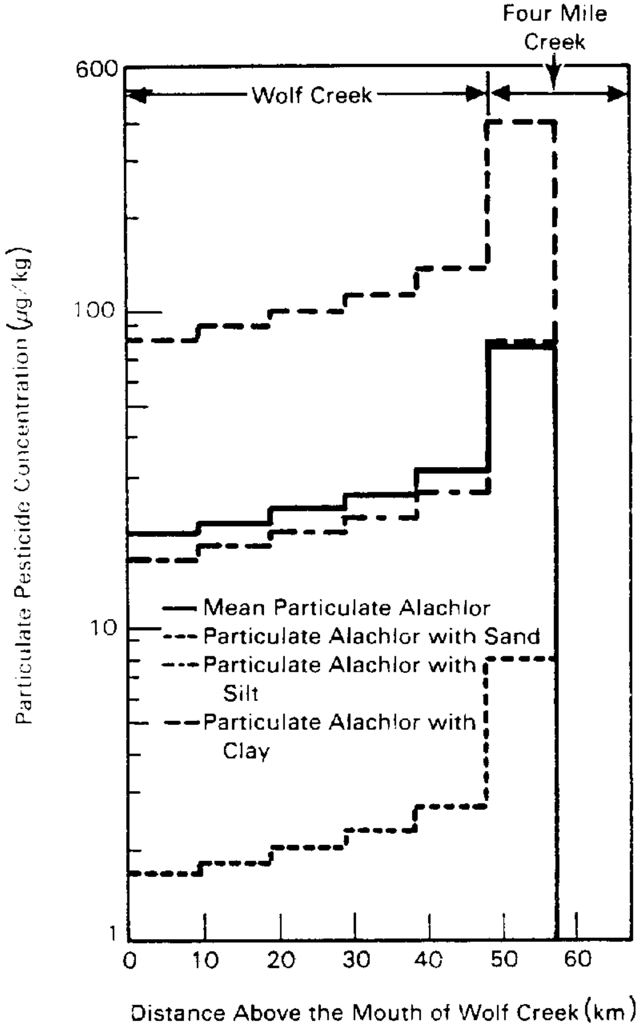

Fig. 16. Variations of predicted sediment-sorbed Alachlor in the top bed layer accumulated during the three-year simulation period.

mouth of Four Mile Creek, predicted dissolved and particulate Alachlor consisted of 22% and 78% of the total concentration, respectively. Because most of Alachlor transported from the agricultural land was in a dissolved form, sediment uptake in the receiving water reduced the dissolved pesticide amount by 78% in Four Mile Creek. As shown in Fig. 15, the percentage of sediment-sorbed Alachlor to the total Alachlor steadily decreased from 59% to 8% with the downstream distance. The decrease resulted mostly from the deposition of contaminated sediment before it reached the mouth of Wolf Creek. The dilution of the pesticide by clean Wolf Creek water (coming from upstream of the confluence with Four Mile Creek) also induced desorption of the pesticide from sediments into the water column. Reduction of total Alachlor concentration with distance reflects these aspects.

The effect of sediment migration on contaminant distribution is also demonstrated in Fig. 16. This figure shows predicted longitudinal sediment-sorbed Alachlor distributions associated with the three sediment-size fractions and their weighted average in the top bed layer after the three-year simulation. Because no Alachlor was initially assumed in the stream bed, the accumulation of Alachlor in the bed must have occurred during the three-year period through deposition and resuspension of contaminated sediment and direct adsorption and desorption with overlying water column. Consequently, even if the use of Alachlor was terminated, already contaminated bed sediment would continue to introduce Alachlor back to the water column. This figure also reveals that, because of the available sediment surface area and organic coating, clay had the highest Alachlor concentration, while sand adsorbed the least amount of Alachlor.

Risk assessment

The risk assessment portion of the application involved determining the acute and chronic toxicity of Alachlor on rainbow trout (*Salmo gairdneri*). The following LC50 and MATC values were used for this case:

24-h LC50 = 9.2 mg/l
48-h LC50 = 3.5 mg/l
96-h LC50 = 1.8 mg/l
MATC = 0.44 mg/l

To determine the possible lethal and sublethal impact of Alachlor on rainbow trout near the mouth of Wolf Creek, the LC50 and MATC values were selected as specific levels of concentration and duration in the statistical computer program, FRANCO.

As shown in Fig. 17, an analysis of the three-year dissolved Alachlor concentration indicated that no Alachlor concentration exceeded even the MATC value for rainbow trout during the entire three-year duration. Because the MATC value is defined as the concentration below which there are no measureable impacts on biota, it can be concluded that the

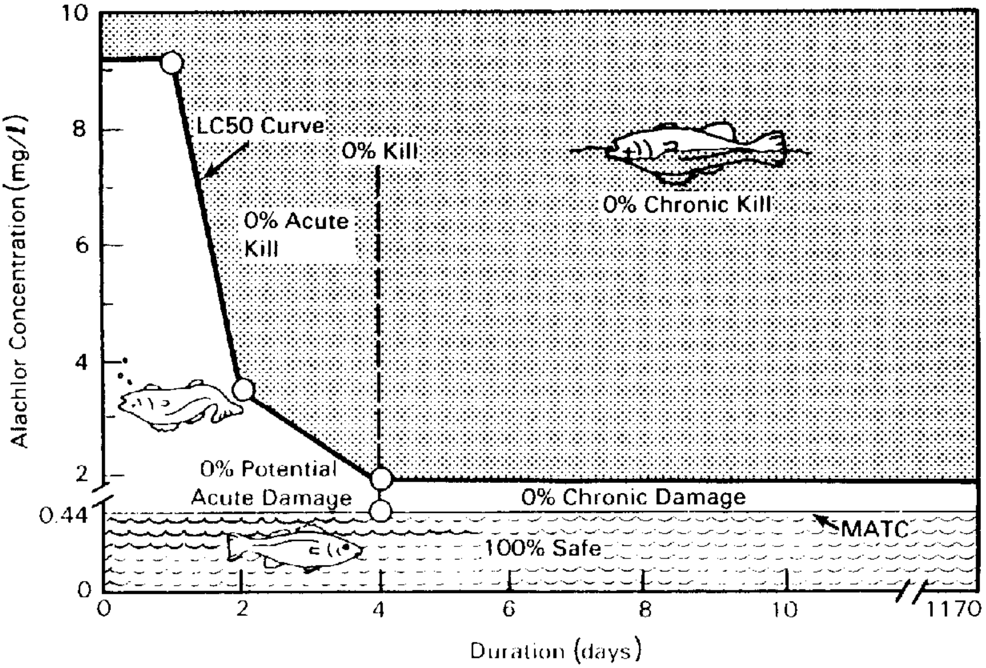

Fig. 17. Probabilistic risk assessment of Alachlor for rainbow trout.

dissolved Alachlor near the mouth of Wolf Creek did not pose any threat of toxicity to rainbow trout or any other species with an MATC greater than 0.44 mg/l. However, as we previously stated, because the Alachlor contribution to Four Mile and Wolf Creeks was assumed to come from only a small portion of the Four Mile Creek Watershed, this assessment should be regarded as the demonstration of the CMRA methodology, rather than as the true risk assessment of Alachlor at the study site.

Conclusions

The CMRA methodology was developed to provide a scientific basis for risk assessment and decision making. It consists of a series of the state-of-the-art mathematical models and simulates the migration and fate of toxic contaminants on land surface and in surface waters and evaluates the probability of acute and chronic impacts on aquatic biota. Its applications for pesticides (toxaphene in the Yazoo River Basin, Mississippi, and Alachlor in the Wolf Creek Basin, Iowa) demonstrated its usefullness as both a decision-making and research tool by integrating complex contaminant transport and fate mechanisms and toxicity into a single framework. This was evidenced by the U.S. government's decision to ban toxaphene, partially based on the results of this assessment study. These applications also demonstrated that when (1) a contaminant has a high affinity to sediment, (2) a receiving water has a high concentration of sediment, especially fine sediment, or (3) a long-term contaminant accumulation in a water body is a main concern, the sediment/contaminant interactions (e.g., adsorption/desorption and transport, deposition, and resuspension of contaminated sediment) become important to the contaminant distribution and thus risk assessment.

Acknowledgments

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