

it does not ordinarily induce a large local reduction of CO<sub>2</sub>. By contrast, macrophyte production can induce large local changes in CO<sub>2</sub> partial pressure, because the turnover rate of carbon from macrophytes is slow due to carbon accumulation in biomass. Coastal CO<sub>2</sub> anomalies are both temporally and spatially patchy, because macrophyte distribution and production are not homogeneous. Water-column CO<sub>2</sub> partial pressures, calculated from hourly pH and alkalinity sampling in a Western Australia seagrass bed, varied by about 30 μatm (10 percent) over 24 hours in response to community metabolism (Fig. 2). Mean CO<sub>2</sub> partial pressures for sites on a Western Australia coral reef rich in macroalgae varied between winter and summer by approximately 120 μatm and between sites by 20 to 50 μatm (Table 1). Because areas of high macrophyte production are often buffeted by breaking waves, gas transfer coefficients at coasts are likely to be elevated above open ocean values.

Marine macrophyte organic carbon production, biomass storage, burial, oxidation, oxidation-induced CaCO<sub>3</sub> dissolution, and metabolically accelerated gas exchange across the air-sea interface are alternative expressions for a single, complex carbon sink. Although the components of this sink do exist, their quantitative significance on a global scale is not yet known.

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## Fate and Transport of Dieldrin in Coralville Reservoir: Residues in Fish and Water Following a Pesticide Ban

**Abstract.** A model for the fate and transport of pesticide has been calibrated with field data from 1968 to 1978. The results have aided in a management decision to lift a commercial fishing ban in Coralville Reservoir, eastern Iowa. Dieldrin residues in fish, sediment, and water are all declining at about 15 percent per year. Approximately 50 percent of the pesticide load is exported from the reservoir in the outflow, 40 percent undergoes sedimentation, and 10 percent enters the fish.

Several models have been proposed to assess the fate and transport of pesticides in surface waters, including the Stanford Research Institute (SRI) model (1) and the Exposure Analysis Modeling System (EXAMS) (2). Previous models have not been extensively verified with field data, and they have not combined chemical fate modeling with biological effects. In this report, a model of pesti-

cide fate and bioconcentration is developed and applied to Coralville Reservoir, eastern Iowa, to assess the long-term fate and effects of dieldrin in the ecosystem. Results have aided the Iowa Conservation Commission in their decision to lift a commercial fishing ban.

The insecticide most widely used for corn rootworm and cutworm during the 1960's and 1970's was the chlorinated hydrocarbon aldrin, a derivative of hexachlorocyclopentadiene. Aldrin is rapidly converted to its epoxide dieldrin by biodegradation in natural waters (3). Because of the widespread use of aldrin in Iowa as an insecticide for corn, Iowa waters have become contaminated with dieldrin.

During the middle 1960's aldrin usage in Iowa reached a peak application of 6.5 million pounds (2.9 million kilograms) per year over a total of approximately 5 million acres (2 million hectares). Insect resistance to this chlorinated hydrocarbon became prevalent in the middle to late 1960's and swept from west to east across Iowa, and usage declined to approximately 3.5 million pounds (1.6 million kilograms) per year. In 1975 the Environmental Protection Agency (EPA) cancelled the registration of aldrin and dieldrin insecticides.

Public attention in Iowa to the problems of aldrin and dieldrin reached a peak in 1976, when the EPA and the Iowa Conservation Commission (ICC) placed a ban on commercial fishing in Coralville Reservoir. The primary commercial species affected by the ban was bigmouth buffalo, a bottom-feeding fish. In 1975 dieldrin residues in several big-

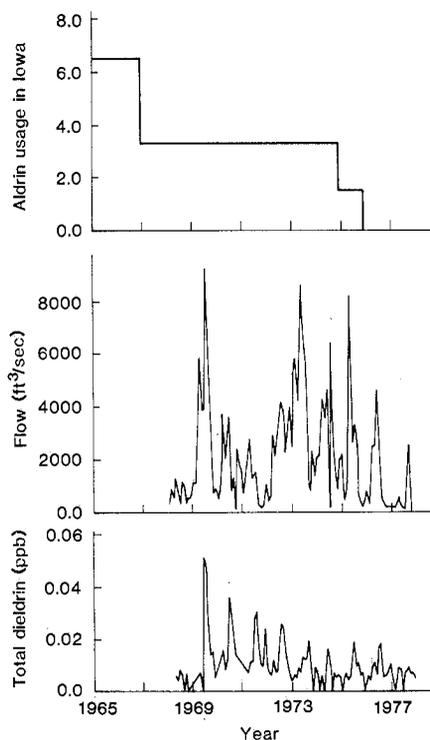


Fig. 1. Estimated aldrin usage (in million pounds) in Iowa and total dieldrin concentrations in the Iowa River at Iowa City, 1968 to 1978.

mouth buffalo, catfish, and carp had been shown to be in excess of the Food and Drug Administration (FDA) guideline value of 0.3 mg/kg in wet, edible tissue. Recent analyses (1978 to 1980) have shown that dieldrin residues in bigmouth buffalo and other bottom-feeding fish have been declining and are below the FDA guideline value in an average composite catch. On 7 November 1979 the ban on commercial fishing in Coralville Reservoir was lifted by action of the ICC in cooperation with the FDA. It is instructive to follow the fate of dieldrin through this chronology of peak precursor application, cancellation of the pesticide registration, ban on commercial fishing, and lifting of the ban. A simple mathematical model was used to analyze these trends and make projections for future water quality management decisions.

Eight major Iowa rivers (the Cedar, Iowa, Little Sioux, Mississippi, Missouri, Nishnabotna, Raccoon, and Skunk rivers) were analyzed for dieldrin in monthly grab samples of unfiltered water (4) from 1968 to the present. In all cases measurable dieldrin concentrations have been decreasing since 1968. Furthermore, logarithmic least-squares regression analyses (log concentration versus time) for the Cedar, Iowa, Little Sioux, Nishnabotna, Raccoon, and Skunk rivers yielded negative slopes and significant correlation coefficients at the 95 percent confidence level. The average decline was 10 percent per year, or a half-life of about 7 years. Mean concentrations were 0.015  $\mu\text{g/liter}$  in 1968 to 1970 and 0.004  $\mu\text{g/liter}$  in 1978, considerably greater than the 24-hour average value of 0.0019  $\mu\text{g/liter}$  in proposed water quality criteria (5, 6). Figure 1 shows dieldrin concentration and flow time series for the Iowa River below Coralville Reservoir. Peak dieldrin concentrations in the water correspond with periods of maximum flow. The mean annual dieldrin concentration and the envelope of the peaks decreased from 1970 to 1978 at a rate of approximately 15 percent per year.

Coralville Reservoir is a mainstream impoundment of the Iowa River approximately three river miles above Iowa City. It is a shallow reservoir with a mean depth of 8 feet (2.4 m) and a mean hydraulic detention time of only 14 days. Because it receives large nutrient inputs from agricultural runoff, it has very high primary productivity and fish production, with a standing crop of more than 1000 pounds per acre in bigmouth buffalo alone (7). Dieldrin concentrations in the sediment, in bottom-feeding fish, and in

the water column have decreased by about a factor of 4 since 1969 and 1970 (Fig. 2). Sorption studies and field data indicate that the equilibrium partitioning of dieldrin between suspended sediments and water ranges from 1000 to 6000  $\mu\text{g/kg}$  in dry sediment per 1  $\mu\text{g/liter}$  in water for fine-grained sediments. The bioconcentration factor (BCF)—that is, the ratio of dieldrin residues in the wet, edible tissue of bottom-feeding fish to the concentration of dissolved dieldrin—is  $\sim 70,000$   $\mu\text{g/kg}$  per 1  $\mu\text{g/liter}$ . All concentrations are decreasing roughly 15 percent per year.

A mathematical model was developed to simulate the fate and transport of dieldrin through Coralville Reservoir. For a completely mixed system, the principle of continuity of mass is formulated in the following equations (1, 8). In the water column

$$\frac{dC_T}{dt} = \frac{W(t)}{V} - \frac{C_T}{t_0} - \Sigma kC - k_s C_p - k_1 C \quad (1)$$

where  $C_T$  is the total dieldrin concentration in unfiltered water;  $t$  is time;  $W(t)$  is the rate of mass input of dieldrin;  $V$  is the reservoir volume;  $t_0$  is the mean hydraulic detention time;  $\Sigma k$  is the sum of the pseudo-first-order rate constants for decay including biological degradation,

chemical hydrolysis, direct photolysis, and volatilization;  $C$  is the dissolved dieldrin concentration;  $k_s$  is the mean sedimentation rate constant;  $C_p$  is the particulate dieldrin concentration; and  $k_1$  is the biouptake rate constant = (600 liters filtered per kilogram of fish per day)  $\times$  ( $4.7 \times 10^{-5}$  kilogram of fish per liter).

The total concentration of dieldrin in whole water is the sum of the concentrations in the particulate and dissolved phases

$$C_T = C + C_p \quad (2)$$

Adsorption and desorption rates are orders of magnitude greater than the rates of the decay and transport processes considered in formulating Eq. 1; hence instantaneous sorptive equilibrium is achieved between the two phases very rapidly in comparison to sedimentation, washout, volatilization, photolysis, hydrolysis, biological degradation, and biological uptake. Therefore  $C$  and  $C_p$  may be replaced by their equivalents in terms of  $C_T$  provided the equilibrium adsorption isotherm is known. Linear adsorption isotherms have been reported by Karickhoff *et al.* (9)

$$r = K_p C \quad (3)$$

where  $K_p$  is the linear adsorption partition coefficient and  $r$  is the amount of pesticide adsorbed per unit mass of dry

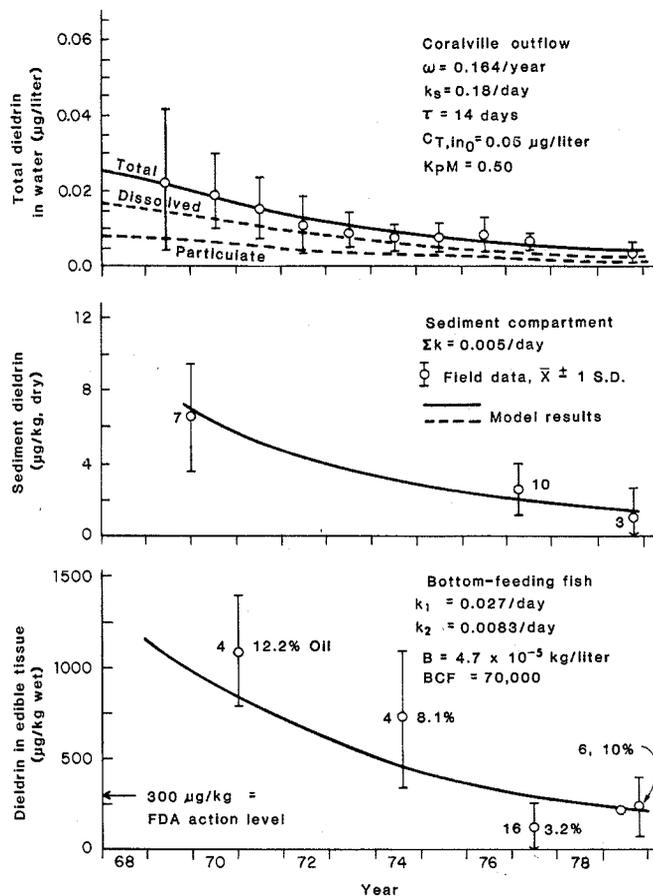


Fig. 2. Field data and model results for dieldrin in Coralville Reservoir. Percentages represent the oil or lipid content of the catch; numbers give the number of data points.

sediment. It follows from Eqs. 2 and 3 that  $C$  and  $C_p$  may be expressed in terms of  $C_T$  under conditions of sorptive equilibrium in which the concentration of suspended solids,  $M$ , is known

$$C = \frac{C_T}{1 + K_p M} \quad (4)$$

$$C_p = \frac{C_T K_p M}{1 + K_p M} \quad (5)$$

Substituting these expressions for  $C_p$  and  $C$  into Eq. 1 gives the mass balance differential equation

$$\frac{dC_T}{dt} = \frac{W(t)}{V} - \frac{C_T}{t_0} - \frac{\sum k + k_1}{1 + K_p M} C_T - \frac{k_s K_p M}{1 + K_p M} C_T \quad (6)$$

Bioaccumulation follows the linear kinetics of uptake minus depuration

$$\frac{dF}{dt} = k_1 f_1 C_T / B - k_2 F \quad (7)$$

where  $f_1 = C/C_T = 1/(1 + K_p M)$  is the fraction of dissolved dieldrin;  $k_2$  is the depuration rate constant, estimated as  $k_1/B(\text{BCF})$ ;  $F$  is the whole-body fish residue level; and  $B$  is the fish biomass concentration (wet weight).

Equations 6 and 7 may be solved analytically for constant coefficients and simple pesticide loading functions,  $W(t)$ , or they may be integrated numerically. In the case of a pesticide ban,  $W(t)$  might typically decline exponentially because of degradation by soil organisms. For a loading function declining exponentially at rate  $\omega$ , the analytical solutions to Eqs. 6 and 7 are

$$C_T = C_{T_0} e^{-\delta t} + \frac{C_{T, \text{in}_0}}{\varepsilon} (e^{-\omega t} - e^{-\delta t}) \quad (8)$$

$$F = F_0 e^{-k_2 t} + \frac{k_1 f_1}{B} \times$$

$$\left( \frac{C_{T_0}}{\gamma} e^{-\delta t} + \frac{C_{T, \text{in}_0}}{\varepsilon \theta} e^{-\omega t} - \frac{C_{T, \text{in}_0}}{\varepsilon \gamma} e^{-\delta t} \right) - \frac{k_1 f_1}{B} e^{-k_2 t} \left( \frac{C_{T_0}}{\gamma} + \frac{C_{T, \text{in}_0}}{\varepsilon \theta} - \frac{C_{T, \text{in}_0}}{\varepsilon \gamma} \right) \quad (9)$$

where  $f_2 = C_p/C_T = K_p M/(1 + K_p M)$  is the fraction of particulate pesticide,  $C_{T_0}$  is the initial pesticide concentration in the lake,  $C_{T, \text{in}_0}$  is the initial total pesticide inflow concentration,  $\omega$  is the rate of the exponentially declining inflow concentration,  $\alpha = (\sum k) f_1 + k_1 f_1 + k_s f_2$ ,  $\gamma = k_2 - \alpha - (1/t_0)$ ,  $\delta = \alpha + (1/t_0)$ ,  $\varepsilon = \alpha t_0 + 1 - \omega t_0$ , and  $\theta = k_2 - \omega$ .

Equations 6 and 7 are written for only one water compartment with sedimentation of suspended solids into the sediment compartment. It is straightforward

to extend the analysis to a number of compartments with flow and bulk dispersive transport between compartments (10). The equations are linear and may be solved analytically or numerically.

Model coefficients and results are presented in Fig. 2. From the analysis it was determined that ~ 40 percent of the dieldrin that enters the reservoir is lost to the bottom by sedimentation and 50 percent is released through the dam gates of the reservoir, which has a short detention time. Uptake by fish accounts for ~ 10 percent of the dieldrin input due to the extremely large biomass of biota. The partitioning of dieldrin in the water column is 74 percent in the fish, 25 percent dissolved in the water, and less than 1 percent adsorbed by suspended solids. Mean residues in the edible tissue of bottom-feeding fish have declined below the FDA guideline value of 300 ppb. Photodegradation, volatilization, and biological degradation rates are negligible in the water column compared to transport rates, but an overall dieldrin degradation rate of 0.1 percent per day in sediment contributes to the gradual decline of sediment concentrations. Concentrations in fish and sediment are essentially in equilibrium with mean concentrations of dissolved dieldrin. Bottom-feeding fish accumulate dieldrin in proportion to their oil content (petroleum ether extraction). Therefore averages or composites for very oily fish tended to be higher than model predictions.

The prospect for a continued decline in dieldrin residues is good. Model projections indicate that by 1986, the resi-

dues in the flesh of bottom-feeding fish should average less than 100  $\mu\text{g}/\text{kg}$ . Research is continuing on the role of sediment resuspension and food items on the bioaccumulation potential of the fishery.

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10. Equations 1 to 6 can be written for a number of water compartments that are connected by flow and suspended sediment exchanges. Therefore it is not necessary to assume completely mixed conditions for the entire reservoir, only for a given control volume. One, two, and five interconnected water compartments have been used in this analysis. Results are shown for a two-compartment model of water and sediment with exchanges in Fig. 2. Addition of water and sediment compartments results in very minor changes to the calculations of Fig. 2.
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## Protein Antigens from *Staphylococcus aureus* Strains Associated with Toxic-Shock Syndrome

**Abstract.** *Staphylococcus aureus* isolates from patients with toxic-shock syndrome have two antigenic proteins that distinguish these strains from isolates obtained from patients who do not have this syndrome and who are colonized or infected with *S. aureus*. These proteins may either represent antigenic markers, the toxin (or toxins), or toxic subunits that cause the clinical manifestations of this disease.

The toxic-shock syndrome (TSS) is a recently recognized illness that primarily affects previously healthy young women (1, 2). The syndrome most often occurs during the menstrual period and is characterized by acute onset of high fever, vomiting, diarrhea, an erythematous rash with subsequent desquamation, and severe hypotension. The syndrome occurs with a frequency of approximately three in 100,000 women and has been associated with a 10 percent mortality (3). Clinical and epidemiologic studies of

TSS have implicated vaginal colonization with *Staphylococcus aureus* and the use of tampons as risk factors for development of disease (3).

Although *S. aureus* has been implicated in TSS, this microorganism colonizes a significant proportion of the general population, and, in one study, vaginal colonization occurred in 7 percent of menstruating women (3). Thus far no useful distinction has been reported between *S. aureus* isolates from patients with TSS and those from either the nor-