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PREDICTION OF TOXICITY OF SEDIMENTS CONTAINING COMPLEX CONTAMINANT MIXTURES

Depositional-zone sediments in urban and industrial areas are often heavily contaminated with complex mixtures of chemicals from historic discharges of toxic pollutants. We developed a model that estimates aquatic toxicity from information on sediment chemistry to evaluate the potential toxicity of sediments that may contain combinations of many contaminants.

MODEL DEVELOPMENT

We needed a method for evaluating the combined effects of sediment mixtures comprising numerous contaminants of varying toxicity. Historically, concentrations of individual metals in mixtures were expressed in relation to incipient lethal concentrations—the concentrations of individual constituents beyond which organisms cannot survive for an indefinite period. These ratios, or toxic units, were then summed over all constituents in the mixture to estimate the total toxicity of that mixture. The toxic units approach remains in use for metals.

We expanded the toxic units method to incorporate information on organic contaminants, bioavailability (i.e., the proportion of a contaminant in a sediment that is available for uptake by organisms), and chronic toxicity. For sediments, this bioavailable fraction is the concentration in the interstitial waters of the sediment—the pore-water concentration. We define a toxic unit as the ratio of the estimated concentration of a

contaminant in the pore water of a test sediment to an estimate of the chronic toxicity of that contaminant in water. We used water quality standards and criteria, mostly the U.S. Environmental Protection Agency Ambient Water Quality Criteria (AWQC), for chronic toxicity. These criteria are founded on information from a wide range of taxa and, where appropriate, incorporate bioaccumulation potential (i.e., the potential for concentrations to increase in upper trophic level organisms). The equation for toxic units is

$$\text{Toxic unit} = \frac{C_{wp}}{C_{wqs}}$$

C_{wp} = *Estimated pore-water concentration*

C_{wqs} = *Water quality standard*

We estimate toxic units attributable to selenium according to a proposed sediment criteria. The toxic units for all contaminants in a sediment are then summed to produce a total toxicity estimate for that sediment.

For organic contaminants, we used information on the differential solubility of compounds in water and in organic carbon and the amount of organic carbon present

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in the sediment to estimate the pore-water concentration. We assumed that the concentration of organic contaminants in water is controlled by organic carbon, and that the contaminant concentrations are in equilibrium with sediment organic carbon and pore water. Analogous to the approach used for organic contaminants, we used the concentration of sulfide released along with metals when the sediments were leached with a weak acid; that is, the acid-volatile sulfides (AVS) and simultaneously extracted metals (SEM), as estimates of the bioavailable fraction of each metal present in the sediments. In using the AVS approach, we assumed that equilibrium concentrations of metals in pore waters are controlled by the presence of sulfides, which combine with the metals to produce relatively insoluble sulfide salts, much as organic carbon controls pore-water concentrations of organic chemicals. For mercury, soluble and highly toxic in its methylated form, we assumed that all methyl mercury was soluble and hence bioavailable; for the remainder, bioavailable mercury was estimated using the AVS-SEM approach.

MODEL TESTING AND EVALUATION

To evaluate the ability of the model to predict toxicity from chemical information we examined data from 12 sites located in three Great Lakes harbors and tributaries—Indiana Harbor, Indiana; Saginaw River, Michigan; and Buffalo River, New York—containing different mixtures of contaminants. Sediments were collected with a Ponar grab and split into two portions—one for laboratory toxicity tests, the other for chemical analysis. Laboratory toxicity tests were performed with fish, zooplankters, benthic macroinvertebrates, phytoplankters, macrophytes, and microbes. The list of contaminants measured included polychlorinated biphenyls, polycyclic aromatic hydrocarbons, organochlorine pesticides, simultaneously extracted metals, total metals, and others. Organic carbon and acid volatile sulfide content of the sediments were also measured.

We evaluated the predictions of the toxic units model by comparing it with sediment toxicity determined in the laboratory. To estimate toxicity for each sediment sample as determined in the laboratory, the data from each of the series of toxicity tests, including multiple endpoints measured within some tests, were scaled similarly to the

toxic units scaling performed on the chemistry measures—by normalizing the measured response associated with an endpoint to the control sediment response (i.e., the same test, run simultaneously with sediment from a clean site) for that endpoint:

$$\text{Control-adjusted laboratory toxicity response} = 1 - \frac{\text{Endpoint value for test sediment}}{\text{Endpoint value for control sediment}}$$

These estimates of hazard—the control-adjusted laboratory toxicity responses for each endpoint—were averaged (i.e., arithmetic mean) over all measured endpoints for a site to estimate the mean hazard for each site on the basis of laboratory-determined toxicity.

TOXIC UNIT ESTIMATION FOR CONTAMINANT MIXTURES IS A VALUABLE TOOL

The relation between laboratory toxicity and toxic units was nearly linear, but included a quadratic term that was marginally significant (Figure). This model accounted for more than 93% of the variability present in mean laboratory toxicity. Our findings support the hypothesis that toxicity, as measured by short-term toxicity tests, is mediated by pore-water contaminant concentrations and that toxicity may be additive, as has been suggested by others. The short-term laboratory toxicity tests by themselves reflect toxicity of the sediments in the immediate vicinity from which they are collected, but not necessarily the ecosystem risk represented by the transfer of the contaminants they contain through the food chain. However, short-term laboratory toxicity tests, as documented in the strength of the relation between toxic units and toxic response, do seem to characterize the overall extent to which sediments are contaminated.

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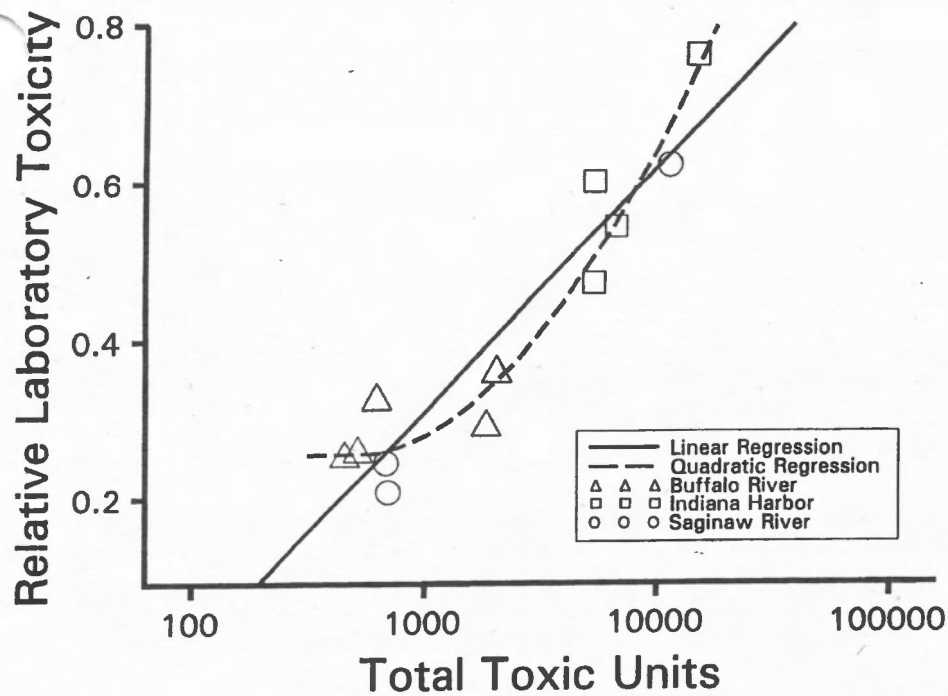


Figure. Relative toxicity of sediment versus total toxic units estimated from bioavailable fractions of all contaminants (for the line $R^2 = 0.88$; for the curve $R^2 = 0.94$; for the line and the curve, $n = 12$, $P = 0.0001$).