Spiked Sediment Toxicity Testing with Hydrophobic Organic Chemicals: Dioxin and Hexachlorobenzene

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Introduction

Many evaluations intended to estimate safe levels of hydrophobic organic chemicals in sediments have been based on studies that do not account for such confounding factors as covariance among chemicals and differences in physical habitat quality. Spiked sediment toxicity tests have been used to conduct controlled experiments that are not confounded by these factors, in some cases producing dramatically different estimates of chemical effects thresholds. Studies with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and hexachlorobenzene (HCB) exemplify the importance of verifying results of field studies using spiked sediment tests.

In a study of sediment toxicity in the lower Passaic River and Newark Bay (New Jersey, USA), the National Oceanic and Atmospheric Administration found a highly significant correlation between 2,3,7,8-TCDD concentrations and mortality observed in 10-day whole-sediment toxicity tests with the amphipod *Ampelisca abdita* [1]. The highest measured 2,3,7,8-TCDD concentration in this investigation was 0.62 μg/kg. However, studies testing the toxicity of 2,3,7,8-TCDD to other invertebrates, including multiple insect, crustacean, mollusc, and worm species, have shown no significant adverse effects at the highest concentrations tested in food, water, flooded spiked soil, and sediment. Therefore, a spiked sediment toxicity test was implemented [2] to distinguish whether (1) *A. abdita* is unusual among invertebrates in its susceptibility to 2,3,7,8-TCDD, or (2) the toxicity observed in the Passaic River was due to other chemicals with concentrations that covaried with 2,3,7,8-TCDD in the sediment samples tested.

A similar contrast provided the impetus for spiked sediment toxicity testing with hexachlorobenzene (HCB). Screening-level sediment quality guidelines of approximately 20 μg/kg normalized to 1% TOC ($\mu g/kg_{1\%OC}$) have been developed for HCB based on evaluations of benthic community composition and laboratory toxicity test results associated with sediment chemical concentrations [3,4]. However, a substantial body of literature has shown a lack of significant adverse effects due to aqueous exposure to HCB at concentrations up to the solubility limit [5]. Thus, the equilibrium partitioning approach, which compares aqueous effects thresholds to dissolved chemical concentrations in sediment porewater, predicts that HCB could not produce direct toxicity as a sediment contaminant. Spiked sediment toxicity testing provided a controlled experimental technique for resolving this contradiction.

Methods

Sediment Spiking. Methods used to spike uncontaminated sediment samples with 2,3,7,8-TCDD and HCB were based on Society of Environmental Toxicology and Chemistry – Europe guidance [6]. Estuarine sediment containing primarily silt and clay was used for the 2,3,7,8-TCDD study, while sandy riverine sediment was used for the HCB study. Both sediments contained approximately 1.8% total organic carbon (TOC). Nominal spiked concentrations were 1, 5, 10, and 25 µg/kg for 2,3,7,8-TCDD and 10, 25, 50, 100, and 250 mg/kg for HCB. An appropriate amount of chemical was added to a minimal amount of hexane, and the spiked solution was added to the surface of an aliquot of wet sediment. The hexane was allowed to evaporate, and the spiked sediment was then mixed thoroughly using a rolling mill. The spiked sediment was distributed to toxicity test chambers and allowed to equilibrate for 14 days under toxicity test conditions (temperature, overlying water) before test organisms were added.

Chemical Analysis. Sediment was collected for chemical analysis at the end of the equilibration period, immediately prior to the addition of test organisms. 2,3,7,8-TCDD was analyzed using U.S. Environmental Protection Agency (USEPA) method 8280 [7], modified using a Dean Stark soxhlet extraction system (USEPA method 1613A [7]). The Dean Stark soxhlet extraction improves extraction efficiency by removing water and thereby increasing solvent contact with the sediment. HCB was analyzed using USEPA method 8080 [7] (extraction by sonication).

Toxicity Testing. Whole-sediment, static bioassays were conducted measuring test organism survival and growth (dry weight). 2,3,7,8-TCDD-spiked sediment samples were tested using the estuarine amphipod *Ampelisca abdita* (10-day exposure [8]). HCB-spiked sediment samples were tested using the freshwater amphipod *Hyalella azteca* and the midge *Chironomus tentans* (14-day exposures [9]).

Results and Discussion

Chemical Concentrations. Measured concentrations of 2,3,7,8-TCDD were approximately equal to the nominal spiked concentrations, whereas measured HCB concentrations were approximately 50% lower than the nominal concentrations. A review of nominal versus measured concentrations in published spiked sediment studies indicates that a variety of factors may affect the ability to achieve target test concentrations in spiked sediment studies, including complex sediment characteristics, chemical volatilization, adsorption to glassware, biodegradation, or extraction method [10]. HCB in particular may be lost through volatilization [11] immediately following sediment spiking, although another recent spiked sediment study with HCB showed no significant additional loss of HCB during the course of toxicity testing [12]. Although the difference between nominal and measured concentrations may be difficult to predict *a priori*, chemical losses are relatively consistent for a given combination of sediment, chemical, and spiking/extraction methodology, such that preliminary spiking and analysis may facilitate achievement of target test concentrations [10].

Toxicity. No significant toxicity was observed in either the 2,3,7,8-TCDD or HCB-spiked sediment samples. The maximum no-effect concentrations were equal to the highest concentrations tested: 25 µg/kg (14 µg/kg normalized to 1% TOC) for 2,3,7,8-TCDD and 75 mg/kg (42 mg/kg normalized to 1% TOC) for HCB.

Bioavailability. The ability to compare the results of spiked sediment studies and field studies for 2,3,7,8-TCDD and HCB depends on an understanding of potential differences in chemical bioavailability among studies. Two key factors are (1) sediment TOC content and (2) the extent and strength of chemical adsorption to TOC. Normalizing chemical concentrations to a constant TOC content (*e.g.*, 1%) addresses the first of these factors. A review of studies examining bioaccumulation of hydrophobic organic chemicals from sediment and chemical partitioning between sediment particles and interstitial water indicates that, given a constant TOC content, spiked chemicals may be more bioavailable than chemicals that have been present for extended periods of time in the field [10]. In the studies evaluated for 2,3,7,8-TCDD and HCB, the spiked chemical concentrations were more than an order of magnitude higher than the concentrations measured in field-collected sediments (concentrations normalized to 1% TOC). Given the large differences in concentrations and the possible bias toward higher bioavailability in the spiked sediment samples, it is apparent that toxicity observed in field-collected sediment samples was not due to 2,3,7,8-TCDD or HCB.

Implications. The evaluation of sediment toxicity to benthic invertebrates using associations (rather than controlled experiments) frequently constitutes the primary basis for the management of contaminated sediments. However, controlled experiments have shown that for some hydrophobic organic chemicals, association-based studies may greatly overestimate toxicity. Spiked sediment toxicity tests provide a practical means of verifying field-based sediment toxicity assessments. For chemicals such as 2,3,7,8-TCDD and HCB, which may not affect benthic invertebrates at environmentally relevant concentrations, sediment management decisions should be based on the risk of effects due to bioaccumulation through the food web rather than direct sediment toxicity.

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