

**Assessing Contaminant Migration and Risk  
through Passive Interstitial Water Samplers - 9347**

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**ABSTRACT**

Soils and sediments account for a large proportion of the contaminated materials being managed under cleanup programs across the country, including at sites addressed by the U.S. Department of Energy and U.S. Army Corps of Engineers. Costs for managing a single sediment site can approach \$1 billion, and overall program costs could exceed the trillion-dollar mark. Thus, using realistic information for contaminant levels in the risk calculations used to guide cleanup decisions for these sites is crucial. The risk-based decisions for contaminated soils and sediments are typically based on bulk solid concentrations. The reason for using that metric in the equations applied to estimate exposure and risk to biota and humans is that it is relatively easy to measure. However, the bulk concentration does not address the actual bioaccessibility or bioavailability of the contaminants. This can result in a substantial overestimate of risk, leading to cleanup decisions that are much more conservative than warranted. Such decisions can translate to unnecessary excavation or dredging that causes significant environmental damage to those natural systems, thus having the opposite effect intended by health and environmental protection programs. More realistic values that represent the bioavailable fraction of contaminants in soil and sediment are clearly needed to guide more effective cleanup decisions. Passive interstitial water samplers have emerged as a practical way to address this need.

**INTRODUCTION**

Federal agencies such as the U.S. Department of Energy and U.S. Army Corps of Engineers are conducting and overseeing extensive cleanup programs at sites across the country with contaminated soils and sediments. These sites typically involve large volumes of solids with relatively low levels of contamination. Environmental management of soils and sediments can be very expensive, especially for sediments that are inherently difficult to characterize and remediate. Cleanup costs for single large sediment projects have been estimated at \$1 billion, and total program costs have been estimated to reach \$5 trillion [1-3]. Further complicating the problem is that cleanup decisions for these materials have been guided by exposure and risk assessments that reflect bulk solid concentrations, as represented by milligrams of contaminant per kilogram soil or sediment (mg/kg). However, the solid phase is normally neither mobile nor readily available to biota, so it is not a realistic measure of the exposure term.

The contaminant concentration in the mobile phase would be a much better indicator of exposure and risk, notably the concentration in the interstitial water. Unfortunately, tools have not been available to provide reliable measures of these pore water concentrations. The result is that risks are commonly overestimated, which can lead to cleanup decisions that are considerably more conservative than warranted. Such decisions can translate to unnecessary excavation or dredging, which typically cause significant environmental damage to those natural systems, thus having the opposite effect intended by health and environmental protection programs. An additional problem is that in-situ management of these materials

is normally accomplished by containment systems, and the low mobility of these compounds has made it difficult to assess and monitor the effectiveness of those systems.

Passive gradient samplers have recently become available that allow sensitive measurement of pore water concentrations and migration, for use in risk calculations and to monitor the performance of sediment containment systems. For example, solid phase microextraction (SPME) samplers can measure nanogram/liter (ng/L) levels of hydrophobic organic compounds with resolution on the order of centimeters (cm), and diffusion gradient thin (DGT) film devices offer a similar capability for metals, including radionuclides. Thus, new tools exist that can help address critical program needs.

## APPROACH

This section presents an overview of (1) the standard method for calculating exposures and risks for contaminated soils and sediments, (2) the common approach for deriving the concentration term to be used in the calculation, and (3) the approach followed to develop and field test passive samplers.

### Exposure and Risk Calculation

The equations used to calculate health risk follows the standard EPA guidance [4]:

$$I_i = \frac{C_i \times IR \times ET \times EF \times ED}{BW \times AT} \quad (\text{Eq. 1})$$

where:

- $I_i$  = intake of contaminant  $i$ , in mg/kg per day (mg/kg-d).
- $C_i$  = concentration of contaminant  $i$ , e.g., mg/kg soil or sediment
- IR = intake rate, e.g., incidental ingestion of 50 mg contaminated soil/sediment per day (mg/d)
- ET = exposure time, e.g., events/day (for chronic incidental ingestion, ET is included with IR)
- EF = exposure frequency, e.g., 350 d/year (d/yr) for a resident
- ED = exposure duration, e.g., 30 yr for chronic (residential) exposure
- BW = body weight (kilograms, kg), e.g., 70 kg for an adult
- AT = averaging time (d): 10,950 d for noncancer effects; 25,550 d for lifetime cancer risk

(A conversion factor may also be needed to adjust mass units, depending on how the concentration measure is reported.)

To assess potential health effects from exposure, the intake calculated using site-specific inputs is then combined with a toxicity value specific to that chemical, route, and duration of exposure. Two types of toxicity values exist: one to address the cancer endpoint (probability of incurring cancer over a lifetime), and the other to address the potential for a noncancer effect (from continuous daily exposures over a lifetime). For contaminants that cause both types of effects, both calculations are conducted using the respective toxicity values.

The EPA has established standard toxicity values to quantify potential health effects from the estimated environmental exposures. These reference values are available online in the Integrated Risk Information System (IRIS) database [5]. Most of the IRIS values address chronic exposures (assumed to extend over a lifetime), but some exist for other durations. To assess whether an exposed individual might incur adverse noncancer effects from chronic daily exposures, the estimated intake is divided by the noncancer toxicity reference value. When the ratio exceeds 1, suggests further consideration. To assess the potential for a person to develop cancer over a lifetime from the estimated exposure, the intake is multiplied by the

unit risk factor The EPA target range for contaminated sites is  $10^{-4}$  to  $10^{-6}$ , and when the calculated risk exceeds  $10^{-4}$  further consideration is warranted.

### Concentration Term

The concentration term in the risk calculation (Eq. 1) is typically a modeled value. This value can be estimated from the distribution coefficient ( $K_d$ ) for a given chemical (including radioactive chemicals). The  $K_d$  represents the amount adsorbed to solid phase (soil/sediment) compared to the amount in interstitial or pore water at equilibrium. A high  $K_d$  indicates that the contaminant is tightly bound to the sediment and little is present in interstitial water. The  $K_d$  can be adjusted to account for the impact of organic material on adsorption, by multiplying the organic carbon partition coefficient ( $K_{oc}$ , representing the partitioning between organic carbon in soil/sediment and water at equilibrium) by the fraction of organic carbon ( $f_{oc}$ ). Thus, assuming equilibrium, contaminant partitioning can be modeled as follows.

$$K_d = \frac{C_{\text{solid phase}}}{C_{\text{pore water}}} = K_{oc} \times f_{oc} \quad (\text{Eq. 2})$$

Because pore water concentrations are not easily measured, values modeled from these equilibrium partitioning equations are commonly used to estimate exposure and risk for contaminated soils and sediments. However, the pore water concentration is usually much lower than what is estimated by these equilibrium models because of desorption-resistant phenomena. Therefore, risk estimates based on these inputs are often unrealistic. This limitation can be addressed by using appropriate site-specific measurements of contaminant concentrations in pore water instead of modeled values.

### In-Situ Passive Samplers

The development and novel application of field-deployable versions of DGT devices offers the potential for evaluating contaminant availability in soils and sediments using pore water concentrations, to support more realistic exposure and risk calculations and guide more practical cleanup decisions. These tools would also be valuable for assessing the performance of in-situ containment systems as part of integrated risk management. Because field-deployable profiling SPME sampling tools were not available commercially and had not been previously reported, extensive development studies were needed for this device.

An number of laboratory studies were conducted to develop and refine the passive samplers, to assure sensitive and reliable measurement of contaminant concentrations in interstitial water. Following this suite of studies, passive sampling tools were deployed at several field sites on the east and west coasts to assess contaminant availability in situ. The passive samplers were used to measure contaminant levels in interstitial waters at these locations, to provide a more appropriate metric for the concentration term used to calculate exposure and health risk.

## RESULTS

The laboratory studies demonstrated the ability to detect sub-ng/L concentrations of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) with cm resolution. Detection limits were inversely proportional to hydrophobicity, with high molecular weight PCBs detectable at approximately 10 picogram (pg)/L with 1 cm resolution. Reproducibility was found to be above 90% for all compounds for which equilibrium had been achieved. Equilibrium sorption was observed in less than 2 to 7 days for PAHs but was considerably longer for PCBs. High molecular weight PCBs required a sampling time of at least 30 days to achieve >90% of equilibrium concentrations.

The field data demonstrate the promise of the passive sampling approach for assessing the availability and ultimately risk to organisms exposed to the contaminated soils and sediments [6-8]. Interstitial water concentrations were found to correlate well with bioaccumulation in macroorganisms in intimate contact with the soils, and also in organisms at least one trophic level higher. Lipid-normalized bioconcentration factors were found to be well estimated by the octanol-water partition coefficients of the compounds. (The octanol-water partition coefficient,  $K_{ow}$ , represents the partitioning between octanol and water at equilibrium, with octanol serving as a surrogate for lipids or fat.) The lack of lipid-normalized biomagnification at higher trophic levels even for PCBs suggests that interstitial waters can be used to indicate an upper bound of availability at all trophic levels within the food chain pathway for risk assessments, although further studies are needed to confirm this behavior.

Studies with the DGT devices to measure available metal concentration profiles in soils and sediments were less clearly related to organism uptake. Mechanisms for metal uptake exist that are substantially more complicated than the partitioning into lipids observed for organic compounds. Nevertheless, measurement of interstitial water profiles of available metals provided valuable information on metal availability, at least to lower trophic levels – including species used for biomonitoring. At several field locations, the passive sampling measurement of interstitial water concentrations was compared directly to bioaccumulation in caged organisms.

## CONCLUSIONS

These data also hold considerable promise for human health risk assessments. In fact, realistic measures of contaminants in soil and sediment that are predictive of bioavailability represent a critical need for health risk assessments. Currently, screening assumptions and conservative default values are commonly used to estimate the exposure term. The result is that risk estimates could be an order of magnitude higher (or more) compared with when appropriate input concentrations are used – i.e., levels in interstitial water rather than bulk sediment data. The consequence is that literally millions of dollars could be wasted on unnecessary cleanup in areas where realistic estimates would indicate the risk is below target levels for action. This can be especially important for sites at which the food pathway is of concern to local communities, such as at the U.S. Department of Energy Hanford site, where foods of interest range from native plants to salmon and higher trophic levels.

The novel passive sampling tools and techniques have shown that pore water concentration is a better indicator of bioavailability for hydrophobic contaminants in soil and sediment compared with bulk concentrations, even for active benthic uptake or ingestion. The recent laboratory and field data indicate that these concentrations can be used to support risk assessments in several ways: (1) direct comparisons to chronic water toxicity values for a more realistic assessment of ecological risk; (2) estimates of bioaccumulation potential, by multiplying the pore water concentration by the bioconcentration factor; and (3) estimates of the fraction of contaminant bioavailable, as the ratio of the measured pore water concentration to that predicted by equilibrium partitioning theory.

In addition to defining pore water concentrations for more realistic estimates of ecological and human health risks, these newly available field tools and techniques data provide an equally valuable basis for assessing remedies. That is, the effect on pore water concentration can be included as a performance metric for evaluating the effectiveness of containment and other management strategies.

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