GRADIENT
TRENDS
Risk Science & Application

Winter 2019
Issue 74

Billion Dollar Dilemma

By Jessie Kneeland, Ph.D. and Manu Sharma, M.S., P.E.

Contaminated sediment megasites continue to pose serious challenges to investigate and remediate.

Despite some progress in addressing sediment sites in the last two decades, significant challenges remain. Twenty years ago in *Trends* Issue 15, Gradient assessed the state of the science and practice for characterizing and remediating sediment sites. Since then, the scientific understanding of potential human health and environmental risks has improved and some large rivers and urban waterways have been remediated. This article provides an update on our previous assessment, including some of the challenges that remain for large sediment cleanup sites and insights on what might be coming in addressing affected sediments.

New concerns about emerging contaminants and climate change impacts may trigger additional investigation at previously remediated sites.

A U.S. EPA report to Congress in 1997 characterized sediment quality in 65% of watersheds and identified 96 areas of potential concern (APCs). There are now over 1,000 sites on the Superfund National Priorities List and approximately 30% of these sites contain sediment contamination (U.S. EPA, 2017). Many of these sites are large and expensive "megasites" costing over $50 million – the largest sediment cleanups can cost well over a billion dollars to investigate and remediate (National Research Council, Committee on Sediment Dredging at Superfund Megasites, 2007).

During a recent three-year period (FY 2012-2014), 39 sediment remedies were finalized, of which 87% included dredging, excavation, or *in situ* containment of the sediments; many sites used a sediment cap to isolate contaminated sediments (U.S. EPA, 2017). The most common contaminants of concern addressed by recent remedial decisions were metals (77% of sites), polychlorinated biphenyls (PCBs; 44%), and polycyclic aromatic hydrocarbons (PAHs; 44%) (U.S. EPA,

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I N S I D E

Letter from the Editors

January 2019

Dear Colleague,

In this issue of *Trends*, we discuss sediments, providing readers with an update (since we last discussed this topic 20 years ago in *Trends* Issue 15) on the complexities of sediment remediation and source identification/allocation.

The first article discusses the substantial costs and complexities associated with remediating sediments, the evolution of remediation methods over the last few decades, and future sediment management challenges, especially in the face of climate change. The second article discusses how scientists use age-dating and weathering techniques to understand the history of chemicals in sediment and to identify and allocate the sources of sediment impacts. The third article discusses the identification of appropriate background chemical concentrations and the impact that this has on defining cleanup goals at sediment sites.

Gradient contributors to this issue include Manu Sharma, M.S., P.E.; Drs. Jessie Kneeland, Jeffrey Rominger, Caroline Tuit, and Tim Verslycke; and Julie Lemay, M.P.H. Instead of a guest author, we decided to write the editorial ourselves with Kurt as author. It introduces ways to improve the evaluation of cleanup costs for complex sediment sites.

We hope that this issue of *Trends* provides you with insights on this topic.

Yours truly,

Kurt Herman, M.Eng., P.G. and Chris Long, Sc.D., DABT
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Billion Dollar Dilemma

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2017). While still a target of remediation at 23% of recent sites, pesticides are somewhat less of a concern than they were 20 years ago. Based on their environmental persistence and long history of widespread use, we can expect that legacy contaminants will continue to be important concerns at sediment sites even as emerging contaminants (*e.g.*, flame retardants) are subjected to new regulatory and media focus.

Sediment sites can be particularly challenging to investigate and remediate for several reasons. Flowing water can transport and mix contaminated sediments from multiple sources, particularly during storm events. Sediment environments vary widely in the type of habitat they represent and uniform screening levels are not available. As a result, expensive site-specific studies are often needed to characterize risks and develop appropriate remedial goals. Some sediment sites (*e.g.*, marshes) feature thick vegetation and inundated areas that complicate site investigation and remediation. Other sites are active harbors and waterways that pose other complications. The U.S. EPA acknowledges these challenges, particularly at large "Tier 1" and "Tier 2" sediment sites, relying on the National Remedy Review Board and Contaminated Sediments Technical Advisory Group for oversight and consistency.

Looking ahead, large contaminated megasites will continue to demand attention. With the increase in phased remediation and the significant remedial costs, the U.S. EPA seems to be considering a more pragmatic approach at some megasites. For example, at Portland Harbor, the U.S. EPA recently proposed new cleanup levels for PAHs based on a reconsideration of toxicity criteria, resulting in a somewhat smaller remedy footprint. Given the scale and complexity of large sediment sites, a recent trend in Superfund remedial approaches is to favor adaptive remediation, including early action to control contamination hotspots. Site-specific studies and phased remediation can help manage the most significant risks and result in overall cost savings, but can also prolong the cleanup process.

Climate change is expected to cause new concerns at many sediment sites. The Associated Press (Dearen *et al.*, 2017) recently identified 327 Superfund sites prone to flooding or likely to be impacted by sea level rise resulting from climate change (see figure). New concerns about emerging contaminants and climate change impacts may trigger additional investigation at previously remediated sites. Though much work remains to be done to control risks at contaminated megasites, we expect that adaptive management will be favored by both the U.S. EPA and industry going forward, as a way to effectively control the most pressing risks while also controlling costs and accelerating the cleanup pace.

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Dearen, J., M. Biesecker, A. Kastanis. 2017. AP finds climate change risk for 327 toxic Superfund sites. December.

National Research Council. Committee on Sediment Dredging at Superfund Megasites. 2007. Sediment Dredging at Superfund Megasites: Assessing the Effectiveness. National Academy Press. 236p.

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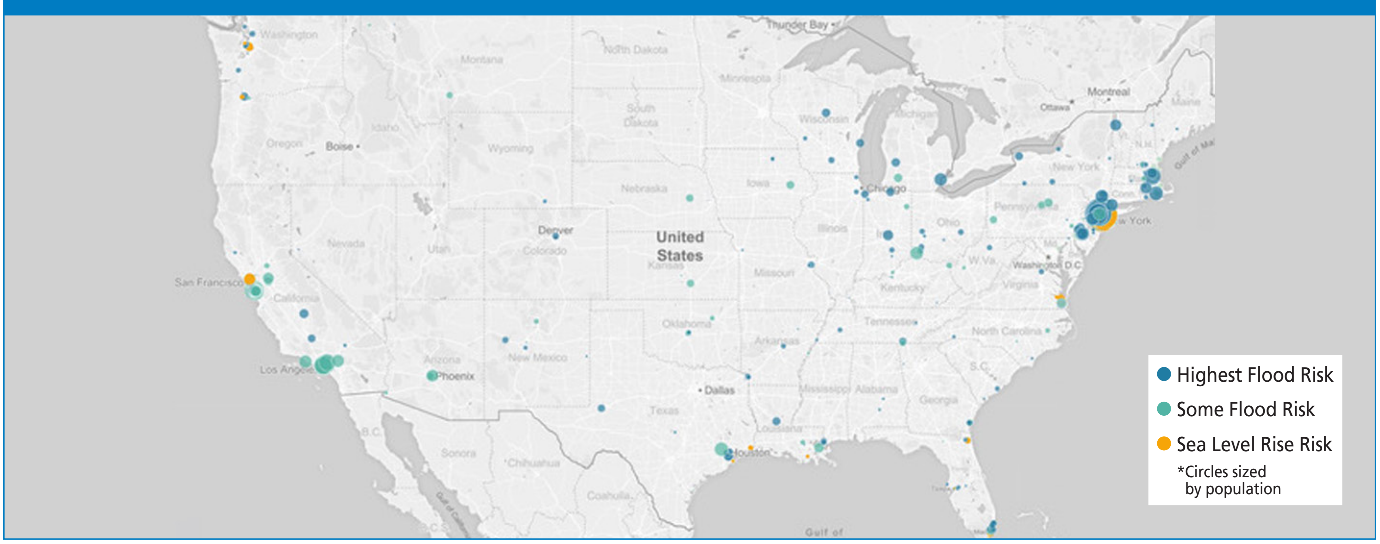
Superfund Sites at Risk for Flooding As a Result of Climate Change



Patterns in the Mud

By Jeffrey Rominger, Ph.D. and Caroline Tuit, Ph.D.

Both the sediment age and the effects of weathering processes should be considered when performing source identification and allocation at sediment sites.

Time is a critical factor in evaluating the source and distribution of chemicals in sediment systems. It is important to be aware of the critical ways that the passage of time can alter chemical compositions and distributions. As sediments are deposited in waterways, the history of chemical releases are recorded in the sediment column. The simultaneous exposure to weathering processes in the environment can also alter the chemical fingerprints. Researchers seeking to identify sources of chemicals should carefully consider both the history of chemical releases and how those chemical fingerprints may have been altered, as well as the numerous confounding factors that may affect both interpretation and usage of both age-dating and weathering information.

Paradoxically, weathering processes can both decrease and increase chemical concentrations in the sediment.

Sediment age-dating techniques allow scientists to read the history of chemicals in the sediment and compare it to known historical operations and releases. Often, this information can be crucial in source identification and allocation. For example, if sediment age-dating shows that contaminated sediments were deposited prior to a company's operations, they are unlikely to be responsible for contamination of that sediment even if they handled similar chemicals. The most widely accepted sediment age-dating techniques rely on the presence of two radioactive chemical isotopes present in the atmosphere: Pb-210 and Cs-137. While used in slightly different ways, both of these tracer chemicals allow researchers to assign historical dates to different sediment depths. For example, a sediment depth of 20 cm below the sediment surface may be associated with a specific year, meaning that sediments found deeper than 20 cm at this location were deposited prior to that year. Identification of these time horizons can provide significant insight into contamination history of a site. However, these age-dating techniques are often inadequate in areas with significant sediment mixing, dredging, bioturbation, or sediment resuspension, all of which can obscure the historical record in the sediment cores and render age-dating unreliable.

As chemicals in sediments are exposed to the environment, a wide range of weathering processes (such as evaporation, water washing, photolysis, and aerobic and anaerobic biodegradation) can alter the concentrations and chemical fingerprints over time. Importantly, chemical fingerprints that have undergone weathering may no longer match the original source fingerprints. In some cases, these weathered chemical fingerprints could be mistaken for other sources. Unlike age-dating techniques, which can rely on the constant decay rate of the indicator chemical isotopes, sediment-weathering rates can vary significantly with time and thus are not proxies for age. Weathering is generally

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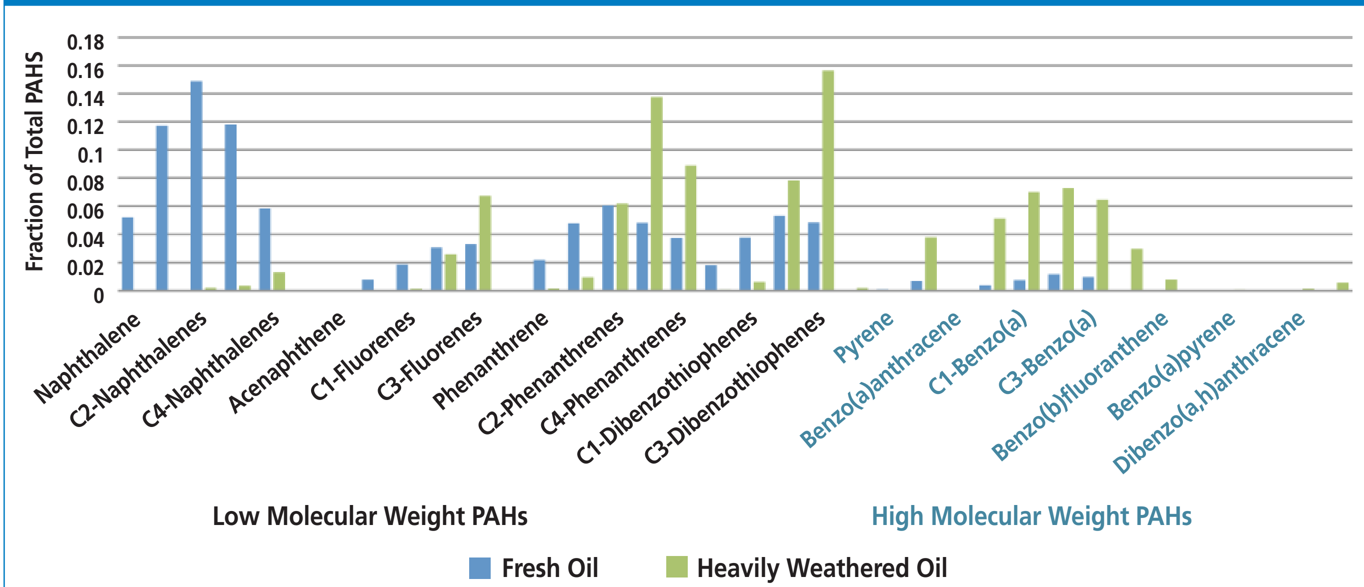
How Weathering Processes Affect The PAH Fingerprint of Crude Oil



Source: Burns *et al.*, 1997 (98-5378).

Is Urban Background an Urban Myth?

By Julie Lemay, M.P.H. and Tim Verslycke, Ph.D.

Sediment site cleanup goals should address where and how background data will be collected and evaluated.

Identification of appropriate background concentrations can be a major challenge in the selection of protective, reasonable, and implementable cleanup goals at contaminated sediment sites. The U.S. EPA defines background as "[s]ubstances or locations that are not influenced by the releases from a site and are usually described as naturally occurring or anthropogenic…" (U.S. EPA, 2002). Naturally occurring background levels are ambient concentrations of substances present in the environment that have not been influenced by human activities. Arsenic is an example, occurring naturally in the environment, frequently above risk-based concentrations. Anthropogenic background levels are concentrations of substances that are present in the environment as a result of human activity, unrelated to site sources. Polycyclic aromatic hydrocarbons (PAHs) are an example of ubiquitous urban chemicals that may be present from natural (*e.g.*, forest fires, natural coal deposits) and anthropogenic (*e.g.*, motor vehicle exhaust, residential wood burning) sources.

> ***The U.S. EPA… does not typically set cleanup levels below background levels.***

The U.S. EPA recognizes that consideration of appropriate background levels is important and does not typically set cleanup levels below background levels (U.S. EPA, 1996). While several states have defined background soil concentrations within their contaminated site programs, such values are generally lacking for sediment. In 2008, NOAA published frequently used sediment background concentrations in their Screening Quick Reference Tables (SQuiRTs). However, these values are based on soil concentrations and they do not consider anthropogenic background. A number of national monitoring programs have produced sediment chemistry data (*e.g.*, the U.S. EPA's Environmental Monitoring and Assessment Program [EMAP] and National Aquatic Resource Surveys [NARS]), but not with the objective of developing sediment background concentrations. As a result, site-specific sediment background sampling is typically needed to support contaminated site investigation and remediation. The U.S. EPA has general guidance on determining background levels at contaminated sites, although soils and not sediments are the primary focus of this guidance. Several states have developed guidance specific to sediments, such as the Washington Department of Ecology (WA, 2017). These guidance documents provide information on selecting appropriate background sample locations (*e.g.*, outside of influence of site/upstream of site, in areas with similar habitat/sediment characteristics) and using appropriate statistical methods to derive site-specific or regional background sediment concentrations. However, in most cases, sampling data quality objectives and the methodology for interpreting collected background data are developed on a site-by-site basis. Often, there is inadequate discussion between the responsible party conducting the remedial investigation and the risk manager on the approach for incorporating background into remedial decision-making. This can result in disagreement over appropriate background locations and concentrations in the later stages of the remedial investigation or even during remedy selection.

To successfully address background at a sediment site, early discussions between the responsible party and risk manager can result in a detailed plan for selecting appropriate background or reference areas. This should also include details on how background data will be evaluated (*e.g.*, statistical approach) and used to support the risk assessment decisions as well as the development of mutually acceptable cleanup goals.

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References:

U.S. EPA. 1996. Office of Solid Waste and Emergency Response. Soil Screening Guidance: User's Guide. EPA-540-R-96-018. July.

U.S. EPA. 2002. Office of Emergency and Remedial Response. Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites. EPA-540-R-01-003. September.

WA Dept. of Ecology. 2017. Sediment Cleanup User's Manual II (SCUM II). Guidance for Implementing the Cleanup Provisions of the Sediment Management Standards. Chapter 173-204 WAC. December.

Join Gradient for a live webinar on Sediments.

Details and registration information for this Sediments-themed 2019 webinar will be sent in a separate mailing.

What's New at Gradient

Awards and Announcements

Joel Cohen has been certified as a Diplomate of the American Board of Toxicology.

Julie Goodman received the Best Poster Award in the Environment, Health & Safety Poster Session at the Polyurethanes Technical Conference in October 2018.

Publications

Fantke, P., ..., **L. Rhomberg**, ..., T.E. McKone. 2018. Advancements in life cycle human exposure and toxicity characterization. *Environmental Health Perspectives*. doi:10.1289/EHP3871.

Handler, J.I., S.R. Gutierrez, **M.J. Mayo, M.C. Pollock.** 2018. INSIGHT: Geographic Information Systems for Environmental Litigation. *Bloomberg BNA*.

Upcoming Presentations

New Orleans, LA. February 11-14, 2019. Battelle 2019 Sediments Conference.

- **"Diagenetic Magnification of Persistent Organic Pollutants from Combined Sewage Overflow Sources."** C. Tuit, K. Herman.
- **"Incorporation of a Chemical Weathering Model in Sediment Source Apportionment Models."** J. Rominger, C. Tuit.
- **"Occurrence, Distribution, and Bioaccumulation of Per- and Polyfluoroalkyl Substances (PFAS) in Minnesotan Freshwater Environments."** J. Lemay, N. Slagowski, L. Kerper, M. Sharma.
- **"Quantitative Methods for Allocating Multiple Contaminant Types in Sediments."** K. Herman, C. Tuit, M. Sharma, J. Kneeland.
- **"Source Allocation of PCBs Derived from Quantile Analysis of Cumulative Response Curves Combined with Monte Carlo Analysis."** E. Butler, J. Rominger, R.J.-C. Remy.

Orlando, FL. February 11-14, 2019. Society for Protective Coatings Conference 2019.

- **"Warning! Technical Challenges of Compliance with the New Proposition 65 Regulations."** A. Lewis, K. Reid.

Baltimore, MD. March 10-14, 2019. Society of Toxicology 58th Annual Meeting.

- **"A Conceptual Model for Predicting How Acutely Toxic Exposure Levels Should Relate to Those Associated with Toxicity from Longer-Term Exposures, Suggesting Approaches to Using *in vitro* Data in Exposure-Duration Extrapolation."** L. Rhomberg.
- **"Comparison of Lung Cancer Risks from Environmental Exposures to Arsenic and from Those Associated with Medical Monitoring Criteria for Smokers."** K. Zu, L. Bailey, M. Seeley, B. Beck.
- **"Considerations for Grouping Different PFAS Together to Develop Guidance Values."** L. Kerper, M. Seeley, D. Pizzurro, H. Lynch, B. Beck.
- **"Critical Evaluation of Human Evidence for the Potential Reproductive and Developmental Toxicity of Nickel and Nickel Compounds."** R. Prueitt, L. Shi, K. Zu, J. Goodman.
- **"Evaluating the Impact on IQ of Short-Term Increases in Blood Lead Levels."** T. Bowers, X. Liu.
- **"Evaluation of the Carcinogenic Mode of Action and Proposal for an Occupational Exposure Limit for Tetrachloroethylene."** L. Bailey.
- **"Evaluation of the Mesotheliogenic Potential of Fibrous Talc Relative to Amphibole Asbestos in *in vitro* and *in vivo* Studies."** D. Dodge, M. Peterson.
- **"Looking Under the Hood – Expert Review of *in silico* Carcinogenicity Predictions."** J. Cohen, B. Hansen.
- **"Physiologically Based Pharmacokinetic Modeling of the Impact of Intermittent Oral Exposures to Lead on Blood Lead Levels and Associated Health Risks."** J. Cohen, R. Mattuck, B. Beck.
- **"Risk Assessment to Determine Proposition 65 Compliance for a Consumer Product: Diisononyl Phthalate."** S. Pacheco Shubin, I. Mohar, T. Lewandowski.

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Editorial: Cost Considerations at Sediment Sites

By Kurt Herman, M.Eng., P.G.

Complex sediment sites may benefit from a new paradigm for evaluating costs.

As discussed in the first article, the costs associated with characterizing and remediating complex sediment sites can be staggering. Yet, in addition to the potential environmental improvements associated with sediment cleanup, remediating blighted waterbodies can become the cornerstone of urban revitalization efforts that provide significant societal and economic benefit. With such high costs in play, and the potential for significant benefit, it begs the question: how are costs evaluated in the context of sediment site remediation, and is there room for improvement?

Other U.S. EPA programs, such as the Clean Air Act, rely on cost-benefit analysis…

Currently, many of the most complex sediment sites are managed under the federal U.S. EPA Superfund program. Under the Superfund program, the U.S. EPA estimates both the capital and long-term operations and maintenance costs for different remedy alternatives. It then selects a remedy alternative, in part, based on an evaluation of cost-effectiveness; that is, evaluating whether the costs are proportional to the "overall effectiveness" of the remedy alternative (U.S. EPA, 1996). Overall effectiveness is defined on the basis of three criteria (long-term effectiveness; short-term effectiveness; and the degree of contaminant toxicity, mobility, or volume reduction), which is then compared to the cost of implementing and maintaining the remedy. The U.S. EPA also considers certain other criteria (*e.g.*, overall protection of human health and the environment) as part of its comparative analysis of remedy alternatives. In addition, the U.S. EPA provides the public and potentially responsible parties (PRPs; *i.e.*, those potentially footing the bill) the opportunity to comment on proposed remedies, including their costs. The U.S. EPA factors their comments into its final decision.

However, there are other cost-related considerations that are relevant and could be considered in making sediment remedy decisions:

Cost-benefit analysis: Other U.S. EPA programs, such as the Clean Air Act, rely on cost-benefit analysis, which requires that economic benefit outweigh cost. By explicitly performing a cost-benefit analysis on each remedy alternative, the U.S. EPA could ensure an optimal return on the significant resources invested for sediment cleanup.

Opportunity cost: The U.S. EPA could evaluate the opportunity cost associated with remedy alternatives and the timing of their implementation. This means that the loss of potential gain from other alternatives would be evaluated when one alternative is chosen, as well as the potential gain (or loss of potential gain) associated with the timing of an alternative. For example, should a high-cost, short-term remedy be implemented to trigger commercial/residential redevelopment with associated long-term economic gain?

Transactional cost: Sediment Superfund sites typically involve many PRPs, multiple regulatory agencies, and community groups. As the remedy is implemented, there are potentially significant transactional costs associated with determining how the site cleanup costs are allocated to the PRPs and ensuring that stakeholder input is adequately accommodated. Getting there often results in litigation or dispute resolution proceedings. The differential transaction costs associated with the alternatives could be considered by the U.S. EPA in its remedy decisions.

Nearly four decades after the U.S. EPA's Superfund program began, there are clear benefits to society and the environment from cleaning up sediment sites. The question is whether it is now time to revisit the approach to evaluating cleanup costs, based on the lessons learned since that time.

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References:

U.S. EPA. 1996. Office of Solid Waste and Emergency Response. The Role of Cost in the Superfund Remedy Selection Process. EPA-540-F-96-018; PB96-963245. 8p. September.

By The Way…

The Mississippi River carries approximately 500 million tons of sediment into the Gulf of Mexico each year.

Source: https://earthobservatory.nasa.gov/images/1257/mississippi-river-sediment-plume.

What's New at Gradient

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- **"Strategies and Innovations for Addressing the Requirements of Proposition 65 and Other Consumer Product Regulations."** Exhibitor Hosted Session. T. Lewandowski, M. Peterson.
- **"Updating the Delaney Clause: Mode of Action Considerations for Carcinogens."** B. Beck.

Orlando, FL. March 31-April 4, 2019. American Chemical Society Spring 2019 National Meeting & Exposition.

- **"Understanding Background Conditions as a First Step in Developing Remediation Goals."** K. Radloff, T. Bowers.

Patterns in the Mud

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most intense during sediment transport and deposition and slows as sediments are buried. An example of how weathering processes alter the chemical fingerprints of oil is the loss of low molecular weight PAHs and the concomitant relative increase in high molecular weight PAHs in sediment chemical fingerprints (see figure).

Paradoxically, weathering processes can both decrease and increase chemical concentrations in the sediment. Weathering of a chemical involves its degradation, destruction, or removal. These processes will decrease the absolute chemical mass in the sediment, but if the original sediment source is rich in readily degradable (labile) carbon, such as fecal material from combined sewage overflows or fish farms, the rapid removal of the readily biodegradable material can simultaneously increase the relative concentrations of persistent chemicals in the sediment. This process is called "diagenetic magnification," and can lead to a twofold to fivefold increase in chemical concentration in surface sediments when compared to suspended particulates. Diagenetic magnification can allow even relatively low concentration chemical sources to result in sediment concentrations above risk levels and cleanup goals.

Ultimately, the dynamic nature of sediments requires that the effects of sediment age and chemical weathering, as well as the potential for diagenetic magnification, be incorporated into source identification and allocation at sediment sites.

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