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Accelerated Implementation of Harbor Processes Research

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14. ABSTRACT

Estuarine and marine sediment investigations should employ oceanographic sampling strategies to provide information that is ecologically relevant and useful in understanding the significance of contaminants on Navy property relative to the rest of the industrialized watershed. Though it is expedient to rely on intensive one-time samplings and analytical chemistry, this strategy is expensive given the amount of interpretation and support the RPM typically receives. Current state of toxicology and environmental forensics does not allow the RPM to develop a strong case regardless of the actual facts. However, it is currently possible to compare the amount of contaminants in Navy sediments to those in the rest of the industrialized watershed, including those suspended in the overlying water column. It is also possible to develop lines of evidence to support intrinsic bioremediation and measure turnover rate of contaminants in sediment. Combining measures of transport and biodegradation with seasonal and watershed-level sampling approaches can provide an ecological understanding of error, source, and ecological relevance of site contaminants.

15. SUBJECT TERMS

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I. EXECUTIVE SUMMARY

Estuarine, aquatic and marine sediment investigations should employ oceanographic sampling strategies and methods if they are to provide information that is ecologically relevant and useful in understanding the significance of contaminants on Navy property relative to the rest of the industrialized watershed. Though it is currently expedient to rely on intensive one-time samplings and analytical chemistry, this strategy is expensive given the amount of interpretation and support the Remedial Program Manager (RPM) typically receives and is often open ended. The onus is on the RPM to either prove that Navy operations did not result in environmental impact or that the contaminant concentrations are ecologically irrelevant. The current state of toxicology and environmental forensics does not allow the RPM to develop a strong case regardless of the actual facts. However, it is currently possible to compare the amount of contaminants in Navy sediments to those in the rest of the industrialized watershed, including those suspended in the overlying water column. It is also possible to develop lines of evidence to support intrinsic bioremediation and to measure the turnover rate of these contaminants in the sediment. Combining measures of transport and biodegradation with a seasonal and watershed-level sampling approach can provide the RPM with an ecological understanding of the error, source, and ecological relevance of the contaminants on Navy sites. Once this information is published in peer-reviewed journals, the RPM will likely be in a very advantageous position given the paucity and lack of site specificity of the published data available for a counter argument. The application of specific methods will be presented in context of the Chief of Naval Operations (CNO) policy on sediment site investigation and response action (5090 Ser N453E/2U589601).

II. BACKGROUND

Remedial Investigations (RIs) of Navy estuarine sediment typically involve sampling strategies based on those used at shore side groundwater sites and on the paradigms derived from those investigations. The most damaging to the Navy, and the least scientifically based, are those that relate sediment contaminants to historic shore side releases into waterways without some measure of contaminant transport. In addition to these problems, there is dearth of microbiological methods for collecting lines of evidence for intrinsic bioremediation despite the near universal acceptance of the ecological importance of such processes. Current evaluations of biological processes rely almost entirely on geochemical and analytical chemical inference of such rates, despite large variance in the intended time scales of geochemical measurements (months, years, decades) verses those known to change on microbiological time scales (minutes, hours). These critical methodological shortfalls result in Navy RPMs having to abandon any scientifically defensible attempt to estimate rates of intrinsic bioremediation. As a result, it is nearly impossible to scientifically validate any conceptual model involving the transport of organic contaminants to a Navy site and their subsequent biodegradation by intrinsic bacteria. This would not be such a significant issue if it were technically and fiscally expedient to track the flux or determine a mass balance for a contaminant through Navy sediments.

Various methods for establishing these lines of evidence are being developed through Office of Naval Research (ONR) supported programs and are currently used at Navy field sites.

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Normally, these lines of evidence would be considered too research-based for inclusion in site evaluations. Considering the lack of counter evidence supplied by the regulators and stakeholders and the large stakes involved in the Remedial Investigations (RIs), bioprocess and transport information may provide the most responsible and scientifically defensible use of taxpayer money. These lines of evidence will be presented as part of an oceanographic sampling strategy to directly compare contaminant biodegradation rates across a watershed. Stations were selected on the basis of both Rapid Sediment Characterization projects (SPAWAR Systems Center; SSC) and data from seven previous cruises in the lower Chesapeake Bay and its tributaries (Naval Research Laboratory; NRL). Taken alone, a single line of evidence is as uninterpretable as ambient contaminant concentrations in the sediment, thus, we present a strategy for coupling the evidence of biodegradation with estimates of contaminant transport and measurement of watershed contaminants outside of the Navy area of concern (background or reference locations). Historical adversity to measuring contaminant concentration at more than a few reference sites outside of the Navy fence line has diminished our understanding of watershed background levels and sources. The strategy presented here ignores traditional boundaries in RI sample collection and thus provides a more ecologically relevant understanding of Navy sediments in the context of industrialized watersheds.

At many submerged, tidally-influenced Navy sites, the primary evidence linking Navy operations to the contaminant levels are anecdotal reports of historical releases and lists of contaminants collocated in the adjacent shore side facility. The traditional strategies have also over relied on single, intensive sampling events, while ignoring processes that cause seasonal changes in ambient contaminant concentration. Understanding the magnitude of seasonal change alone can render comparison with Environmental Risk Low (ERL) values irrelevant. Although this document is not intended to encompass all methods for measuring and interpreting organic contaminant sources to sediments, bioprocesses must be put in context of other transport and transformation rates, as well as, a sampling strategy to be useful to the RPM. Brief descriptions of the specific methods used in this study will be presented and put in context of the oceanographic sampling strategy, as well as, suggestions on where these methods may apply to CNO policy.

III. METHODS

- PCA analyses of compound ratios (Point of Contact (POC): J. Leather, SSC)

One method for identifying or ruling out potential sources of organic contaminants to sediments involves analytical chemical measurement followed by Principle Component Analyses (PCA) of the ratios of individual compounds within the mixture. Much of the Naval Engineering Facilities Command (NAVFAC) Y0817 supported work focuses on polycyclic aromatic hydrocarbons (PAHs) but this method can also apply to polychlorinated biphenyls (PCBs). Various sources of organic contaminants have distinct ratios of certain compounds and these ratios can be maintained with deposition into sediment. The strategy may be most effective for comparing sediments with elevated PAH levels and similar organic matter composition. An advantage of this analysis is that it can be performed on data that has already been collected as part of a typical Navy RI.

- Compound specific stable isotope fingerprinting (POC: R. Coffin, T. Boyd, NRL)

An additional strategy for contaminant source identification among mixtures of organic compounds involves compound specific stable isotope fingerprinting. This method has been recently developed for PAHs and trinitrotoluene (TNT) in sediments under Y0817 and ONR programs (Coffin et al. 2001). In addition to measuring the ambient concentration of individual compounds, the ratio of $^{13}C::^{12}C$ for each compound is determined. These ratios can be specific to isolation or synthesis methods or geographic origins of the source material and they are often preserved despite biological, chemical or physical processes acting on the compounds once released into the environment. This analysis is more expensive than standard concentration measurements for sediment but it can provide much higher resolution than other more equivocal source determinations. It is also less sensitive to differences in organic matter concentrations that can change extraction efficiency between samples.

- Rapid Characterization of PAHs and PCBs (POC: J. Leather, SSC)

Several of the lines of evidence of intrinsic bioremediation involve relatively large sample volume and need to be performed on sediment over a large range of PAH or PCB concentrations. With standard analytical chemical analysis, the ambient contaminant concentration would not be known to the investigator for several weeks after the sampling event. Rapid characterization techniques were used to estimate PAH and PCB concentration during the initial survey and then, the following day, selected stations were resampled for the more detailed genetic and biochemical analyses. The rapid characterization immunoassays can be performed in less than 24 h which allows it to be used in conjunction with a two-day watershed sampling event.

- Watershed sampling strategy (POC: M. Montgomery, NRL)

Navy sediment RIs typically involve a sampling strategy based on that used for investigation of shore side groundwater sites. Almost all of the samples are taken within the Navy boundary along with one of two reference or background samples from outside the Navy area of concern. In addition, economic concerns often lead to a reduction in the total number of samples and sampling events. The complexities of the aquatic ecosystems and especially the importance of contaminant transport render the current strategy inadequate in providing a scientifically-defensible understanding of the Navy's role in sediment contamination. Since 1997, NRL has used a strategy for selecting stations and sampling events based on an oceanographic understanding of processes likely to play a role in the estuary. These considerations include hydrodynamic issues based on water flow and physical characteristics of the area surrounding the Navy sediment site; seasonal fluctuations in temperature and rainfall (e.g. tropical verses temperate); and, more even distribution of sampling stations across the watershed. This strategy was applied to the lower Chesapeake Bay, Charleston Harbor, San Francisco Bay, and the upper Delaware and Schuylkill Rivers near Philadelphia. More information is currently available on the Philadelphia study (Pohlman et al. 2002, Boyd et al. 1999).

- Seasonal sampling strategy for contaminant input and reference material (sediment traps, seston, nepheloid layer) (POC: M. Montgomery, NRL)

Typical Navy sediment RIs focus on an individual survey of sediment and/or surface water stations. If subsequent samplings show lower contaminant concentrations, it is assumed to be due to heterogeneity in the sediments. In contrast, oceanographic-based sampling strategies provide quantitative information on normal seasonal variation in contaminant input and biotransformation. The two primary features of this proposed strategy involve sampling the same watershed stations over several seasons and sampling organic contaminants bound to water column particles. Sampling the watershed several times annually allows one to assign ecologically-relevant error bars to the measured contaminant concentration at a site. The seasonal error is generally several orders of magnitude greater than the analytical error normally used for determining contaminant mass at a site. In addition, it can be important to measure the contaminants bound to particles in the water column (seston), moving over the sediment (nepheloid, or bottom boundary layer), or depositing onto the surface sediments (sediment traps). These parameters can be measured as part of the sediment survey and used to bound values for seasonal variation in the sediment contaminant concentrations. For instance, in several Navy relevant ecosystems, PAH concentrations in the sediment traps were 10-15 times higher (based on dry weight or total organic concentration) than in the surface sediments. The sediment trap material may provide a more site-specific and ecologically-relevant reference material than non-industrialized areas that are often chosen as reference sites. These measures can also be coupled with data on water flow to estimate contaminant transport through a specific area of the watershed. Further information on sampling and evaluating these media is available on the Anacostia River watershed (Coffin et al. 1999).

- Organotolerance of bacterial assemblage (POC: M. Montgomery, NRL)

Although semi-volatile organic contaminants (SVOCs) are often not a regulatory issue in estuarine sediments, they are often associated with higher molecular weight organics at their source (e.g. PAHs). These latter compounds can often impact the environment, so identifying the source of SVOCs to sediment may lead to identification of non-Navy PRPs that contribute the higher molecular weight organics to Navy sediments. Because of the episodic nature of industrial releases of SVOCs to surface waters and sediments, it is difficult to determine if areas of the ecosystem are being exposed to SVOC release from other PRPs. One strategy is to employ a radiotracer assay that measures the response of the bacterial assemblage to SVOC exposure. As sedimentary bacteria are repeatedly exposed to SVOCs, many of them become organotolerant. The degree of organotolerance can be directly measured by exposing subsamples of the natural assemblage to increasing amounts of a SVOC (e.g. naphthalene). The bacterial growth rate in chronically exposed sediments was not affected by naphthalene whereas that from more pristine sediment was dramatically affected. More information on this assay and its application to sediments at Charleston Harbor, San Diego Bay, and the Philadelphia area is available as a technical report (Montgomery et al. 2003).

- Lines of evidence of continued natural recovery (POC: L. Chrisey, ONR).
    i. Genetic analyses for PCB degradation (POC: K. Sowers, Univ. MD; H. May, Medical Univ. SC)
    ii. Genetic analyses for PAH degradation (POC: L. Kerkhof, L. Young, Rutgers Univ.)
    iii. Presence of metabolic intermediates (POC: J. Suflita, Oklahoma Univ.; L. Young, Rutgers Univ.)
    iv. Alternate electron acceptor availability (POC: D. Lovely, Univ. MA)
    v. Survey and depth profile of PAH mineralization (POC: M. Montgomery, T. Boyd, NRL)

Despite the widespread recognition of the importance of measuring intrinsic contaminant biodegradation rates, there are few methods currently used in Navy RIs. Just as with other components of the site investigation, no single method is likely to yield unequivocal results. The most compelling argument for evidence of intrinsic bioremediation will involve the convergent conclusions of several independent methods. Lines of evidence in this study fall into one of four categories: genetic capacity for biodegradation; presence of metabolic biodegradation intermediates; change in ambient contaminant concentration in response to electron acceptor availability; and, radiotracer contaminant (e.g. ^{14}C-PAHs) mineralization by the natural bacterial assemblage. Determining whether or not the natural bacterial assemblage has the capacity for metabolizing PAHs and PCBs can be determined by direct extraction of the sediment sample and genetic characterization. The advantage of this strategy is the assay measures the *in situ* community with little manipulation that changes the assemblage prior to evaluation. The disadvantage is that it provides no degradation rate estimate and the degrading bacteria may be present but not active. The second line of evidence involves quantifying the metabolic intermediates of contaminant degradation. The advantage is that the assay reflects *in situ* community activity, though the disadvantage is that an actual rate for degradation is not determined. The third measure looks to see how biodegradation rate changes in response to the addition of a limiting electron acceptor. The advantage is that parent compound biodegradation rates are directly measured and can be done aerobically or anaerobically, but the disadvantage is that the assay is performed *ex situ.* The final method measures intrinsic biodegradation rates using radiotracer additions of the contaminant (Montgomery & Osburn 2003, Montgomery et al. 2003). The advantage is that actual transformation and turnover rates are measured and can then be compared with transport rates. The disadvantage is that the assay is *ex situ* and the rates may be influenced by conditions that are changed during the 24 hour incubation. The best strategy for identifying sediment sites that are undergoing intrinsic bioremediation is to determine that the genetic capacity exists, find *in situ* evidence that metabolism is occurring (e.g. presence of intermediates), and then estimate the *in situ* rate via radiotracer additions. The estimated degradation rate or contaminant turnover time should then be compared with contaminant transport rates (e.g. sediment trap data) and ambient contaminant concentration to determine if the biodegradation rate is ecologically feasible.

IV. APPLICATION OF HARBOR PROCESSES' METHODS TO CNO POLICY

In February 2002, CNO release a policy of sediment site investigation and response action (5090 Ser N453E/2U589601) that may provide a framework for applying some or all of the methods and strategies described above. The policy statements are first summarized and then the specific statement to which the method may apply is listed (Table 1).

1) All sources shall be identified to determine if the Navy is solely responsible for the contamination.
2) All investigations shall primarily be linked to a specific Navy CERCLA/RCRA site.
3) All sediment investigations and response actions shall be consistent with Navy polices on risk assessment and background chemical levels.
4) Sediment cleanup goals shall be developed based on site specific information and shall be risk-based.
5) The Navy shall not clean up contamination from a non-Navy source where the Navy has not contributed to the risk in sediments. The Navy will not clean up a site before the source is contained. Any potential re-contamination by non-Navy sources shall be documented.
6) A monitoring plan with exit strategies shall be developed before collecting the first monitoring sample.

Table 1. CNO policy listed seven statements describing the types of information that should be gathered during a sediment site investigation.

Method	CNO Policy Statement					
	1	2	3	4	5	6
PCA Analyses	X	X			X	
Stable Isotopes Fingerprint	X	X			X	
Rapid Characterization		X			X	
Watershed Sampling			X			X
Seasonal Sampling & Source Input	X	X	X		X	X
Organotolerance		X				
Evidence for Intrinsic Bioremediation				X		X

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VI. DISCLOSURE

The opinions and assertions contained herein are not to be construed as official or reflecting the views of the US Navy or the Federal Government at large. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.