Integrated Forensics Approach to Fingerprint Sediment PCB Sources using RSC and ACF

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ESTCP

ABSTRACT – ESTCP Project ER0826

Determining the original source of contamination to a heterogeneous matrix such as sediments is a requirement for both Clean-up and Compliance programs within the military. Understanding the source of contaminants to sediment in industrial settings is a prerequisite to implementing any proposed sediment remedial options under Clean-up programs. This is due to the fact that the sources must be controlled prior to remedial efforts to ensure that recontamination can be avoided. An additional reason for source identification includes ensuring that costs of any remedial efforts can be fairly allocated among multiple principle responsible parties. In some instances, elevated levels of polychlorinated biphenyls (PCBs) in sediment have led to impairment designations requiring the development of total maximum daily loads (TMDLs) and subsequent waste load allocations under Compliance programs. Because of this, development of site-specific forensic investigations and TMDLs are closely linked. The need to develop these types of TMDLs also requires the development and use of a forensics approach to fingerprint contaminant sources so that potential load reductions can be allocated. Without a forensics study, the standard approach is to assume the most "visible" nearby facility is the source of contamination, which often turns out to be a military facility. The forensics technology to be demonstrated includes two primary components: 1) rapid sediment characterization (RSC) technologies that provide for wide spatial and temporal coverage to delineate sediment contaminant gradients and semi-quantitative characterization in a cost effective manner; and 2) advanced chemical fingerprinting (ACF) on a selected subset of samples to delineate sources. ACF includes both advanced laboratory congener analysis of samples, and the application of sophisticated data analysis and interpretation methods to fingerprint sources.

METHODS

Technology Components

To determine the source of sediment contamination, we link two components:

1) Rapid Sediment Characterization (RSC) to provide spatial and temporal coverage for cost effective concentration gradient mapping. For PCBs we will use immunoassay methods modified from EPA Method 4020; and

2) Advanced Chemical Fingerprinting (ACF) on selected subset of samples to delineate sources using advanced laboratory methods with sophisticated data analysis and interpretation methods. For PCBs we will use high resolution GC/MS including a combination of EPA Methods 680/1668a.

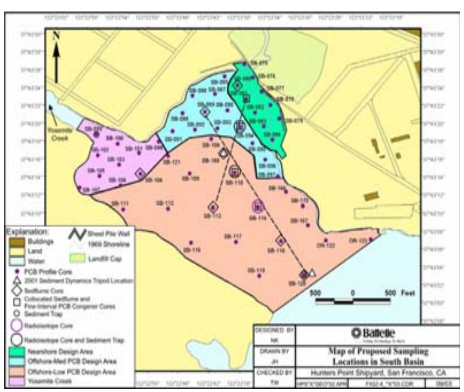
User-Friendly 6 Step Procedure

The forensics study can be divided into a six step process, entered at different points in the process depending on how much existing data are present at a site:

1) Site selection (Forensics not for every site, are multiple sources likely at site?)
2) Develop Conceptual Site Model (CSM) and forensic questions
3) Develop defensible sampling plan to answer forensic questions
4) Demonstrate RSC methods (Do concentration gradients suggest source locations?)
5) Demonstrate ACF methods (Do unique congener patterns differentiate sources?)
6) Presentation of results (Can forensics data be presented in understandable way?)

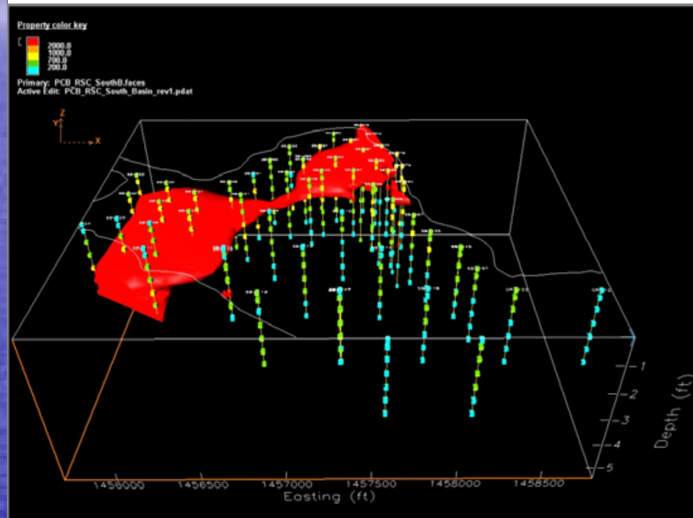
Steps 1-3: Select Site, Develop CSM and Sampling Plan

Select site and develop defensible sampling plan to answer forensic questions from CSM. RSC will collect higher density data near potential sources, less dense data farther out in basin for source apportionment. A subset of RSC samples are selected for ACF and source fingerprinting. Over 500 immunoassay (RSC) and 100 GC/MS (ACF) samples are identified in this sampling plan, plus additional samples for the regulatory project.



Step 4 – Demonstration of RSC

The RSC data are shown below in EarthVision software to delineate the 3-dimensional block diagram of the 2000 ppb PCB contour interval. Additional contours were drawn at 1000, 700, and 200 ppb to visualize other PCB contaminated sediment volumes and select representative samples for ACF. The map view shown in the Step 3 sampling plan can be seen on the top the this block which has been tilted at 45 degrees to show the seven depth horizons measured in each core (color indicates concentration). The 2000 ppb contour shows two large volumes of contaminated sediment, one to the west near the creek and the second to the northeast near the former landfill.



Step 5 – Demonstration of ACF

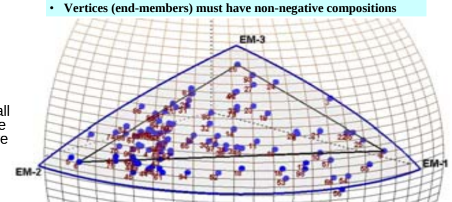
Multivariate Data Analysis and Visualization Methods are used to determine three parameters:

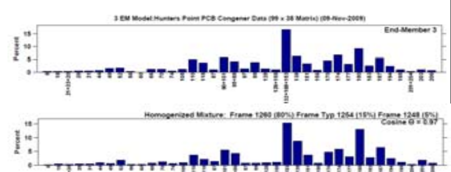
1) The number of sources (EM fingerprints) contributing to the system.
2) The chemical composition of each EM fingerprint.
3) The relative contribution of each EM fingerprint in each sample from the site.

Polytopic Vector Analysis (PVA) is shown here to resolve three end-member (EM) sources. Samples fall within the blue triangle and indicate they can be represented by positive linear mixtures of the end-member sources.

PVA provides an EM congener fingerprint that can be compared to Aroclor patterns from different sources. Here the proposed EM3 composition is compared to a mixture of Aroclor 1260/1254/1248 composition, with a "goodness of fit" metric (cosine theta) close to 1.0 indicating this mix of Aroclors represents the best fit for sources of this EM. Similar fitting of the other triangle corner compositions indicate EM1 best matches a pure Aroclor 1254 and EM2 best matches a pure Aroclor 1260.

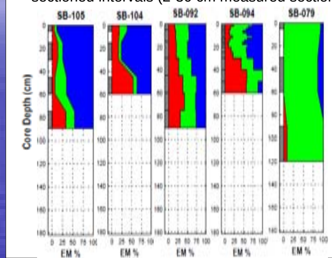
- **Principal Component Space used as Reference Space**
- **Iteratively resolves a simplex (a triangle in this case where there are 3 sources) that surrounds the data cloud.**
- **Samples are positive linear combinations of End-Member sources**
- **Vertices (end-members) must have non-negative compositions**

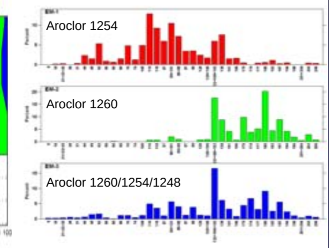


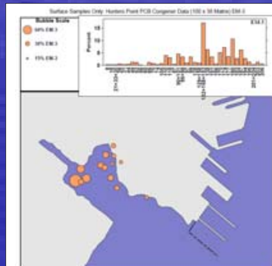


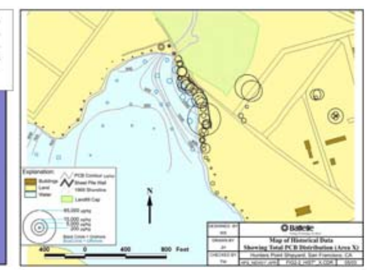
Step 6 – Preliminary Results

Preliminary Polytopic Vector Analysis (PVA) resolved three end-member sources (bottom right). The relative contribution of each end-member (EM%) is shown below for five cores in an east-west transect (see core locations on Step 3 map). East side core (SB79) shows mainly Aroclor 1260 (green EM2), west side core (SB105) shows mainly Aroclor 1260/1254/1248 mixture (blue EM3), and center cores show mix of all three sources with more Aroclor 1254 (red EM1) in older sections of the cores. The dated core SB-94 shows sharp compositional shift at 30cm (in about 1970), others smoothed due to larger sectioned intervals (2-30 cm measured sections shown in gray on left of each core).

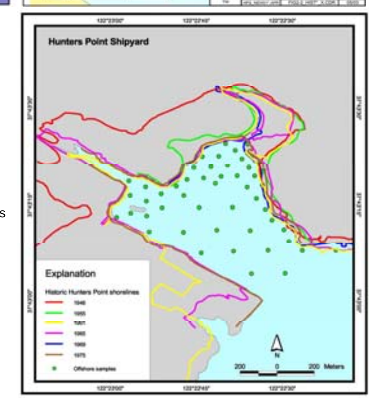








EM source locations are highly speculative, but forensics data can be compared with concentration gradients, sediment transport data, and additional upstream studies to provide evidence. Upper left bubble plot suggests higher EM3 proportions at the creek, and additional upstream studies suggest even higher proportions farther upstream. Upper right bubble plot suggests contaminated fill in front of former landfill is source for EM2 at least back to about 1970 when shoreline filled. Shoreline fill history at right shows how bay was filled from 1946 through1975 when the present shoreline was established. Old Combined Sewage Outfall (CSO) channel was filled in by landfill from 1955 to 1975, and the city reorganized all CSOs into creek area in the 1970s with larger storage capacity (the "Moat") to reduce sewage overflows. Before 1970, EM3 was less common and EM1 was more common which could indicate a link to reorganization of the CSOs. Or this greater EM1 could be associated with older fill that was covered by later fill events with material contaminated with more Aroclor 1260.



Preliminary Conclusions

Forensics studies to fingerprint PCB sources in sediments can be constructed following a simple six step process. It is important to develop a conceptual site model (CSM) to focus forensic questions on specific objectives so that a technically defensible sampling plan can be designed to obtain useful data. RSC data can provide the 3-dimensional spatial (and temporal if dated cores are used) coverage to delineate gradients and help select the ACF locations. The ACF data will determine the number of sources in the system, congener fingerprints of these sources, and relative contributions of these source fingerprints in each of the site samples. The forensic study can be accomplished in a cost-effective manner, especially if pre-existing data or concurrent sediment assessment studies are available to leverage into the study.