USE OF X-RAY FLUORESCENCE (XRF) AND IMMUNOASSAY RAPID SEDIMENT CHARACTERIZATION RESULTS FROM TWO SITES

John Hardin[1], Theresa Himmer[2], Greg Durell[3], and Heather Thurston[4]

ABSTRACT

Traditional sampling and analysis approaches for aquatic ecosystem environmental characterization studies operate within time periods of weeks and months. Rapid sediment characterization (RSC) methods have been developed to speed up site characterization processes by identifying the nature and extent of contamination and to reduce costs. These advanced screening methods can improve sampling in general by characterizing a large sampling area to reduce uncertainty at several steps in the assessment process.

At two sites, the Marine Corps Base in Quantico, Virginia, and Hunters Point Shipyard in San Francisco Bay, California, immunoassay and/or field portable X-ray fluorescence spectrometry (FPXRF) methods were used to augment laboratory measured concentrations of organic contaminates (polychlorinated biphenyls (PCBs) and pesticides) and metals. RSC data are being used to increase the resolution of sediment characterization for use in defining areas potentially requiring remediation. Combined with laboratory results defining or confirming the characterization of contaminates, RSC data were utilized with the goals of improving the resolution of contamination extent, providing cost savings, and defining potential remediation areas.

INTRODUCTION

The USEPA, DoD, Interstate Technology and Regulatory Council (ITRC), and other organizations are currently promoting the use of more effective strategies for characterizing, monitoring, and cleaning up hazardous waste sites, with particular emphasis on a triad approach to plan and implement data collection and decision making at field sites. The triad consists of:

- Systematic planning
- Dynamic work plans
- Real-time measurement technologies

The position of USEPA is that "the lower costs and real-time information value of field analysis permits much greater confidence in the representativeness of data sets due to greater sampling density and the ability to delineate a hot spot...in real time" (Crumbling et al, 2003; Crumbling 2001). The USEPA cites cases in which the use of real-time data collection resulted in projects being completed significantly under-budget. The review also noted that all schedules had been met, the defensibility and implementability of technical plans had been improved, client satisfaction increased, and relations and communications with regulatory agencies improved. Rapid screening methods have been so useful that field analysis now has a dedicated, peer-reviewed journal (*Field Analytical Chemistry and Technology)* as well as the recently formalized Field Activities Committee within the National Environmental Laboratory Accreditation Council (NELAC) (Crumbling, 2001). The April 2005 DoD Environmental Monitoring Data Quality Workshop included discussion of real-time, field-based measurements.

There are currently EPA approved methods, as well as ASTM guidelines, for the use of rapid characterization tools and techniques such as immunoassays for PCBs, PAHs, and selected pesticides, and FPXRF for selected metals. However, these methods were developed primarily for analysis of soil samples. These techniques have been refined by the U.S. Navy SPAWAR laboratory to achieve lower detection limits and greater accuracy for sediment samples. The lower detection limits are particularly important for sediment sites, where cleanup goals are generally lower than those at contaminated soil sites.

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[1] Principal Research Scientist, Battelle, 5205 Avenida Encinas, Suite J, Carlsbad, CA 92008, T: 760-476-1415, Fax: 760-476-1602, Email: hardinj@battelle.org

[2] Researcher, Battelle, 397 Washington St., Duxbury, MA 02332, T: 781-952-5398, Fax: 781-952-5332, Email: himmert@battelle.org

[3] Program Manager, Battelle, 397 Washington St., Duxbury, MA 02332, T: 781-952-5233, Fax: 781-952-5433, Email: durell@battelle.org

[4] Research Scientist, Battelle, 397 Washington St., Duxbury, MA 02332, T: 781-952-5394, Fax: 781-952-5334, Email: thurstonh@durell@battelle.org

In 2001, the Navy completed the project "Integrated Screening for Rapid Sediment Characterization," which was conducted under the Technology Demonstration and Validation Program (referred to as Y0817), with joint funding from the Environmental Security Technology Certification Program (ESTCP). Technology transfer is an important goal for both the Y0817 and ESTCP programs.

The Navy and Battelle have worked separately and together to disseminate the methods, strategy of use, and results of several RSC methods. Efforts have included comparative sample analysis, preparation of a user's guide, conference presentations, peer-reviewed publications, presentation at the Navy's Remediation Innovative Technology Seminars (RITS), and transition of SOPs to Navy contractors. The Navy and Battelle are working to streamline the process and train additional staff to improve RSC data collection and processing in the field to make real-time sampling decisions.

This work was funded by Naval Facilities Engineering Command Washington (Marine Corps Base, Quantico, VA) and Naval Facilities Engineering Command, Southwest (Hunters Point Naval Shipyard). The work was conducted by Battelle, the U.S. Navy Space and Naval Warfare Systems Command (SPAWAR) San Diego, CA; Neptune and Company, NM, and Applied Marine Sciences, TX. The two projects described in this paper focused on using RSC methods at offsite laboratories to increase the quantity of information gathered at a much reduced cost.

BRIEF SITE HISTORIES

MCB Quantico

MCB Quantico in Virginia is located approximately 35 miles south of Washington, D.C., and approximately 75 miles north of Richmond, Virginia. The Base is approximately 60,000 acres, and lies within southern Prince William, northern Stafford, and eastern Fauqier Counties in Virginia. The Base is bounded to the north by Cedar Run and Virginia State Route 646; to the east by the Potomac River, to the south by Tank Creek, Aquia Creek, and Virginia State Route 610; and to the west by Darrels Run and Virginia State Route 612. Three creeks drain portions of MCB Quantico into the Potomac River and are identified as Chopawamsic Creek, Quantico Creek, and Little Creek.

Chopawamsic Creek is one of several creeks on Base that flow into the Potomac River. The portion of the creek investigated in this study is characterized as a shallow, approximately 400-acre tidal, open water, riverine wetland (TtNUS, 2004). Along the northeast portion of the creek, a Former Rifle Range and a Former Skeet Range are located. Runoff from the Former Rifle Range drains to marshy wetlands adjacent to the Creek, and then to the creek itself. Activities at the Former Skeet Range resulted in lead shot falling directly into Chopawamsic Creek and an adjacent wetland. The creek and wetlands adjacent to these two areas were investigated within this study.

Abraham's Creek is a tributary to Chopawamsic Creek located near the confluence of Chopawamsic Creek and the Potomac River. Abraham's Creek drains forested Marine Corps exercise areas and parade grounds; barracks, classroom, and equipment storage buildings. Chopawamsic Creek study areas are shown in Figure 1. Abraham's Creek is partially influenced by tidal fluctuations in the northern section of the creek but a land bridge and beaver dam restrict tidal influence in the upstream portions of the creek. Historical evidence indicated sediments within the Creek contained elevated levels of some pesticides and PCBs (TtNUS 2004).

Battelle and Neptune and Company were contracted by the Navy to collect and analyze additional data from these creeks to fill in data gaps and provide enhanced characterization of the horizontal and vertical extent of potential sediment contamination. This characterization will guide formulation of a remedial footprint and volume estimation to compare potential remedial alternatives in the areas of interest.

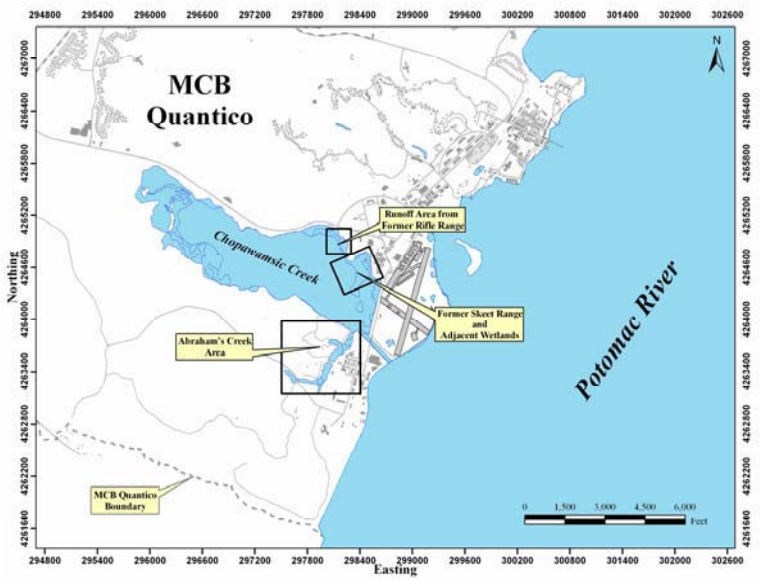

Figure 1. MCB Quantico Abraham's Creek and Chopawamsic Creek study areas.

Hunters Point

HPS is a former Navy installation located on a peninsula in the southeast section of San Francisco, CA (Figure 2). The peninsula is bounded on the north, east, and south by San Francisco Bay and on the west by the Bayview Hunters Point district. HPS comprises about 866 acres, with approximately 457 acres of offshore sediment (Parcel F). From 1945 to 1974, the Navy maintained and repaired ships at HPS. The facility was deactivated in 1974 and remained relatively unused until 1976, when it was leased to Triple A Machine Shop, a private ship repair company. In 1986, the Navy resumed occupancy of HPS. The facility was closed in 1991 under the Defense Base Realignment and Closure Act of 1990 (BRAC) and is in the process of conversion to non-military use.

Past site activities at HPS resulted in the release of chemicals to the environment, including offshore sediments. Various studies have been conducted since 1991 to evaluate shoreline and offshore contamination (ATT, 1991; PRC, 1994; PRC, 1996; TtEMI, 1997; TtEMI and LFR, 1998; TtEMI, 2003a and 2003b). The Parcel F Validation Study was conducted to more clearly define the areas of offshore sediment requiring evaluation in the Parcel F FS (Battelle et al., 2005). The Validation Study concluded that offshore sediments in South Basin (Areas IX-X) and Point Avisadero (Area III) pose potentially unacceptable ecological risks to upper trophic level receptors from ingestion of contaminated prey. The primary chemicals of concern for ecological receptors are PCBs in South Basin, and metals (copper and mercury) at Point Avisadero. The risk assessment results indicated that consumption of shellfish from the South Basin contained potential human health risk from PCBs. Additionally, debris, metal slag, and/or riprap along the shoreline in Area I (India Basin), Area III (Point Avisadero), Area VIII (Eastern Wetland Area), and Area X (South Basin) are of concern because they may act as future sources of contamination to offshore sediments. These shoreline areas are being addressed in conjunction with activities in the adjacent upland parcels (i.e., Parcels B and E).

Environmental restoration activities are being conducted in accordance with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) as amended by the Superfund Amendments and Reauthorization Act of 1986 (SARA).

Battelle, Blasland, Bouck & Lee, Inc. (BBL), and Neptune and Company were contracted by the Navy to collect and analyze additional data from Hunters Point to fill in data gaps and provide enhanced characterization of the horizontal and vertical extent of sediment contamination. This characterization will guide formulation of a remedial footprint and volume estimation for use in the Parcel F Feasibility Study.

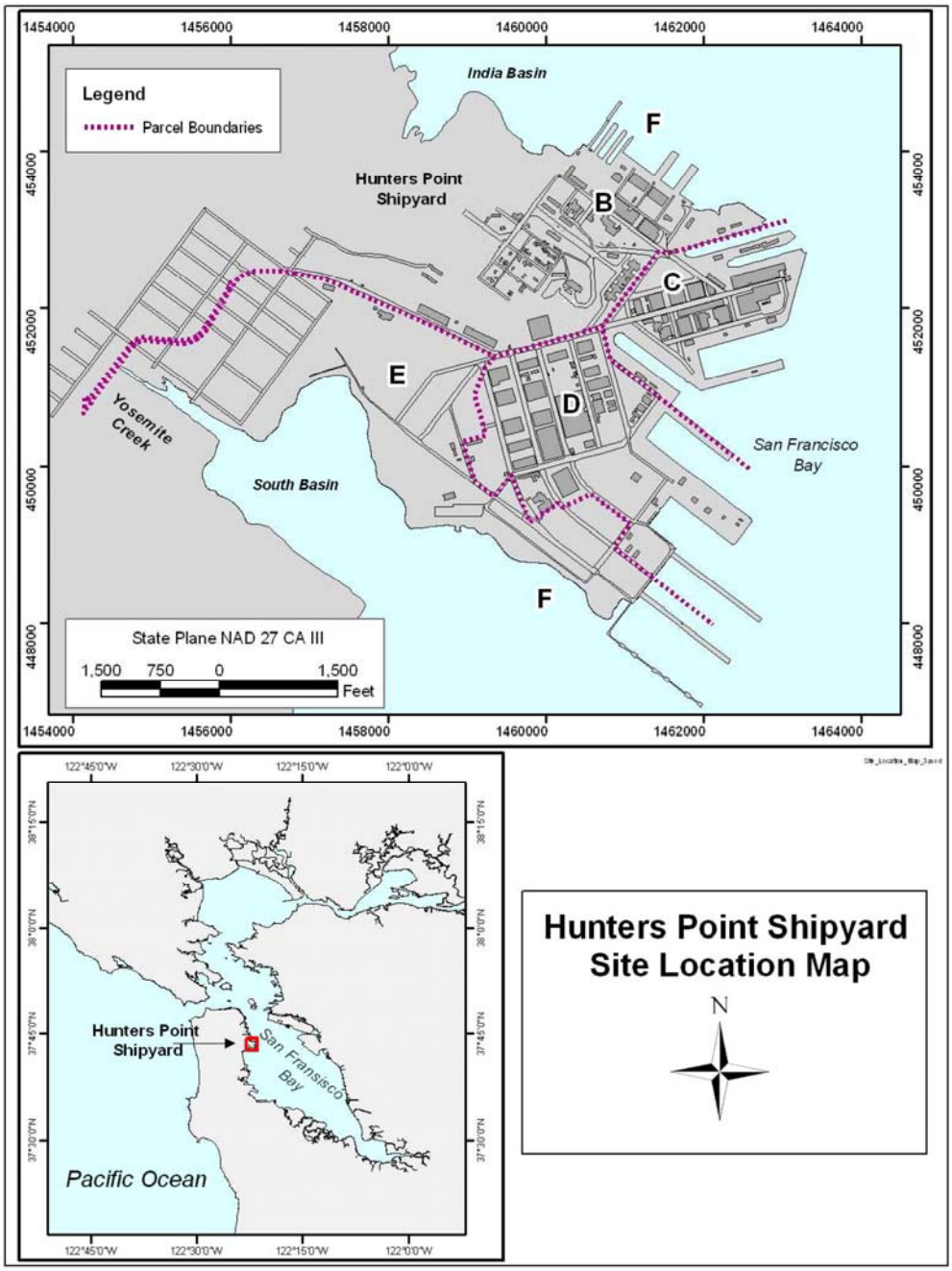

Figure 2. Hunters Point Shipyard site overview map.

PROJECT OBJECTIVES AND STUDY DESIGNS

Marine Corps Base (MCB) Quantico RSC Study Objectives

Two objectives of the Chopawamsic Creek Investigation at the MCB Quantico were approached with RSC methods: 1) collect sediments from Chopawamsic Creek and Abraham's Creek to define the extent of contamination both vertically and horizontally; and 2) evaluate possible remedial alternatives at the two sites. In each of these areas, a combination of RSC analysis and laboratory characterizations were conducted to spatially delineate the areas of elevated contamination. Polychlorinated biphenyls (PCB) and DDx compounds (including the pesticides DDD,

DDE, and DDT) were investigated within Abraham's Creek utilizing immunoassay methods. Lead (Pb) concentrations within Chopawamsic Creek sediments were delineated with the aid of FPXRF.

Quantico Study Design

The MCB Quantico data discussed here are limited to data collected from Chopawamsic Creek and Abraham's Creek as part of a larger study (Battelle and Neptune, 2005b). These data are being used to evaluate possible remedial alternatives at these sites. In these two areas, sediment sampling and characterization incorporating RSC methods were conducted to spatially delineate the areas of elevated DDx compounds and PCBs within Abraham's Creek or lead (Pb) concentrations within Chopawamsic Creek sediments.

To address these areas of potential remedial action, the following tasks were completed as part of the field sampling effort:

- Sediment cores were collected from 58 locations within Chopawamsic Creek area (Figures 3, 4 and 5). Samples from the top 6 inches from one foot sections of each core were analyzed for Pb analysis by FPXRF. Ten subsamples encompassing the data range intervals were analyzed by laboratory methods to confirm FPXRF data. In addition, a subset of the sediment samples were analyzed for grain size, TOC, Atterberg limits, and specific gravity based on the FPXRF results.
- Sediment cores were collected from 17 locations in Abraham's Creek (Figure 6). Samples from the top 6 inches of each foot of each core collected were analyzed for total DDx and total PCBs by immunoassay-based RSC methods. Based on immunoassay data, ten samples encompassing the range of results were analyzed by traditional laboratory methods for confirmation of DDx compounds and total PCBs. Subsamples of these intervals were also analyzed for grain size, total organic carbon [TOC], Atterberg limits, and specific gravity based on the immunoassay data.

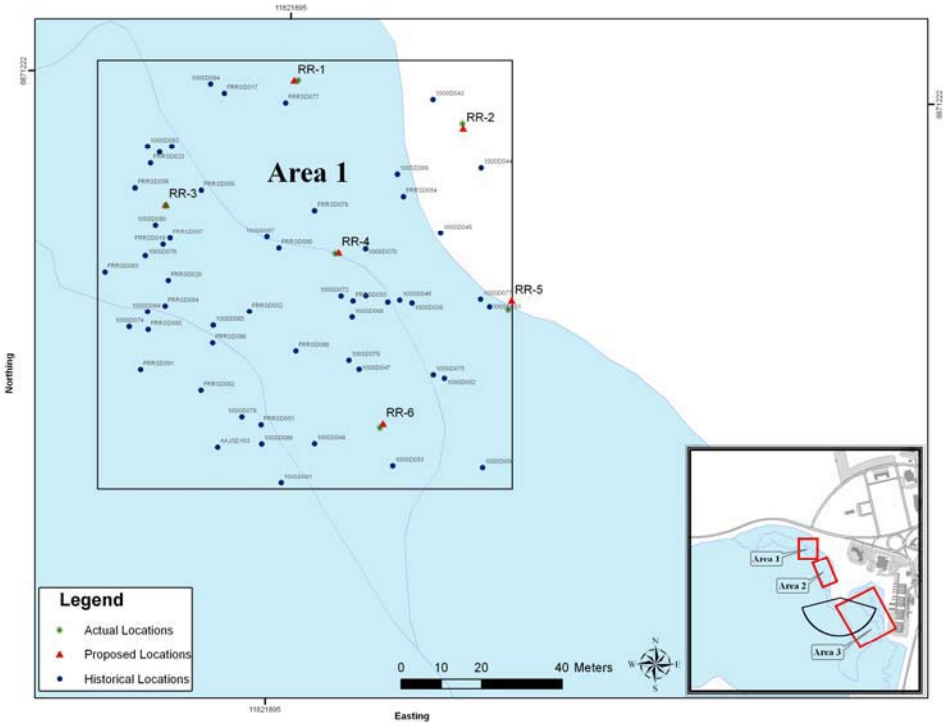

Figure 3. Chopawamsic Creek Area 1 sample locations.

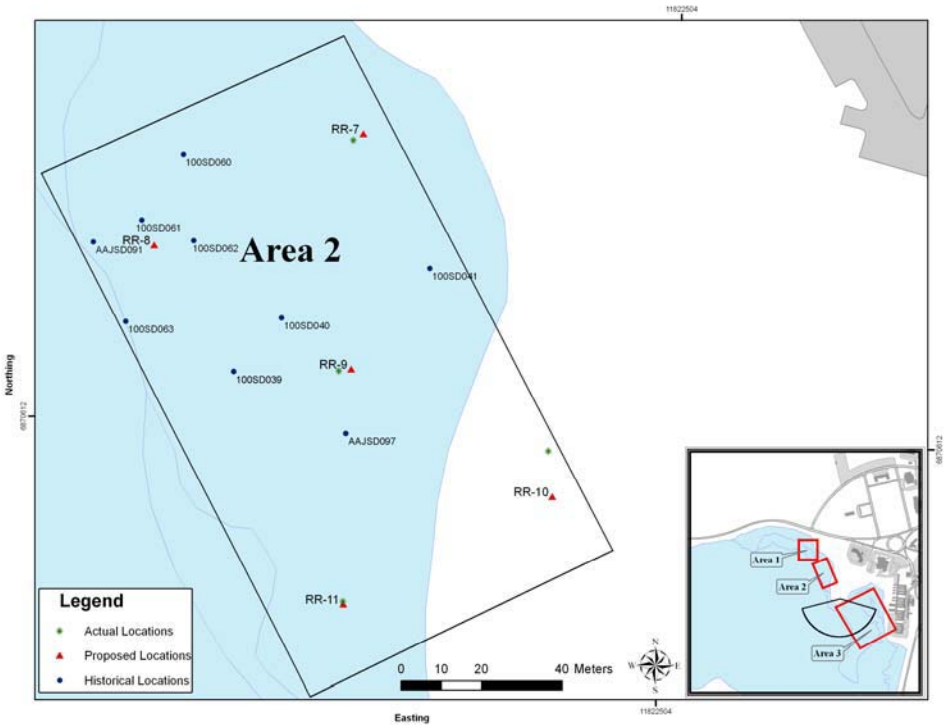

Figure 4. Chopawamsic Creek Area 2 sample locations.

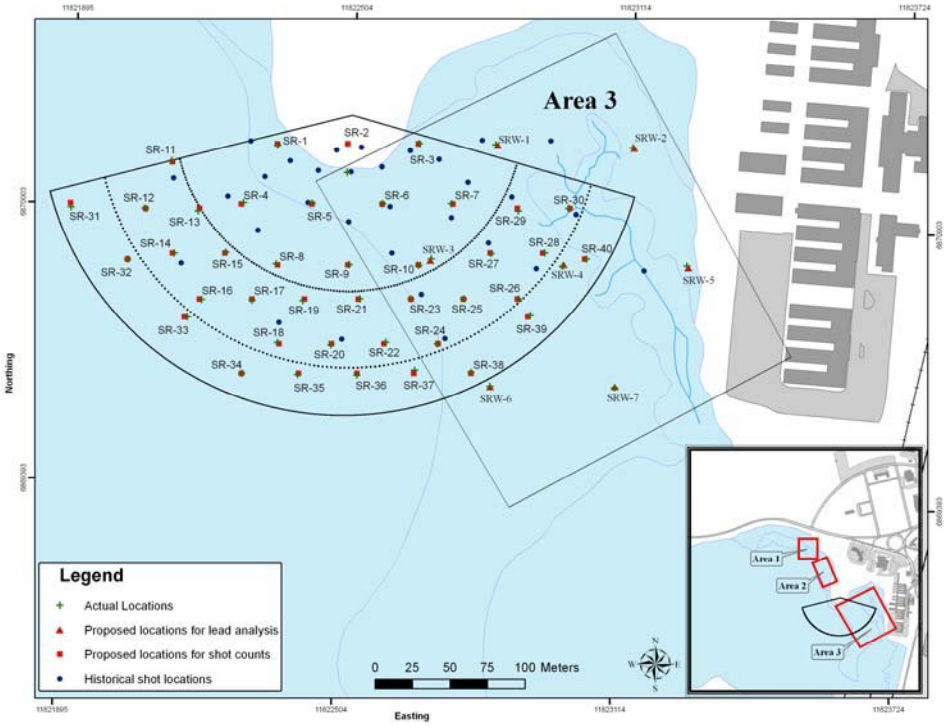

Figure 5. Chopawamsic Creek Area 3 sample locations.

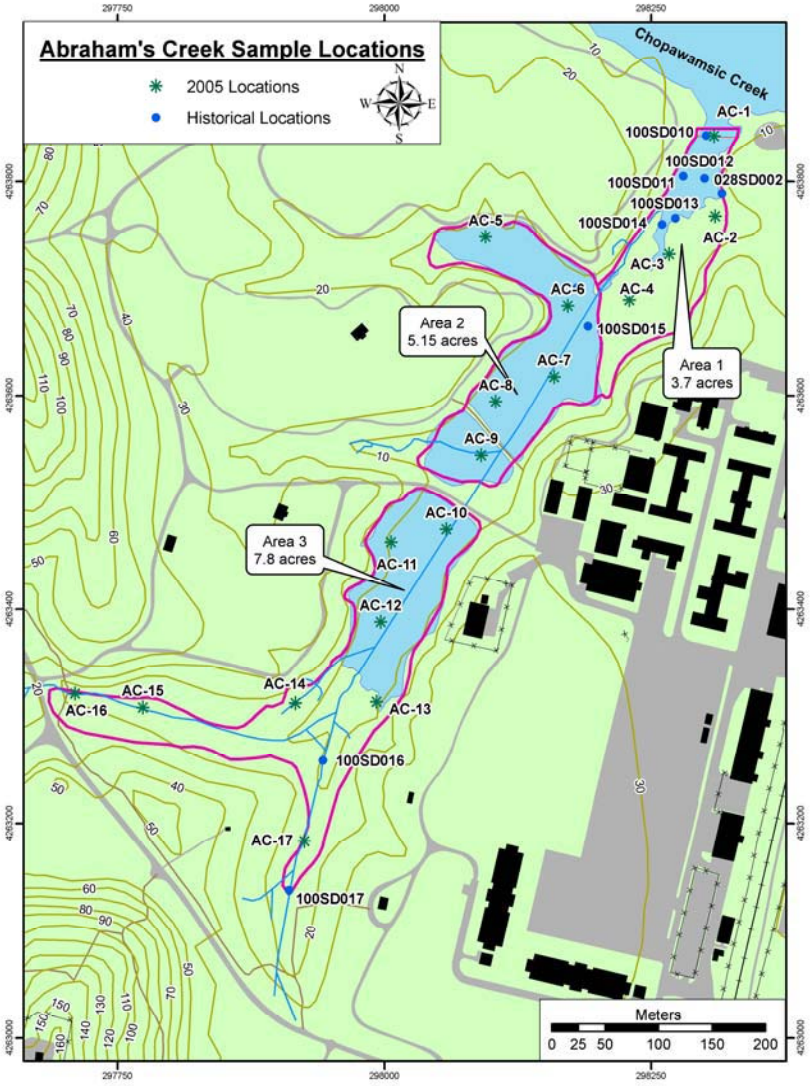

Figure 6. Abrahams Creek sample locations.

Hunters Point RSC Study Objectives

At Hunters Point, RSC methods were used to address three objectives included in the FS Data Gaps sampling effort: 1) improve the resolution of the horizontal and vertical distributions of total PCBs in the South Basin and along the adjacent shoreline; and 2) identify all major sources of PCBs to offshore sediments in South Basin; and 3) determine whether any sources are still actively releasing PCBs. These three objectives were addressed by using horizontal and vertical PCB concentration gradients, relying heavily on RSC generated data, in shoreline and offshore areas to infer the nature and location of PCB source areas. In addition, PCB compositional data from Parcel E-2, Parcel F, and Yosemite Creek were evaluated to determine chemical similarity.

Hunters Point Study Design

Hunters Point information presented in this paper is limited to results for PCB concentrations in samples collected from the South Basin area. These data are included in the 2003 Feasibility Study Data Gaps Investigation Technical Memorandum (this document is undergoing final review in response to comments).

The primary objective of the FS Data Gaps sampling effort in South Basin was to determine the location and volume of sediment requiring evaluation in the FS based on the preliminary remediation goals (PRGs) presented in the Parcel F Validation Study Report (Battelle et al., 2005a). Five other objectives were presented in the FS Data Gaps Work Plan (Battelle et al., 2003), as follows:

- Identify all major source areas of PCBs to offshore sediments;
- Characterize the depth of the mixing/biologically active zone;
- Predict erosion of the sediment bed under typical and extreme hydrodynamic conditions, including depth of scour;
- Estimate the flux of dissolved-phase PCBs from the sediment bed due to bioturbation, diffusion, and porewater advection; and
- Evaluate whether natural processes will effectively cap contaminated sediments.

Core samples were collected from 51 locations in and around South Basin in 2003 (Figure 7) to address project objectives. Four types of analyses were performed on a subset or all of the core samples:

- **PCB profiles.** Fifty-one cores were collected and subsampled into a total of 407 samples (370 primary plus 37 duplicates). Samples were analyzed for total PCBs using the immunoassay rapid sediment characterization method. Ten percent of the samples underwent laboratory analysis for PCB congeners by gas chromatography/mass spectrometry to confirm the accuracy of the RSC results. Data were used to better define horizontal and vertical distribution of PCBs.
- **Sedflume.** Twelve cores from eleven stations were analyzed in a mobile Sedflume laboratory to provide information on sediment erosion rates under typical and extreme hydrodynamic conditions.
- **Fine-interval PCBs.** Four cores were sectioned into high-resolution vertical segments that were analyzed for PCB congeners and total organic carbon. PCB congener data were used to calculate the flux of dissolved-phase PCBs from the sediment bed over time due to diffusion, bioturbation, and advection.
- **Radioisotope.** Three cores were subsampled and analyzed for 210Pb, 137Cs, 7Be, and 234Th to provide age data to confirm the previously estimated sediment accumulation rate of approximately 1 cm/yr for South Basin.

Cores were segmented as shown in Figure 8.

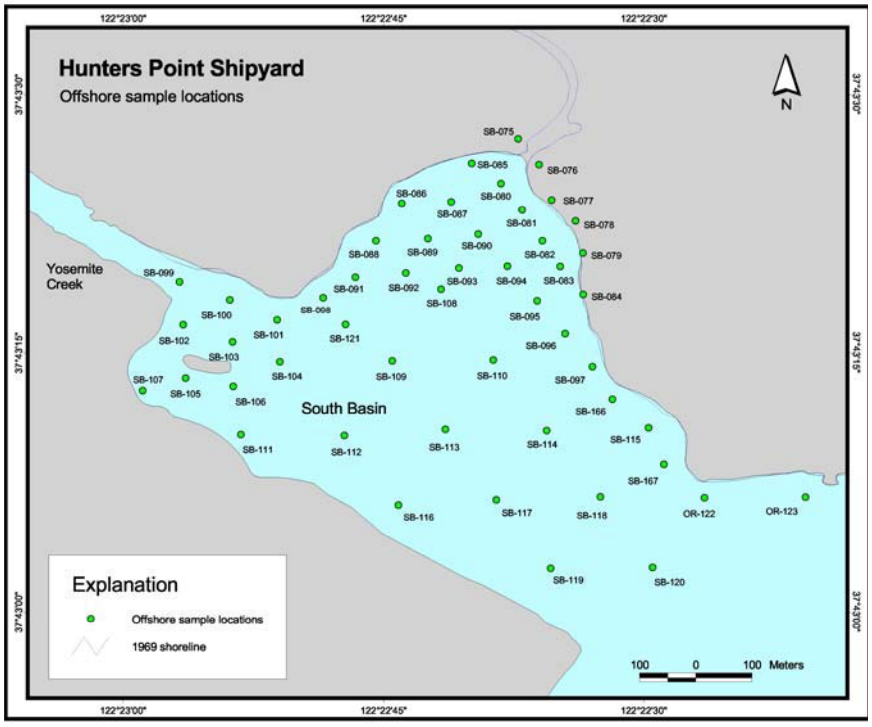

Figure 7. Parcel F FS data gaps sample stations in South basin.

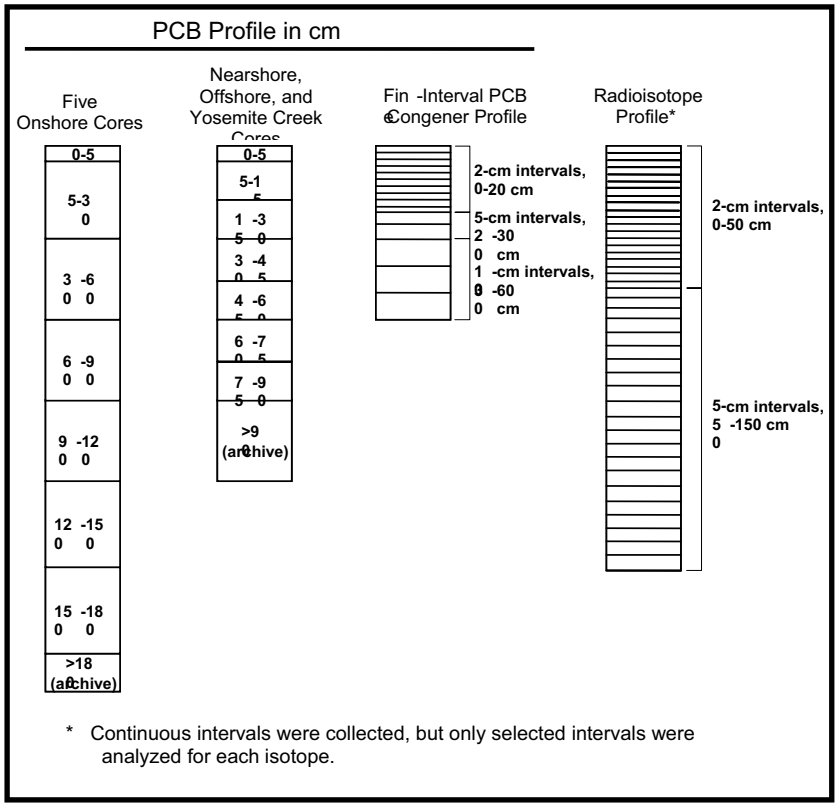

Figure 8. Vertical profiles for South basin core chemical analyses.

RSC AND LABORATORY METHODS

FPXRF- Lead

The FPXRF technology uses sealed radioisotope sources to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. When absorption occurs (the photoelectric effect) electrons are dislodged from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence. The FPXRF technique measures the various fluorescent signatures and quantifies concentrations of 26 elements (including Pb) in soil and sediment samples.

For samples collected from Chopawamsic Creek at MCB Quantico, sample aliquots were homogenized and analyzed at the SPAWAR laboratory using the FPXRF technique described in EPA Method 6200 (EPA, 1996) and SPAWAR SOP. Data generated from the FPXRF analysis included concentrations of metals not identified as COCs for the Chopawamsic Creek study areas, but only lead is discussed in this document. Fifteen percent of the samples were analyzed for confirmatory Pb analysis by Battelle to develop a correlation between the RSC and quantitative Pb concentrations. Critical values for the RSC measurements to report with confidence at MCB Quantico were the site specific Alternative Technology Screening Threshold (ATST) values. ATSTs were values generated using the no observable adverse effects level (NOAEL) and lowest observable adverse effects level (LOAEL) toxicity reference values (TRVs) for specific ecological receptors to back-calculate a sediment concentration to be considered for remedial alternatives. Samples for confirmatory analysis were selected taking into consideration the following criteria:

- Samples include the full range of concentrations obtained from RSC measurements (i.e., high, medium, and low detected concentrations and nondetected results);
- Include at least two negative RSC result samples (if negative values are part of the data set);
- Include RSC samples from locations critical for confirming the extent of sediments with Pb concentrations exceeding the ATST;
- Samples with percent moisture of greater than 30% were air dried until water content was less than 30%.

Battelle Sequim Laboratory performed confirmatory analysis of low-level Pb concentrations using inductively coupled plasma optical emissions spectroscopy (ICP-OES) according to Battelle SOP MSL-I-033, Determination of Elements in Aqueous and Digestate Samples by ICP-OES.

RSC DDx and PCBs

Immunoassay test kits use antibody molecules to detect and quantify the antibody reaction to specific substances in a test sample. The testing kits combine the specific binding characteristics of an antibody molecule with a detection chemistry that produces a quantifiable response used for interpretation. In general, antibody molecules specific for the method's intended target are provided at a predefined concentration. A reporter (i.e., signal generating) reagent, composed of the target compound conjugated to a signal producing compound or molecule (e.g., enzymes, chromophores, fluorophores, luminescent compounds, etc.), is also provided. The concentration, affinity, and specificity of the products' antibody influences performance, as does the chemistry of the reporter reagent. For project specific objectives, several situations can occur that limit the effectiveness of immunoassay methods:

- Contaminates of concern (COCs) can be present below the detection limit of a specific kit
  - This is not necessarily a critical problem if the project benchmark for the COC is above the detection limit
- COC can be present at high levels that quench the antibody response
  - Sample dilution can be used to adjust range of response, with some reduction in accuracy
  - This is not a problem if the 'quench' level is greater than the project benchmark for the COC
- Complex contaminates, such as PCBs and DDx, have multiple constituents that do not bind equally on antibody receptor sites. Thus, RSC estimates of total concentration of a compound class can exceed or be less than non-RSC measured values.

  - Degradation products, such as what occurs with DDT, may have a greater affinity for antibodies than the target compounds (i.e., DDX > DDMU).
- Matrix interferences can be problematic. Extracts typically do not undergo chemical clean up (e.g. HPLC). Only simple physical methods such as filtering or centrifugation are used to clean up matrix interfering compounds.

Samples from Abraham's Creek at MCB Quantico and Hunters Point were analyzed at the Navy's SPAWAR San Diego CA laboratory for Total PCBs and Total DDx using RSC (i.e., immunoassay) techniques based on EPA Method 4020 *Screening for Polychlorinated Biphenyls by Immunoassay* (EPA, 1998; EPA, 1996) and on EPA Method 4042 *Soil Screening for DDT by Immunoassay* (EPA, 1996a), respectively. Once the RSC screening was complete, 10-20% of the samples were selected for quantitative confirmatory analysis by gas chromatography/electron-capture detector (GC/ECD) of individual compounds to develop a correlation between the RSC and quantitative PCB or DDx concentrations.

Samples for confirmatory analysis were selected taking into consideration the following criteria:

- Samples include the full range of concentrations obtained from RSC measurements (i.e., high, medium, and low detected concentrations and nondetected results);
- Include at least two negative RSC values (if negative values are part of the data set);
- Include RSC samples from locations that are critical for confirming the extent of sediments with PCB or DDx concentrations exceeding the ATST;
- Samples with percent moisture of greater than 30% were air dried until the water content was less than 30%.

Battelle Duxbury Laboratory performed the confirmatory analysis of PCBs and pesticides (specifically DDx) using GC/ECD and low-level methods developed for the NOAA Status and Trends Program (Lauenstein and Cantillo, 1993). A standard suite of PCB congeners and chlorinated pesticides were acquired during analysis but only the target PCB congeners and/or DDx compounds (DDT, DDE, and DDD) were quantified.

Hunters Point PCB Calculations

There are 209 possible PCB congeners comprising 'Total PCB' estimates, and many methods and formulas used to quantify and describe PCB contamination in the environment. Several common systems were examined before selecting the National Oceanic and Atmospheric Administration's (NOAA) National Status and Trends Mussel Watch Program list of 18 non-coplanar congeners (PCB08, PCB18, PCB28, PCB44, PCB52, PCB66, PCB101, PCB105, PCB118, PCB128, PCB138, PCB153, PCB170, PCB180, PCB187, PCB195, PCB206, and PCB209). The sum of the NOAA 18 congeners typically constitutes 40-55% of the total PCB in most environmental samples. This means that the sum of the concentrations of the other 191 possible PCB congeners typically constitutes 45-60% of the total PCB concentration. In reality, all the PCBs that are typically found in the environment can be accounted for with a little over 100 PCB congeners, the remaining 100 or so congeners were either never part of any Aroclor formulations to begin and/or are not formed in the environment to any detectable degree.

These 18 congeners are also the target PCB compounds in the Environmental Protection Agency's Environmental Monitoring and Assessment Program (EMAP). These congeners were selected to (1) cover a relatively broad range of PCB composition (includes at least one congener from each level of chlorination, except the less environmentally relevant monochlorobiphenyls) and (2) congeners that are relatively abundant in most typical environmental PCB contamination. These are also the congeners that were in common to the laboratory analyses performed when the five different data sets used for the analysis were generated.

Total PCBs were calculated as follows:

- PCB RSC data: screening result adjusted by a correction factor of 1.1 based on the correlation between RSC and confirmatory laboratory data (Battelle 2005).
- PCB congener data: two times the sum of detected concentrations for 18 PCB congeners monitored in the National Oceanographic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Mussel Watch Program.
- PCB Aroclor data: sum of detected concentrations for individual Aroclors.

RSC and Laboratory Method Calibration

The following procedure was generally followed to calibrate RSC data to laboratory analyses. The total concentrations determined by the RSC analysis were corrected based on a comparison of RSC concentration with the concentration determined by confirmatory ICP-OES (Pb) or GC/ECD (PCBs and DDx) analyses. Using linear regression analysis, the correction slope and intercept were determined. The regressions were based on the following equation:

Total Concentration (from RSC) = slope × Total Concentration (confirmatory value) + intercept

To correct the RSC values, the following equation were used:

Corrected RSC total concentrations = [RSC total concentrations - intercept]/slope

The significance of the regression analysis must be <0.05 and the r^2 must be 0.70 or higher in order for the calibration to be applied to the data. If not, the data were reviewed to identify non-representative values or outlier data that were removed from the regression. Regardless of outlier finding, all data were reported. The "calibrated" RSC results are censored at the limits of detection for the immunoassay method prior to combining these data with other historical data and plotted to evaluate the spatial distribution of contaminants in each area. Previous studies demonstrated that this approach provides a conservative estimate of concentrations and variability for sediment chemistry.

RESULTS BY SITE

MCB Quantico

Chopawamsic Creek Lead Distribution

Sixty-seven samples from Chopawamsic Creek were analyzed at the Navy's SPAWAR San Diego facility using RSC techniques for Pb. The number of samples, 67, was established through the development of data quality objectives by a combination of the original plan, FPXRF results, and conditions in the field (e.g. refusal). This flexibility within the sampling plan was used to best describe the horizontal and vertical extent of lead contamination. Ten samples were analyzed using ICP-OES at the Battelle Sequim laboratory for use in the confirmation and calibration process.

The regression of FPXRF results with ICP-OES results was highly significant. The regression results produced a correction formula of Reported value = 1.241 * (FPXRF result) + 2.748. The detection limit for lead using the FPXRF method was determined to be 50 mg/kg dry weight and 64.8 after correction. Reported lead concentrations ranged from 17.1 mg/kg (ICP-OES) to 3,503 mg/kg (FPXRF).

Historical surface concentrations of lead were used to design a new sampling design to determine the horizontal and vertical extent of contamination.

Surface concentrations by four ranges with contours generated from the data are shown in Figures 9 and 10. Orange boxes represent Areas 1, 2, and 3. The blue line marks the transition from open water of Chopawamsic Creek to wetland areas and the green line indicates the transition from wetland to upland.

The high density of low cost sample data enabled the contouring to provide smooth and narrowly banded intervals.

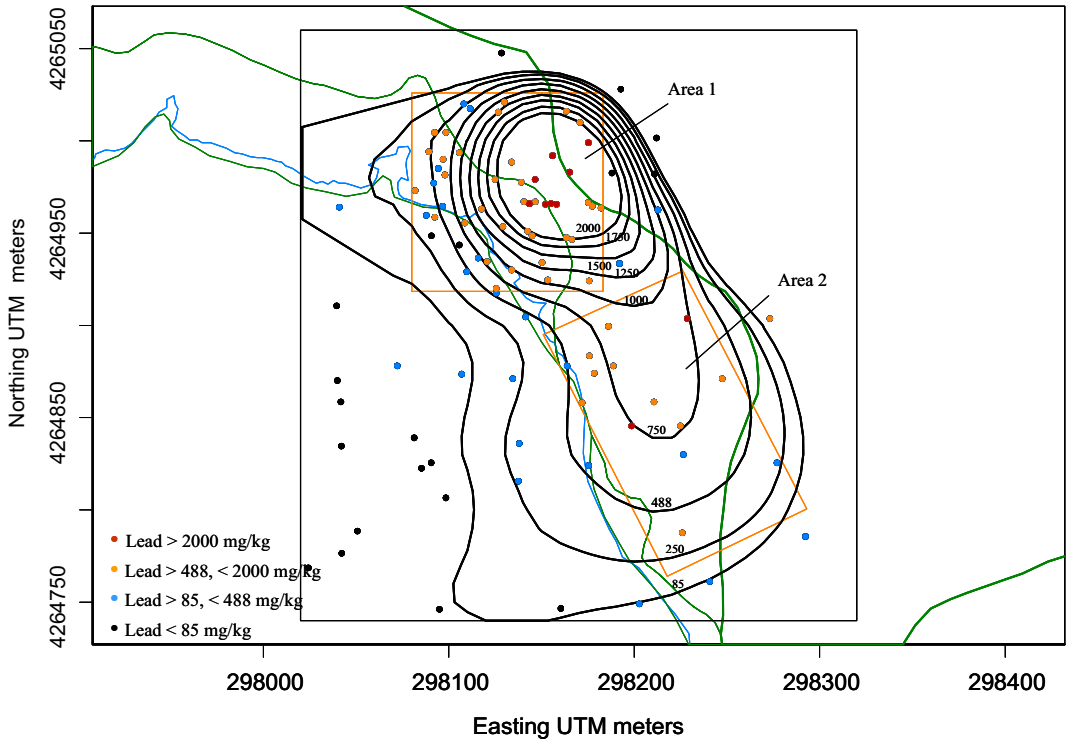

Figure 9. Lead contours (mg/kg) for areas 1 and 2 in the former rifle range runoff area.

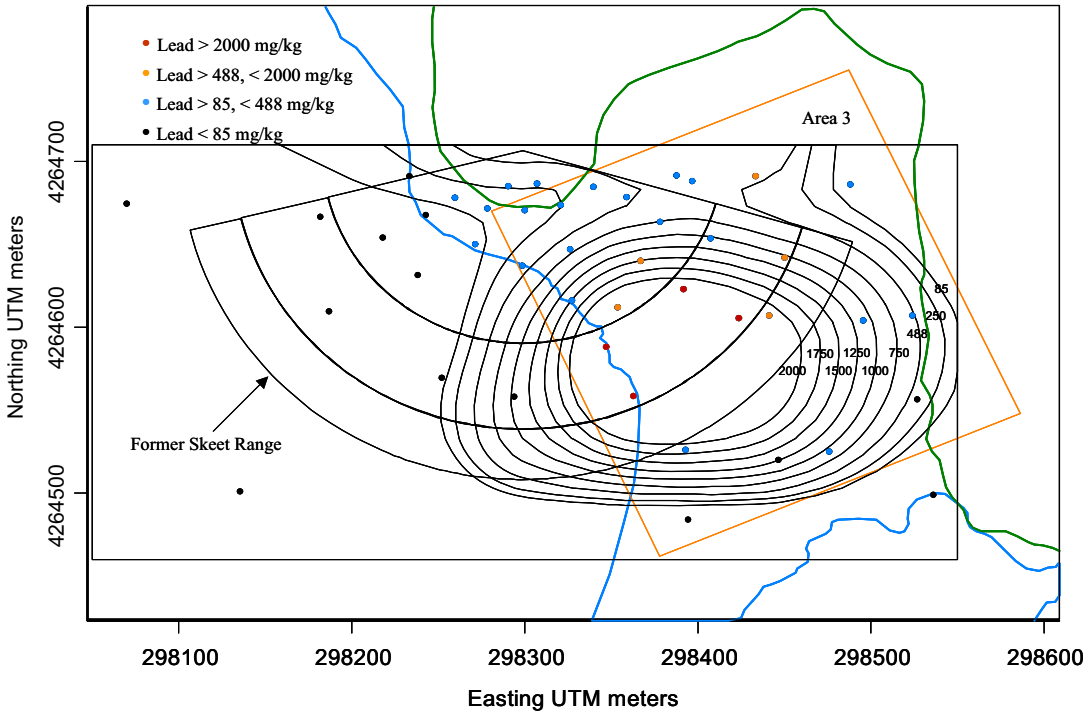

Figure 10. Lead contours (mg/kg) for area 3 in the former skeet range area.

Abraham's Creek DDx Distribution

Eighty-six samples (including field duplicates) from Abraham's Creek were analyzed for total DDx and total PCB analysis using RSC methods. A subset of 23 samples was analyzed in the laboratory for confirmation of RSC values. To better understand the relationship between RSC and fixed laboratory results and to provide sufficient understanding of surface DDx concentrations, an additional 20 surface samples (11 from Abraham's Creek and 9 from another Quantico site, Potomac River) were submitted for fixed laboratory analyses.

The comparability of laboratory and RSC DDx results were not as strong as the RSC and confirmatory results in other historical studies. The ratio between the immunoassay and laboratory Total DDT data ranged from 0.3 to 748. This ratio, and the variability in the ratio, appeared to be slightly larger for Abrahams Creek samples than for the Potomac River samples. However, the variability was so large across the board that no clear difference could be established between the two datasets, and they were therefore handled together to increase the sample size and power of the data analysis.

The ratio between the immunoassay and laboratory results would be approximately one (1) if the laboratory generated concentrations were accurately represented by the immunoassay test. After excluding non-detects and samples that clearly appear to be outliers, and/or have unidentified analytical issues with the laboratory and/or the immunoassay analysis, the average ratio between the immunoassay and laboratory results becomes approximately 3.2 (Figure 11). This is a reasonable ratio, considering the fact that the DDT compound composition is dominated by 4,4-DDD, which responds four times as well as 4,4-DDT in the immunoassay test (the immunoassay test is calibrated against 4,4-DDT). However, the difficulty with the data was the very large variability in the relationship between the immunoassay and laboratory based results; a standard deviation of 2.4 (75% relative standard deviation) is associated with the average ratio of 3.2.

There are a number of reasons why this discrepancy may be occurring. Potential sources of variability include the composition of DDT degradation products within the samples, and large or subtle sample-to-sample fluctuations in this composition. The EnviroGard DDT test kit was developed, and calibrated, based on the compound 4,4-DDT, which was the primary compound in the original DDT pesticide formulation. The original technical DDT formulation was generally about 85% 4,4-DDT and about 15% 2,4-DDT, with only traces of the 2,2-isomer, DDD, and DDE. However, once released to the environment, DDT breaks down to DDD, DDE, and a number of other degradation products depending on conditions (e.g., DDA and DDMU when anaerobic). Furthermore, these different DDT-related compounds have dramatically different responses in the EnviroGard DDT test kit (see Table 1), resulting in very different "Total DDT" concentration results depending on the composition of these compounds.

Table 1: Detection limits and relative response for different DDT-related compounds using the EnviroGard immunoassay test kit.

Compound	EnviroGard DDT Immunoassay Kit Sensitivity	
	MDL (ppb; ng/g)	Relative Response
2,4-DDD	1,760	0.11
2,4-DDE	14,900	0.013
2,4-DDT	14,900	0.013
4,4-DDD	50	4
4,4-DDE	600	0.33
4,4-DDT	200	1
DDA	10	20
4,4-DDMU	?	?

DDD was the most abundant of the three DDT-related compounds, constituting between 60 and 80% of the "Total DDT" (defined as the sum of all DDT, DDD, and DDE compounds) in most samples. DDE was generally the second most abundant, constituting between 10 and 15% of the Total DDT, and the specific DDT compounds (4,4-DDT and 2,4-DDT) together only constituted between 5 and 15% in most samples. The DDT compound composition was relatively consistent spatially (between surface sediment samples) and also with sediment depth. The samples with a composition that deviated from these general observations were samples with DDT compound concentrations near detection limits and lower than many other samples. Therefore, these samples contained greater

relative analytical uncertainty. However, there may also be other explanations for differing composition in these samples.

The observed composition of DDT-related compounds, with relatively low proportions of DDT compared to DDD and DDE, is common for sediments contaminated with historic inputs of DDT. The DDT compound composition would not be expected to significantly impact the relationship between laboratory and immunoassay results, because of this relatively uniform DDT compound composition; the ratio between the immunoassay and laboratory-based results should be fairly consistent, if the immunoassay results were driven by the concentrations of these six compounds and the analysis was reliable.

However, the large differences in the response of the six DDT compounds, and other compounds, in the immunoassay test can greatly impact the total concentration values that are determined, which may affect the relative difference between immunoassay and laboratory results. Based on the sensitivity and specificity specifications reported for the EnviroGard kit (Table 1), a 10 mg/kg concentration of 4,4-DDT should result in a measured Total DDT concentration of 10 mg/kg, while a 10 mg/kg concentration of 4,4-DDD will result in a measured Total DDT concentration of 40 mg/kg. The laboratory will, correctly, report a Total DDT concentration of 10 mg/kg for both those samples, while the immunoassay analysis will yield one value of 10 mg/kg and one of 40 mg/kg Total DDT. The test is even more sensitive to the DDT degradation product DDA; a 10 mg/kg concentration of DDA will result in a measured Total DDT concentration of 200 mg/kg. DDA was not determined in the laboratory analyses, but is reasonable to expect that these samples contain DDA at varying concentrations. It is not known how sensitive the test is to the other common degradation product – DDMU. DDMU was measured in the laboratory, and was generally found at concentrations higher than both DDT and DDE; there is clearly a significant potential for both DDMU and DDA to have a large impact on the immunoassay results. Large absolute differences between the immunoassay and laboratory results can be expected if the composition includes compounds other than 4,4-DDT, as is the case for these and most environmental samples.

The laboratory results were converted to "Immunoassay 4,4-DDT Equivalents" to further investigate the potential impact on the results of the compound-specific sensitivities and responses. The laboratory determined individual compound concentrations that were multiplied by the relative response of the compound in the immunoassay test (Table 1), and the resulting adjusted concentrations were summed to generate an overall Total DDT concentration, corrected for the response difference. These results were then compared to the immunoassay Total DDT results. The average immunoassay concentration was, as expected, more comparable to this new "immunoassay 4,4-DDT equivalent" laboratory value; the average ratio between the immunoassay and laboratory results was now approximately 1.4 (Figures 11 and 12). However, the sample-to-sample variability in the relationship did not decline (Figure 11); the standard deviation was 1.2, which is equivalent to 86% relative standard deviation.

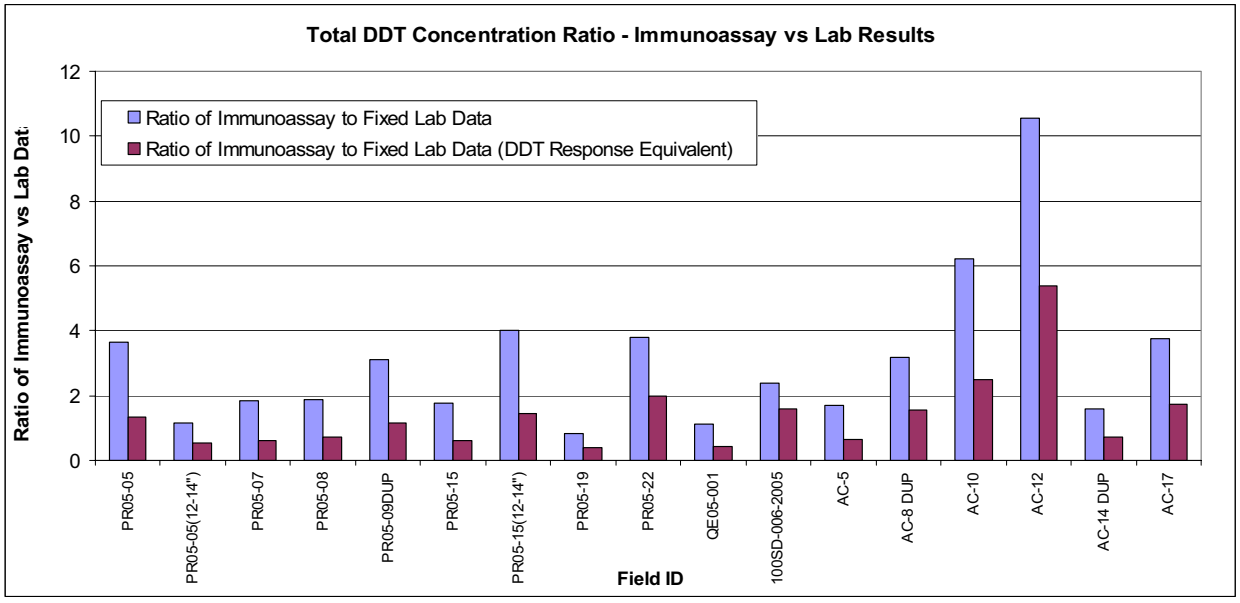

Figure 11: Ratio between DDT concentrations determined by immunoassay and laboratory method.

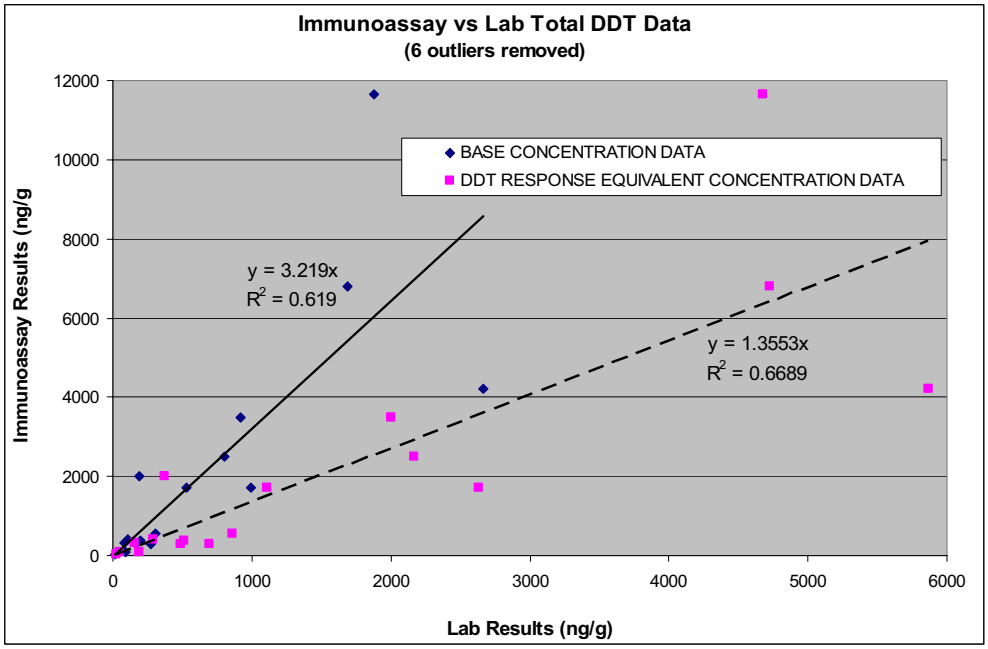

Figure 12: Correlation between DDT concentrations determined by immunoassay and laboratory method.

Use of a straight linear relationship method assumes that the ratio is constant across the range of sediment concentrations and that the line goes through the origin (also called zero intercept when sediment concentration by laboratory is zero, then sediment concentration by RSC is zero). The zero intercept assumption is consistent with the data as shown in Figure 13 and confirmed statistically by testing that the linear regression intercept is not significantly different from zero (the test produced p-value=0.18, where $p<0.05$ implies significantly different). Review of the regression residuals in terms of the error variance criteria stated above indicated that the ratio estimator is preferred. The residual errors are clearly not constant and the sum of squared residuals is largest when the mean of the point ratios is used. The ratio estimator (Cochran, 1963) was chosen to estimate the ratio between the methods.

The ratio estimator is the average (or mean) of the laboratory results divided by the average (mean) of the RSC results. Figure 13 shows the data from Figure 12 (with X & Y reversed) and presents the ratio estimator by plotting a straight line through the origin with slope equal to the ratio estimator. The colored points (and lines) in the plot on the left identify the results (and ratio estimators) calculated for the two groups (Abraham's Creek and Other areas). The clusters of points seen in the breakouts of two groups do not suggest a different relationship between methods. The fact that 95% confidence intervals about the group ratio estimators overlap (reported in legend at top) verifies that the slopes (ratio estimators) are not statistically significantly different, confirms that the fixed lab-RSC relationship in the groups is the same, and indicates that that the groups can be combined to provide an overall estimate. The line for the combined ratio estimator is plotted in black.

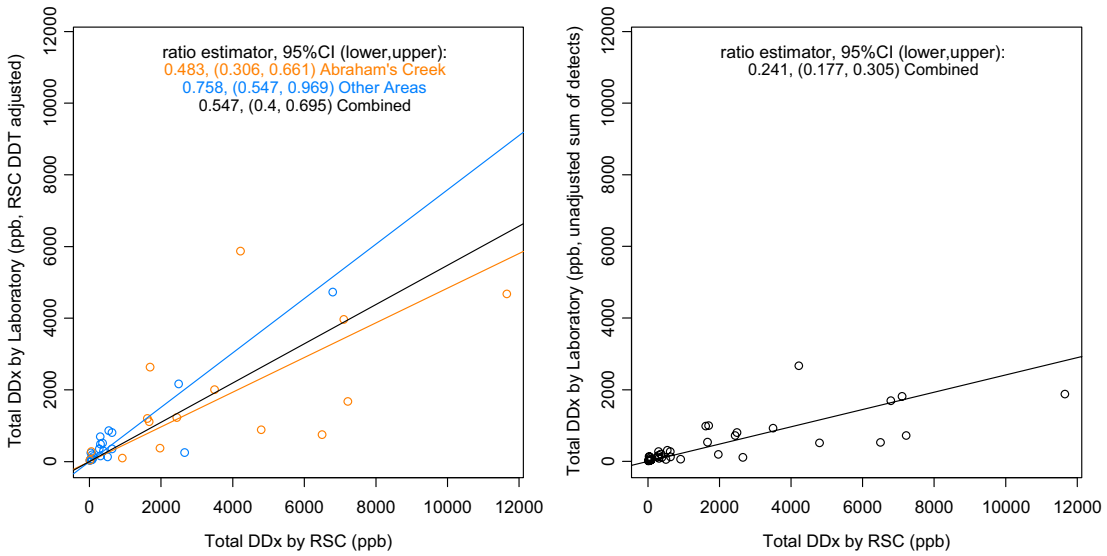

Figure 13. Plots of RSC immunoassay results versus laboratory total DDx concentrations with lines at the ratio estimate.

The majority of the data were not analyzed by laboratory methods, so a ratio estimator that relates the RSC results to the unadjusted laboratory Total DDx results is needed. The plot on the right shows the data and ratio estimator for the needed setting. There is scatter or variability about the line but the correlation (r=0.755) is as strong as it was for the adjusted laboratory results (r=0.754). The y-value concentration on the line represents the concentration that would be predicted or produced on average by an RSC result with that x-value concentration.

RSC data and GC/ECD generated data were combined and presented in a post plot (Figure 14) and contours (Figure 15). Contours were created only within Area 3; no contours were developed for Areas 1 and 2 because these entire areas likely represent unacceptable ecological risk.

Sample data from GC/ECD methods were used to represent the sample concentration when available. For samples that were analyzed by RSC only, the ratio estimate was used to adjust RSC raw results to generate estimates of compound concentrations. To assist in the development of remediation action levels, six contours were drawn using a local regression model based on all available surface sediment results from the TtNUS and Battelle/Neptune dataset, including historic sampling efforts beginning in 1998 up through the most recent samples taken in 2005 (Figure 15). Included in the six contour levels were three Alternative Technology Screening Threshold (ATST) concentrations endpoints: 1) DDx NOAEL (No Observed Adverse Effects Level) ATST based on risk to piscivorous birds; 2) DDx LOAEL (Lowest Observed Adverse Effects Level) ATST based on risk to piscivorous birds; and 3) Minimum ATST (5th percentile LOAEL) based on risk to fish.

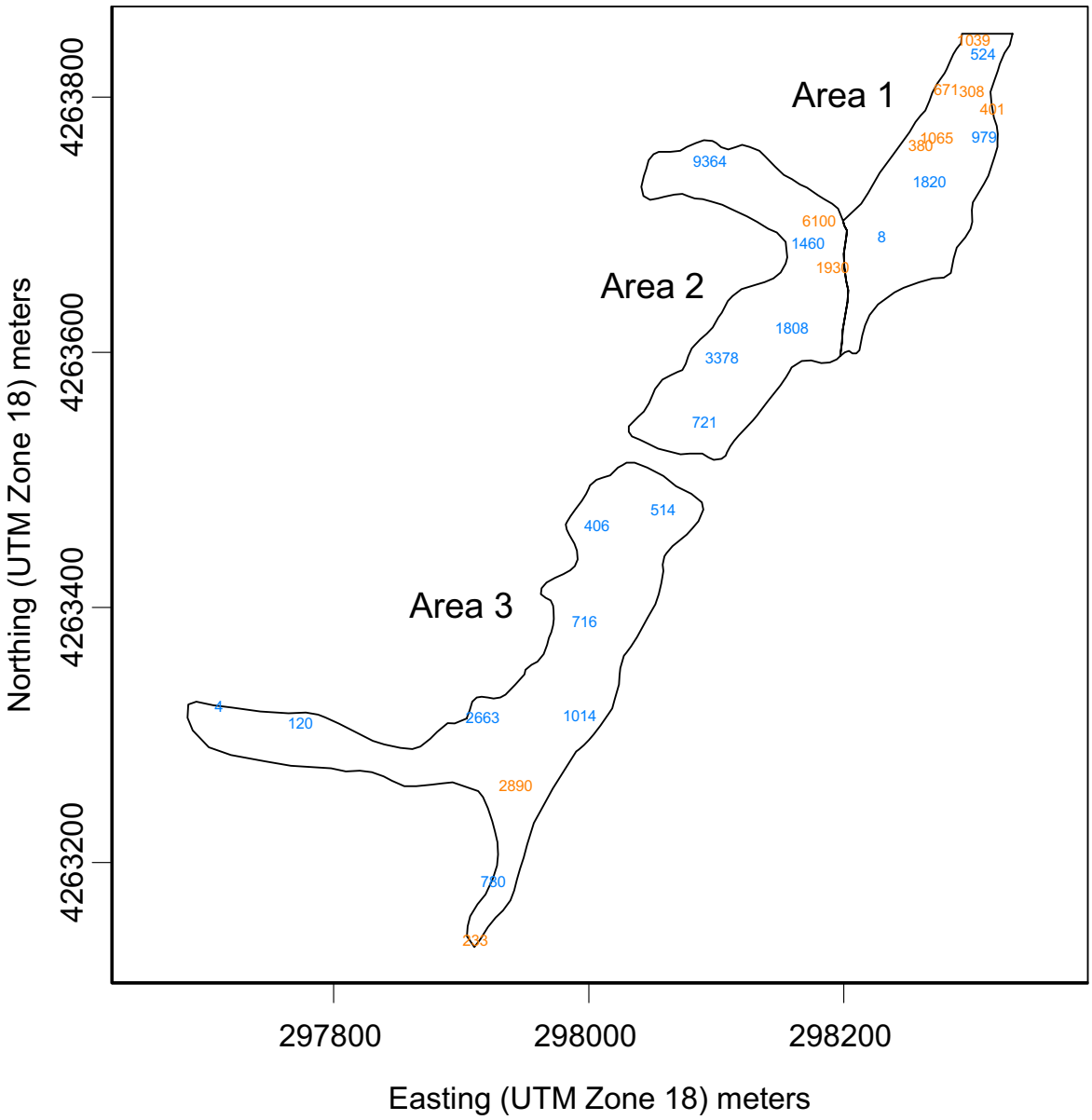

Figure 14. Posting plot of surface concentration of total DDx in Abraham's Creek.

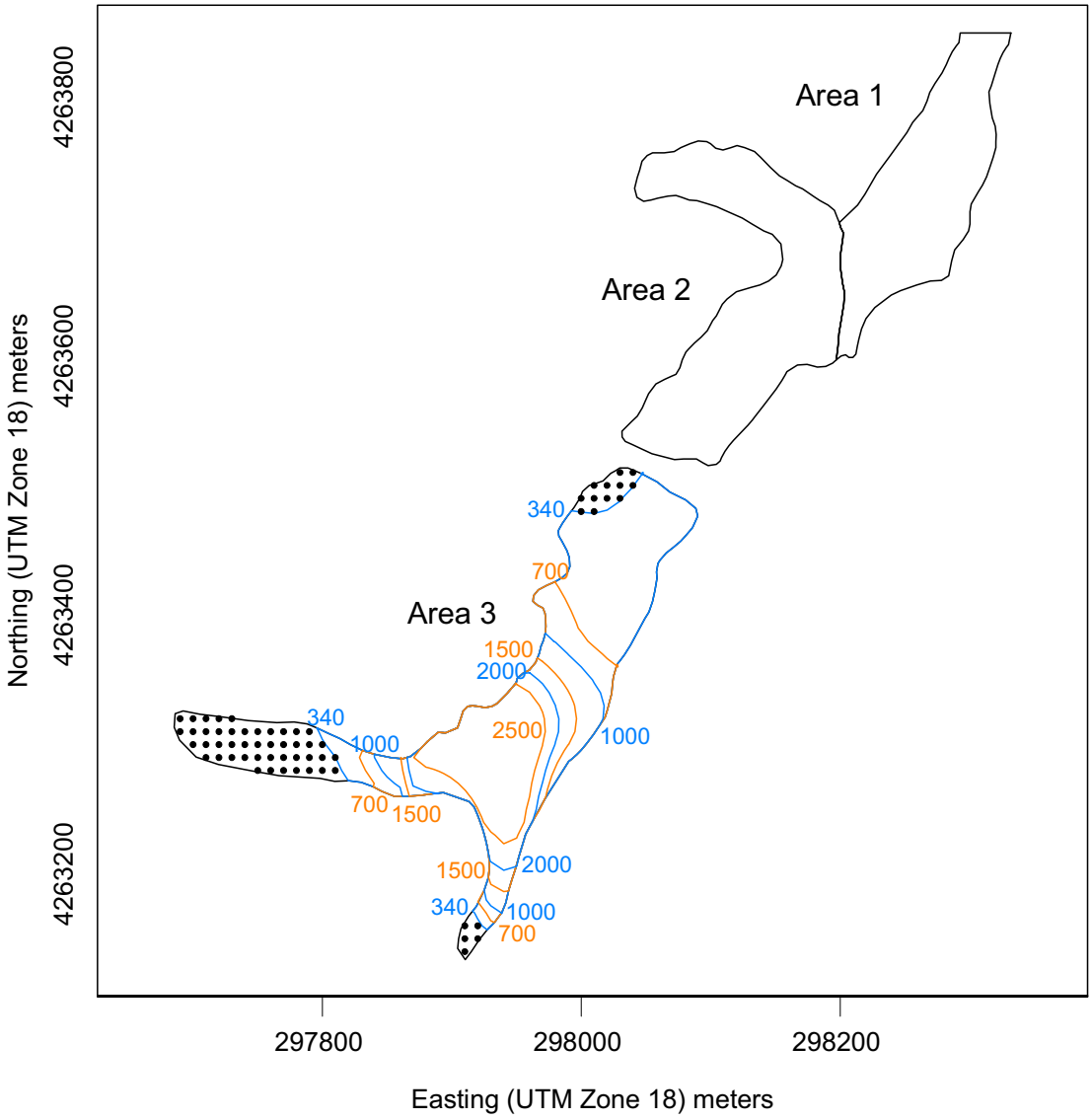

Figure 15. Contour plot of surface concentrations of total DDx at Abraham's Creek area 3.

Hunters Point

PCB Distribution

Horizontal and vertical distribution maps and cross-sections of total PCBs in the South Basin and along the adjacent shoreline were processed using combined RSC and fixed laboratory (PCB congener) data. Figures 16 through 19 are three-dimensional models of total PCB concentrations with increasing depth below the mudline based on the 2003 FS Data Gaps data only. Where available, PCB congener data were used to represent total PCB concentrations; otherwise, adjusted PCB RSC data were used. Based on the data plotted in these figures, the following observations were possible:

- PCB concentrations in surface sediment are highest (>2,000 µg/kg) along the northern shoreline of South Basin, near the area where the former slough connected with South Basin (near Stations SB-075 and SB-076).

- At a depth of 1 ft below the mudline, the area with PCB concentrations >2,000 µg/kg is more extensive, both at the northern portion of South Basin and at the mouth of Yosemite Creek. Overall, concentrations are higher 1 ft below the surface than at the surface.
- At 1.5 ft below the mudline, the area of highest PCB concentrations decreases in extent at the northern portion of South Basin, and increases in extent at the mouth of Yosemite Creek.
- At 2.6 ft below the mudline, PCB concentrations of >2,000 µg/kg at the north end of South Basin are limited to the vicinity of Station SB-076, whereas the affected area at the head of Yosemite Creek has not diminished substantially. The vertical extent of PCB concentrations >2,000 µg/kg at the head of Yosemite Creek was not delineated in this investigation.
- Cross-sections show that the areas of high PCB concentrations in the northern portion of South Basin do not appear to be continuous with the contamination found at the mouth of Yosemite Creek, and the deposit near the mouth of Yosemite Creek is at a greater depth.

PCB Composition

PCB composition in sediment samples collected throughout South Basin was analyzed using several methods including hierarchical cluster analysis (HCA) and principal component analysis (PCA) to determine if any differences could be attributed to different PCB sources. This analysis included an overall review of the PCB concentrations and composition in surface and subsurface sediment samples, and an evaluation of the similarities and differences in the PCB congener composition and how the observed composition(s) may relate to source(s). The analysis is summarized below.

The following data sets were included in the analysis:

- Parcel F Validation Study data (Battelle et al., 2005a)
- FS Data Gaps investigation data, including PCB congener data for fine interval core samples and confirmatory samples analyzed to support the RSC data (Battelle 2005)
- Surface sample data obtained from Space and Naval Warfare Systems Command (SPAWAR) Systems Center San Diego
- Parcel E-2 shoreline data (TtEMI, 2003b)
- Yosemite Creek data collected by CCSF from 1998-2000.

The PCB compositions of most of the field samples were similar to that of one Aroclor formulation; Aroclor 1260. The PCB composition data suggest that there may also have been partial contributions from Aroclor 1254 source(s), particularly in the Yosemite Creek area, but the vast majority (i.e., >90%) of the PCB clearly appears to be from an Aroclor 1260 source in most of South Basin. The resemblance to Aroclor 1260 was particularly good in samples collected along the shore in the area near Stations SB-20 to SB-23 (Figure 7). Samples from Yosemite Creek and the westernmost part of the basin showed evidence of PCB other than Aroclor 1260 contributing to the dominant Aroclor 1260 signature. Lower molecular weight PCB congeners, such as from Aroclor 1254 and possibly also 1242/1248, were evident in samples from stations 1N and 4C, for example, and from stations outside the mouth of Yosemite Creek (e.g., SB 01 and SB-100) (Figure 7). The influence of Aroclor 1254 was evident in all samples from and near Yosemite Creek, and the PCB composition was similar throughout the Creek. In contrast, the Aroclor 1260 signature dominated the PCB composition in the surface sediments throughout the basin, including the western parts.

The PCB composition of the subsurface samples was, for the most part, similar to the PCB composition of the surface sediments. There were, proportionately, slightly higher concentrations of less chlorinated PCB congeners in the subsurface sediments than in the surface sediments. Slightly higher levels of Aroclor 1254 in historic loadings to the basin may partly explain the subtle difference. However, it is also possible that natural dechlorination of the more chlorinated congeners contributed to the relatively small change in composition that is observed for most of the basin.

The consistency of Aroclor 1260 as the primary PCB source compound enhances the power of the RSC results to augment the laboratory results.

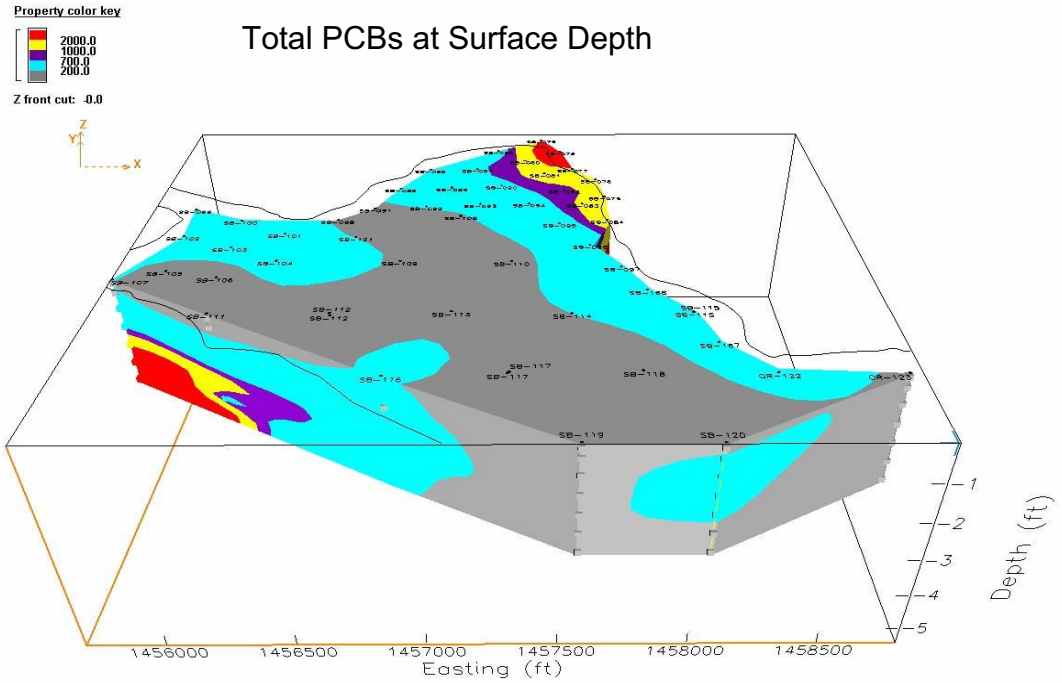

Figure 16. PCB concentrations (µg/kg) in surface sediments in South Basin.

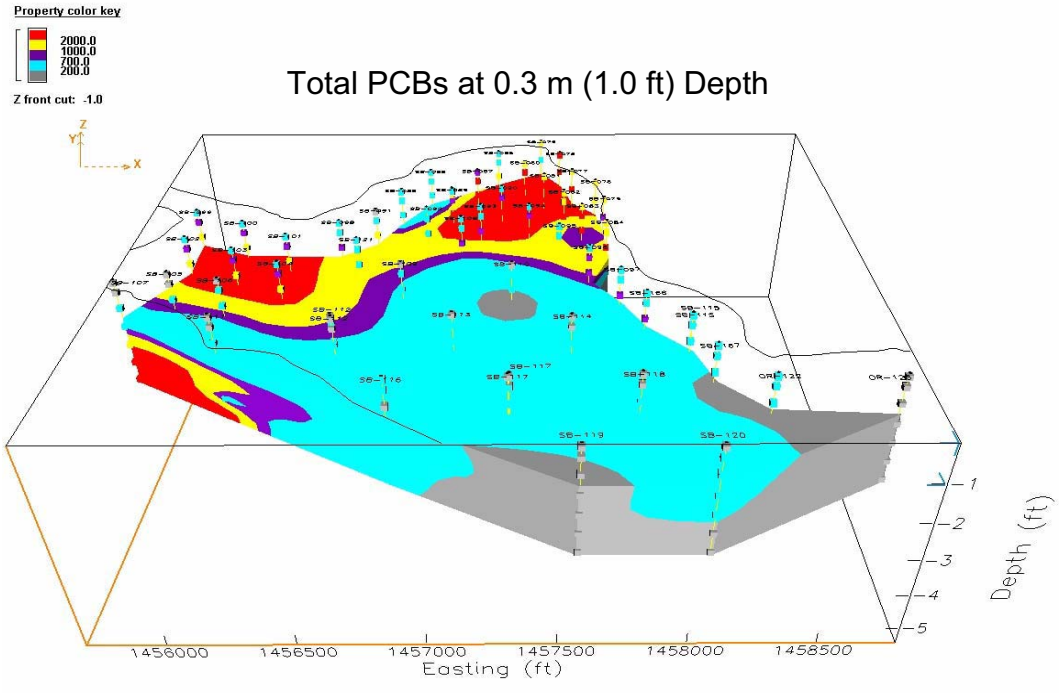

Figure 17. PCB concentrations (µg/kg) at 1.0' core interval in South Basin.

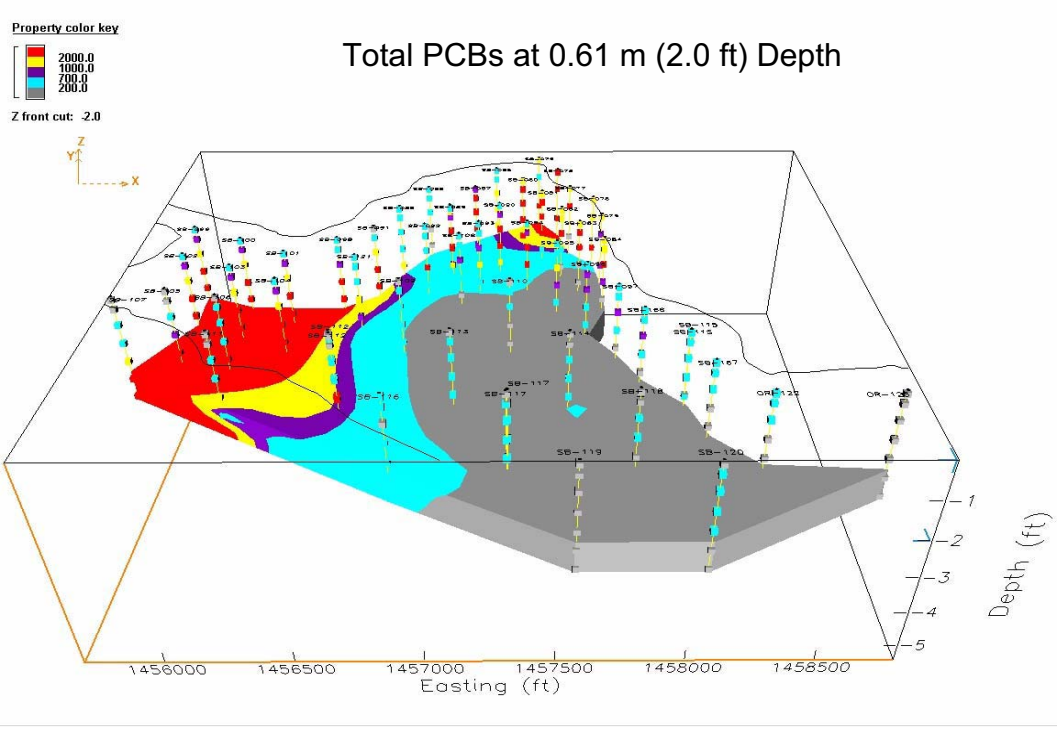

Figure 18. PCB concentrations (µg/kg) at 2.0 ft core interval in South Basin.

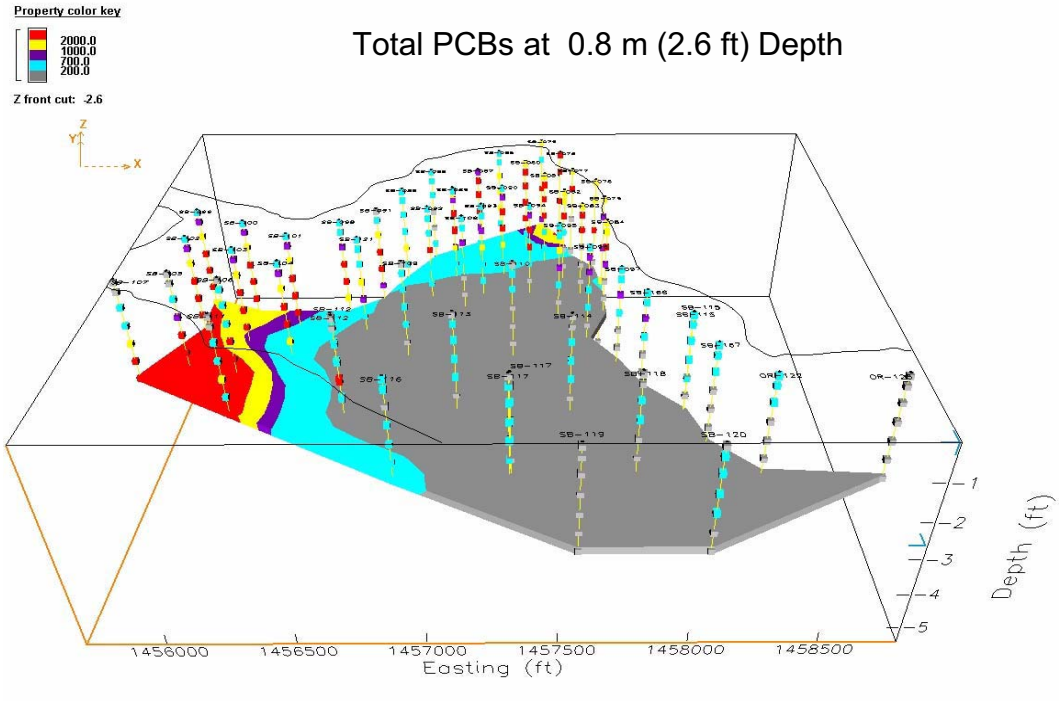

Figure 19. PCB concentrations (µg/kg) at 2.6 ft core interval in South Basin.

CONCLUSIONS

RSC methods were very successful in characterizing lead concentrations in sediments and soils from MCB Quantico and PCBs in sediment from Hunters Point.

RSC methods were not as successful in analyzing DDx in sediments from Abraham's Creek at MCB Quantico. Variable immune response to DDx compounds and potentially confounding interference from other organic compounds reduced the confidence of the results to ineffective levels.

Benefits of RSC methods are not simply the direct cost savings compared to fixed laboratory methods. When RSC methods are appropriate, as they were for lead at MCB Quantico and PCBs at Hunters Point, there are several interrelated areas that add value to contaminant characterization studies such as the following:

1. Immediate (*in-situ*) or very rapid turn-around times
2. Tiering the analyses at the lab or in the field provides flexible sampling plans and maximizes value return on the field and laboratory investment.
3. Cost savings
    a. Reduced per sample costs
    b. Efficient number of samples
    c. Increased efficiency of data management, reporting, and management labor

The benefits of an adaptive sampling plan are especially valuable for large study areas. Extensive sites often contain hot spots; RSC methods can prevent or minimize multiple sample and analysis events

Following are conclusions by area of the direct and indirect cost savings, and descriptions of value added by RSC analysis methods.

MCB Quantico Lead

The FPXRF provided very useful data at MCB Quantico. The high density of data horizontally and vertically provided by the RSC flexibility was the foundation for developing tight contours and minimizing the footprint of material potentially designated for evaluation in the Feasibility Study. A large cost savings for the Navy was achieved by reducing the per-sample cost and the numbers of samples compared to analyzing all the samples that were collected by fixed laboratory methods.

To increase efficiency, analysis of lead was tiered vertically and horizontally at MCB Quantico in 2005. In general, when a value above the action level was recorded with FPXRF, the next deepest sample interval was analyzed. This approach saved a significant amount of project cost and analyses occurred almost real-time (within days). With only a fixed laboratory analysis resource, the same focused results would have required many iterations of laboratory requests and extractions. Several months of activity with the associated additional labor for management and database efforts, and a far greater number of QC samples would have been required to reach the same results. RSC methods reduced not only the number of fixed laboratory analyses, but they allowed a reduced number of RSC analyses as well.

Due to logistical constraints, we were unable to use the FPXRF in the field. If available in the field, even tighter resolution would have been possible. Once the field team is mobilized and on site, additional samples are relatively inexpensive to collect, which is the ultimate objective of the method

MCB Quantico DDx

Information derived from the DDx immunoassay tests was not as beneficial as anticipated. Confounding factors were suspected to be a combination of unequal immune responses due to differential degradation products of DDT and matrix interferences from other organic compounds. The confounding factors triggered inconsistent data results with associated high relative standard deviation between immunoassay and fixed laboratory results.

DDA and DDMU breakdown products are suspected as triggers in inconsistent relative proportions causing variable immune response. DDMU was measured in the laboratory, and was generally found at concentrations higher than both DDT and DDE.

Further development of the DDx immunoassay method should include calibrating results to a mixture of DDT compounds that closely resembles the composition at the site. However, that would also require knowledge of the concentrations of the less commonly determined DDT degradation products that are likely to be present and contribute to the immunoassay results. Even with this analytical improvement of accuracy, it is likely that much of the poor precision that was observed for the immunoassay analysis would remain. It appears that much of the data variability, and resulting lack of confidence in the immunoassay results, is due to inherent precision issues with the test in complex organic rich samples, or something that has not yet been identified. Aside from the difficulties of the DDx immunoassay test methods, for the MCB Quantico, the DDx data was sufficient to identify the areas of evaluation of potential remedial alternatives in a Feasibility Study.

Hunters Point PCB

The RSC PCB method worked very well at Hunters Point, partially due to the consistency of the Aroclor/Congener composition across the site. Immunoassay methods were able to save a significant amount of money within the per-sample cost reduction.

The PCB immunoassay kit works best with consistent PCB contamination with an average molecular weight of Aroclors 1254/1260 because the immune response is based on the detection and analysis of a just a few biologically important congeners. If those congeners are present at relative concentrations dissimilar to "fresh" Aroclor 1254/1260, then the immunoassay derived data will not correlate well with laboratory analysis of total PCBs.

To confidently apply the immunoassay screening method, it is prudent to understand the expected PCB composition based on high quality Aroclor or Congener analysis. The existing data must cover the range of conditions at the site, including the depth range of interest. PCB composition can be dramatically different based on source input and the degradation environment; the degradation conditions in surface sediment are often very different compared to subsurface sediment. If the immunoassay kit is used in sediments with PCBs that are highly dechlorinated, the immunoassay method can produce total PCB concentration data an order of magnitude lower than for samples without the same level of dechlorination. In reality, these samples may have the same total PCBs.

The assessment of the site conditions as they apply to the immunoassay kits needs to be performed prior to finalizing a sample plan (e.g., analysis of existing data, lab analysis of archived samples, lab analysis of a small set of newly collected representative samples) to ensure the use of immunoassay approach and methods are appropriate. Additionally, the immunoassay kits have optimum concentration ranges. Study objectives must be consistent with the test kit limitations.

As with the Quantico lead FPXRF study, the cost savings and value added by the PCB immunoassay methods at Hunters Point were not limited to the direct analysis costs. Flexibility in analysis and efficiencies available with the RSC method conserved costs as well.

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