The Use of X-ray Fluorescence Spectrometry to Support Long-term Monitoring of Heavy Metals Migration at a Wetlands Site.

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Abstract: Rapid sediment characterization (RSC) tools (X-ray Fluorescence for metals, UV Fluorescence for PAHs, Immunoassay for PCBs) are being used at sediment sites to facilitate the Ecological Risk Assessment process. Two different applications of X-ray Fluorescence Spectrometry (XRF) were used in support of a five-year periodic review assessment at the Litigation Area at Naval Weapons Station Seal Beach Detachment Concord, California. The objectives of the field investigation were to support a Baseline Ecological Risk Assessment and to provide additional data to support the evaluation of migration of heavy metals in the wetlands. During the first phase of the field investigation, field portable XRF was used on site to provide rapid measurements of the relative concentrations of Zn and Cu at the most contaminated portions of the site. These data were used to select samples for the amphipod bulk sediment bioassays. The second phase of the project involved the vertical delineation of metals concentrations on the marsh surface and in the ditches and sloughs. For this phase, a benchtop XRF analyzer was used in the laboratory to quantitatively evaluate concentrations in sections of the surface sediment core samples. The versatility of this analytical technique provided the ability to address different data requirements in a cost- and time-effective manner.

In the late 1980s, a remedial investigation and feasibility study recommended that a remediation focused on heavy metals should be conducted at the Litigation Area sites at Naval Weapons Station Seal Beach Detachment Concord, California. Between 1992 and 1995, the Navy completed four remedial actions to remove contaminated soil at these sites. A periodic review assessment was developed to monitor the success of the remediation and has been implemented annually for the past five years. In October 2000, field activities were conducted at the Litigation Area to provide information necessary to complete the five-year review process (Tetra Tech EM Inc. 2000). The main tasks of the field investigation were to support a Baseline Ecological Risk Assessment (BERA) and to provide additional data to support the evaluation of migration of heavy metals in the wetlands. Two different applications of X-ray Fluorescence Spectrometry (XRF) were used to support both objectives.

Bioassay samples collected in prior years did not include samples taken from the most contaminated regions of the site. At these locations, high concentrations of metals, particularly Cu and Zn, had been identified. To support the BERA, sediment samples were collected for conducting amphipod bulk sediment bioassays. The additional bioassays were conducted to ensure that the risk assessment included areas with the highest metals concentrations (Tetra Tech EM Inc. 2000). Thirty-three sampling locations were identified as candidates for bioassay analyses. Only those locations identified by XRF analysis with the highest concentrations of Cu or Zn would be subsequently sampled for the bioassay analyses. In order to minimize the time

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between the collection of sediment and the shipment of the sample off site for bioassay analysis, it was vital to provide metals analysis in a time-effective manner. For this reason, a field portable XRF unit (Spectrace 9000 portable XRF spectrometer, Spectrace Instruments, Sunnyvale, CA, USA) was used on site to satisfy the requirement of providing rapid measurements of the metals concentrations.

Sediment samples were collected from 33 locations along the ditches and slough at the site for XRF analysis. A subsample of sediment from each location was dried and ground on site to minimize the effects of moisture and sample heterogeneity on the XRF analysis. After XRF measurements were obtained for all samples, the Cu and Zn concentrations were tabulated and plotted (Figure 1).

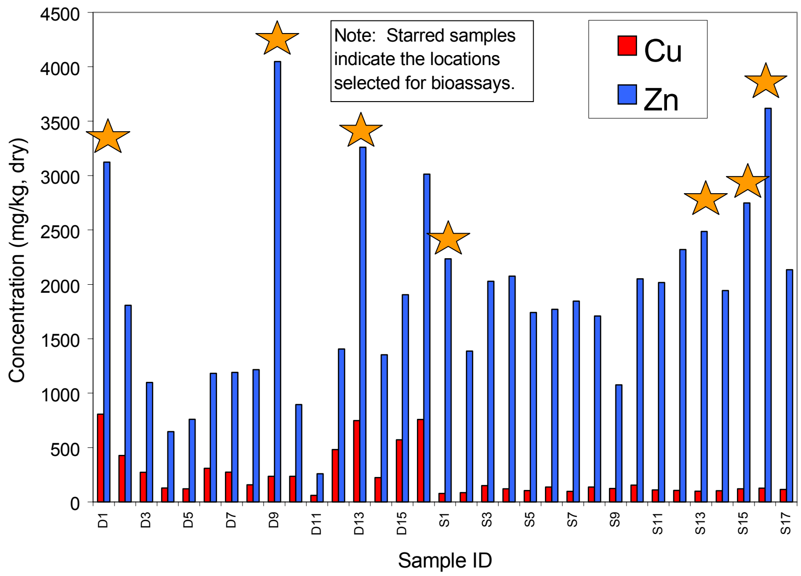

Figure 1 – Field portable XRF measurements of ditch and slough sampling locations.

Areas of high concentrations of Cu and Zn were identified by the field portable XRF measurements. Based on these results, three locations in the ditches and four locations along the slough were selected for further sampling to obtain sufficient sediment for bioassay analyses. In this phase of the field investigation, the ability to guide the selection of the bioassay samples in near real-time, based on measurements of Cu and Zn, was demonstrated by the deployment of a field portable XRF.

The second objective of the site investigation was to provide additional data to support the evaluation of the migration of heavy metals. The focus of the field activities was the collection of core samples, which would be used to determine vertical profiles of metals contamination on the marsh surface and in the ditches and sloughs (Tetra Tech EM Inc., 2000). Forty-four ten-inch deep sediment core samples were collected from various locations of the site, frozen with dry ice, and sent to the Space and Naval Warfare Systems Center, San Diego (SSC SD) laboratory for metals analysis using a benchtop EDXRF (Energy Dispersive XRF) spectrometer. The benchtop EDXRF (QuanX EDXRF spectrometer, Spectrace Instruments, Sunnyvale, CA, USA) was used to quantitatively evaluate the concentrations of Cu, Zn, Pb, As, Cd, and Se in sections of the sediment core samples. Several factors led to the decision to use the benchtop

EDXRF for this phase of the site investigation. First, it was necessary to section the ten-inch deep cores into one-inch segments in order to measure metals concentrations throughout the depth of the core. The controlled conditions of the laboratory provided the desired environment for precisely sectioning the cores. The autosampler contained on the benchtop EDXRF allowed overnight measurements of the samples. For the measurements of a large number of samples (over 300 samples in this phase of the project), the benchtop EDXRF was determined to be the most cost- and time-effective candidate for the analysis of metals concentrations.

After sectioning each core into one-inch segments, the segments were dried and ground in the laboratory to achieve higher data quality. After XRF measurements were obtained for all core segments, the concentrations of the chemicals of concern (Zn, Cu, Pb, As, Cd, and Se) were tabulated and plotted (Figure 2).

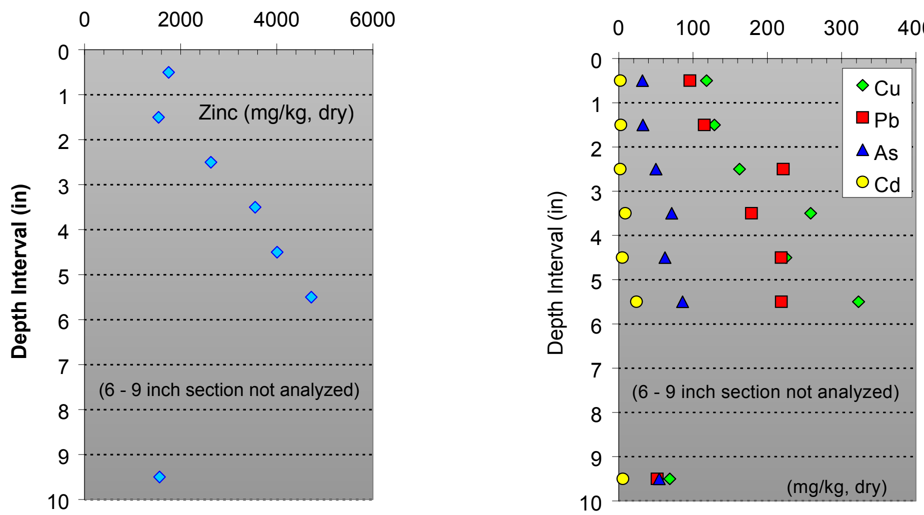

Figure 2 – Vertical profile of metals concentrations of a marsh surface sediment core.

Figure 2 shows the results from the XRF measurement from seven core sections (6 - 9 inch section not analyzed according to workplan) for one of the marsh surface sediment cores. Se was below the detection limit of the benchtop EDXRF and therefore not plotted. For this particular core, it was observed that metals concentrations increased to a depth of 6 inches and decreased at the deepest depth.

The goals of this field investigation were to support a Baseline Ecological Risk Assessment and to provide additional data to support the evaluation of migration of heavy metals in the wetlands. Specific data requirements were defined for each phase of this investigation. The versatility of X-ray Fluorescence Spectrometry provided the means of satisfying these requirements. By employing different XRF analytical techniques (field-based measurements and laboratory measurements) to each phase, the data requirements were attained in a cost- and time-effective manner.

Reference:

Tetra Tech EM Inc. 2000. "Work Plan for Five-Year Periodic Review Assessment for Litigation Area, Naval Weapons Station Seal Beach Detachment Concord, California."