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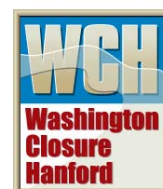
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## **Radionuclides, Trace Metals, and Organic Compounds in Shells of Native Freshwater Mussels Along the Hanford Reach of the Columbia River: 6000 Years Before Present to Current Times**

**January 2006**

**Washington Closure Hanford**

Prepared for the U.S. Department of Energy, Richland Operations Office  
Office of Assistant Manager for River Corridor



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## River Corridor Closure Contract

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# Radionuclides, Trace Metals, and Organic Compounds in Shells of Native Freshwater Mussels Along the Hanford Reach of the Columbia River: 6000 Years Before Present to Current Times



**January 2006**

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## EXECUTIVE SUMMARY

Shell chemistry of naiads can reflect the chemistry of the surrounding water. Information concerning background levels (in the absence of anthropogenic activities) of radionuclides, trace metals, and organic compounds in biotic media is scarce at best. This report documents concentrations of radionuclides, trace metals, and semivolatile organic compounds measured in shell samples of the western pearl shell mussel (*Margaritopsis falcata*) collected along the Hanford Reach of the Columbia River.

Radiological and chemical concentrations measured in the mussel shell samples were examined from three general time periods: ~6000 to 4000 radiocarbon years before present (B.P.); ~3000 to 250 B.P. (as determined by radiocarbon dating); and current (through collection of shells of organisms during the spring of 2005 that had recently died). The periostracum (external surface) of all shell samples were removed and nacreous tissues were cleaned and submitted for radiological and chemical analyses. Ten samples were submitted for analyses of 14 gamma-, beta-, or alpha-emitting radionuclides. Radio-strontium and uranium-234/238 were the only radionuclides reported above analytical detection, and no apparent increasing or decreasing patterns were observed across time periods. Eight shell samples were submitted for analyses of 71 semivolatile organic compounds; however, none of the sample results were reported above the analytical detection limits, suggesting this media may not be a sensitive indicator of changing environmental levels for these compounds. Nine of 12 trace metals analyzed in 9 samples of mussel shell tissue were reported above analytical detection limits, but barium was the only trace metal where a temporal trend was apparent. The mean, minimum, and maximum concentrations of barium were highest in shell samples from the oldest time period (~6000 to 4000 B.P.) and lowest in samples from the most recent time period (current). Plausible mechanisms involving the accumulation of barium in shells from the oldest environments examined in this study include hydrothermal, biogenic, and diagenetic processes. Decreasing glacial melt run-off and scouring of basalt formations in the Columbia River basin during the time periods studied likely play a role in decreasing barium levels in mussel shells.

Collectively, this study illustrated the utility of monitoring selected radionuclides and trace metals in shells of native freshwater mussels to assess long-term trends and background levels of these pollutants in the environment. Results reported here represent river-wide contaminant loading patterns and provide insight to background levels expected for this media in the Columbia River basin.

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## 1.0 INTRODUCTION

For more than 40 years, Hanford Site facilities were dedicated to the production of special nuclear materials for national defense. In 1944, the first plutonium production reactor on the Hanford Site began discharging radionuclides, organic compounds, and trace metals into the Columbia River via cooling water effluents. In succeeding years, as many as nine reactors were introducing various amounts of these materials into the Columbia River. Although Hanford Site production operations have ceased and Hanford's mission is focusing on environmental cleanup and restoration, the movement of the Hanford Site's legacy materials continues to be released to the environment via contaminated shallow groundwater that emerges into the Columbia River. Some examples of the primary contaminants of potential interest include radionuclides (e.g., strontium, plutonium, and uranium), trace metals (chromium, zinc, and mercury), and organic compounds (polychlorinated biphenyls [PCBs]) (Poston et al. 2004). However, environmental media have not been sampled and analyzed for contaminants to examine baseline changes in contaminant loading along the Columbia River spanning thousands of years to include pre-operational, operational, and post-operational time periods.

Several studies have shown that shell chemistry of naiads reflects the chemistry of the surrounding water and are nicely summarized by Mutvei and Westermarck (2000). Freshwater mussels have several life-history traits that make them excellent sentinels and/or indicators of the long-term health of the aquatic ecosystems: (1) individuals are relatively long-lived (sometime exceeding 100 years), and their populations may reflect cumulative effects of environmental conditions and extreme events over time; (2) adults are relatively immobile and may only move a few yards during their entire life, providing insight of the local conditions; (3) they are relatively sensitive to environmental quality, habitat, and fish communities; 4) being long-lived, filter-feeding animals, mussels have a propensity to accumulate chemical pollutants in their bodies and shells; and (5) they are relatively easy to collect, identify, and measure. However, information concerning the uptake and accumulation of Hanford Site's legacy materials in native freshwater mollusks has not been previously studied.

Eight recognized mussel species are considered endemic to the western United States (Turgeon et al. 1998). Seven native mussel species have been identified in Washington State, six of which occurred historically in the mainstem of the Columbia River, including the following: *Anodonta californiensis*, *A. kennerlyi*, *A. oregonensis*, *A. nuttalliana*, *Gonidea angulata*, and *Margaritopsis falcata* (Frest and Johannes 1995). Archeological evidence with radiocarbon dates from ~6000 years before present (B.P.) to ~250 B.P. supported the premise that western pearlshell mussels (*Margaritopsis falcata*) persisted on the Hanford Reach (Marceau and Sharpe 2002). However, Tiller et al. (2005) characterized native freshwater mussel species compositions, densities, and distributions along the Hanford Reach during 2004 and found relatively large populations of three species of *Anodonta* genera existing there today. Shells of the western pearlshell mussel (*Margaritopsis falcata*) that had recently died were found in two areas along the Hanford Reach, but the authors reported that the species appeared to be largely absent in current times.

The goal of this project was to integrate archeological findings and recent biological characterization efforts to provide an initial assessment of the levels of radionuclides, trace metals, and semivolatile organic compounds found in the Columbia River environment before and during Hanford Site operational periods. As such, shell tissue of the freshwater mussels

that have occupied the Hanford Reach of the Columbia River for thousands of years were used to assess these long-term patterns.

## 2.0 METHODS

### 2.1 STUDY AREA

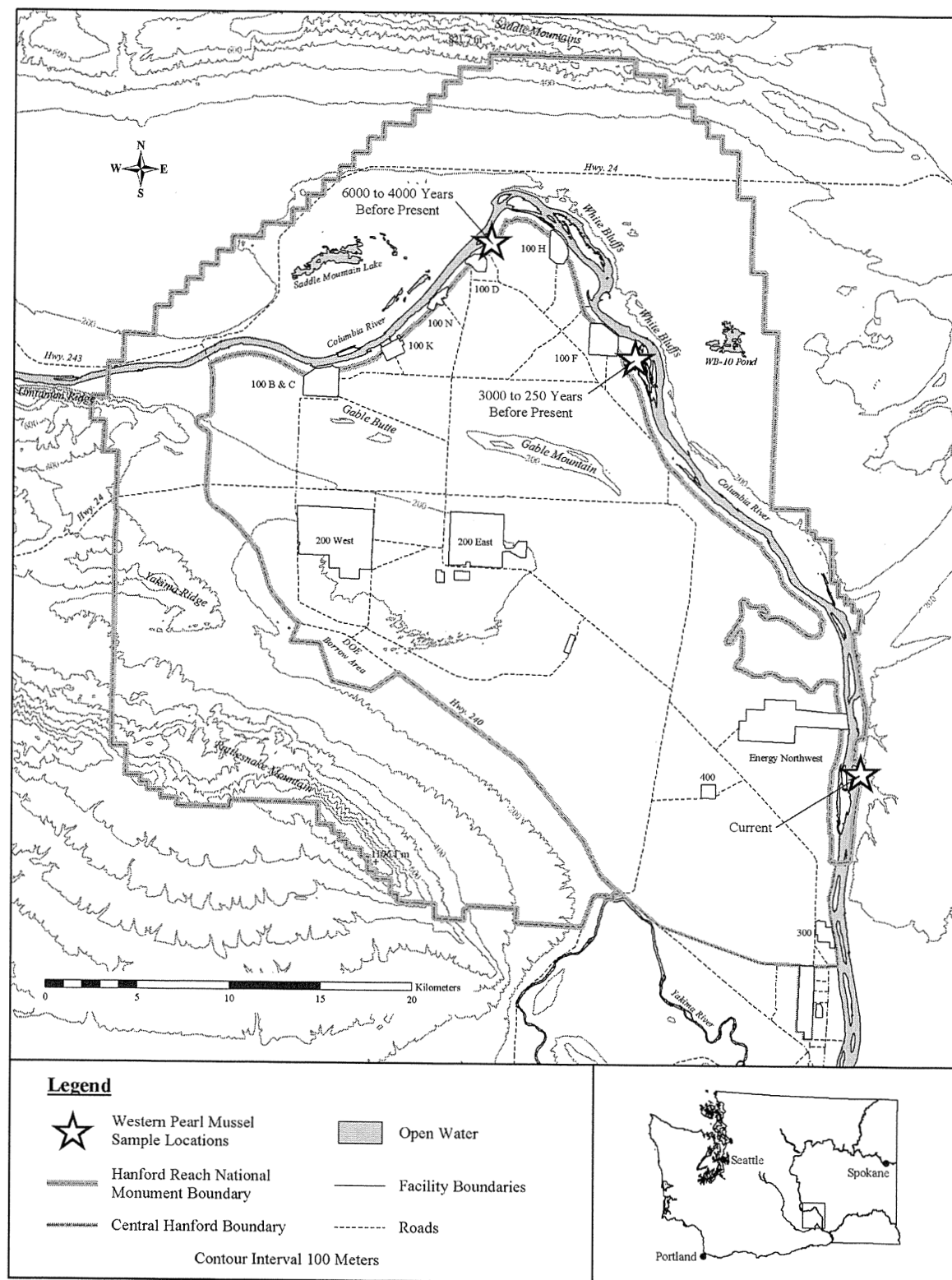
The Hanford Site is located within the Columbia Basin of southeastern Washington State (Figure 1) and is a semiarid region of the Pacific Northwest. The area, in general, is characterized by steppe vegetation (Daubenmire 1970) with approximately 16 cm of annual precipitation (Hoitink and Burk 1994). The Columbia River runs through the Columbia Basin. Approximately 90 km (56 mi) of the Columbia River runs through the Hanford Site, and this portion of the river was designated the Hanford Reach National Monument in 2000 (Figure 1). The Hanford Reach is one of the last free-flowing portions of the Columbia River and contains substrate characteristics (cobble, gravel, sand/silt) suitable for a number of the native freshwater mussels that are known to exist in the Pacific Northwest.

Figure 1 illustrates three locations where native mussel shell samples were collected along the Hanford Reach and represent three general periods of time (Table 1). Two sets of shell samples representing two pre-operational time periods were obtained for this study and were located near 100-D and 100-F facilities. Ten archeological test units were excavated near 100-D, a concentrated site contained within a shallow depression on a high terrace above the Columbia River. Seven radiocarbon dates from materials recovered from this test site indicated three occupational periods extending from 5950 B.P. to 1410 B.P. Shell samples obtained from the 100-D site used in this analysis were dated from  $5880 \pm 70$  B.P. to  $4880 \pm 80$  B.P. Thirty-three archeological test units were excavated near 100-F, an expansive site distributed across a low terrace of the Columbia River. Ten radiocarbon dates from materials recovered from this site indicated as many as six occupational periods extending from 3000 B.P. to 100 B.P. Shell samples obtained from the 100-F site used in this analysis were dated from  $2750 \pm 30$  B.P. to 250 B.P. Tiller et al. (2005) found indications of remnant populations of the western pearl shell mussel along the Hanford Reach. Shells from animals that had recently died were collected along the eastern shoreline of the river near the Energy Northwest facility (see Figure 1) and analyzed to represent uptake and accumulation of radionuclides and chemicals when the Hanford Site was operational.

### 2.2 SAMPLE COLLECTIONS

Mussel shell samples were identified to genera based on morphological characteristics of the shell recognized by Turgeon et al. (1998) and further defined according to Smith et al. (2001). Pre-operational shell samples of the western pearlshell mussel were collected from 100-D and 100-F archeological sites during February to May 2001. These shell samples were briefly washed in tap water and then placed in plastic bags and placed in locked storage at the Washington State University's Consolidate Information Center until this study began in April 2005.

Figure 1. Mussel Shell Sample Sites Along the Hanford Reach of the Columbia River.



**Table 1. Mussel Shell Sample Sets Used to Classify Contaminant Concentrations by Time Period.**

| <b>Radiocarbon Years Before Present</b> | <b>Time Period Estimation Technique</b>   | <b>Collection Technique</b>                                 | <b>General Location (See Figure 1)</b> |
|---|---|---|--|
| 5880 ± 70 to 4880 ± 80                  | Radiocarbon dating  | Excavation site 45BN888 (2 to 20 cm below ground surface)   | 100-D Area                             |
| 2750 ± 30                               | Radiocarbon dating  | Excavation site 45BN606 (90 to 110 cm below ground surface) | 100-F Area                             |
| 2610 ± 30 to 2180 ± 40                  | Radiocarbon dating  | Excavation site 45BN606 (70 to 110 cm below ground surface) | 100-F Area                             |
| 1100 to 250                             | Estimated based on multidimensional analysis relative to radiocarbon dates in deeper and shallower soil | Excavation site 45BN606 (4 to 40 cm below ground surface)   | 100-F Area                             |
| Current                                 | Shell condition (coloration of periostracum and nacreous tissue, hinge integrity)                       | Snorkeling  | Energy Northwest                       |

Snorkel-based surveys were employed to locate, identify, and collect mussel shells that had recently died during September 2004 (Strayer and Smith 2003). Three shell samples of the western pearlshell mussel were collected during October 2004 and were stored in zip-lock plastic bags under lock and key until this study began in April 2005. The coloration of periostracum (external surface of the shell), nacreous tissues (inside portions of the shell), and integrity of the intact hinge ligament provided evidence that the pearlshell mussel specimens had died within the past decade, and likely within the past three years (Frest 2005).

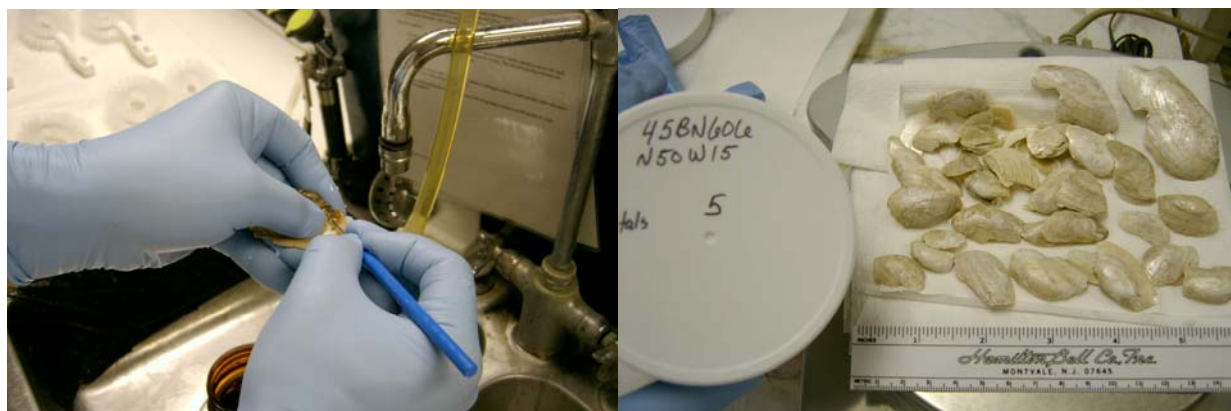
### 2.3 AGE DETERMINATION OF SPECIMENS

Adult western pearlshell mussels have been known to live 60 to 100+ years (Toy 1998). Age estimates can be determined by counting the annuli growth rings on the external surface (periostracum) of the shells (Neves and Moyer 1988, Dunca and Mutvei 2001). Specimens that were collected during 2004 (i.e., those living during Hanford Site operational period) were aged by an expert malacologist (T. J. Frest, Deixis Consultants). The mussel shells obtained from archeological sites (i.e., those representing two pre-operational periods) were not fully intact valves and much of the periostracum had been eroded, preventing annuli growth rings to be accurately counted to estimate their ages at time of death.

## 2.4 SAMPLE PREPARATIONS

To prepare shell samples for analyses, the sampling team donned nitrile powder-free surgical gloves that were pre-cleaned using liquinox™ and de-ionized water solution and then thoroughly rinsed free of the detergent residues. A stainless steel dissecting needle and scalpel (pre-cleaned between each sample) were used to remove periostracum tissues and dirt on the surfaces of all shells (Figure 2). Water equipment blanks were prepared for each sample analyses. Sample weights ranged from ~30 to 150 g. A number of shell fragments were combined to represent a single sample, depending on the sample mass required by the analytical laboratories.

**Figure 2. Mussel Shell Sample Preparations.**



*The photograph on left depicts removal of excess dirt and periostracum tissues, and the photograph on the right shows shell tissue sample after periostracum surfaces were removed.*

## 2.5 SAMPLE ANALYSES

Shells samples were analyzed for a suite of 14 radionuclide, 12 trace metals, and 71 organic compounds using techniques listed in Table 2. Detailed descriptions of each of the analytical methods are described in Appendices A, B, and C.

**Table 2. General Compound Classes, Analytical Techniques, and Analytes Examined in Shell Tissues. (2 Pages)**

| General Compound Class         | Analytical Method   | Analyte(s)  |
|--------------------------------|---|---|
| Total radio-strontium          | Gas proportional counting (GPC)   | Strontium   |
| Plutonium and uranium isotopes | Alpha spectroscopy (AEA)  | Pu-238, Pu-239/240, U-234, U-235, U-238                       |
| Gamma-emitting isotopes        | Gamma energy analysis (GEA)   | Cs-137, Co-60, Eu-152, Eu-154, Eu-155, Ra-226, Ra-228, Th-228 |
| Trace metals                   | Inductively coupled plasma atomic emission spectrometry (ICP-AES) 6010B | Sn, As, Ba, Cd, Cr, Cu, Pb, Li, Ag, Zn                        |
| Mercury                        | Cold-vapor atomic absorption (CVAA) 7471A                               | Hg  |

**Table 2. General Compound Classes, Analytical Techniques, and Analytes Examined in Shell Tissues. (2 Pages)**

| General Compound Class           | Analytical Method                                  | Analyte(s)  |
|----------------------------------|--|---|
| Polychlorinated biphenyls (PCBs) | Gas chromatography (GC) 8082                       | Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260 |
| Semivolatile organics            | Gas chromatography/mass spectrometry (GC/MS) 8270C | See Appendix C                                    |

## 2.6 DATA ANALYSIS

Descriptive statistics of the trace metals and organic datasets included means, minimum, and maximum observed concentrations. Median values were used to represent central tendencies of radiological concentrations. The nonparametric multi-response permutation procedure (Mielke 1991) was used to test for significantly different ( $p \leq 0.05$ ) tissue concentrations between time periods. Linear regressions were also calculated using Microsoft™ Excel software to further assess possible correlations between the contaminant concentrations measured in shell tissue samples and time periods dated by radiocarbon techniques (Marceau and Sharpe 2002) when the organisms were thought to be living.

## 3.0 RESULTS

The following sections summarize radionuclides, organics, and trace metal sample results reported for mussel shells submitted during this study.

### 3.1 RADIONUCLIDE CONCENTRATIONS

A total of 10 composite shell samples were submitted for radionuclide analyses. Table 3 summarizes the number of samples submitted for each general time period and the frequency of radionuclide results reported above the analytical detection limits. Radionuclides were not typically detected above the analytical limits achieved (Table 3), with the exception of uranium-234, where 4 out of 10 samples showed uranium-234 levels slightly above the analytical detection limits (0.041 to 0.094 pCi/g wet weight). Radio-strontium and uranium-238 was detected in a few mussel shell samples as well, but none of the radionuclide levels reported indicate increasing or decreasing concentrations across each time period ( $p > 0.1$ ) examined during this study. Actual radionuclide results are provided in Appendix A.

**Table 3. Number of Mussel Shell Samples Submitted and Frequency of Radiological Results Reported Above Analytical Detection Limits for Three General Time Periods Examined.**

| Analyte         | Analytical Detection Limit(s)<br>(pCi/g wet wt.) | ~ 6000 to 4000 B.P.<br>(100-D Site) |   | ~ 3000 to 250 B.P.<br>(100-F Site) |   | ~ Current<br>(Energy Northwest) |   |
|-----------------|--|-------------------------------------|---|------------------------------------|---|---------------------------------|---|
|                 |  | Number of Samples                   | % Results Reported Above Analytical Detection | Number of Samples                  | % Results Reported Above Analytical Detection | Number of Samples               | % Results Reported Above Analytical Detection |
| Cs-137          | 0.03 - 0.6                                       | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Co-60           | 0.03 - 0.7                                       | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Eu-152          | 0.077 - 1.48                                     | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Eu-154          | 0.09 - 1.23                                      | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Eu-155          | 0.05 - 0.96                                      | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Pu-238          | 0.007 - 0.033                                    | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Pu-239/240      | 0.007 - 0.033                                    | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Ra-226          | 0.075 - 1.1                                      | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Ra-228          | 0.12 - 2.4                                       | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Th-228          | 0.09 - 1.36                                      | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Radio-strontium | 0.072 - 0.088                                    | 3                                   | 33  | 3                                  | 0%  | 4                               | 0   |
| Ur-234          | 0.041 - 0.094                                    | 3                                   | 33  | 3                                  | 33%   | 4                               | 50  |
| Ur-235          | 0.035 - 0.094                                    | 3                                   | 0   | 3                                  | 0%  | 4                               | 0   |
| Ur-238          | 0.047 - 0.087                                    | 3                                   | 0   | 3                                  | 33%   | 4                               | 25  |

### 3.2 ORGANIC COMPOUND CONCENTRATIONS

Eight samples were prepared and submitted for analyses of organic compounds, and all results were less than the analytical detection limits achieved (Appendix B). Lacking any PCBs or semivolatile organic results that were reported above their respective analytical detection limits, trends between the three time periods examined during this study could not be observed.

### 3.3 TRACE METAL CONCENTRATIONS

Nine mussel shell samples were submitted for analyses of twelve trace metals, comprising three samples from each time period as shown in Table 4. Concentrations of antimony, arsenic, cadmium, lead, mercury, and uranium were typically at or below analytical detection limits achieved (Table 4). Conversely, sample results reported for barium, copper, lithium, and zinc were all found at levels above the analytical detection limits. Sample results reported for chromium and silver were also measured at levels typically above the analytical detection limits (Table 4).

**Table 4. Mussel Shell Sample Sizes, Trace Metal Analytes, and the Frequency of Trace Metal Results Reported Above Analytical Detection Limits.**

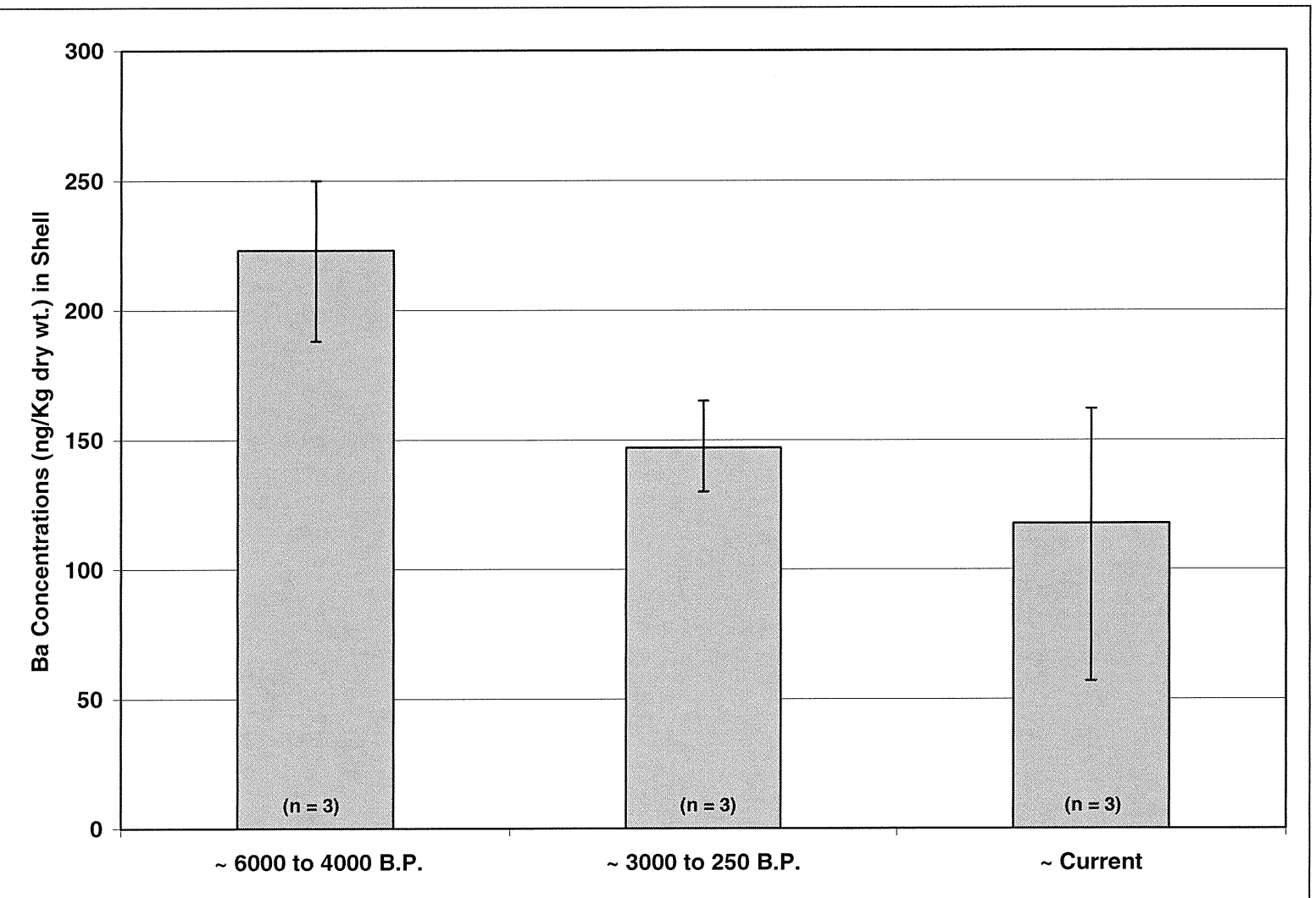
| Analyte               | Analytical Detection Limit(s)<br>(ng/kg dry wt.) | ~ 6000 to 4000 B.P.<br>(100-D Site) |   | ~ 3000 to 250 B.P.<br>(100-F Site) |   | ~ Current<br>(Energy Northwest Site) |   |
|-----------------------|--|-------------------------------------|---|------------------------------------|---|--------------------------------------|---|
|                       |  | Number of Samples                   | % Results Reported Above Analytical Detection | Number of Samples                  | % Results Reported Above Analytical Detection | Number of Samples                    | % Results Reported Above Analytical Detection |
| Antimony <sup>a</sup> | 0.94 - 1.3                                       | 3                                   | 0   | 3                                  | 33  | 3                                    | 0   |
| Arsenic               | 1.2 - 2.3  | 3                                   | 33  | 3                                  | 0   | 3                                    | 0   |
| Barium                | 0.22 - 0.26                                      | 3                                   | 100   | 3                                  | 100   | 3                                    | 100   |
| Cadmium <sup>a</sup>  | 0.17 - 0.24                                      | 3                                   | 0   | 3                                  | 0   | 3                                    | 33  |
| Chromium              | 0.17 - 0.24                                      | 3                                   | 66  | 3                                  | 100   | 3                                    | 66  |
| Copper                | 0.21 - 0.29                                      | 3                                   | 100   | 3                                  | 100   | 3                                    | 100   |
| Lead <sup>a</sup>     | 0.81 - 1.1                                       | 3                                   | 0   | 3                                  | 0   | 3                                    | 0   |
| Lithium               | 0.05 - 0.06                                      | 3                                   | 100   | 3                                  | 100   | 3                                    | 100   |
| Mercury <sup>a</sup>  | 0.01 - 0.02                                      | 3                                   | 0   | 3                                  | 0   | 3                                    | 0   |
| Silver                | 0.21 - 0.3                                       | 3                                   | 0   | 3                                  | 66  | 3                                    | 33  |
| Uranium <sup>a</sup>  | 3.5 - 4.9  | 3                                   | 0   | 3                                  | 0   | 3                                    | 0   |
| Zinc                  | 0.21 - 0.3                                       | 3                                   | 100   | 3                                  | 100   | 3                                    | 100   |

<sup>a</sup>Data sets typically reported at or below analytical detection.

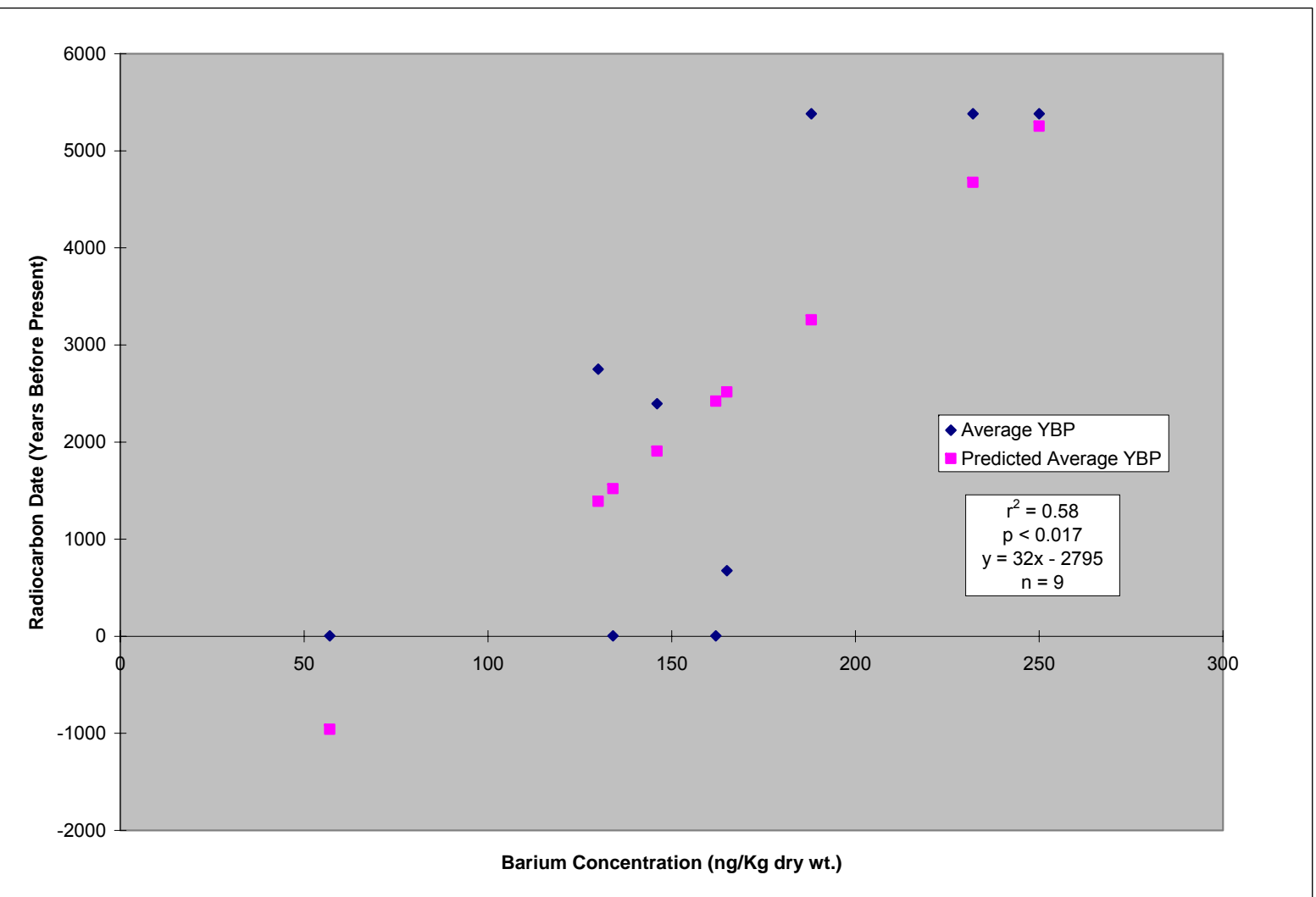
Statistically significant ( $p \leq 0.05$ ) patterns were limited to barium, showing substantial decrease from pre-operational periods (6000 to 4000 B.P.) to current times (Figure 3). The individual barium concentrations were also inversely related to the dates when the animals were assumed to be living (Figure 4).



**Figure 3. Mean, Minimum, and Maximum Barium Concentrations Measured in Mussel Shell Samples Across Three Time Periods.**



**Figure 4. Relationship of Barium Concentrations Measured in Mussel Shell Samples and Time Period when Organisms Were Living.**



## 4.0 DISCUSSION

The utility of biota to monitor and assess contaminant levels in the environment has been recognized since the turn of the century (Phillips and Segar 1986, Johnson et. al 1993). However, we found no studies to date that have attempted to assess pre-historic trends of radionuclides, trace metals, or organic pollutants in the environments using biota tissues. The current study integrated archeological archives with current biological sampling efforts to examine the utility of mussel shell tissues in assessing the long-term patterns of various pollutants in the environment that may have changed as the result of Hanford Site operations.

Overall, mussel shells appear to be a useful tool for assessing long-term patterns of some radionuclides and trace metals in the current study, and provided some insight into background concentrations that may be expected in the absence of anthropogenic sources of these contaminants in the Columbia River environment. The three western pearlshell mussel specimens that were used in this study to represent accumulation of pollutants during Hanford Site operations were estimated to be 59, 61, and 65 years  $\pm$  3 years of age at death. The external surfaces of the mussel tissues were successfully removed using the scraping techniques employed in this study and probably reduced variability of the results and cross-contamination of soil particles embedded in the periostracum portion of the shells. Ultrasonic tools such as those used in the orthodontics industry or laser ablation techniques may be more effective and less time intensive than the techniques used during this study.

The species of mussel found at both archeological sites (*Margaritopsis falcata*) reported in Marceau and Sharpe (2002) are no longer common in much of the Columbia River system today (Tiller et al. 2005). It is unclear why there has been a decline of this species in these free-flowing portions of the Columbia River. The habitat of this species is generally described to be a mixture of gravel, sand, and boulders with relatively cold fast running water and little to no sedimentation. A number of regions along the Hanford Reach of the Columbia still have these substrate characteristics today, but increasing water temperatures during the summer and fall seasons, siltation, and eutrophication rates, as well as decreases in dissolved oxygen, have likely occurred with the advent of Columbia Irrigation project for farming and four major hydroelectric dams being established upstream of this region during the mid- to late 1900s. The decline of native freshwater mussels in North America has been primarily attributed to a number of anthropogenic activities, including physical habitat destruction, pollution (particularly including eutrophication), and commercial exploitation (Patzner and Muller 2000, Young et al. 2000).

Environmental levels of PCBs, lead, and cesium-137 are known to have increased during the advent of the 1900s but were not detected in mussel shell samples measured during this study (Whicker and Shultz 1982, Magnus 1993). As such, these results indicate mussel shells may not be a sensitive indicator of changing environmental levels of compounds with short environmental half-lives or those that are not expected to sequester in calcium-rich tissues. However, long-lived radionuclides such as radio-strontium, plutonium, or uranium were not elevated in the mussel shell tissue samples that were living during Hanford Site operations. As well, trace metals results in the mussel shell samples reported above analytical detection limits did not suggest a substantial increase of these elements during Hanford Site operations.

Decreasing barium concentrations in mussel shell tissues over the 6,000-year period examined suggest macro-climatic factors have played a role in changing the river environment. The lack

of similar decreases in other crustal elements such as zinc and lead make it unlikely that the barium trends observed were artifacts of sample preparation procedures from cross-contamination of soil particles embedded in the archeological shell samples. The removal of virtually all periostracum tissues on the mussel shell samples before they were submitted for chemical and radiological analyses greatly reduced this possible source of error. Plausible mechanisms involving the accumulation of barium in the oldest mussel shells examined in this study include hydrothermal, biogenic, and diagenic processes (Mannan 2002). Substantial climatic changes have been described for the Columbia Basin during this time period (Chatters 1995, Chatters and Hoover 1992). Archeological and hydrogeological evidence provided in these studies demonstrate that this region has undergone dramatic shifts of climatic warming following a period of climatic cooling after about 3500 B.P. Historically high rates of snowmelt, run-off, and subsequent scouring of basaltic rock material containing barite, an element known to occur throughout the northern ranges of the Columbia River Basin (Valentine 1949), is one plausible mechanism explaining relatively higher levels of dissolved forms of barium that was available to mussels living in the Columbia River 6000 B.P. Another plausible source of barium in the Columbia Basin environments around the time the oldest mussel shells were living originates from the eruption of Mount Mazama, which occurred about 7680 B.P. and deposited ash containing silicates.

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**APPENDIX A**

**RADIONUCLIDE METHODS AND CONCENTRATIONS  
IN MUSSEL SHELLS**

## **APPENDIX A**

### **RADIONUCLIDE METHODS AND CONCENTRATIONS IN MUSSEL SHELLS**

#### **GAMMA ENERGY ANALYSIS (GEA)**

Gamma rays interact with germanium-based high-resolution detectors to produce electron-hole pairs (as in transistors) that are collected by an applied electric field. The system determines the energy of specific gamma rays associated with gamma-emitting radionuclides. Computer integration and conversion yields individual isotope identification and quantitation.

#### **ACTINIDE ANALYSIS (PLUTONIUM AND URANIUM ISOTOPES)**

Actinide analysis requires dissolution/chemical separation/purification of the sample to minimize solids (presence of more than trace amounts of solids on the counting "mount" results in severe attenuation of the alpha activity and broadens the energy "peak" reducing resolution), concentrate the activity from the element of interest, and eliminate overlap of activity energies from mixed elements present. Separation is typically performed using ion exchange, solvent extraction, or element-specific absorbers. The resulting material is mounted and submitted for alpha energy analysis.

#### **ALPHA ENERGY ANALYSIS (AEA) (ALSO KNOWN AS ALPHA SPECTROSCOPY)**

Typical instrumentation relies on solid state silicon-based detectors. AEA detectors not only record the presence of an alpha particle, but also measure the energy of the particle. Computer integration and conversion yields individual isotope identification and quantitation.

#### **TOTAL RADIOACTIVE STRONTIUM ANALYSIS**

Total radioactive strontium analysis requires dissolution/chemical separation/purification of the sample to minimize excess solids (presence of significant amounts of solids on the counting "mount" results in attenuation of the beta activity), concentrate the activity from the element of interest, and eliminate any beta emissions from any other elements present. (Typically, any beta activity present in the mount will be detected.) Separation is typically performed using repetitive precipitation/dissolution of strontium salts. No additional separations are performed for specific isotopes of strontium. For any sample greater than 5 years old, the only remaining strontium beta activity is from strontium-90. The resulting material is mounted and submitted for beta analysis using gas proportional counting.

#### **GAS PROPORTIONAL COUNTING (GPC)**

Based on operation of an ionization type detector (decay particle enters the detector and ionizes a molecule of internal gas) in a range where the output is proportional to the activity of the sample.



Table A-1. Concentrations (pCi/g wet wt.) in Mussel Shells for Radionuclides.

| Customer ID               | 45 BN 888:N158 W4 |      |        | 45 BN 888:N158 W4 |      |        | 45 BN 888:N157.5 W6.5 |      |        | 45 BN 606:N170 W90 |      |        | 45 BN 606:N50 W15 |      |        | 45 BN 606:N62 W16 |      |        | None      |      |        | None      |      |        | None      |      |        | None      |      |        |
|---------------------------|-------------------|------|--------|-------------------|------|--------|-----------------------|------|--------|--------------------|------|--------|-------------------|------|--------|-------------------|------|--------|-----------|------|--------|-----------|------|--------|-----------|------|--------|-----------|------|--------|
| Time period (YBP)         | 4880 to 5880      |      |        | 4880 to 5880      |      |        | 4880 to 5880          |      |        | 2750               |      |        | 2180 to 2610      |      |        | 250 to 1100       |      |        | Recent    |      |        | Recent    |      |        | Recent    |      |        | Recent    |      |        |
| HEIS ID                   | J030H0            |      |        | J030H1            |      |        | J030H2                |      |        | J030H3             |      |        | J030H4            |      |        | J030H5            |      |        | J030H6    |      |        | J030H7    |      |        | J030H7-A  |      |        | J030H8    |      |        |
| Date of Analyses          | 05-Apr-05         |      |        | 05-Apr-05         |      |        | 05-Apr-05             |      |        | 05-Apr-05          |      |        | 05-Apr-05         |      |        | 05-Apr-05         |      |        | 20-Apr-05 |      |        | 11-Apr-05 |      |        | 11-Apr-05 |      |        | 20-Apr-05 |      |        |
| Constituent               |                   | Qual | PQL    |                   | Qual | PQL    |                       | Qual | PQL    |                    | Qual | PQL    |                   | Qual | PQL    |                   | Qual | PQL    |           | Qual | PQL    |           | Qual | PQL    |           | Qual | PQL    |           | Qual | PQL    |
| Cs-137                    | -0.203            | U    | 0.449  | -0.0167           | U    | 0.602  | 0.149                 | U    | 0.597  | -0.0811            | U    | 0.108  | -0.0459           | U    | 0.137  | 0.0625            | U    | 0.177  | -0.00657  | U    | 0.055  | -0.0443   | U    | 0.224  | 0.0373    | U    | 0.135  | 0.00725   | U    | 0.032  |
| Co-60                     | -0.00018          | U    | 0.587  | 0                 | U    | 0.159  | 0.157                 | U    | 0.728  | 0.124              | U    | 0.574  | 0.00841           | U    | 0.131  | 0.01              | U    | 0.213  | 0.0255    | U    | 0.067  | -0.0441   | U    | 0.239  | -0.00296  | U    | 0.15   | -0.00915  | U    | 0.033  |
| Eu-152                    | 0.45              | U    | 1.48   | 0.0192            | U    | 0.947  | 0.126                 | U    | 0.91   | 0.00461            | U    | 1.13   | -0.047            | U    | 0.347  | 0.0238            | U    | 0.382  | -0.0559   | U    | 0.125  | 0.079     | U    | 0.599  | 0.104     | U    | 0.335  | -0.0341   | U    | 0.077  |
| Eu-154                    | 0                 | U    | 0.583  | -0.16             | U    | 0.429  | -0.203                | U    | 0.574  | 0.168              | U    | 1.23   | 0.176             | U    | 0.507  | -0.0496           | U    | 0.462  | 0.0198    | U    | 0.195  | 0.00785   | U    | 0.736  | -0.141    | U    | 0.39   | -0.0164   | U    | 0.094  |
| Eu-155                    | 0.273             | U    | 0.958  | -0.133            | U    | 0.79   | -0.0484               | U    | 0.731  | -0.0404            | U    | 0.738  | -0.0257           | U    | 0.274  | -0.0142           | U    | 0.295  | -0.0193   | U    | 0.09   | -0.0077   | U    | 0.443  | -0.0469   | U    | 0.249  | 0.00382   | U    | 0.054  |
| Pu-238                    | 0.00506           | U    | 0.0069 | 2.2E-07           | U    | 0.0192 | 0                     | U    | 0.0053 | -0.00318           | U    | 0.0295 | 1.8E-07           | U    | 0.02   | -0.00637          | U    | 0.0239 | 0.00496   | U    | 0.0155 | -0.00712  | U    | 0.0331 | 0.00331   | U    | 0.019  | -0.00477  | U    | 0.0222 |
| Pu-239/240                | 0.00505           | U    | 0.0068 | 2.17E-07          | U    | 0.0192 | -0.00196              | U    | 0.0144 | -0.00317           | U    | 0.0234 | -0.00271          | U    | 0.0326 | 0.00454           | U    | 0.0211 | -0.0036   | U    | 0.0193 | 0.00356   | U    | 0.0096 | -0.00221  | U    | 0.0289 | -0.00334  | U    | 0.0236 |
| Ra-226                    | -0.609            | U    | 0.991  | -0.0799           | U    | 0.668  | -0.00982              | U    | 1.11   | 0.0896             | U    | 0.97   | 0.265             | U    | 0.416  | 0.082             | U    | 0.446  | 0.0248    | U    | 0.135  | 0.123     | U    | 0.598  | 0.287     | U    | 0.304  | 0.135     | U    | 0.075  |
| Ra-228                    | 0.34              | U    | 2.41   | -0.284            | U    | 0.4    | -0.196                | U    | 0.547  | -0.317             | U    | 0.434  | -0.309            | U    | 0.582  | 0.137             | U    | 0.73   | -0.154    | U    | 0.27   | -0.488    | U    | 0.963  | -0.12     | U    | 0.446  | 0.0441    | U    | 0.124  |
| Th-228 GEA                | -0.251            | U    | 1.14   | 0.277             | U    | 0.995  | 0.379                 | U    | 1.36   | 0.151              | U    | 1.16   | 0.00207           | U    | 0.462  | 0.401             | U    | 0.616  | 0.00133   | U    | 0.182  | 0.155     | U    | 0.861  | 0.113     | U    | 0.379  | 0.0472    | U    | 0.09   |
| Total beta radiostrontium | 0.026             | U    | 0.084  | 0.315             |      | 0.079  | -0.0023               | U    | 0.086  | 0.0135             | U    | 0.077  | -0.0255           | U    | 0.081  | -0.0067           | U    | 0.072  | -0.0002   | U    | 0.088  | 0.0239    | U    | 0.082  | 0.0233    | U    | 0.075  | 0.0167    | U    | 0.077  |
| U-234                     | 0.0483            | U    | 0.094  | 0.075             |      | 0.041  | 0.0225                | U    | 0.09   | 0.00881            | U    | 0.066  | -0.00129          | U    | 0.054  | 0.389             |      | 0.072  | 0.00884   | U    | 0.07   | 0.105     |      | 0.047  | 0.256     |      | 0.054  | -0.00051  | U    | 0.046  |
| U-235                     | -0.00538          | U    | 0.0941 | -0.003            | U    | 0.0718 | -0.00474              | U    | 0.067  | -0.00126           | U    | 0.0527 | -0.00258          | U    | 0.0618 | 0.0136            | U    | 0.0631 | 0.0109    | U    | 0.0594 | -0.00175  | U    | 0.0731 | 0.0258    | U    | 0.0349 | 0.0122    | U    | 0.0463 |
| U-238                     | 0.0322            | U    | 0.0857 | -0.003            | U    | 0.0718 | -6.9E-06              | U    | 0.0872 | -0.00757           | U    | 0.0795 | 0.0103            | U    | 0.0618 | 0.436             |      | 0.0631 | 0.0245    | U    | 0.0562 | 0.07      | U    | 0.0474 | 0.269     |      | 0.0539 | 0.0372    | U    | 0.0512 |

## **APPENDIX B**

### **POLYCHLORINATED BIPHENYLS AND SEMIVOLATILE ORGANIC METHODS AND CONCENTRATIONS REPORTED IN MUSSEL SHELLS**

## **APPENDIX B**

### **POLYCHLORINATED BIPHENYLS AND SEMIVOLATILE ORGANIC METHODS AND CONCENTRATIONS REPORTED IN MUSSEL SHELLS**

#### **POLYCHLORINATED BIPHENYLS (PCBs) BY GAS CHROMATOGRAPHY – METHOD 8082**

A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique. Aqueous samples are extracted at neutral pH with methylene chloride using separatory funnel, continuous liquid-liquid extractor, or other appropriate technique. Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Soxhlet, automated Soxhlet, or other appropriate technique.

Extracts for polychlorinated biphenyl analysis may be subjected to a sulfuric acid/potassium permanganate cleanup designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine or organophosphorus pesticides.

After cleanup, the extract is analyzed by injecting a 2- $\mu$ L aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD). The chromatographic data may be used to determine the seven aroclors using "fingerprint" matching of chromatographic peaks and peak area summation.

#### **SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) – METHOD 8270C**

The samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) and are extracted with methylene chloride using separatory funnel, continuous liquid-liquid extractor, or other appropriate technique and then concentrated.

The semivolatile compounds are introduced into the GC/MS by injecting the sample extract into a gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) connected to the GC. Analytes eluted from the capillary column are introduced into the MS via a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

Table B-1. Concentrations (µg/Kg) in Mussel Shells for Organics. (3 Pages)

| Customer ID                    | 45 BN 888:N158 W4 |      |      | 45 BN 888:N158 W4 |      |      | 45 BN 888:N157.5 W6.5 |      |      | 45 BN 606:N170 W90 |      |      | 45 BN 606:N50 W15 |      |      | 45 BN 606:N62 W16 |      |      | None          |      |      | None          |      |      |
|--------------------------------|-------------------|------|------|-------------------|------|------|-----------------------|------|------|--------------------|------|------|-------------------|------|------|-------------------|------|------|---------------|------|------|---------------|------|------|
| Time period (YBP)              | 4880 to 5880      |      |      | 4880 to 5880      |      |      | 4880 to 5880          |      |      | 2750               |      |      | 2180 to 2610      |      |      | 250 to 1100       |      |      | Recent        |      |      | Recent        |      |      |
| HEIS ID                        | J030F0            |      |      | J030F1            |      |      | J030F2                |      |      | J030F3             |      |      | J030H4-A          |      |      | J030H5-A          |      |      | J030H7-C      |      |      | J030H7-D      |      |      |
| Date of Analyses               | 4/5/05 12:12      |      |      | 4/5/05 13:45      |      |      | 4/5/05 13:10          |      |      | 4/5/05 14:00       |      |      | 4/5/05 14:45      |      |      | 4/5/05 15:20      |      |      | 4/11/05 12:30 |      |      | 4/11/05 12:30 |      |      |
| Constituent                    |                   | Qual | PQL  |                   | Qual | PQL  |                       | Qual | PQL  |                    | Qual | PQL  |                   | Qual | PQL  |                   | Qual | PQL  |               | Qual | PQL  |               | Qual | PQL  |
| <b>PCBs</b>                    |                   |      |      |                   |      |      |                       |      |      |                    |      |      |                   |      |      |                   |      |      |               |      |      |               |      |      |
| Aroclor-1016                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1221                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1232                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1242                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1248                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1254                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| Aroclor-1260                   | 200               | U    | 200  | 500               | U    | 500  | 130                   | U    | 130  | 73                 | U    | 73   | 370               | U    | 370  | 470               | U    | 470  | 500           | U    | 500  | 500           | U    | 500  |
| <b>SVOAs</b>                   |                   |      |      |                   |      |      |                       |      |      |                    |      |      |                   |      |      |                   |      |      |               |      |      |               |      |      |
| 1,2,4-Trichlorobenzene         | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 1,2-Dichlorobenzene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 1,3-Dichlorobenzene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 1,4-Dichlorobenzene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2,4,5-Trichlorophenol          | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 2,4,6-Trichlorophenol          | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2,4-Dichlorophenol             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2,4-Dimethylphenol             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2,4-Dinitrophenol              | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 2,4-Dinitrotoluene             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2,6-Dinitrotoluene             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2-Chloronaphthalene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2-Chlorophenol                 | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2-Methylnaphthalene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2-Methylphenol (cresol, o-)    | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 2-Nitroaniline                 | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 2-Nitrophenol                  | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 3+4 Methylphenol (cresol, m+p) | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 3,3'-Dichlorobenzidine         | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |

Table B-1. Concentrations (µg/Kg) in Mussel Shells for Organics. (3 Pages)

| Customer ID                      | 45 BN 888:N158 W4 |      |      | 45 BN 888:N158 W4 |      |      | 45 BN 888:N157.5 W6.5 |      |      | 45 BN 606:N170 W90 |      |      | 45 BN 606:N50 W15 |      |      | 45 BN 606:N62 W16 |      |      | None          |      |      | None          |      |      |
|----------------------------------|-------------------|------|------|-------------------|------|------|-----------------------|------|------|--------------------|------|------|-------------------|------|------|-------------------|------|------|---------------|------|------|---------------|------|------|
| Time period (YBP)                | 4880 to 5880      |      |      | 4880 to 5880      |      |      | 4880 to 5880          |      |      | 2750               |      |      | 2180 to 2610      |      |      | 250 to 1100       |      |      | Recent        |      |      | Recent        |      |      |
| HEIS ID                          | J030F0            |      |      | J030F1            |      |      | J030F2                |      |      | J030F3             |      |      | J030H4-A          |      |      | J030H5-A          |      |      | J030H7-C      |      |      | J030H7-D      |      |      |
| Date of Analyses                 | 4/5/05 12:12      |      |      | 4/5/05 13:45      |      |      | 4/5/05 13:10          |      |      | 4/5/05 14:00       |      |      | 4/5/05 14:45      |      |      | 4/5/05 15:20      |      |      | 4/11/05 12:30 |      |      | 4/11/05 12:30 |      |      |
| Constituent                      |                   | Qual | PQL  |                   | Qual | PQL  |                       | Qual | PQL  |                    | Qual | PQL  |                   | Qual | PQL  |                   | Qual | PQL  |               | Qual | PQL  |               | Qual | PQL  |
| 3-Nitroaniline                   | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 4,6-Dinitro-2-methylphenol       | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 4-Bromophenylphenyl ether        | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 4-Chloro-3-methylphenol          | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 4-Chloroaniline                  | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 4-Chlorophenylphenyl ether       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| 4-Nitroaniline                   | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| 4-Nitrophenol                    | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| Acenaphthene                     | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Acenaphthylene                   | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Anthracene                       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Benzo(a)anthracene               | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Benzo(a)pyrene                   | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Benzo(b)fluoranthene             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Benzo(ghi)perylene               | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Benzo(k)fluoranthene             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Bis(2-chloro-1-methylethyl)ether | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Bis(2-Chloroethoxy)methane       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Bis(2-chloroethyl) ether         | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Bis(2-ethylhexyl) phthalate      | 210               | JB   | 1200 | 100               | JB   | 870  | 200                   | JB   | 1200 | 65                 | JB   | 1000 | 270               | JB   | 1900 | 130               | JB   | 1900 | 140           | JB   | 1900 | 1800          | U    | 1800 |
| Butylbenzylphthalate             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Carbazole                        | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Chrysene                         | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Di-n-butylphthalate              | 1200              | U    | 1200 | 870               | U    | 870  | 80                    | JB   | 1200 | 55                 | JB   | 1000 | 310               | J    | 1900 | 130               | J    | 1900 | 120           | J    | 1900 | 1800          | U    | 1800 |
| Di-n-octylphthalate              | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Dibenz[a,h]anthracene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Dibenzofuran                     | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Diethylphthalate                 | 1200              | U    | 1200 | 870               | U    | 870  | 70                    | J    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |

Table B-1. Concentrations (µg/Kg) in Mussel Shells for Organics. (3 Pages)

| Customer ID                  | 45 BN 888:N158 W4 |      |      | 45 BN 888:N158 W4 |      |      | 45 BN 888:N157.5 W6.5 |      |      | 45 BN 606:N170 W90 |      |      | 45 BN 606:N50 W15 |      |      | 45 BN 606:N62 W16 |      |      | None          |      |      | None          |      |      |
|------------------------------|-------------------|------|------|-------------------|------|------|-----------------------|------|------|--------------------|------|------|-------------------|------|------|-------------------|------|------|---------------|------|------|---------------|------|------|
| Time period (YBP)            | 4880 to 5880      |      |      | 4880 to 5880      |      |      | 4880 to 5880          |      |      | 2750               |      |      | 2180 to 2610      |      |      | 250 to 1100       |      |      | Recent        |      |      | Recent        |      |      |
| HEIS ID                      | J030F0            |      |      | J030F1            |      |      | J030F2                |      |      | J030F3             |      |      | J030H4-A          |      |      | J030H5-A          |      |      | J030H7-C      |      |      | J030H7-D      |      |      |
| Date of Analyses             | 4/5/05 12:12      |      |      | 4/5/05 13:45      |      |      | 4/5/05 13:10          |      |      | 4/5/05 14:00       |      |      | 4/5/05 14:45      |      |      | 4/5/05 15:20      |      |      | 4/11/05 12:30 |      |      | 4/11/05 12:30 |      |      |
| Constituent                  |                   | Qual | PQL  |                   | Qual | PQL  |                       | Qual | PQL  |                    | Qual | PQL  |                   | Qual | PQL  |                   | Qual | PQL  |               | Qual | PQL  |               | Qual | PQL  |
| Dimethyl phthalate           | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Fluoranthene                 | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Fluorene                     | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Hexachlorobenzene            | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Hexachlorobutadiene          | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Hexachlorocyclopentadiene    | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Hexachloroethane             | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Indeno(1,2,3-cd)pyrene       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Isophorone                   | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| N-Nitroso-di-n-dipropylamine | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| N-Nitrosodiphenylamine       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Naphthalene                  | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Nitrobenzene                 | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Pentachlorophenol            | 2900              | U    | 2900 | 2200              | U    | 2200 | 3000                  | U    | 3000 | 2500               | U    | 2500 | 4800              | U    | 4800 | 4600              | U    | 4600 | 4800          | U    | 4800 | 4500          | U    | 4500 |
| Phenanthrene                 | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Phenol                       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |
| Pyrene                       | 1200              | U    | 1200 | 870               | U    | 870  | 1200                  | U    | 1200 | 1000               | U    | 1000 | 1900              | U    | 1900 | 1900              | U    | 1900 | 1900          | U    | 1900 | 1800          | U    | 1800 |

**APPENDIX C**

**TRACE METAL METHODS AND CONCENTRATIONS  
MEASURED IN MUSSEL SHELLS**

## **APPENDIX C**

### **TRACE METAL METHODS AND CONCENTRATIONS MEASURED IN MUSSEL SHELLS**

#### **SAMPLE DIGESTION – SW-846 3050B**

For the digestion of samples, a representative 1 to 2 g (wet weight) or 1 g (dry weight) sample is digested with repeated additions of nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).

#### **INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY – METHOD 6010B**

Prior to analysis, samples must be solubilized or digested using appropriate sample preparation methods (e.g., acid digestion). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

This method describes multi-elemental determinations by inductively coupled plasma (ICP)-atomic emission spectrometry (AES) using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. In one mode of analysis the position used should be as free as possible from spectral interference and should reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

#### **MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE) – METHOD 7471A**

Prior to analysis, the solid or semisolid samples must be prepared using an aqua regia/potassium permanganate digestion. Method 7471 is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury.



Table C-1. Concentrations (ng/Kg dry wt.) in Mussel Shells for Metals.

| Customer ID       | 45 BN 888:N158 W4 |      |      | 45 BN 888:N158 W4 |      |      | 45 BN 888:N157.5 W6.5 |      |      | 45 BN 606:N170 W90 |      |      | 45 BN 606:N50 W15 |      |      | 45 BN 606:N62 W16 |      |      | None     |      |      | None     |      |      | None    |      |      | Equipment Blank |      |      |
|-------------------|-------------------|------|------|-------------------|------|------|-----------------------|------|------|--------------------|------|------|-------------------|------|------|-------------------|------|------|----------|------|------|----------|------|------|---------|------|------|-----------------|------|------|
| Time period (YBP) | 4880 to 5880      |      |      | 4880 to 5880      |      |      | 4880 to 5880          |      |      | 2750               |      |      | 2180 50 2610      |      |      | 250 to 1100       |      |      | Recent   |      |      | Recent   |      |      | Recent  |      |      | --              |      |      |
| HEIS ID           | J030F0            |      |      | J030F1            |      |      | J030F2                |      |      | J030F3             |      |      | J030H4-A          |      |      | J030H5-A          |      |      | J030H7-C |      |      | J030H7-D |      |      | J030F8  |      |      | J030H9          |      |      |
| Date of Analyses  | 4/5/05            |      |      | 4/5/05            |      |      | 4/5/05                |      |      | 4/5/05             |      |      | 4/5/05            |      |      | 4/5/05            |      |      | 4/11/05  |      |      | 4/11/05  |      |      | 4/20/05 |      |      | 4/11/05         |      |      |
| Constituent       |                   | Qual | PQL  |                   | Qual | PQL  |                       | Qual | PQL  |                    | Qual | PQL  |                   | Qual | PQL  |                   | Qual | PQL  |          | Qual | PQL  |          | Qual | PQL  |         | Qual | PQL  |                 | Qual | PQL  |
| Antimony          | 1.2               | U    | 1.2  | 1.3               | U    | 1.3  | 1.3                   | U    | 1.3  | 1.3                | U    | 1.3  | 1.4               |      | 1.2  | 1.2               | U    | 1.2  | 1.2      | U    | 1.2  | 0.94     | U    | 0.94 | 1.3     | U    | 1.3  | 1.3             | U    | 1.3  |
| Arsenic           | 1.6               | U    | 1.6  | 1.7               | U    | 1.7  | 2.3                   |      | 2.3  | 1.7                | U    | 1.7  | 1.6               | U    | 1.6  | 1.5               | U    | 1.5  | 1.6      | U    | 1.6  | 1.2      | U    | 1.2  | 1.7     | U    | 1.7  | 1.7             | U    | 1.7  |
| Barium            | 188               |      | 0.24 | 250               |      | 0.25 | 232                   |      | 0.26 | 130                |      | 0.25 | 146               |      | 0.24 | 165               |      | 0.24 | 162      |      | 0.24 | 134      |      | 0.22 | 57      |      | 0.25 | 0.25            | U    | 0.25 |
| Cadmium           | 0.22              | U    | 0.22 | 0.24              | U    | 0.24 | 0.24                  | U    | 0.24 | 0.23               | U    | 0.23 | 0.22              | U    | 0.22 | 0.21              | U    | 0.21 | 0.22     | U    | 0.22 | 0.17     | U    | 0.17 | 0.24    |      | 0.23 | 0.23            | U    | 0.23 |
| Chromium          | 0.22              | UC   | 0.22 | 0.45              | C    | 0.24 | 0.36                  | C    | 0.24 | 0.25               | C    | 0.23 | 0.39              | C    | 0.22 | 0.62              | C    | 0.21 | 0.53     | C    | 0.22 | 0.17     | UC   | 0.17 | 0.36    | C    | 0.23 | 0.23            | UC   | 0.23 |
| Copper            | 3.3               | C    | 0.27 | 2.3               | C    | 0.28 | 4                     | C    | 0.29 | 0.94               | C    | 0.28 | 1.9               | C    | 0.27 | 1.6               | BC   | 0.26 | 7.3      | C    | 0.27 | 3.8      | C    | 0.21 | 2.4     | C    | 0.28 | 0.61            | C    | 0.28 |
| Lead              | 1                 | U    | 1    | 1.1               | U    | 1.1  | 1.1                   | U    | 1.1  | 1.1                | U    | 1.1  | 1                 | U    | 1    | 1                 | U    | 1    | 1        | U    | 1    | 0.81     | U    | 0.81 | 1.1     | U    | 1.1  | 1.1             | U    | 1.1  |
| Lithium           | 0.42              | C    | 0.05 | 0.3               | C    | 0.06 | 0.33                  | C    | 0.06 | 0.35               | C    | 0.06 | 0.29              | C    | 0.06 | 0.45              | C    | 0.06 | 0.21     | C    | 0.06 | 0.18     | C    | 0.06 | 0.19    | C    | 0.06 | 0.08            | C    | 0.06 |
| Mercury           | 0.01              | U    | 0.01 | 0.02              | U    | 0.02 | 0.01                  | U    | 0.01 | 0.02               | U    | 0.02 | 0.02              | U    | 0.02 | 0.02              | U    | 0.02 | 0.01     | U    | 0.01 | 0.01     | U    | 0.01 | 0.02    | U    | 0.02 | 0.02            | U    | 0.02 |
| Silver            | 0.27              | U    | 0.27 | 0.29              | U    | 0.29 | 0.3                   | U    | 0.3  | 0.31               |      | 0.29 | 0.39              |      | 0.27 | 0.26              | U    | 0.26 | 0.28     | U    | 0.28 | 0.21     | U    | 0.21 | 0.32    |      | 0.29 | 0.34            |      | 0.29 |
| Uranium           | 4.4               | U    | 4.4  | 4.8               | U    | 4.8  | 4.9                   | U    | 4.9  | 4.7                | U    | 4.7  | 4.5               | U    | 4.5  | 4.3               | U    | 4.3  | 4.5      | U    | 4.5  | 3.5      | U    | 3.5  | 4.9     | U    | 4.9  | 4.7             | U    | 4.7  |
| Zinc              | 2.2               | C    | 0.27 | 4.5               | C    | 0.29 | 1.3                   | C    | 0.3  | 1.2                | C    | 0.29 | 1.1               | C    | 0.27 | 1.4               | C    | 0.26 | 1.9      | C    | 0.28 | 1.4      | C    | 0.21 | 2.5     | C    | 0.29 | 1.1             | C    | 0.29 |

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