

3.0 Results

3.1 Contaminant Sources

Source samples were collected throughout the study area at several locations representing potential contaminant input sources such as oil and gas activities (crude oil and produced water), coals, municipal discharges, boat harbors, riverine and coastal inputs (Section 2.1.3). The results were used to compare concentrations and distributions of contaminants found in the sediment samples from zones 0, 1, 2, 3, and 4 to potential known contaminant sources. The source samples from surface sediment, oil, coal, and water matrices were analyzed for organics and metals. In addition, the source sample sediments were analyzed for grain size and TOC.

3.1.1 Physical Measurements

The TOC content for bottom sediments from the Susitna and Copper Rivers, two primary sediment sources to outermost Cook Inlet and the Shelikof Strait, average 0.20 ± 0.01 percent and 0.14 ± 0.02 percent, respectively (Table 3-1). Low TOC values in sediments from these two rivers reflect the high sand content. For example, bottom sediment from the Susitna River has 56.2 percent sand, 37.9 percent silt and only 5.9 percent clay. The Copper River contains 35.8 percent sand, 48.7 silt and 15.5 percent clay. In contrast, bottom sediment recovered from Homer Harbor, also a potential source of sediment to the study area, contains 1.6 percent TOC, 5.6 percent sand, 43.6 percent silt and 50.7 percent clay. The TOC content of a coal sample from Homer, Alaska is 67.1 percent (Table 3-1).

3.1.2 Organics

Analyses for SHC, PAH, and S/T target analytes were conducted on the various source samples, and included the following: crude oil from Cook Inlet; Swanson River Field oil; seep oil from Well Creek; coals from Cook Inlet, Homer coals, Ninilchik, Matanuska, Coyote Lake, and Beluga; sediments from the Susitna River, Copper River, Homer Harbor, Matanuska River, Alaska Coastal Current, and Augustine Island; Trading Bay produced water; and Point Woronzof municipal effluent. Inputs from crude oil (e.g., seeps), produced water, municipal effluent, and coal were all considered to be the potential source(s) of organic hydrocarbons to outermost Cook Inlet and the Shelikof Strait (Boehm *et al.*, 1998).

Results for each source sample are summarized in Table 3-2 as total PAH, total petroleum hydrocarbons (PHC), and total S/T concentrations. Where more than one sample was analyzed for a source (e.g., Copper River, Susitna River, and Homer Harbor), an average is presented. For the Cook Inlet crude oil, the source sample as well as all Cook Inlet crude “check” oils that were analyzed with respective PAH, SHC, and S/T field sample analyses were averaged together. The complete organics results data tables are presented in Appendix B. Figures 3-1 through 3-18 provide a representative GC/FID chromatogram (top), PAH distribution histogram (middle), and S/T extracted ion chromatogram (bottom) for each source sample type. The GC/FID chromatograms represent the total signal detected by the instrument (GC/FID) during the sample analysis. The extracted ion chromatogram is similar, but represents the signal of only one ion or

mass (in this case mass 191 which is characteristic of triterpanes) from the total signal detected by the mass spectrometer (GC/MS) during the sample analysis.

3.1.2.1 Source Oils

Cook Inlet Crude. Results for the Cook Inlet crude oil show an average total PHC concentration of $700,000 \pm 34,000 \mu\text{g/g}$ ($n=24$). The Cook Inlet crude oil sample chromatogram (Figure 3-1) reveals a predominance of resolved n-alkanes in the C8 through C34 carbon range, typical for a fresh crude oil. An unresolved complex mixture (UCM - seen as a baseline rise) extends across the entire n-alkane range. The distribution of alkanes gradually tapers from highest concentrations of lower molecular weight carbon alkanes (C12) down to the higher molecular weight carbon compounds (C34). The crude oil source results may be used to typify possible hydrocarbon contributions from fresh crude oil and/or seep areas in the Shelikof Strait and Cook Inlet in the sediment samples.

The results of GC/MS analyses of Cook Inlet crude oil show an average total PAH concentration of $13,000 \pm 1,000 \mu\text{g/g}$ ($n=29$), or 1.3 percent PAH. The distribution of the PAH analytes (Figure 3-1) shows a typical petrogenic PAH signature, with an abundance of 2- and 3-ring PAH (naphthalenes through phenanthrenes), substantially lower levels of 4-ring PAH (fluoranthenes/pyrenes and chrysenes) and only traces of 5- and 6-ring PAH. The Cook Inlet crude oil has a low sulfur content as indicated by the low levels of the 3-ring, sulfur-containing dibenzothiophenes. The observed PAH distribution with the C-2 or C-3 alkyl homologues greater than the parent PAH is also characteristic of petroleum PAH.

The steranes and triterpanes in the Cook Inlet crude averaged $510 \pm 81 \mu\text{g/g}$ ($n=21$) and exhibit a characteristic petroleum pattern dominated by the C30-triterpane, $17\alpha(\text{H})$ -hopane (Figure 3-1). In addition, the triterpane $18\alpha(\text{H})$ -oleanane, an indicator of higher plant (e.g., angiosperm) input to crude oils from the upper Cretaceous period and later (Peters and Moldowan, 1993), is absent. Thus the presence of oleanane can be used as an indicator of non-Cook Inlet crude oil inputs.

Swanson River Field Oil. The total petroleum hydrocarbons determined for the Swanson River Field oil sample was comparable to the Cook Inlet crude oil, at $630,000 \mu\text{g/g}$ (Table 3-2). The GC/FID chromatogram also portrays a virtually identical pattern of the resolved n-alkanes.

The total PAH concentration of $12,000 \mu\text{g/g}$ (Table 3-2) and overall PAH distribution (Figure 3-2) are also similar to that determined for the Cook Inlet crude oil, i.e., an increased abundance of alkyl homologues relative to both the parent PAH and higher molecular weight PAH.

Comparable concentrations and S/T distribution of the Swanson River Field oil with the Cook Inlet crude oil sample (Figures 3-2 and 3-1, respectively), lend further support to the consistencies found within each of the hydrocarbon subclasses.

Well Creek Seep Oil. On average, the Well Creek oil samples contained $660,000 \pm 130,000 \mu\text{g/g}$ ($n=2$) of total PHC. The sample chromatogram (Figure 3-3) exhibits a deficiency of resolved n-alkanes, likely due to the fair amount of weathering expected for a sample of this type. The UCM predominates the chromatogram and extends across the entire range of the GC/FID analysis.

The average total PAH for the Well Creek seep oil was $4,400 \pm 2,000$ $\mu\text{g/g}$ ($n=2$). As seen with the SHC chromatogram, the PAH distribution (Figure 3-3) also shows some degree of weathering. Losses of the low molecular weight PAH such as naphthalene, fluorene, and their alkyl homologues are common due to their heightened solubility/volatility when compared with the higher molecular weight compounds such as the alkylated phenanthrenes and fluoranthenes.

Steranes and triterpanes averaged 250 ± 5.6 $\mu\text{g/g}$ ($n=2$) in the Well Creek seep oil and, similar to observations in the Cook Inlet crude oil S/T extracted ion chromatogram, is also dominated by the C30-triterpane, $17\alpha(\text{H})$ -hopane and lacks the triterpane $18\alpha(\text{H})$ -oleanane (Figure 3-3).

3.1.2.2 Source Coals

Homer Spit Coal. This coal source sample was collected from a beach in the Kachemak Bay area and contained low concentrations of total PHC (1,200 $\mu\text{g/g}$) relative to the Cook Inlet crude oil. The GC/FID chromatogram of the coal reveals a complex mixture of hydrocarbons in the C26 to C34 carbon range; however, there is no homologous pattern of normal alkanes observed (Figure 3-4). Although the concentrations of PHC are low, the coal represents a potentially significant source of hydrocarbon input to the marine sediments of the region.

The PAH analysis of the coal sample reveals a substantially lower total PAH concentration (5.3 $\mu\text{g/g}$) than the Cook Inlet crude oil. The PAH distribution of the coal is comprised of 2- and 3-ring PAH, with a predominance of alkyl naphthalenes. Perylene, a biogenic PAH, which occurs naturally as a product of diagenesis of terrigenous organic matter in sediments, is one of the most abundant PAH compounds. The sulfur-containing dibenzothiophenes are low relative to the phenanthrenes, but appear to be slightly more abundant than in the Cook Inlet crude oil.

The S/T in the coal are distinctive and very different from Cook Inlet crude oil. The triterpanes are dominated by moretane (the largest peak in Figure 3-4), which is an indicator of recent biogenic material. In comparison, C30-hopane, the primary triterpane in Cook Inlet crude oil, is a relatively minor component in the coal. The large relative abundance of the C31-homohopane 22R isomer over the 22S isomer (peaks T22 and T21 in Figure 3-4, respectively) is further evidence of the immature/recent biogenic nature of the coal.

Homer Coal. This coal sample was very similar to that described above for the Homer Spit coal in that it contained low concentrations of total PHC (660 $\mu\text{g/g}$). In addition, the GC/FID chromatogram of the coal reveals a complex mixture of saturated hydrocarbons in the C26 to C34 carbon range (Figure 3-5).

The total concentration of PAH is fairly low, at 2.4 $\mu\text{g/g}$, and is comprised mainly of the parent and alkylated naphthalenes and phenanthrenes (Figure 3-5). However, the biogenic component (perylene) is fairly large in this coal, at a concentration of 0.25 $\mu\text{g/g}$ or just above 10 percent of the total PAH.

The amount of S/T is also comparable to the Homer Spit coal, with a total S/T of 2.1 $\mu\text{g/g}$. Additionally, the C30-hopane is present, although not dominant as was seen with the Cook Inlet crude. The relative abundance of the C31-homohopane 22R isomer over the 22S isomer (peaks T22 and T21 in Figure 3-5, respectively), is the reverse of that seen in the Homer Spit coal, perhaps evidence of a more mature nature of this coal sample.

Ninilchik Coal. Total PHC for this coal source (4.7 µg/g) is comparable to that of the Homer coals (Table 3-2). The GC/FID chromatogram (Figure 3-6) also illustrates the similar heightened distribution of saturated hydrocarbons in the C26 to C34 carbon range.

The concentration of total PAH in the Ninilchik coal was also similar to the other coal source samples, but was clearly dominated by the biogenic PAH, perylene (Figure 3-6), comprising nearly 80 percent of the total PAH distributions.

Results for Ninilchik coal total S/T were 0.95 µg/g, within the range spanned by the other coal source samples (Table 3-2). The extracted ion chromatogram shows the presence of the C30-hopane (peak T19, Figure 3-6), in addition to a minor triterpane 18α(H)-oleanane component.

Matanuska Coal. The TPH results for the Matanuska coal are comparable to the other coals (1,200 µg/g). The GC/FID chromatogram (Figure 3-7) reveals the presence of a wider range of the resolved n-alkanes, generally extending across the domain of the analysis (from C9 through C36), compared with the other coal samples.

The total PAH for the Matanuska coal was the highest compared to all other coals, at 62 µg/g (Table 3-2). The overall PAH distribution is similar to a petrogenic source, with a predominance of the low molecular weight naphthalenes and phenanthrenes; however a clear absence of fluorenes and dibenzothiophenes render it quite unique. There are also only trace amounts of the 4- and 5-ring PAH, in addition to a minimal biogenic PAH component (Figure 3-7).

Results for the S/T concentrations are comparable to the Homer coals, with a total S/T of 2.1 µg/g. The distribution of analytes, however, is not similar and is noted by maximums at the C-31-homohopanes, with the 22S isomer dominant over the 22R isomer (Figure 3-7).

Coyote Lake Coal. The total concentration of petroleum hydrocarbons was the lowest of the coal samples measured in this study (400 µg/g). The GC/FID chromatogram is very similar to that of the Matanuska coal, although there appears to be a degree of weathering associated with the loss of some of the resolved n-alkanes (Figure 3-8).

Total PAH for the Coyote Lake coal source sample was about one-third that of the Matanuska coal (23 µg/g), but still substantially higher than the other coals (Table 3-2). The coal sample from Coyote Lake (Figure 3-8) also exhibits similarity to the Matanuska coal (Figure 3-7) regarding the high abundance of the alkylated naphthalenes and phenanthrenes and lack of most other PAH measured here.

Comparable distributions of S/T, e.g., the dominance of the C-31 homohopanes, the lack of oleanane and similarities among the other hydrocarbon analytes, lead to the conclusion that these two source coals (Coyote Lake and Matanuska) are from the same coal-bearing formation.

Beluga Coal. Results for the TPH concentration are within the range of the other coals measured in this study (750 ± 180 µg/g). The GC/FID chromatogram contains a complex mixture of saturated hydrocarbons in the C26 to C34 range, much like that of the Homer and Ninilchik coals, but the concentrations of the resolved n-alkanes are much lower (Figure 3-9).

The Beluga coal sample contained a low concentration of total PAH ($4.4 \pm 0.44 \mu\text{g/g}$) and, just as observed with the Ninilchik coal, was dominated by the biogenic PAH perylene (Figure 3-9). The similarities between these two coals also extend to the S/T distribution, with a dominance of the 22S isomer of C31-homohopane and the presence of oleanane (Figures 3-6 and 3-9).

3.1.2.3 Source Sediments

Homer Harbor Sediment. Results of SHC analyses for the two Homer boat harbor sediment source samples were very similar at the surface (0- to 2-cm) and subsurface (4- to 6-cm) depth intervals. This sediment was a black, anoxic, silt-clay, and as expected, the SHC and other organic hydrocarbon concentrations were approximately 3 to 10 times greater than the riverine and surficial sediments collected throughout the study region. The average total PHC concentration was $120 \pm 7.1 \mu\text{g/g}$ (Table 3-2). The SHC chromatogram (Figure 3-10) shows a predominance of higher molecular weight alkanes in the C27 to C31 range and a corresponding UCM. The assemblage of saturated hydrocarbons in these samples is predominated by the plant wax alkanes; however, there are also indicators of weathered petroleum as well.

The mean total PAH concentration in the Homer Harbor sediments is $0.78 \mu\text{g/g}$. The PAH distribution is comprised primarily of petroleum PAH and perylene, with a minor combustion PAH contribution (Figure 3-10). The relative distribution within the series of alkyl naphthalenes indicates that the petroleum PAH are moderately weathered (e.g., the C4-naphthalenes > C3-naphthalenes > C2-naphthalenes). The predominance of perylene is indicative of recent diagenesis of terrestrial hydrocarbons in the sediments, or alternatively may be linked to a coal source (i.e., Homer coals, Figures 3-4 and 3-5). The abundance of the C4-phenanthrenes, which are the dominant PAH analyte in the distribution, is likely due to an interferent which may be related to combustion sources.

The S/T distributions of the Homer Harbor sediments are clearly different from the other source samples. An unidentified triterpane, perhaps normoretane, is the most abundant compound, followed by the C31-homohopane 22R isomer (Figure 3-10). C30-hopane and oleanane are only minor components. Some similarities in the triterpane distributions between the Homer Harbor sediments and the Homer coals (e.g., the large relative abundance of the C31-homohopane 22R isomer versus the 22S isomer) indicate that Homer Spit coal (Figure 3-4) may be a major component of the observed hydrocarbon assemblage.

Copper River Sediment. The total PHC concentrations in the Copper River sediment samples were very low in 4 of the 5 samples and ranged from 2.6 to $68 \mu\text{g/g}$, with an average total PHC concentration of $18 \pm 28 \mu\text{g/g}$. The SHC distributions in all the samples were dominated by terrigenous alkanes in the C25 to C33 range (Figures 3-11 and 3-12). None of the samples exhibited evidence of a petroleum hydrocarbon signature based on the GC/FID chromatograms. In comparison to the total PHC concentrations in the oil, coal, and Homer Harbor sediment source samples, the PHC levels in these riverine sediments were quite low. The one exception is the CR-1 sample collected near the Million Dollar Bridge. This sample had a total PHC concentration approximately 15 times higher than the other 4 samples (CR-2 to -5), and is likely the result of incorporation of terrigenous/plant material in this sample.

The total PAH concentrations from the Copper River sediments were very low, with many target compounds below the detection limit of the method (i.e., not detected). The mean total PAH concentrations of the Copper River sediments were $0.041 \mu\text{g/g}$ (Table 3-2). The PAH

distribution of the Copper River sediments (Figure 3-11) contains trace levels of petrogenic 2- and 3-ring PAH, as well as combustion-related 4-, 5-, and 6-ring PAH. Furthermore, the Copper River sediment also contains a significant biogenic PAH component, i.e., perylene (Figure 3-12).

S/T are present at only trace levels in the Copper River sediments and many compounds were not detected (Figures 3-11 and 3-12). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples. Overall, the trace levels of SHC and PAH in these riverine samples indicate that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

Susitna River Sediment. The Susitna River sediment samples have low total PHC concentrations ($3.4 \pm 1.3 \mu\text{g/g}$). The Susitna River sediment SHC distributions are similar to the Copper River samples and are characterized by a predominance of terrigenous alkanes in the C27 to C31 carbon range (Figure 3-13). There is no evidence of petroleum hydrocarbons in these sediments based on the GC/FID chromatograms.

In contrast to the Copper River sediment, the PAH distribution of the Susitna River sediment shows only trace levels of total PAH ($0.0074 \pm 0.00094 \mu\text{g/g}$), composed primarily of the combustion-related PAH (phenanthrene, fluoranthene, and pyrene) and the biogenic PAH, perylene.

S/T are present at only trace levels in the Susitna River sediments and many compounds were not detected (Figures 3-13). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples. Overall, the trace levels of SHC and PAH in these riverine samples indicate that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

Matanuska River Sediment. Sediment collected from the Matanuska River contained low concentrations of total PHC ($6.3 \mu\text{g/g}$). The SHC distributions are similar to the Copper and Susitna River samples and are characterized by a predominance of terrigenous alkanes in the C24 to C31 carbon range (Figure 3-14). There is no evidence of petroleum influence in these sediments based on the GC/FID results.

The PAH concentrations in these sediments were higher than the other two rivers but still less than that of the Homer Harbor sediment (Table 3-2). The PAH distribution of the Matanuska River sediment (Figure 3-14) contains trace levels of petrogenic 2- and 3-ring PAH, as well as combustion-related 4-, 5-, and 6-ring PAH.

S/T are present at only trace levels in the Matanuska River sediments and many compounds were not detected (Figures 3-14). This further supports the observation that petroleum is not a significant component of the total hydrocarbons in the samples and indicates that they are not likely to be a significant source of petroleum hydrocarbon input to the Cook Inlet and Shelikof Strait region.

Alaska Coastal Current Sediment. Results for the ACC sediment revealed a total PHC concentration of $47 \pm 3.0 \mu\text{g/g}$ (Table 3-2). The pattern of saturated hydrocarbons extends across the range of GC/FID analysis (Figure 3-15), with a similar distribution of the lower n-alkanes and terrigenous C27 to C31 alkanes, as seen in Cook Inlet and Shelikof Strait sediments.

GC/MS results showed the highest PAH concentrations ($1.7 \pm 0.06 \mu\text{g/g}$) compared with each of the other source sediments analyzed (Table 3-2). The distribution of PAH analytes represents a mixture of both petrogenic (i.e., 2- and 3-ringed alkylated PAH) and typical pyrogenic (5- and 6-ringed PAH) signatures (Figure 3-15).

The concentrations of S/T in the ACC sediments were moderately low, at $0.049 \pm 0.0021 \mu\text{g/g}$. The extracted ion chromatogram exhibits a biomarker distribution similar to that of the oils, with a dominance of the C30-triterpane, 17 α (H)-hopane (Figure 3-15), although the sediments did contain a significant amount of oleanane. These results indicate that these sediments are likely influenced by both “background” petroleum and pyrogenic sources of hydrocarbons.

Augustine Island Sediment. Total petroleum hydrocarbons in the Augustine Island sediments were $12 \mu\text{g/g}$ (Table 3-2). The overall SHC (Figure 3-16) distribution reflects the influence of terrigenous plants (C23 through C30) just as observed with each of the river sediments.

PAH concentrations for these sediments were moderate ($0.17 \mu\text{g/g}$), with a distribution reflecting the influence of petrogenic, pyrogenic, and biogenic (perylene) PAH (Figure 3-16).

The concentration of S/T for the Augustine Island sediments was $0.019 \mu\text{g/g}$, with a profile containing similar dominance of the 22R isomer of C31-homohopane (Figure 3-16), as was observed with the Homer Spit coal and Homer Harbor sediments (Figures 3-4 and 3-10, respectively).

3.1.2.4 Aqueous Sources

Point Woronzof Municipal Effluent. The total PHC concentration for the Point Woronzof (Anchorage) municipal effluent was $2,300 \mu\text{g/L}$ (Table 3-2). The chromatogram of the municipal effluent sample reveals a predominance of higher molecular weight alkanes (C27 to C34) which are typical of terrigenous hydrocarbon sources (i.e., plant wax alkanes), and only a trace PHC signature.

The Anchorage municipal effluent has a total PAH concentration of $6.7 \mu\text{g/L}$, with a PAH distribution characterized by a full suite of 2-, 3-, and 4-ring PAH, with considerably lower levels of 5- and 6-ring PAH (Figure 3-17). Three of the most abundant compounds in the PAH distribution are phenanthrene, fluoranthene, and pyrene, which are indicative of pyrogenic or combustion-related sources (e.g., urban runoff). The effluent also contains a complete series of C1- through C4-alkyl naphthalenes, phenanthrenes, and dibenzothiophenes, which is characteristic of petroleum sources.

The full suite of triterpanes, dominated by hopane (Figure 3-17), is also characteristic of PHC material. Based on the SHC, PAH, and S/T data, the Anchorage effluent contains a mixture of petroleum and combustion-related hydrocarbons.

Trading Bay Produced Water. Total SHC in the produced water sample from the Trading Bay Production Facility had a concentration of $6,200 \mu\text{g/L}$ (Table 3-2). The chromatogram for the produced water (Figure 3-18) displays a homologous series of alkanes and a UCM similar to the Cook Inlet crude oil (Figure 3-1), although the produced water is depleted in the low molecular weight alkanes (C9 to C14).

The total PAH concentration of 380 μL in the TBPf produced water sample is substantially higher than the municipal effluent, but within the range for other produced water samples from Cook Inlet (Hyland, *et al.*, 1995). The PAH distribution (Figure 3-18) is characterized by an abundance (>90 percent) of naphthalene and alkyl naphthalene relative to the 3- and 4-ring PAH (phenanthrenes and chrysenes). The observed enrichment of the naphthalenes is due to the higher solubility of these 2-ring PAH relative to the 3-, 4-, 5-, and 6-ring PAH. The distribution of the 3-, 4-, and 5-ring PAH and the S/T (Figure 3-18) in the produced water are comparable to the Cook Inlet crude (Figure 3-1).

3.1.3 Metals

Twenty-three source samples were analyzed for trace metals and major elements including the following: Susitna River bottom sediment (2), Copper River bottom sediment (4), Homer Harbor bottom sediment (1), Susitna River suspended solids (2), Knik River suspended solids (2), Matanuska River suspended solids (2), Copper River suspended solids (2), coal (5), Cook Inlet crude oil (1), Cook Inlet produced water (1), and Point Woronzof municipal effluent (1). Samples of sediment, water, and oil were collected during 1997 and samples of suspended solids and coal were collected during 1997 and 1998. At the beginning of this study, riverine inputs were hypothesized to be the dominant source of sediment and sediment metals to outermost Cook Inlet and the Shelikof Strait (Boehm *et al.*, 1998). Thus, the Susitna and Copper Rivers, two primary sources of metals to the study area, were sampled for bottom sediment and suspended solids.

3.1.3.1 Source Sediments and Suspended Solids

Results for bottom sediment from the Susitna and Copper Rivers (Table 3-1) show that concentrations of nine metals (Al, Be, Cr, Fe, Hg, Ni, Pb, Sn, Tl, and Zn) are comparable to or less than values for average continental crust (Table 3-3). In contrast, and again relative to average continental crust, concentrations of As, Ba, Cd, Cu, Sb, and Zn are higher in bottom sediment from both rivers, Ag and Se are greater in Susitna River sediments, and Mn and V are higher in Copper River sediments (Table 3-1). However, when these metals in river sediment are compared with native sedimentary, volcanic, and plutonic rocks from Alaska (Table 3-3), the river sediments contain comparable or lower levels of all metals.

During 1998, suspended solids were collected from the Susitna, Knik, Matanuska, and Copper Rivers. All concentrations of As, Cd, Cu, Fe, Hg, Mn, Sb, V, and Zn in river suspended solids are higher than levels reported for average continental crust (Table 3-3). However, relative to Alaskan rocks, only concentrations of Al, Cr, and Ni are higher in most samples of river suspended solids (Tables 3-1 and 3-3). This enrichment is most likely due to higher natural levels of these three metals in the fine-grained aluminosilicate clays carried in suspension. Maximum concentrations of Ba and Pb in suspended solids are about 30 percent higher than Alaskan rocks for just one or two isolated instances that may be tied to natural or anthropogenic processes. Collectively, metal values for bottom sediments and suspended solids from the important source rivers provide one valuable frame of reference that will be used to help identify inputs of contaminants to sediments as they are carried through Cook Inlet and on to the Shelikof Strait.

Bottom sediment from Homer Harbor also was chosen as a potential source material to outermost Cook Inlet and the Shelikof Strait. This sediment is fine-grained, black mud (94.3 percent silt plus clay) with 1.6 percent organic C. Despite the nature of this material,

concentrations of all metals in river suspended solids are greater than levels found in sediments from Homer Harbor. When Homer Harbor sediments are compared with river sediments, concentrations of Hg, V, and Zn are elevated in Homer Harbor (Table 3-1). However, bottom sediment from the Susitna River contains 56 percent sand and may not be representative of the material carried seaward from the river system. At this point, Homer Harbor sediment will be considered an additional potential source of Hg, V, and Zn to the study area. The degree of anthropogenic additions of Hg, V, and Zn to Homer Harbor will be discussed in Section 4.1.

3.1.3.2 Source Coals

Coal is an important deposit in the drainage basin of the study area (MMS, 1996).

Concentrations of metals in five samples of coal are generally lower than in bottom sediment from the Susitna or Copper Rivers (Table 3-1). Notable exceptions to this observation are higher levels of Cd, Cu, and Hg in the Ninilchik coal and elevated concentrations of Sb in the Matanuska coal relative to river bottom sediment and suspended solids. When source coals for this study are compared with the USGS (1998) database for coal in Alaska (Table 3-1), the following metals (samples) are above the range of observed concentrations: Al (Homer), Cd (Ninilchik), Cr (Beluga), Cu (Matanuska and Ninilchik), Fe (Homer), Hg (Ninilchik), Mn (Homer), Pb (Beluga and Ninilchik), and Sb (Matanuska). However, coal is unlikely to be an important source of metals to any of the sediments in outermost Cook Inlet and the Shelikof Strait because the highest TOC values in sediment (TOC \approx 2 percent) are more than 30 times lower than in coal (TOC > 60 percent). Even if all the TOC in the sediment was from coal, metals in the coal would be diluted by a factor of 30 or more. Thus, concentrations of Sb, with a 3-fold enrichment in coal, would not be enhanced in sediment due to the presence of a small fraction (< 3 percent) of coal.

3.1.3.3 Aqueous and Oil Sources

Metal concentrations in the source sample of TBPF produced water (salinity = 25 g/L), Cook Inlet crude oil, and final effluent from Point Woronzof WWTF (Table 3-4) are low, with concentrations > 1 mg/L only for Ba and Mn in the produced water, Fe and Ni in the crude oil, and Fe in the final effluent. At these low concentrations and discharge rates, the aqueous and oil samples are unlikely to serve as a detectable source of metals to sediments in the study area. Trefry *et al.* (1996) found no statistical differences ($\alpha = 0.05$) in concentrations of Ba, Cd, Cu, Fe, Mn, Ni, Pb, V, or Zn in fish collected from oil production platforms in the Gulf of Mexico where there were discharges of produced water versus non-discharging sites. Furthermore, metal levels of produced water from the Gulf of Mexico were considerably higher than those found in the sample from TBPF.

3.2 Surface Sediments

3.2.1 Physical Measurements

A total of 170 surficial sediments were analyzed for TOC and percent sand, silt, and clay. The TOC values in surficial sediments range from 0.26 percent to 1.49 percent (Table 3-5). Relative to TOC concentrations in bottom sediment from the Susitna (0.20 ± 0.01 percent) and Copper (0.14 ± 0.02 percent) Rivers, TOC levels in sediment from outermost Cook Inlet and the Shelikof Strait are significantly higher. Average TOC values are similar in zones 0 and 1, increasing by about 40 percent in zones 2 and 3 (Table 3-5). Highest TOC levels (> 1 percent TOC) are

observed at Z0F1 and Z0F14 (Homer Harbor), at selected sites in zones 2 and 3, and throughout zone 4 (Appendix A).

Sand values in surficial sediments average about 42 percent in zone 0 and 41 percent in zone 1 (Table 3-5). However, the sand content decreases dramatically in the remaining three zones. For example, sediment from zone 2 averages about 7 percent sand, zone 3 contains only 2 percent sand, and zone 4 has about 1 percent sand. In contrast, the silt+ clay levels in surficial sediments from outermost Cook Inlet and the Shelikof Strait increase from 57.9 percent in zone 0 to >97 percent in zones 3 and 4 (Table 3-5).

3.2.2 Organics

In this section, the surface sediment grab sample results and general trends in the data will be discussed for the outermost Cook Inlet and Shelikof Strait study area as a whole, as well as within each of the five zones.

Average concentrations of total PAH, total PHC, and total S/T were calculated for each zone by first averaging replicates, where appropriate, to obtain a value for each station location, and then averaging the station location values within each zone to obtain an average total concentration for each zone. The data presented reflect concentrations on a dry sediment weight basis. The concentrations presented for the combined years (1997 and 1998) are simply the average of the zone for each sample period (n=2). The study area-wide grand average concentrations were obtained by averaging the average total concentration for each zone (i.e., n=4 for 1997, n=5 for 1998, n=5 for 1997 and 1998). The range of values presented for each grand average includes the minimum and maximum concentration values for all station locations. These calculated means and ranges for the summary organic parameters in all zones are presented in Table 3-6. The complete organics data for all surface sediments are included as data tables in Appendix B. In addition, the key diagnostic parameters for the organics data, as defined in Table 3-7, which were used in the statistical analysis of the surface sediment data for both years, are summarized in Table 3-8.

To facilitate the presentation and discussion of the organics data, GC/FID chromatograms, PAH distribution plots, and triterpane extracted ion chromatograms that are representative of surface sediments in zones 0, 1, 2, 3, and 4 were selected, and are presented in Figures 3-19 through 3-27. The stations selected for presentation are as follows:

- **Zone 0** - Fixed station locations F1 - Kachemak Bay (sample 97-0-F1-01-00-PHC-S, Figure 3-19), station F4 - center of outermost Cook Inlet (samples 97-0-F4-02-00-PHC-S, Figure 3-20 and 98-0-F4-01-00-PHC-S, Figure 3-21), and F5 - Kamishak Bay (samples 97-0-F5-02-00-PHC-S, Figure 3-22 and 98-0-F5-01-00-PHC-S, Figure 3-23)
- **Zone 1** - Random station 09 - North Shelikof Strait (sample 97-1-08-01-00-PHC-S, Figure 3-24)
- **Zone 2** - Random station 08 - Middle Shelikof Strait (sample 97-2-08-01-00-PHC-S, Figure 3-25)
- **Zone 3** - Random station 10 - South Shelikof Strait (sample 97-3-10-01-00-PHC-S, Figure 3-26)
- **Zone 4** - Fixed station location F2 - Outside Shelikof Strait (sample 98-4-F2-01-00-PHC-S, Figure 3-27)

Surface sediments were also collected in triplicate at two embayment stations located within Kodiak Island (Figure 2-1). Due to their close proximity to the shore and the presence of a sill between them and the open strait (as indicated by the water depths of the two embayment stations), these stations were not included in the statistical zone analysis, but are discussed separately.

3.2.2.1 Saturated Hydrocarbons

Concentrations of total PHC in surficial sediments from outermost Cook Inlet and Shelikof Strait ranged from 6.8 to 71.0 µg/g throughout the study area. The total PHC concentrations were generally at low to moderate levels with average total PHC concentration across the four zones of 28.5 µg/g in the sediments collected in 1997, with a coefficient of variation (CV) of 18 percent (Table 3-6). The total PHC concentrations for surface sediment averaged across the five zones collected in 1998 was 28.8 µg/g, with a CV of 19 percent (Table 3-6). The grand average total PHC for the study area over the entire sampling period was 29.4 ± 5.41 (Table 3-6). Comparison of both sample periods reveals little variation across both years, with the CV for zones ranging from 0.2 percent to 7.4 percent. A more detailed comparison of the analysis of variance among measured and calculated parameters between years is presented in Section 3.5. Among samples in each zone, the average total PHC concentration was highest in zones 3 and 4 (34.8 µg/g and 35.8 µg/g, respectively), with somewhat lower average concentrations in zones 0, 1, and 2 (25.5 µg/g, 24.9 µg/g, and 26.0 µg/g, respectively).

In general, the surficial sediments collected in zones 1, 2, 3, and 4 (GC/FID chromatograms in Figures 3-24 through 3-27) exhibit a mixture of terrestrial and marine hydrocarbons dominated by an assemblage of plant wax alkanes in the C27 through C33 carbon range. This is further demonstrated by Carbon Preference Index (CPI - calculated as:

$$\frac{C26 + C28 + C30}{C27 + C29 + C31}$$

values, on average, ranging from 2.3 to 3.6, and is characteristic of sediments influenced by terrigenous plant inputs (Wakeham and Carpenter, 1976; Boehm, 1984). Traces of lower molecular weight alkanes (LALK), indicative of petroleum, are visible in the chromatograms only as a minor component relative to the plant wax alkanes. The GC/FID chromatograms from three stations in zone 0 (Figures 3-19 through 3-23) show a similar distribution of terrestrial hydrocarbons (an average CPI of 3.2 and 5.4 for 1997 and 1998, respectively), but show even less evidence of lower molecular weight petroleum hydrocarbons.

The sediment for the two embayment stations adjoining zone 2, but within Kodiak Island sills, contained substantially higher total PHC concentrations of SHC's, with a mean total PHC of 71.3 ± 17.5 µg/g and 47.7 ± 10.7 µg/g for stations Z2F3 and Z2F4, respectively. The composition of SHCs however, was similar to the other zone 2 sediments although primarily influenced by terrigenous plants. Each chromatogram (not shown) was dominated by the plant wax alkanes along with a large corresponding UCM, and revealed low abundances of the nC9 through nC20 alkanes (LALK) relative to the entire suite of alkanes (between 18 and 23 percent), compared with a mean abundance of 42 percent for the LALK in the zone 2 sediments.

3.2.2.2 Polycyclic Aromatic Hydrocarbons

In general, low to moderate levels of PAH were found across the study area. The average total PAH concentration in sediment for all four zones collected in 1997 was $0.457 \mu\text{g/g}$ (CV of 32 percent) and $0.432 \mu\text{g/g}$ (CV of 38 percent) for the five zones collected in 1998. The grand average for total PAH in the entire study region across both years was $0.459 \pm 0.151 \mu\text{g/g}$, with minimal variation between the sampling period within zones (CV of 2.2 to 21 percent). In outermost Cook Inlet (zone 0), the average total PAH concentration was $0.235 \mu\text{g/g}$, while the average total PAH concentrations in Shelikof Strait (zones 1, 2, 3, and 4) gradually increased with distance from Cook Inlet ($0.376 \mu\text{g/g}$, $0.534 \mu\text{g/g}$, $0.548 \mu\text{g/g}$, and $0.604 \mu\text{g/g}$, respectively). These levels of PAH are consistent with previously reported values for the Cook Inlet/Shelikof Strait region, as well as other Alaskan coastal sediments (e.g., Prince William Sound and the Beaufort Sea - Table 3-9).

The PAH distributions for most surficial sediments show that the PAH are primarily of a combined fossil fuel origin (i.e., petroleum and coal), with a somewhat variable biogenic component (perylene) and lesser contribution of pyrogenic or combustion-related compounds (4-, 5-, and 6-ring PAH). Perylene concentrations were relatively high in most surficial sediments, but varied widely from zone to zone and among samples within a zone. Perylene is a naturally occurring PAH formed during early diagenesis in sediments from biological source precursors (Wakeham and Farrington, 1980; Wakeham, *et al.*, 1980). It may also be found in crude oil at very trace concentrations. In past studies, perylene was found at comparable concentrations in the sediments of Cook Inlet and Alaska nearshore sediments (Boehm *et al.*, 1998).

The variations in PAH composition in the surface sediments of zone 0 are shown in PAH distribution plots in Figures 3-19 through 3-23. In Kachemak Bay (Station Z0F1, Figure 3-19) the PAH assemblage is dominated by perylene, with a full suite of 2-, 3-, and 4-ring petroleum PAH, and lower levels of combustion PAH. In contrast, in the center of Cook Inlet (Station Z0F4, Figures 3-20 and 3-21) only traces of perylene are found, and the PAH distribution is primarily comprised of moderately weathered petroleum PAH (i.e., naphthalenes generally < phenanthrenes), with trace combustion PAH. In Kamishak Bay (Station Z0F5, Figures 3-22 and 3-23), the PAH concentration is somewhat lower and is characterized by a full suite of petrogenic PAH, a significant perylene component, and only trace combustion PAH.

The PAH distributions in zones 1, 2, 3, and 4 are generally similar throughout, and are characterized by the presence of a full suite of relatively “unweathered” petroleum PAH (i.e., naphthalenes \geq phenanthrenes). Perylene is present at somewhat variable concentrations, and does not appear to correlate with the total PAH concentrations. Trace levels of 4-, 5-, and 6-ring combustion PAH are present, but are generally only a minor component of the overall PAH composition.

The total PAH concentrations for sediments located within the Kodiak Island embayment area were consistent and within the range of all zones (Table 3-8), with a mean of $0.530 \pm 0.043 \mu\text{g/g}$ and $0.415 \pm 0.033 \mu\text{g/g}$ for the stations Z2F3 and Z2F4, respectively. The composition of PAH were similar to the other Shelikof Strait sediments, containing a mixture of the relatively “unweathered” petroleum PAH combined with a minor combustion PAH component similar to that observed for the adjacent zone 2 sediments, as well as, sediments from zones 1, 3, and 4 (Figures 3-24 through 3-27).

3.2.2.3 Steranes and Triterpanes

In general, the S/T appear somewhat different in zone 0 than in zones 1, 2, 3, and 4, where the S/T results were generally similar. Figures 3-19 through 3-27 show the distribution of triterpanes for surficial sediments in all 5 zones of the study area. The average total S/T concentrations for zones 1, 2, 3, and 4 range from 0.016 to 0.029 $\mu\text{g/g}$ (CV of 31 to 71 percent) for surface sediment collected in 1997, while the range of average S/T concentrations for the sediment collected in 1998 was 0.016 to 0.030 $\mu\text{g/g}$ (CV of 4 to 81 percent). The grand average for total S/T for all zones across both years was $0.024 \pm 0.005 \mu\text{g/g}$, with minimal year-to-year variation within zones (CV of 0 to 23 percent).

Generally, there were low levels of S/T characteristic of petroleum found at all stations in zones 1, 2, 3, and 4 with C30-hopane (T19) present and often the most abundant compound in the overall triterpane distribution. Oleanane (T18) was detected in all samples in zones 1, 2, 3, and 4, indicating the presence of a non-Cook Inlet post-Cretaceous/Tertiary petroleum source (i.e., T18 is absent in Cook Inlet crude). In addition, the relative abundance of $T22 > T21$ and the presence of the moretananes are indicators of recent organic matter inputs to the surficial sediments.

The S/T concentrations at station Z2R22 (1997) and Z3R11 (1998) were substantially higher than all other stations, thus contributing to relatively heightened CVs for these zones (Table 3-6). A closer evaluation of the triterpane distribution in these samples indicates the presence of a different petroleum source (or a mixture) than in the other samples and currently suggests that these stations may be an outlier in the data set for triterpanes (all other organic parameters were within the range of other samples from the study area).

The S/T analyses from zone 0 (outermost Cook Inlet) stations reveal a slightly different pattern of triterpanes, particularly in Kachemak Bay (Figure 3-19). The triterpanes from this station show an abundance of recent biogenic triterpanes and the greater abundance of T22 versus T21 is similar to that observed for the Homer Spit coal source sample (Figure 3-4). While a characteristic petroleum triterpane distribution is present, it is only a minor component, indicating that coal may be the primary source of the S/T. Three other samples taken from the Kachemak Bay area (Z0F2, Z0F13, and Z0F14) also have similar triterpane distributions, indicating the influence of a coal source. In general, the remaining stations in zone 0 (Figures 3-21 through 3-23) have triterpane patterns more similar to those observed in zones 1, 2, 3, and 4 (Figures 3-24 through 3-27). However, there appears to be a greater component of coal influence as indicated by the $T22 > T21$ abundance. Oleanane was also present in all of the zone 0 samples, indicating a non-Cook Inlet petroleum contribution. At station Z0F6 only trace oleanane was detected, indicating a different petroleum source (discussed below).

The total S/T concentrations for sediments located within the Kodiak Island embayment area were similar to those measured in all zones (Table 3-8), with a mean of $0.023 \pm 0.003 \mu\text{g/g}$ and $0.020 \pm 0.005 \mu\text{g/g}$ for the stations Z2F3 and Z2F4, respectively. The composition of S/T were similar to the other Shelikof Strait sediments, i.e., dominated by the C30-hopane and containing a minor presence of oleanane, in addition to having a relative abundance of $T22 > T21$.

3.2.2.4 Hydrocarbon Sources in Surface Sediments

As mentioned previously, selected diagnostic ratios and parameters were used in the statistical evaluation and to support the interpretation of the organics data (SHC, PAH, and S/T). The data

sets were analyzed separately by year due to the additional zone (zone 4) included in the 1998 sampling survey. The initial statistical analysis of the hydrocarbon data focused on identifying differences between zones for the selected diagnostic parameters, in order to evaluate potential source trends i.e., higher concentrations of hydrocarbons closer to Cook Inlet oil and gas production activities.

The statistical results (Student Newman-Keuls test on non-normalized data) of the organics diagnostic parameters for the surface sediments collected in 1997 are shown in Table 3-8 (complete details of the statistical results are included in Appendix I Table H-I). Zones were not significantly different for 8 of the 23 parameters measured. For 11 of the remaining 16 parameters, zone 0 was significantly different from zones 1, 2, and 3. The remaining parameters resulted in some overlap in significant differences between zones. Results for the 1997 surface sediment data normalized by TOC were not substantially different, with zone 0 again statistically separate from the other zones, which were overlapped among each other.

The statistical results (Student Newman-Keuls test on non-normalized data) of the organics diagnostic parameters for the surface sediments collected in 1998 are also shown in Table 3-8. Two additional parameters were introduced during this sample period, i.e., the presence of oil degrading bacteria and mean heterotrophic bacterial population (Section 2.2.5.4). All zones were not significantly different for 18 of the 25 parameters measured. For 2 of the remaining 7 parameters, zone 0 was significantly different from zones 1, 2, 3 and 4. The remaining parameters resulted in some overlap in significant differences between zones. Results for the 1998 data normalized by TOC were, once again, not substantially different with zone 0 statistically separate from the other zones, which were themselves overlapped among each other.

Generally, these results show that zone 0 was different from the other zones due to lower concentrations of the total or summed hydrocarbon parameters (e.g., Total PAH, petrogenic PAH, isoprenoids, LALK). Zone 0 had significantly higher concentrations of perylene and a higher pyrogenic/petrogenic ratio (for the 1997 and 1998 sediments), showing that zone 0 is more subject to biogenic and combustion inputs than zones 1, 2, 3, and 4. The naphthalene/phenanthrene (N/P) ratio in zone 0 was lower in the 1997 sediment analysis, supporting earlier observations that the PAH in zone 0 appeared more weathered than zones 1, 2, 3, and 4. The Carbon Preference Index (CPI) was not significantly different between zones in the sediment collected in 1997, while in 1998 the zone 0 sediment had a significantly higher CPI, confirming a consistent influence of terrigenous hydrocarbon input throughout the area, particularly in zone 0. The key petroleum source parameters (e.g., C2D/C2P, C3D/C3P, oleanane/hopane, and Ts/Ts+TM,) were either not different or resulted in overlap between zones, indicating a common source of petroleum hydrocarbons to the study area. Overall, these statistical results indicate that zone 0 was generally different from the other zones due to lower concentrations of organic parameters, and there is no reproducible trend showing higher levels of organics closer to Cook Inlet oil and gas production activities.

Based on a review of the key diagnostic parameters for organics, an evaluation of the petroleum hydrocarbon sources in the surface sediments is best described by the double-ratio plot of the alkyl dibenzothiophenes and alkyl phenanthrenes (C2D/C2P versus C3D/C3P). This double ratio has been well documented as an accurate source indicator in other studies investigating the sources of petroleum hydrocarbons in the environment (Brown and Boehm, 1993; Page *et al.*, 1996; Bence *et al.*, 1997).

A double-ratio plot of the source samples and all the surface sediment samples collected during both surveys is shown in Figure 3-28. The plot reveals that North Slope crude oil (i.e., *Exxon Valdez* crude) and Point Woronzof effluent have significantly higher ratios than any of the study samples, effectively eliminating either of these sources as significant contributors to the surface sediments. Four of the Copper River and both of the Susitna River source samples contained only trace concentrations of most individual PAH, while the alkyl dibenzothiophenes and phenanthrenes were not detected. As a result, both of these sources plot at the origin and are likewise eliminated as a source of petroleum hydrocarbons. One of the Copper River samples, however, did contain detectable alkyl PAH, and the subsequently calculated ratio did fall near many of the sediment samples. As stated earlier though, the PAH levels present in this source are insufficient to be considered as an influential contributor of PAH. Furthermore, the Well Creek seep oil and the Matanuska and Coyote Lake coals can also be discounted as primary sources of hydrocarbons based on their positioning within the double-ratio plot (Figure 3-28).

Several of the other source samples, the Homer Harbor sediment, St. Augustine Island sediment, Alaska Coastal Current sediment, Homer Spit coal, Ninilchik coal, TBPF produced water, Cook Inlet crude oil, and Swanson River Field oil, all have source ratios within the range observed for all the surface sediments. The TBPF produced water sample has a similar ratio to the Cook Inlet crude oil and falls within the ellipse representing 1 standard deviation (SD) around the mean of the 29 replicate Cook Inlet crude oil analyses. In contrast, nearly all the samples appear in a cluster above and to the right of the Cook Inlet crude (Figure 3-28), and only 4 of the surface samples plot within the Cook Inlet crude oil ellipse.

An evaluation of the same source ratios from other studies of offshore sediments and oil seeps to the east of the study area revealed that the sediments associated with the Katalla and Yakataga seeps and petroleum-bearing formations have C2D/C2P and C3D/C3P ratios that are similar to the major cluster of samples from this study (Page, *et al.* 1995; Page *et al.*, 1996; Bence *et al.*, 1997). The Katalla production oil has C2D/C2P and C3D/C3P ratio values which are central to the main cluster of samples, and the same ratio was determined for the deep subtidal “background” sediments in Prince William Sound (Bence *et al.*, 1997). Results from “background” subtidal sediments off the Alaska Peninsula to the south of the study area have also yielded similar C2D/C2P and C3D/C3P ratios (Manen *et al.*, 1993). The Alaska Coastal Current sediment sample collected east of Cook Inlet in 1998 as part of this study also has C2D/C2P and C3D/C3P ratios which plot centrally to the main cluster of sediment samples. These results, coupled with the known sediment transport to the area by the Alaska Coastal Current (Boehm *et al.*, 1998), demonstrate that petroleum hydrocarbons, likely from the Katalla and Yakataga region formations, are the primary source of petroleum hydrocarbons in the outermost Cook Inlet and Shelikof Strait sediments. Others have suggested that coal particles may also represent a source of hydrocarbons to the Alaska Coastal Current sediments (Short, *et al.*, 1999; Hostettler, *et al.*, 1999). However, a recent comprehensive study of Alaska Coastal Current and Prince William Sound sediment sources, concluded that erosional sediments and glacial flour from tertiary shales, and seep oils to the east (e.g., Katalla and Yakataga region, Malspina Glacier), are the primary source of hydrocarbons to the sediment loading of the Alaska Coastal Current (Boehm, *et al.*, 2001).

When the double-ratio plots of the surface sediments are examined by zone, a pattern of hydrocarbon sources becomes apparent. In zone 0 the double-ratio plot reveals a greater scatter of samples. This scatter is likely due to the influence of coal and Homer Harbor source(s)

mixing with the influx of “background” sediment and seep oil hydrocarbons (Figure 3-29). The sediments plotting most distant from the Cook Inlet ellipse and proximal to the Homer Harbor source samples were consistently collected from locations in or near Kamechak Bay (Z0F14, Z0F1).

In zone 1 there is substantially less scatter of the ratio as it approaches the “background” sediment value of seep-associated petroleum hydrocarbons with minimal coal source influence (Figure 3-30). Four of the surface sediment samples from zone 1 occur within the Cook Inlet crude source ellipse, indicating a possible contribution or mixing from Cook Inlet crude or related seep oil(s) from Cook Inlet (Iniskin Peninsula). In zones 2 and 3 the sediment samples generally cluster in the area of the “background” sediments and seep-associated hydrocarbons oil formation (Figures 3-31 and 3-32). Many of the sediments collected from zone 4 also mirror the calculated “background” sources, although several samples did fall outside the range of sources measured as a part of this study (Figure 3-33).

3.2.3 Metals

3.2.3.1 Trace and Major Elements

All surficial sediments were analyzed for total concentrations of Ag, Al, As, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn (Table 3-10 and Appendix C). The 1997 samples also were analyzed for the major elements Ca, K, and Mg for use as possible indicators of differences in composition of material from the Susitna River versus the Copper River. The resulting data show that concentrations of Ag, Al, Be, Cd, Cr, Fe, Mn, Ni, Pb, Sn, Tl, and V in surficial sediments from outermost Cook Inlet and the Shelikof Strait are similar to or less than average continental crust, whereas concentrations of As, Ba, Cd, Hg, Sb, Se, V, and Zn are enriched by a factor of 1.4 to 5 (Table 3-11). When average metal values for these Alaskan sediments are compared with data for sediment from the Susitna and Copper Rivers (Table 3-11), only levels of Fe, Hg, Mn, Pb, Tl, V, and Zn are 16 to 50 percent higher (Table 3-11). Further comparison of average metal concentrations for the surficial sediments from this study (Table 3-11) with available values for sedimentary, volcanic, and plutonic rocks from Alaska (Table 3-3) and river suspended solids (Table 3-1), show that average levels for all metals in these sediments are within the range of values in potential source rocks and river suspended solids.

Average metal concentrations for surficial sediments from zones 0, 1, 2, 3, and 4 (Table 3-10) are relatively uniform throughout this region which extends over approximately 350 km. For example, the CV [$CV = (\text{standard deviation}/\text{mean}) \times 100 \text{ percent}$] for all metals in all surficial sediments (except zone AC) range from about 9 to 35 percent. As shown in Table 3-12, 14 of the 22 metals have a CV ≤ 20 percent. Only Ag, Hg, and Se have a CV of >30 percent. The high CV for Hg results from high concentrations ($>0.1 \mu\text{g Hg/g}$) in sediments from Homer Harbor.

To make inter-comparisons among sediment samples, it is often necessary to normalize metal values to either Al or Fe, thereby removing variations in metal concentrations that result from changes in grain size and/or mineralogy. Aluminum and Fe exhibit a strong linear relationship when they are introduced by a common suite of aluminosilicate and/or Fe-bearing minerals to a sedimentary basin. This trend results from progressive dilution of Al- and Fe-rich minerals with quartz sand and/or shell carbonates that are depleted in these two elements. In addition, trace metals tend to be enriched in aluminosilicate minerals and depleted in quartz sand and shell

carbonates, thereby showing a positive relationship with Al and/or Fe.

In contrast with typical marine sediments, no distinct relationship between Fe and Al (Figure 3-34) is observed for surficial sediments from zones 0, 1, 2, 3, and 4. This lack of a simple trend between Fe and Al suggests that more than one source (or suite) of Al- and Fe-bearing minerals is responsible for observed concentrations of these elements. For example, abundant magnetite (Fe-rich, Al-poor) was observed in some sediment samples. Furthermore, no strong positive linear trends between trace metals and Al were obtained for these surficial sediments, suggesting that Al is not a dependent variable for most trace metals. Metal/Fe plots for the surficial sediments from zones 0, 1, 2, 3, and 4 showed good linear relationships ($r > 0.70$) for Cr, Cu, Ni, Pb, Sb, V, and Zn (Figures 3-34, 3-35, and 3-36), suggesting that Fe-bearing phase(s) are the more important carriers of these trace metals to the sediments. Less significant trends ($r < 0.70$) between Fe and the trace metals Ag, As, Ba, Be, Cd, Hg, Mn, Se, Sn, and Tl (Figures 3-34 and 3-35) were observed, indicating that a more complex or varied suite of mineral phases carry these metals to the study area.

Twenty-five samples of surficial sediment collected during 1997 were resampled in 1998 to assess interannual variability. Metal concentrations in the 1997 samples agreed within ± 10 percent with results from 1998 for Al, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl, and Zn. For As, Sn, and TOC, agreement between years was within $\pm 20\%$. Only concentrations of Ag and Se varied by >20 percent, at 39 percent and 23 percent, respectively.

Statistical analysis (1997 Student Newman-Keuls test) of the metal/Fe ratios by zone for the surficial sediments showed that the metals divided into three separate groups (Table 3-13). In the first group, values for Ag/Fe, Mn/Fe, Ni/Fe, and Tl/Fe show no significant differences at $\alpha = 0.05$ among the four zones in outermost Cook Inlet and the Shelikof Strait. Within the second group, comprising As, Ba, Cr, Cu, Hg, Pb, Sb, Sn, V, and Zn normalized to Fe, two different subgroupings (A and B) could be identified. For example, Pb/Fe and Sn/Fe ratios in zone 0 are statistically different from zones 1, 2, and 3, whereas Cr/Fe and Cu/Fe ratios in zone 2 differ from zone 1, but are similar to zones 0 and 3 (Table 3-13). Beryllium, Cd, and Se normalized to Fe make up the third group with three different groupings (A, B, and C). In this group, the metal/Fe ratio in one zone is statistically different from two other zones (Table 3-13). For example, the Be/Fe ratio in zone 0 is statistically different at $\alpha = 0.05$ from zone 2 and 3 and zone 2 differs from zone 3. The statistical results by zone show that the metal/Fe ratios in zones 0, 1, 2, and 3 are all similar with the exception of Cd and Se in zone 0 and Be in zone 2.

Statistical analysis (1997 and 1998 Combined Student Newman-Keuls test) of the metal/Fe ratios by zone for the surficial sediment data for 13 of the 17 metals (Ag, As, Ba, Be, Cr, Cu, Hg, Pb, Ni, Sb, Se, Tl, and V) showed no significant differences at $\alpha = 0.05$ among the four zones in outermost Cook Inlet and the Shelikof Strait (Table 3-13). For Cd, Mn, Sn, and Zn ratioed to Fe, two different sub-groupings (A and B) could be identified. In each case, higher metals values are observed for zone 3 relative to zone 1, possibly the result of sediment with a greater surface area in zone 3. However, in the cases of Cd, Sn, and Zn, standard deviations (SD) for average metal concentrations in a given zone are often quite low ($CV < 2\%$ or absolute value of $SD < 0.05 \text{ ug/g}$). Thus, relatively small absolute differences between metal values from zone to zone test as being statistically significant. For Mn, variation may be related to differences in the degree of Mn remobilization, as previously discussed.

Statistical results for metal/Fe ratios for 1997 versus 1998 show no annual differences (at $\alpha = 0.05$) for 15 of the 17 metals (Appendix I Table I-29). In the case of Sn, the absolute difference in mean concentrations for 1997 ($1.67 \pm 0.07 \mu\text{g/g}$) versus 1998 ($1.46 \pm 0.07 \mu\text{g/g}$) was small and is not considered to be related to any defensible shifts during the sampling periods. A similar, small absolute difference was observed in Ag levels for 1997 ($0.08 \pm 0.01 \mu\text{g/g}$) versus 1998 ($0.05 \pm 0.01 \mu\text{g/g}$). Much of this statistical result for Ag results from an interannual difference of $0.03 \mu\text{g/g}$ for zones 0 and 3. The overall mean (\pm standard deviation) for Ag in all surface samples of 0.07 ± 0.02 supports no easily detectable differences in Ag levels.

3.2.3.2 Acid-Volatile Sulfide/Simultaneously Extracted Metals

Concentrations of AVS and SEM were determined for 29 samples of surficial sediment (0 to 2cm) collected during 1997. Results for AVS range from $<0.005 \mu\text{moles/g}$ (the detection limit) at four stations (Z0F6, Z0F8 [1 of 3 field replicates], Z1F1, and Z1R8) to $18.6 \mu\text{moles/g}$ at station Z0F14 (Figure 3-37). This maximum value is much higher than the next closest value of $3.1 \mu\text{moles/g}$ (at both Z0F1 and Z3R20). Only six values in the data set are $>1 \mu\text{mole/g}$, the level considered to be the threshold of applicability for the SEM-AVS technique (DiToro *et al.*, 1990). The overall mean value of $1.2 \pm 3.6 \mu\text{moles/g}$ decreases to $0.6 \pm 0.8 \mu\text{mole/g}$ when the maximum value is excluded. The six samples with $>1 \mu\text{mole AVS/g}$ are scattered across all these zones with no simple trend except that the two highest values are for zone 0.

Analyses for SEM included the following metals: Cd, Cu, Ni, Pb, and Zn. Of the 5 SEM metals, Zn is the most abundant in all cases, comprising 50 percent or more of the total SEM (Figure 3-38 and Appendix D). Copper and Ni are the second and third most abundant metals in the SEM summation, with typical contributions of about 10 to 35 percent of the total SEM. In contrast, Pb and Cd account for <7 percent and <1 percent, respectively, of the total SEM in all samples.

The underlying principle for this technique is to use the value for SEM minus AVS as an interpretative tool. For these samples, values of (SEM-AVS) range from -17.5 to $+2.3 \mu\text{moles/g}$ (Figure 3-37 and Appendix D). In the total data set, six values are negative and the remainder are positive. In those instances where the value for (SEM-AVS) is negative, the amount of sulfide exceeds the total amount of metal and thus these metals should all be bound in the sediments as a sulfide phase. When the (SEM-AVS) value is positive, acid-leachable metals are present in the sediment in other than a sulfide phase. The implications of these results are discussed in Section 4.4.

The data for SEM was used to determine the percent of total metal that is released into 2N HCl with the following overall mean values: Cd, 88%; Cu, 40%; Ni, 20%; Pb, 44%; and Zn, 41% (Table 3b). Cadmium is clearly the most labile of the five metals and Ni is the least labile. The variability in the percent of total metal leached was $<40\%$ (as a coefficient of variance) for each metal except Zn (Table 3b). A complementary study by Gray (1999) showed that $<3\%$ of the total metal was leached at pH levels of 4 (*i.e.*, 0.0001N HCl).

3.2.4 P450 Reporter Gene System Response in Extracts of Sediment

Twenty-seven sediment samples were analyzed by the RGS assay in 1997 and another twenty-seven were analyzed in 1998. The RGS B[a]PEq ranged from 0.8 to $6.3 \mu\text{g/g}$ dry weight (a mean of 3.2 with a CV of 54 percent) in 1997. The RGS B[a]PEq ranged from 0.6 to $3.8 \mu\text{g/g}$ dry weight (a mean of 2.2 with a CV of 38 percent) for 1998 samples.

Values in the range of 1 to 10 µg/g dry weight are generally considered to be at background levels in embayment areas and 1 to 5 µg/g dry weight are considered to be at background levels in coastal marine sediments. Only two samples collected in 1997, Z1R13 and Z3R14, were slightly above the coastal marine background with concentrations of 6.3 and 6.2 µg/g dry weight B[a]PEq, respectively. These results are consistent with the concentrations of the PAH measured in the surface sediment, i.e., generally low concentrations of PAH, as well as the results from the 6hr. vs. 16hr which indicate that the RGS response was due to PAH's rather than chlorinated hydrocarbons (dioxins/furans, coplanar PCB's).

Examination of the trends in the mean values for the zones, including the standard deviations for each set of data indicated that sediments from zone 0 had the lowest level of inducing compounds in comparison to the other zones. Also, the mean values for all zones were somewhat lower in 1998 than in 1997. The complete results of the P450 RGS sediment tests are included in Appendix E.

3.2.5 Sediment Toxicity Tests

Amphipod toxicity tests were conducted using marine amphipods and surface sediments collected during both sample cruises. The test organism for the 1997 sediments was *Eohaustorius estuarius*, while the test organism for the 1998 sediments was *Ampelisca abdita*. The percent survival of the amphipods exposed to sediment collected during the 1997 cruise is presented in Table 3-14. Statistical analysis (using ToxCalc v5.0 software) of the results from the 1997 sediment bioassay conducted by PERL demonstrated that 15 of the 20 sediment samples resulted in survival less than the control at $p < 0.05$. However, most laboratories conducting sediment bioassays only indicate toxicity if the following criteria are met:

- There is a significant difference between the laboratory control and the test using a *t*-test, as was done here.
- Mean organism response in the bioassay test was less than 80 percent of the laboratory control value.

Application of the second criterion eliminates the problem of designation of toxicity based only on comparison to controls with low replicate variance.

The 80 percent of control criterion was established by statistical analysis of many amphipod data sets by other investigators (e.g., Thursby and Schlekert, 1993). The two criterion approach is currently being used by the EPA's EMAP (Schlimmel *et al.*, 1994), by California's State Bay Protection and Toxic Cleanup Program (BPTCP, 1993) and by the Regional Monitoring Program for Trace Substances in the San Francisco Estuary (SFBRMP, 1995).

Applying these criteria to the bioassay results demonstrates that only 7 of the 20 sample sites had sediments with significantly lower survival than the controls: 2 of 8 from zone 0; 1 of 4 from zone 2; and 4 of 4 from zone 3. None of the 4 sites in zone 1 demonstrated significantly lower survival than the controls. A detailed analysis of the data for these toxicity tests (discussed in Sections 3.6 and 4.4) indicates that the significantly lower survival observed in these sediments was correlated with sediment grain size and therefore probably not due to the measured concentrations of metals or organics.

Results for the toxicity tests conducted on the 7 sediment sites collected in 1998 are presented in Table 3-15. Statistical analysis of these results from sediment bioassay demonstrated that 5 of the 7 sediment samples resulted in survival less than the 'home' control at $p < 0.05$. However, not one of the amphipod test exposures to surface sediment had less than 90 percent survival. In addition, none of the exposure groups were significantly less than the Holgate Glacier "reference" sediment, which averaged 91 percent survival. (This reference location was selected since it represented fine grained and glacial sediment and was up current from Cook Inlet and inshore of the influence of the Gulf of Alaska). These results support the theory that the toxicity observed in the 1997 and 1998 sediments was not due to the measured concentrations of metals or organics, but likely the result of grain size effects.

3.2.6 Enumeration of Heterotrophs and Hydrocarbon Degrading Microorganisms

Heterotrophic bacteria ranged from approximately 8×10^3 to 8×10^6 organisms per gram of dry weight sediment. Most samples contained about 10^4 to 10^5 organisms per gram of dry weight sediment. Hydrocarbon degrader populations were very low for all samples - 30 sample results were zero and the 10 remaining results ranged from 26-300 organisms per gram of dry weight sediment. These results indicate that the petroleum hydrocarbons present in the sediment are not readily bioavailable.

Complete information on the sample handling and the mean MPN populations are found in Appendix H Table H-1.

3.2.7 Sediment Profile Imaging Camera

In this section, a summary of the SPI camera analyses is presented. A complete set of all the summary data measured from each image is included in the SPI report, which was issued by MMS as a separate stand-alone document in 1998 (MMS, 1998).

Parameters such as boundary roughness and mud clast data (number, size) provide supplemental information pertaining to the physical regime and bottom sediment transport activity at a site. Even though mud clasts are definitive characteristics whose presence can indicate physical disturbance of some form, the mud clasts noted in the images from this survey were either biogenic in origin or artifacts due to sampling (mud clumps clinging to the frame base) and not indicative of physical disturbance or sediment transport activities. Therefore, mud clast data were not used as individual parameters for interpretation. Rather, they were used to enhance the overall comprehension of characteristics at the various areas sampled in conjunction with other SPI parameters such as RPD and OSI.

3.2.7.1 Grain Size

The sediments throughout the entire area surveyed were primarily fine-grained, with very few occurrences of any substantial amount of sand-sized particles except at 5 of the 57 stations sampled (see Appendix Figure A1). For the majority of stations, the sediment grain-size major mode was $\geq 4 \phi$ (4ϕ is an upper particle size limit of 0.0625 mm, or coarse silt). Appendix Figure A1 shows the spatial distribution of sediment grain-size major mode and bottom kinetic regimes at all stations sampled. Most of the images from zone 1 and all the images from zones 2 and 3 in the Shelikof Strait displayed a grain-size major mode of silt-clay with little to no fine sand as part of the grain-size range; Appendix Figure A2 shows a typical profile image from the area. These well-sorted sediments are most likely derived from glacial till and are indicative of

low-energy, depositional environments.

At the northern end of the Shelikof Strait and moving into outermost Cook Inlet, evidence of fine- to medium-sand surface layers appeared at 5 of the stations (Stations 1, 3, 5, and 20 in zone 1; Station F4 in zone 0); medium sand was also the grain-size major mode at 1 station in Kachemak Bay (Station 2, zone 0; Appendix Figure A3). The cluster of these 5 stations in zones 0 and 1 represented a localized area at depths ranging from approximately 150 to 175 m that was influenced by strong bottom transport and displayed coarser-grained sediment. Station 2 (zone 0) presented a transitional facies of a silt-clay bottom with a 2- to 3-cm layer of fine sand at the surface and a hint of bedforms occurring as the result of bottom currents (Appendix Figure A4). The stations surrounding Station 2 with sandy bottoms (Appendix Figure A1) ranged from those with a level sediment-water interface and a grain-size major mode of medium sand (Appendix Figure A5) to stations with allochthonous surface fine-sand layers that showed evidence of active transport (Appendix Figure A6).

Set against a background that is predominantly fine-grained glacial till, the source of sand in this localized region was not readily apparent; however, the presence of these coarser sediments did not appear to be related to water depths (Appendix Figure A7).

3.2.7.2 Surface Boundary Roughness

Surface boundary roughness ranged from 0.26 to 4.81 cm, principally due to fecal mounds or burrow openings caused by infaunal activities. The large roughness features at the high end of the range were all macro- or megafaunal burrow structures (Appendix Figure A8). Because most of the area sampled was represented by a low-energy, depositional environment, the surface boundary roughness elements were primarily of biogenic origin and not indicative of active transport regimes. The locations that appeared to have active transport had surface boundary roughness values ranging between 0.26 and 2.12 cm.

3.2.7.3 Prism Penetration Depth

With sediment grain-size fairly uniform across the entire study area, the variation in prism penetration was a good indicator of relative sediment shear strength as a function of biological mixing depth. The average prism penetration depth at the fine-grained stations (sediment grain-size major mode $\geq 4 \phi$) in the study area ranged from 3.75 to 20.69 cm; the spatial distribution of mean penetration depth at all stations sampled is shown in Appendix Figure A9. Sediments appeared to be more consolidated (lower penetration) at those stations in outermost Cook Inlet and the northern end of the Shelikof Strait; while this was due primarily to a shift in sediment grain-size major mode to a coarser fraction (very fine to medium sand), there were 5 stations (Stations 7, 8, 15, and F2, zone 1; Station F5, zone 0) in this elliptical region outlined in Appendix Figure A9 that were fine-grained.

The typical variation in sediment water content and shear strength caused by differences in bioturbation intensity at stations with similar grain-size distributions is dramatically illustrated by the two example images in Appendix Figure A10. Fine-grained sediments can be substantially dilated through the activity of deep bioturbating infauna; for example, Station 15 in zone 3 (Appendix Figure A11) shows a dramatic difference in geotechnical properties compared to the sediments shown in Appendix Figures 6 and 8, because of the burrowing activity of head-down, deposit-feeding infauna. Low-shear-strength sediments are susceptible to erosion, and the high frequency of stations with penetration depths in excess of 14 to 15 cm is further evidence of the low-energy, depositional nature of most of this site.

3.2.7.4 Apparent Redox Potential Discontinuity Depth

The distribution of mean apparent Redox Potential Discontinuity depths is shown in Appendix Figure A12; depths from individual image measurements ranged from 0.57 to 8.32 cm. The greatest depths were found in the southern end of the Shelikof Strait. The variation in Redox Potential Discontinuity depth was largely a function of the number, size, and type of infauna present at a particular location; apparent Redox Potential Discontinuity depths were not related to water depth ($r^2 = 0.48$). The lowest apparent Redox Potential Discontinuity depths were found at those stations in the northern end of the Shelikof Strait and in outermost Cook Inlet where the more consolidated sediments, with lower prism penetration due to lower bioturbation rates, were found.

There was no evidence of low-oxygen stress in the overlying water or high SOD caused by excess organic loading at any of the locations sampled. The range of apparent Redox Potential Discontinuity depths encountered did not display any anomalous patterns or unusual variations given the sediment type and amount of biological activity in the surveyed areas, indicating normal sediment with appropriate natural Redox development.

3.2.7.5 Infaunal Successional Stage

The mapped distribution of infaunal successional stages is shown in Appendix Figure A13. There was evidence of head-down, deposit-feeding infaunal taxa (mature Stage III communities) at all locations sampled except for Station F8, zone 0. Only one successful image was obtained from this station, and while it is possible that deposit-feeding taxa were present at this location in low densities, the shallow penetration depth (2.2 cm) prevented the detection of any subsurface feeding voids. This same phenomenon of shallow penetration obscuring the detection of Stage III communities was observed at the adjacent Station F6, zone 0 (Appendix Figure A14).

Because of their location at the sediment-water interface, Stage I taxa are ideal prey items for demersal fish and epifaunal macroinvertebrates. Appendix Figure A15 shows a crab at Station 1 (zone 1) that is most likely foraging on the tubicolous fauna evident at the sediment-water interface. However, the dominant infaunal community at all of the fine-grained stations were head-down, deposit-feeding taxa that were reworking the sediment to depths of 10 to 15 cm or more which is generally consistent with the results of sediment core age dating (Appendix Figure A16). Almost half the images collected (69 out of 156) showed evidence of secondary succession (Stage I fauna recolonizing the sediment surface after Stage III communities are established); Appendix Figure A17 shows an example of Stage I and III taxa present at the same location.

One unique faunal component recorded in this survey was at Station 3 in zone 3 at a depth of 279 m. Appendix Figure A18 shows a rare, in situ photograph of an obscure family of sea cucumbers, the Chirodotidae; the oral ends of the individuals bear a striking resemblance to coelenterates. Very little is known about the life-history of these elongate, worm-like holothurians, but the oral ends of individuals can be seen both above the sediment-water interface and 1 to 5 cm below the sediment surface.

3.2.7.6 Organism-Sediment Index

The spatial distribution of OSI values throughout the study area can be seen in Appendix Figure A19. An OSI of 6 or less typically indicates that a benthic habitat has experienced physical disturbances, eutrophication, or excessive bioavailable contamination in the recent past. The four stations that had median OSI values ≤ 6 were quiescent locations with limited profile information due to shallow camera prism penetration caused by coarser sediments or limited biological reworking. The low OSI at these four locations were attributed more to physical factors such as coarse or overconsolidated sediments than to anthropogenic sources of disturbance. Most OSI throughout the site were very high, reflecting a largely undisturbed environment with a mature biological community.

3.2.7.7 Interpretation of Sediment Profile Imaging Results

All the results from the SPI technology survey supported the conclusion that there was a largely undisturbed, low-energy depositional basin throughout the sampled area of the Shelikof Strait. Water depths throughout most of zones 1 through 3 ranged between 100 and 350 m, well below the depth at which storm energy would typically be able to impact the bottom. Only nine stations sampled at the northern end of the Shelikof Strait (Stations 1, 3, 5, and 20 in zone 1) and in outermost Cook Inlet (Stations F2, F4, F6, F8, and F13) were clearly unrepresentative of a quiescent environment. Station 2 in zone 1 was a transitional zone between the quiescent silt-clay facies found at the majority of stations and the few stations that had a surface sand layer present. Because the sand appeared primarily as a discrete stratum at the sediment surface (Appendix Figure A20), it most likely represented a quantum input of sand-sized particles at some point in the recent past; over time, this surface sand layer should get thoroughly mixed in with the underlying mud by the burrowing and feeding activities of the resident infauna.

Based on the reflectance contrast of the sediment profile, there were no areas obviously suffering from excess organic carbon loading, and no areas that appeared to have their biological communities compromised by any form of excess chemical contamination. One of the images at Station F2 in zone 2 (Appendix Figure A21) shows a localized patch of highly reduced sediment at depth, but this was more likely due to some form of biogenic decomposition rather than anthropogenic contamination. The uniform silt-clay sediment grain size, the prism penetration depths in excess of 12 cm reflecting low-shear strength, dilated sediments, the high OSI, and the high frequency of mature, Stage III infaunal assemblages at most of the stations sampled are all attributes that would be found in a low-disturbance, depositional regime. From the characteristics seen in the profile images, we would predict sediment organic carbon concentrations ranging between 0.5 and 2 percent at the majority of the stations, and annual depositional rates in the Shelikof Strait basin of between 0.2 and 1.5 cm/year.

All the data from the profile images point to both high sediment quality and benthic habitat values at most of the area surveyed throughout the site. From the data available from SPI technology, there appeared to be no detectable adverse impacts to this area from any of the oil and gas development activities in the region.

3.3 Sediment Cores

3.3.1 Geochronology

Sedimentation rates were calculated for 13 cores for which concentrations of organics and/or metals were determined. Sediment ages were determined using the fission-produced radionuclide ^{137}Cs (first introduced to Earth by bomb testing during the early 1950s) in tandem with excess ^{210}Pb (a naturally occurring decay product of ^{238}U ; half-life $^{210}\text{Pb} = 22.3$ y). By using two different independent radioisotopes, sedimentation rates could be verified by separate methods. Results for 9 of the 13 cores that could be dated showed good agreement between the two methods (Table 3-16). The sedimentation rate in the core collected from Z0F1 (Homer Harbor) in 1997 was too fast to obtain a reliable rate over the 34 cm core length and thus a longer, 2-m gravity core was collected during 1998 with successful dating results. The cores from Z0F8, Z1F2, and Z2F1 had discordant ages between the two methods; however, a range of likely sedimentation rates was established using one of the two isotopes.

Results for core Z3F2 (Figure 3-39) show an ideal decay curve (natural logarithm scale) for excess ^{210}Pb . The sedimentation rate calculated using the activities of excess ^{210}Pb is 0.44 cm/yr. A sedimentation rate of 0.45 cm/y calculated from the ^{137}Cs profile is in excellent agreement with the rate determined from the excess ^{210}Pb profile. When the ^{137}Cs activities for the core from Z3F2 are compared with the year determined from excess ^{210}Pb (Figure 3-39), the highest peak for ^{137}Cs corresponds well with the 1963 date of maximum ^{137}Cs input to the atmosphere. Thus, the geochronology results for the core from Z3F2 are considered reliable. Results from the other cores will be evaluated on a zone-by-zone basis below using the same perspective described here.

Sedimentation rates of about 1.3 to 1.5 cm/y are obtained for the 1998 core from Homer Harbor (Z0F1) (Figure 3-40). Thus, a record of contaminant inputs can be traced back to at least 1900 in this 2-m core. Sedimentation rates for all three cores from Kamishak Bay (Z0F5, Z0F6, and Z0F8) are about 0.1 to 0.3 cm/y (Table 3-16 and Figures 3-41, 3-42, and 3-43). Two minor discontinuities (lower activities of ^{210}Pb than predicted by the overall trend) in the activity profile for core Z0F5 occur at 2 to 4 cm and 8 to 10 cm; however, they have been included in the overall calculation of sedimentation rate using excess ^{210}Pb because we did not identify any reason to exclude them. The resultant sedimentation rate for the core from Z0F5 has a lower correlation coefficient than the other sites and an associated error as large as $\pm 25\%$. Results for cores from sites Z0F6 and Z0F8 are much better (Figures 3-42 and 3-43). The activity of ^{137}Cs decreases to zero about 1950 in each of the cores from Kamishak Bay based on the excess ^{210}Pb age. Such concordance verifies the overall reliability of the sedimentation rate for these sites.

Calculated sedimentation rates for cores from zone 1 (Z1F1, Z1F2, and Z1R3B) are all similar at about 0.2 to 0.3 cm/y (Table 3-16 and Figures 3-44, 3-45, and 3-46). The profile for ^{137}Cs in the core from site Z1F1 contains some discontinuities in the upper 5 cm that may be due to post-depositional disturbances and the excess ^{210}Pb profiles support some mixing in the upper 2.5 cm of the core. Using data from below the mixed zone, the sedimentation rates are concordant (Table 3-16). The excess ^{210}Pb profile for the second core from zone 1 (Z1F2, Figure 3-45) exhibits a large discontinuity at a depth of 10 cm where the activity of the ^{210}Pb decreases from approximately 7.5 dpm/g ($\ln = 2.0$ dpm/g on Figure 3-45) to 1 dpm/g ($\ln = 0.0$ dpm/g on Figure 3-45). This large change in activity complicates calculation of a sedimentation rate. If we use the point at which the activity of ^{137}Cs goes to zero (12.5 ± 2.5 cm), then the sedimentation rate is

about 0.27 cm/y. Thus, a general estimate of sedimentation rate can be made at this site. The third core from zone 1 also contains some minor anomalies at ~4 and 14 cm (Figure 3-46).

Sedimentation rates calculated using excess ^{210}Pb and ^{137}Cs for core Z2F2 (Figure 3-47) agree well at 0.62 and 0.65 cm/y, respectively, despite evidence for some mixing at the top of the core. The vertical profile for excess ^{210}Pb in the core from site Z2R16 shows clear indications of mixing over the top 10 cm of the sediment column (Figure 3-48). Excluding the 0 to 10 cm section, the calculated sedimentation rate is 0.53 cm/y relative to 0.72 cm/y using the full data set. The ^{137}Cs profile also does not fit simple interpretation and the sedimentation rate is 0.76 cm/y based on the assumed peak activity at 24.5 cm. Thus, a sedimentation rate of 0.5 to 0.7 cm/y was similar to that found for site Z2F2 and at least 3 times greater than found in zone 1. In contrast with results for Z2F2 and Z2R16, the calculated sedimentation rate for the core from site Z2F1 is 2 times higher at 1.3 cm/y (Table 3-16 and Figure 3-49). The slope of the excess ^{210}Pb profile, along with an incomplete ^{137}Cs profile, supports a high sedimentation rate at site Z2F1. Site Z2F1 was located in a depositional basin in zone 2 that may serve as an effective trap for fine-grained sediments.

Both cores from zone 3 (Z3F1 and Z3F2) had sedimentation rates of 0.60 and 0.44 cm/y, respectively (Table 3-16 and Figures 3-49 and 3-50). These rates are comparable with two sites from zone 2, but 2 to 3 times higher than found in zone 1.

The excess ^{210}Pb profile for one core collected from zone 4 during 1998 (Figure 3-51) may be interpreted as having 2 different sedimentation rates. Using data from the top 20 cm, the calculated sedimentation rate is 1.0 cm/y relative to a rate of 0.52 cm/y for the 20 to 43-cm interval in the core. The ^{137}Cs profile corroborates this perspective. The peak activity for ^{137}Cs at 29.5 cm (1963 or 35 y BP) is consistent with 20 years of sedimentation at 1.0 cm/y and 9 cm of sedimentation at 0.5 cm/y to yield about 38 years.

3.3.2 Physical Measurements

Concentrations of TOC in 14 sediment cores from outermost Cook Inlet (zone 0) and the Shelikof Strait (zones 1, 2, 3, and 4) range from 0.21 percent to 1.24 percent (Table 3-17). The highest TOC values are for cores from sites Z0F1 (Homer Harbor-1997, 1998) and Z4F4 (southernmost Shelikof Strait), whereas the lowest values for TOC are for cores from sites Z1R3B, Z0F6, and Z0F8 (Table 3-17 and Appendix A).

In zone 0, levels of TOC in all four cores (Z0F1, Z0F5, Z0F6, and Z0F8) have remained relatively uniform since the 1940s (Figures 3-52 through 3-56). Data for core Z1F1, with an average of 0.62 ± 0.08 percent TOC, show that inputs of TOC to the sediment column have been fairly constant since the turn of the century (Figure 3-57). In contrast, TOC values for core Z1F2 are more variable (Figure 3-58) since the 1950s. Prior to the 1950s, TOC concentrations increased from 0.60 percent at about 13 cm (~1950s) to 1.01 percent at 29 cm.

Sediment cores from zone 2 average 0.87 ± 0.11 percent TOC, (Z2F1, Z2F2, and Z2R16, Figures 3-60, 3-61 and 3-62). Values of TOC are relatively uniform in cores Z2F1 and Z2R16 (Figures 3-60 and 3-62), whereas in core Z2F2, TOC levels decrease gradually from 1.14 percent in the surficial layer to 0.84 percent at 32 cm (Figure 3-61). Average values for TOC in cores Z3F1 and Z3F2 are comparable at 0.83 percent and 0.81 percent, respectively. However, only values in core Z3F1 are uniform throughout the entire sediment column (Figure 3-63). Values for TOC

in core Z3F2 decrease from 0.89 percent between 0 to 2 cm to 0.70 percent at 32 cm (Figure 3-64). In zone 4, TOC values of 1.08 ± 0.06 percent for core Z4F4 (Figure 3-65), are comparable with those obtained for Homer Harbor (Z0F1) (Table 3-17).

Sand levels in sediment cores from Homer Harbor (1997-total length 35 cm) and zones 2, 3, and 4 average ≤ 6 percent. For these sediment cores, the silt+clay content is >90 percent and values are uniform throughout the length of the core (Figure 3-52 and Figures 3-60 through 3-65). However, the sand content in the sediment core recovered from Homer Harbor during 1998 averages 13.0 ± 9.6 percent from 20 to 235 cm (Table 3-17 and Figure 3-53). The grain-size distribution for the upper 20 cm was not determined. In the remainder of the sediment cores from zone 0 (Z0F5, Z0F6, and Z0F8) and those from zone 1 (Z1F1, Z1F2, and Z1R3B), the sand content averages between 17.8 percent and 59.6 percent (Table 3-17). The silt+clay levels in cores Z0F5, Z0F6, and Z0F8 are fairly uniform, averaging 69.4 ± 5.7 percent, 49.5 ± 6.9 percent and 46.6 ± 4.2 percent, respectively (Figures 3-54, 3-55, and 3-56). Values for silt+clay in core Z1F1 vary between 50 percent and 81 percent in the upper 14 cm, but are relatively uniform over the remaining 10 cm of the core, ranging between 67.1 percent and 71.9 percent (Figure 3-57). Silt+clay concentrations in the sediment core recovered from Z1F2 are fairly uniform throughout the core, with values ranging between 71 percent and 91 percent (Figure 3-58).

3.3.3 Organics

Sediment cores for organics analysis were collected from 11 of the fixed (non-random) stations and from 1 of the random stations in the study region (5 cores from zone 0, 2 cores each from zones 1 and 3, 3 from zone 2, and 1 from zone 4). The sediment cores ranged from 18 to 235 cm in length (depth of the core). Approximately 9 to 12 separate 2-cm sediment intervals were subsampled within a core section and analyzed for the same suite of organic target analytes as the surface sediments (Section 2.2.2). Finer resolution of the core at station Z2R16 was desired, therefore this core was subsectioned at separate 1-cm intervals over the first 15 cm of the core. Approximate sedimentation rates from an earlier core collected at station Z0F1 indicated that subsamples needed to be much larger than 2-cm intervals. A 230 cm core from Z0F1 was obtained during the 1998 sampling survey and was subsectioned between intervals of 5 cm and 35 cm.

The results of the sediment core analyses are summarized in Table 3-18 and detailed results including individual analyte measurements are included in Appendix B. The average concentrations of the three key total organic parameters measured (TPHC, total PAH, and total S/T) are comparable to the values observed in the surface sediments from the 5 zones in the study region (Tables 3-6 and 3-18). Core profiles for selected organic diagnostic parameters (Section 3.2.2) and TOC are shown for all 13 of the sediment cores in Figures 3-66 through 3-78. The selected diagnostic parameters were chosen based on their capacity to show the overall trends in total concentration, composition, and source of hydrocarbons.

In general, the core profiles do not show any clear trends that would indicate increases in the overall petroleum hydrocarbon concentrations over time. Geochronology of the cores has resulted in seven cores of sufficient depth to be dated to 1920 or earlier and four additional cores that can be dated to 1950 or earlier. The established dates for these cores provide sufficient data to evaluate the potential impact of Cook Inlet petroleum exploration and production activities, and is evaluated statistically in Section 3.3.5.

The core profiles of organics from zone 0 (Figures 3-66 through 3-70) do not reveal any patterns of analytes that are consistent between parameters. However, there are several slight patterns or anomalies which merit discussion. In the Z0F1 core (Kachemak Bay) collected in 1997 the CPI increases by a factor of 4 at the 2 to 4 cm depth interval (Figure 3-66). This anomalous increase in CPI is likely associated with particles of plant material (possibly from the wood chip processing operation on Homer Spit) entrained in the sediment. The deeper core from station Z0F1 (1998) does contain a trend of increasing total hydrocarbons over the past decade; however, the CPI is within the range of terrestrial plant influence and the corresponding PAH profile during that time frame is decreasing (Figure 3-67). The core profiles of Z0F5 (Kamishak Bay), Z0F6 (near Oil Bay), and Z0F8 show a recent decrease in the combustion/petroleum PAH ratio (0 to 5 cm depth - ~1970 to present), suggesting a possible shift in PAH composition (Figures 3-68 and 3-70). However, the total PAH decreases slightly in each core at the same depth interval, indicating that the decrease in the combustion/petroleum ratio is due to lower combustion PAH input.

A slight increase in the C2D/C2P source ratio is also apparent in the Z0F6 core at the 0 to 6 cm depth (Figure 3-69). The C2D/C2P ratio for the remainder of the core is considerably lower than other sediments from the study. The Well Creek seep oil sample analyzed as part of this study had a C2D/C2P value of 0.046, which is substantially lower than the value at depth in the Z0F6 core (0.082). This could indicate a mixture of “background” and Well Creek sources, with a greater Well Creek component in the past. In a study of Southern Alaska seeps, Page *et al.* (in press) reported a C2D/C2P ratio for an Oil Bay seep oil of 0.071. This value is close to the ratio at depth in the Z0F6 core (0.082), further indicating that the inputs of Oil Bay seep oil are an important local source of petroleum hydrocarbons in this area. There is also an apparent rise in the C2D/C2P ratio in the Z0F8 core (Figure 3-70) and the Z0F5 core (Figure 3-68), although at depth the ratios are higher than Z0F6 (~0.10) and increase to a value of ~0.20. The rise in the C2D/C2P ratio at the surface of these cores may indicate a greater contribution from “background” petroleum sources more recently.

The core profiles for the six stations in zones 1, 2, 3, and 4 are remarkably similar (Figures 3-71 through 3-78) with some variability in parameters. The total PAH values exhibit minimal variation, with some cores showing a slight decrease in total PAH over time to the present-day sediment (e.g., total PAH at Z1F1 increases as the core date approaches ~1920). The source parameter C2D/C2P ratio is very consistent with depth in all six cores, indicating a continuing and unchanging source of petroleum hydrocarbons from the early 1900s to the present. This is further supported by the Ts/Ts+Tm maturity ratio which is similarly constant throughout the core profiles. Overall, evaluation of the core profiles does not reveal any substantial petroleum hydrocarbon trend (either increase or decrease) which can be attributed to the onset of petroleum exploration and production activities (circa 1963) in Cook Inlet.

3.3.4 Trace and Major Metals

Sediment cores, ranging in length from 15 to 235 cm, were collected for metal analysis from 14 sites in the study area. Two sediment cores were obtained from Homer Harbor in zone 0 (F1), a 35-cm core in 1997 and a 235-cm core in 1998. Three additional cores were collected from zone 0 at sites F5, F6, and F8. In the Shelikof Strait, the following samples were collected: 3 cores from zone 1 (F1, F2, and R3B) and zone 2 (F1, F2, and R16), 2 cores from zone 3 (F1 and F2), and 1 core from zone 4 (F4). Approximately 5 to 12 separate 1- or 2-cm sediment intervals were

subsampled from each core and analyzed for the same suite of metals as the surface samples (Table 3-19, Appendix C).

Average metal concentrations for Al, Ag, As, Ba, Be, Cd, Mn, Pb, Sb, Sn, and Tl from each core site (Table 3-19) are comparable with levels obtained for bottom sediments from the Susitna and Copper Rivers (Table 3-1). For Cr, Cu, Hg, Ni, Se and V, average concentrations for all sediment cores, except Homer Harbor (Z0F1) and Z0F4 (Hg only), also are consistent with results obtained for bottom sediments from the Susitna and Copper Rivers. However, sediments from Homer Harbor are about 14 to 225 percent higher for these 6 metals relative to values for bottom sediments from the Susitna and Copper Rivers. Average Zn concentrations for all 14 cores range from 81.2 to 125 $\mu\text{g/g}$ (Table 3-19). These Zn values are consistently higher than the average Zn level of 75 ± 4 $\mu\text{g/g}$ in bottom sediments from the Susitna and Copper Rivers (Table 3-1). However, as previously discussed (Section 3.2.3 and Table 3-3), concentrations of all metals in suspended solids from the Susitna and Copper Rivers are higher than found in sediment cores. Further consideration of the relative contributions of river-borne sediment from the Susitna River versus the Copper River is presented in Section 4.1.

Sediment in cores from Homer Harbor (Z0F1) are fine-grained (>85 percent silt + clay) and organic-rich (~1.1 percent organic C). Besides having the highest sedimentation rate (~1.4 cm/y), sediments from Homer Harbor also contain the highest levels of Fe, Ag, As, Cr, Cu, Hg, Ni, Sb, and V (Table 3-19). With such a high sedimentation rate, the 235-cm long core from site Z0F1 collected during 1998 (Figure 3-53) records the turn of the twentieth century at ~140 cm. During this past century, concentrations of trace metals have varied only slightly, with most metals having a CV for the entire core of <5 percent, except for Ag and As (~12 percent) and Se (21 percent).

The other 3 cores collected from zone 0 (F5, F6, and F8) were all from the outer portions of Kamishak Bay. The average silt+clay content at these 3 sites (69 percent for Z0F5, 49 percent for Z0F6, and 46 percent for Z0F8) is considerably lower than observed for Homer Harbor (87 percent). Likewise, TOC values are lower at 0.44, 0.34, and 0.36 percent, respectively. Concentrations of trace metals for these 3 cores from zone 0 also are lower than in Homer Harbor (Table 3-19 and Figures 3-54, 3-55 and 3-56); however, they are comparable to metal values for bottom sediments or suspended solids from the Susitna and Copper Rivers. Despite sizeable differences in grain size among these cores from zone 0 (Table 3-19), metal concentrations generally varied by <10 percent. Overall, metal concentrations in sediment from this study do not show a strong positive relationship with levels of silt+clay as commonly observed in many other shelf and slope locations. This trend suggests that the mineralogy is similar among sediments with different grain-size distributions, and thus, only the size of the particles most likely varies as a function of the degree of powdering by glacial activity.

The sedimentation rate of 0.10 to 0.27 cm/y for cores from zone 0 (F5, F6, and F8) facilitates tracing the record of metal inputs back to the 1920s (Figure 3-54). Relatively minor shifts ($\text{CV} \leq 10$ percent) in metal concentrations occur over this ~ 70-y time interval. However, As and Hg levels in the top 2 cm (the 1990s) of the core (from Z0F5), are about 20 and 30 percent higher, respectively, relative to subsurface sediment, with no significant shifts in levels of Fe, Al, and most other metals. In core Z0F8 concentrations of TOC, Ba, Be, Cd, Hg, Sb, and Zn have decreased by 20 to 30 percent over the past 20 years (top 5cm), yet no changes in the Fe and Al content of these sediments was observed (Figure 3-56). Similar to core Z0F5, As levels are

about 20 percent higher in the top 2 to 5 cm of core Z0F8 and Z0F6. Concentrations of Fe, Ca, Cd, Cu, Cr, Mg, Mn, Ni, Sb, V, and Zn (Figure 3-55 and Table 3-19) are ~ 30 percent lower at 4 to 6 cm in the core from Z0F6 relative to other samples from Kamishak Bay. In sharp contrast, concentrations of Be, Sn, and Tl are 20 to 25 percent higher in the same layer. These transitions may be related to input of volcanic material deposited during the rather large time interval of 1947 ± 10 years.

Two of the three cores recovered from zone 1 (F1 and F2) have similar metal concentrations throughout the cores ($CV \leq 10$ percent) (Table 3-19) with the exceptions of about 25 percent higher As and Cd and about 15 percent lower Al in core Z1F2 relative to core Z1F1 (Figures 3-57 and 3-58). These three exceptions match higher TOC levels in core Z1F2 and may be related to deposition of more As- and Cd-rich (Al-poor) organic matter in these sediments. Core Z1F1 (Figure 3-57) records about 100 years of sediment input with little change in metal levels, except for slightly higher Cr levels (10 to 20 percent) prior to the 1920s. Higher concentrations of Fe, Ni, Cr, V, and Zn are observed in core Z1F2 below a depth of about 15 cm, which corresponds to the 1940s (Figure 3-58). The third core from zone 1 (R3B), has the lowest values of As, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Sn, Tl, V, Zn, and TOC observed throughout the study area (Figure 3-59 and Table 3-19). These low levels of trace metals most likely result because sediment from this core averages 60 percent sand-size particles that include extensive amounts of volcanic ash.

Sediment cores from zone 2 (Figure 2-1) were collected near the western (Z2F1) and eastern (Z2F2) sides of the Shelikof Strait, respectively, whereas core Z2R16 was from a central basin. The silt+clay content for these cores is uniform at 95 to 99 percent. No differences greater than ± 5 percent occur for concentrations of Fe and Al (Table 3-19). Trace metal levels also vary by < 10 percent (CV) among these three sites with the exception of Cd (Table 3-19 and Figures 3-60, 3-61, and 3-62). Cadmium concentrations at Z2F2 vary downcore from 0.14 $\mu\text{g/g}$ in the surficial 2 cm interval to 0.27 $\mu\text{g/g}$ at 19 cm (Figure 3-61). A similar increase downcore also is observed in core Z2R16, with Cd values increasing from 0.10 $\mu\text{g/g}$ in the top 1 cm to 0.15 $\mu\text{g/g}$ at 5 cm (Figure 3-62). In contrast, levels of Cd were relatively uniform in core Z2F1 at 0.13 ± 0.01 $\mu\text{g/g}$ over the entire 33 cm length of the core (Figure 3-60). Overall, in zone 2, no changes in concentrations of trace metals, with the exception of Cd in Z2F2 and Z2R16, have occurred over the past 50 years (Figures 3-60, 3-61, and 3-62).

Two cores were recovered along a track extending north (Z3F2) to south (Z3F1) in zone 3 (Figure 2-1). The grain-size distribution (Table 3-19, Figures 3-63 and 3-64), indicates that the sediments in this region are very fine-grained, containing > 98 percent silt+clay. Average Al and Fe for all samples from the two cores vary by < 6 percent, averaging 7.15 ± 0.42 percent and 4.39 ± 0.08 percent, respectively. In addition, average concentrations of Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Sn, Tl, V, and Zn differ by ≤ 10 percent for these sediment cores and about 10 to 20 percent for Ag, As, Be, Mn, and Se. Relative to the other three zones, maximum concentrations of Ba, Mn, Sn, Tl, and Zn were found in sediments from zone 3 (Appendix C).

Sedimentation rates in cores from zone 3 were 0.60 cm/y and 0.44 cm/y. These rates indicate that the history of metal inputs at these sites can be traced to the 1950s in core Z3F1 and the 1920s in core Z3F2 (Figures 3-63 and 3-64). Thus, metal trends throughout these two cores, except for Cd, show that inputs to this region have been uniform over the past 70 to 80 years (Figures 3-63 and 3-64). Cadmium values in Z3F2 increase from 0.14 $\mu\text{g/g}$ in the surficial 2 cm

to 0.25 µg/g at 24 cm (Figure 3-64). The depth of peak Cd values is about the 1940s; however, such peaks may sometimes be explained by biogeochemical processes and may not be time-dependent. For example, in core Z3F1, a 50 percent increase in Mn (and As) values occurs in the top 2 cm of sediment, most likely the result of remobilization as previously shown for Mn in the Shelikof Strait (Massoth et al., 1979) and other depositional environments (e.g., the Gulf of Mexico, Trefry and Presley, 1982).

Sediment recovered from zone 4 (Z4F4), has >98 percent silt+clay and an organic carbon content of 1.08 percent (Figure 3-65), similar to that obtained for sediments collected in Homer Harbor (Table 3-19). Sediments in core Z4F4 have the highest concentrations of Al, Mn and Pb. Average concentrations of Al, Ba, Be, Cr, Cu, Fe, Hg, Ni, Pb, Sb, Tl, V and Zn differ by ≤5 percent and about 10 to 20 percent for Ag, As, Mn, Se, and Sn. Cadmium values vary downcore and range from 0.12 µg/g to 0.20 µg/g (Figure 3-65). The upper 2 to 5 cm of sediment show a 40-percent increase in Mn (and As) values, most likely indicative of remobilization, as previously discussed.

3.3.5 Statistical Results of Core Data

Indices Shifts Associated with the Post-1963 Development Time Period. Trends in metals and organic indices were analyzed to investigate the hypothesis that there was a shift in these indices associated with post-1963 oil development. In this analysis, post-1963 core sections were compared to pre-1963 sections for the 12 cores where appropriate dating and thus sedimentation rates were available. These cores were taken at the fixed stations Z0F1, Z0F5, Z0F6, Z0F8, Z1F1, Z1F2, Z2F1, Z2F2, Z3F1, Z3F2, Z4F4, and the random station Z2R16.

Small changes in the selected indices can also result from geochemical and biochemical processes in the sediments as detailed in Sections 3.2 and 3.3. The major finding here is that there are relatively small variations in the important indices with time or depth within a core and that the empirical association with the post-1963 oil development accounts for a small percentage of the total variation within a core. All 23 organic indices that were used to describe the spatial patterns in the surface sediments were analyzed using a standard randomized block analysis of variance. The results of this analysis are detailed below.

In Table 3-20, the first column gives the organic index analyzed. The second column gives the percent of the variation within a core (after the between-core variability has been removed) that can be attributed to the post-1963 intervention. The third and fifth columns give the mean shift in the index that is associated with the post-1963 intervention. A negative value indicates the index is decreasing historically to current time, a positive value indicates the index is increasing historically to current time. Associated with each of the mean shift columns are their respective results of the two analysis of variance tests, i.e., for the null hypothesis that the mean shift associated with the post-1963 development is zero.

In the first analysis (columns three and four in Table 3-20), the cores are considered fixed (*i.e.*, non-random samples, and the statistical test is for a mean shift associated with the 1963 intervention within these twelve fixed cores. In the second, and more realistic analysis (columns five and six in Table 3-20), the twelve cores are considered as random samples, and the statistical test is for a mean shift associated with the 1963 intervention for the population of all possible sediment profiles from the study area. In this second analysis, the variation in the intervention effect from core to core is modeled as a random effect, contributing to the statistical

uncertainty in estimating the mean intervention effect and thus increasing the P-value. P-value here is defined as the probability (assuming no 1963 intervention effect) of obtaining a mean shift as large or larger than the observed mean shift.

The major statistically significant feature in this table is the increase in perylene with depth in the cores, which is clearly detected in this analysis. For perylene, the higher mean value in pre-1963 core sections is scored as a negative intervention effect. The increase in perylene concentration with depth in all cores is due to well known biogenic processes of early diagenesis in marine sediments (Wakeham *et al.*, 1980).

A few of the other organic indices had statistically significant associations with the post-1963 period. The diagnostic PAH source parameters, C2D/C2P and C3D/C3P exhibited a positive intervention effect and could suggest a slight shift in petroleum source with depth. A decrease in the Ts/Ts+Tm ratio with depth could also be indicative of a shift in petroleum source over time, with the lower Ts/Ts+Tm ratios at depth indicating a greater contribution from a less-mature petroleum source. Several other hydrocarbon parameters also showed significant increases after 1963 (pristane, TPHC, nC27+nC29+nC31, and TOC). However, increases in all of these parameters can be associated with increases in plant wax or terrigenous hydrocarbon inputs. This is supported by the result that there are no corresponding post-1963 significant increases in any of the key petroleum hydrocarbon parameters (e.g., TPAH, petrogenic and pyrogenic PAH, N/P, etc.). This suggests that the observed post-1963 increases in these parameters may be due to increased terrigenous hydrocarbon inputs associated with terrestrial development activities (i.e., logging). Overall, based on this analysis, no increases in the key petroleum hydrocarbon indices were observed that are associated with the onset of petroleum exploration and production activities in 1963.

For post-1963 shifts in metal concentrations, the data were first normalized for iron concentration, generally removing differences between cores due to sediment properties. Table 3-21 presents the same kind of analysis as was done for the organic indices.

Higher concentrations of Mn (normalized to Fe) in surficial sediment (top 5cm) layers are commonly observed in marine sediments at outer continental shelf and slope environments (Trefry and Presley, 1982). Under reducing conditions at depth in the sediment, manganese oxides dissolve and dissolved Mn²⁺ ions diffuse upward until they are reoxidized near the sediment surface. This natural process leads to the surface sediment enrichment of Mn as seen most clearly at the following sites from this study: Z0F6, Z1F2, Z2F2, Z2R16, Z3F1, and Z4F4.

Concentrations of Ba (and the Ba/Fe ratio) in sediment cores show relatively uniform values (<10 percent deviation) from 1963 to the present at most sites. At two sites, Z0F8 and Z4F4, Ba levels were distinctly lower in the surficial layers of the sediment column. No systematic reason can be given for this trend in this study. However, barium sulfate is produced naturally in the tests of some decaying organisms (Bishop, 1988), a portion of which is likely to dissolve at the seafloor. In any case, the observed lower Ba/Fe ratios in surficial sediments at 2 to 3 sites is not likely to be related to any anthropogenic inputs. Cadmium (and the Cd/Fe ratio) shows a similar and more widespread (about 8 cores) trend of lower levels in more recent, surface layers. Cadmium is known to be released from sediment organic matter during early chemical diagenesis (Nriagu and Sprague, 1987). However, no simple reason explains why this process may be more exaggerated in recent times (e.g., why more Cd may be released from sediments

now than in the past). A general decrease in the input of Cd to the sediments of the Shelikof Strait is possible; however, there are no other data to support this explanation.

In addition to more obvious lower levels of Ba and Cd in surficial sediment, decreased concentrations of Sb, Cu and Tl were observed in surface layers from 1 or more cores, thereby yielding a statistical trend of lower metal/Fe ratios since 1963. In the case of Sb and Tl, the actual change in concentrations is small (<0.05 to $0.2 \mu\text{g/g}$) and the generally high analytical precision for these elements (± 0.01 to $0.04 \mu\text{g/g}$) leads to the observation of statistically significant changes. Overall, no increases in metal concentrations have been observed since 1963 that can be related to the anthropogenic activities.

3.4 Fish Tissue

This section documents the collection and analytical results for the fish sampled during the 1997 and 1998 R/V *Alpha Helix* cruises. Time, location, depth, and fish species caught are reported in their respective cruise reports (Arthur D. Little, 1997a; Arthur D. Little 1998a). Details of the number collected, physical measurements (sex, length, and weight), composite information, and the biological results for individual fish are given in Appendix F Tables F-1 through F-3.

3.4.1 Organics (PAH)

During the 1997 cruise, fish samples were collected from 3 different stations across 3 zones (zones 0, 2, and 3), and 3 species of fish were collected (Halibut, Arrowtooth Flounder, and Black Cod). Three stations across 3 different zones were also sampled in 1998 (zones 1, 2, and 3), with 6 species collected (Halibut, Arrowtooth Flounder, Black Cod, Aleutian Skate, Longnose Skate, and Pacific Cod). The catch distribution across the zones, in addition to the total samples for each year, are presented in Table 3-22. Fish liver samples were prepared from collected specimens and analyzed for PAH. Livers were analyzed because the highest concentrations of PAH would accumulate and be detected in this fatty organ if the fish were exposed to petroleum contamination.

Distributions of PAH in most fish tissue samples indicated a combination of petrogenic (e.g., C2-alkylated naphthalenes), pyrogenic (e.g., fluoranthene), and biogenic (perylene, detected at less than $2 \mu\text{g/kg}$ in 2 samples in 1997) hydrocarbons, all at very low concentrations. The individual PAH concentrations in fish tissue samples are included in Appendix B. Method detection limits (MDL), based on laboratory MDL tissue studies, range from approximately 1 to $5 \mu\text{g/g}$ (parts per billion [ppb]) dry weight. Minimum reporting limits (MRL), based on the lowest calibration standard, sample size, and pre-injection extract volume, ranged from approximately 2.8 ppb to 35 ppb dry weight. Values below the MRL are considered estimates and should be treated accordingly.

The concentrations of individual PAH rarely exceeded $20 \mu\text{g/kg}$ (ppb) and values of most individual PAH were near or below the MRL of the method (74 percent in 1997, 78 percent in 1998). Most of the PAH that were detected above the MRL were associated with low ppb blank contamination (66 percent of PAH above the MRL in 1997 tissues and 51 percent in 1998).

Naphthalene and phenanthrene concentrations were high for several fish liver samples. However, analysis of laboratory procedural blanks revealed low concentrations of naphthalene, C1-naphthalenes, phenanthrene, and benzo[g,h,i]perylene (see Section 3.6.2 for complete

laboratory QA/QC results). Table 3-23 compares the PAH detected in procedural blanks to the average PAH concentrations in fish tissue samples in zones 0, 1, 2, and 3.

In most instances, the concentrations of these PAH compounds in fish tissue samples were similar to or less than the concentrations of these compounds found in the procedural blanks. The average phenanthrene concentrations were elevated in Halibut tissue samples from all 3 zones in 1997, with concentrations ranging from 0.027 mg/kg to 0.052 mg/kg which were greater than the phenanthrene concentrations found in the two associated procedural blanks (0.016 and 0.006 mg/Kg). For the 13 tissue samples collected in 1997, the mean percent increase of the detected phenanthrene concentrations relative to the mean of the two procedural blanks (for each sample), is 55 percent. The Halibut tissues again contained the highest concentrations compared to the other species collected in 1998, but there was a smaller difference between the lowest blank and the tissue concentrations, in particular phenanthrene, ranging from 0.006 mg/kg to 0.009 mg/kg (Table 3-23).

The trace concentrations and distribution of PAH detected in the liver samples (Figure 3-79 and Table 3-24) are characteristic of pyrogenic sources (e.g., primarily non-alkylated PAH), most likely derived from atmospheric deposition, land runoff, and creosote pilings (Page *et al.*, 1995). The characteristic petroleum-alkylated homologue distribution (NRC, 1985) was not observed in any of the samples and represents clear evidence that these samples do not contain petroleum-derived hydrocarbons. Due to trace concentrations of PAH in these samples (e.g., most of the data were below the MRL) and the low-level blank contaminants, there are no apparent differences between the background levels of hydrocarbons detected in the fish and the zone from which they were collected.

3.4.2 Metals

Concentrations of trace metals were determined for 36 composite samples of liver from Halibut and Pacific Cod from single sites in zones 0, 1, 2 and 3 (Table 3-25 and Figures 3-80 to 3-83). Overall, metal values for these fish livers are quite variable (Table 3-25). In general, fish length and weight did not correlate well with liver metal concentrations in the Halibut, except for Hg (Figure 3-84). Mercury concentrations in Halibut liver correlated positively with both length and weight ($r = 0.80$ and $r = 0.82$, respectively). Concentrations of Be in all liver samples were below the MDL (0.002 $\mu\text{g/g}$, dry weight).

Metal concentrations in liver samples from the Arrowtooth Flounder (3), Black Cod (2), and skates (2) are within the range of values obtained for the Halibut livers (Table 3-25). However, lower concentrations of Ag, As, Cd, Cu, Se, V, and Zn in Black Cod livers, Ag, Hg, Mn, Ni, and Pb in Flounder livers, and Al, Cd, Hg, Mn, Ni, Pb, Se, Sn, V, and Zn in skate livers are observed relative to the Halibut livers collected in the same zone. In contrast, values of Ag in skate livers and Ag, As, and Sb in Pacific Cod livers are higher than the Halibut livers (Table 3-25).

Fifty-three samples of fish flesh (muscle) from halibut collected in zones 0, 2, and 3 were analyzed separately for total Hg content (Table 3-26). Concentrations ranged from 0.128 to 2.43 $\mu\text{g/g}$ (dry weight) or 0.022 to 0.486 $\mu\text{g/g}$ (wet weight). The highest levels were found in zone 2. In general, the highest Hg levels in halibut flesh are found in longer (older) specimens (Figure 3-85). Concern for adverse effects from Hg during human consumption of fish is based on a daily Hg intake of 0.1 $\mu\text{g/Kg}$ mass of human (EPA, 1999). At typical Hg levels of 0.10-0.15 $\mu\text{g/g}$, as

discussed by EPA (1999), a 70-Kg human could consume 50-70 g (2-2.5 ounces) of fish per day or 350 to about 500 g (about 2-18 ounces) per week. All mean values for Hg in halibut flesh from all zones in the Shelikof Strait are between 0.10 and 0.15 ug/g (wet weight). These are all considered within the range of natural levels. One of the lowest Hg levels of concern noted by EPA (1999) is 0.4 ug/g (wet weight); a point whereat consumption should be adjusted accordingly. Only one sample from this study has a Hg level >0.4 ug/g (wet weight) at 0.486 ug/g (wet weight).

3.4.3 P450 RGS Response in Extracts of Fish Liver

Three replicates of 13 fish liver extracts (10 µl) were analyzed after 16h of exposure using P450 RGS on September 29 and October 17, 1997. Of the 13 samples analyzed, only 3 samples produced a detectable RGS response (i.e., the fold induction > 1.0). These responses were just above background, yielding B[a]PEq of 0.9, 1.0, and 1.6 µg B[a]PEq /g lipid, which is consistent with results from an uncontaminated environment.

Extracts of 12 fish liver samples were analyzed by P450 RGS on January 7-8 and January 11-12, 1999, with the addition of 10 µL of each extract to two replicate exposure wells for both 6h and 16h. Extracts were notably oily, and in some instances, the fold induction responses were very low, indicating possible toxicity to the cells. Additional extract was obtained from the CAS/Kelso laboratory, and the RGS assay was again conducted on January 18-19, 1999, with the addition of 5 µL of each extract. No evidence of toxicity occurred with this test. The wide variation in percent lipids (2.5 to 79 percent) and percent solids (28 to 92 percent) of these samples produced high variability in the calculated equivalency values. Most samples produced very low responses, with 4 samples producing responses that were greater than the solvent blank (fold induction > 1.0). The 6h/16h response patterns were indicative of PAH (6h greater than 16 h). Based on the 16 h responses, these 4 samples yielded B[a]PEq from 0.3 to 6.5 µg/g lipid.

These results indicate that the livers of the fish contain little or no contamination by PAH or chlorinated compounds, which is supported by the very low PAH levels measured in the livers (Section 3.4.1). The complete results of the P450 RGS analyses are included in Appendix E.

3.4.4 CYP1A (P4501A) Response in Different Species and Different Tissues

1997. This section will first address all three species of fish analyzed in 1997 and then discuss the results for Pacific Halibut (*Hippoglossus stenolepis*) in more detail, as this was the species with the greatest number of specimens and geographic coverage and therefore provides the best opportunity (therefore, the most power) to contrast conditions in the three zones as they affect CYP1A response in fish.

All fish species--Fish were captured at 1 station each in zones 0, 2, and 3 (Figure 2-1). The majority of fish analyzed (35) were Pacific Halibut, and these were caught in each of the 3 zones. There were 4 Arrowtooth Flounder (*Atherestes stomias*) captured in zone 2 and 1 captured in zone 3. There were 5 Black Cod, or Sablefish (*Anoplopoma fimbria*), all caught in zone 3.

With few exceptions, CYP1A was detected in 2 organs (liver and kidney) which included responses in 3 cell types--hepatocytes in liver, and tubules and vascular endothelium in the kidney (Table 3-27). A few responses (1/44) were also observed in the liver vascular endothelium and liver bile duct cells (1/44). Likewise, in the gills a few responses were seen:

pillar cells (4/44), epithelial cells (2/44), and vascular endothelium (2/44). In general, however, the gills showed little or no induced CYP1A protein; only hepatocytes in the liver and both kidney cell types were responsive.

In the hepatocytes, responses ranged from 0 to 10.5 out of a possible maximum score of 15. Likewise, in the kidney tubules scores ranged from 0 to 10.5 out of a possible maximum score of 15. In the kidney vascular epithelium scores ranged from 0 to 12, with the same maximal score possible.

Pacific Halibut-- Halibut were collected in zones 0, 2, and 3. The specimens ranged in length from 72 to 145 cm (standard length [SL]). Both males and females were retained. The mean Pacific Halibut IHC scores are provided by zone in Table 3-28. Although for each of the 3 cell types in Table 3-27, there was a trend of highest mean scores in zone 0, intermediate scores in zone 3, and lowest scores in zone 2, in only one cell type, kidney tubules, were these differences significant across all zones ($p=0.007$). The results of the Student Newman-Keuls test indicated that for the kidney tubule, CYP1A response for zones 0 and 3 fell within the same group while zone 2 was lower and significantly different. Sex and length did not explain a significant amount of the variance of CYP1A response in Pacific Halibut cell types.

1998. This section will first address all 6 species of fish analyzed in 1998, and then discuss the results for Pacific Halibut (*Hippoglossus stenolepis*) and Pacific Cod (also called True Cod or Grey Cod) (*Gadus macrocephalus*) in more detail. Both of these latter species were collected in larger numbers than the other species, and from all 3 sites. In 1998, heart was added to the gill, liver, and kidney tissues analyzed for CYP1A response and histopathologies.

All fish species--Fish were collected at 1 station each in zones 1, 2, and 3 (Figure 2-1). The majority of fish analyzed were Pacific Cod (60) and Pacific Halibut (41) which were collected in each of the 3 zones. The sites in zone 2 (Z2 R14A) and zone 3 (Z3 R1A) were the same sites at which Halibut were collected in 1997. There were also 4 Arrowtooth Flounder (*Atheresthes stomias*) collected in zone 3 and 5 collected in zone 2; 4 Black Cod (or Sablefish) (*Anoplopoma fimbria*) collected in zone 3; 1 Aleutian Skate (*Bathyraja aleutica*) collected in zone 3; and 1 Longnose Skate (*Raja rhina*) collected in zone 1.

CYP1A was detected in all 4 organs analyzed (Table 3-27). The majority of the responses (scores other than zero) were in 4 cell types--hepatocytes in liver (45/116), tubules in the kidney (37/116), epithelial cells in the gill (30/116), and endothelial cells in the heart (30/116). Additionally, a few responses were observed in gill pillar cells (3/116).

The possible range of scores for the CYP1A response in each of the cell types analyzed was from 0 to 15. Liver hepatocyte scores ranged from 0 to 4.5; kidney tubule scores ranged from 0 to 9; gill epithelial cell scores ranged from 0 to 4.5; heart endothelial cell scores ranged from 0 to 8; and gill pillar cell scores ranged from 0 to 4.

Aleutian Skate--One Aleutian Skate was collected in zone 3. It was female, weighed 6.6 kg, and was 145 cm long (SL). This skate received a liver hepatocyte score of 1.5, a gill pillar cell score of 4, a gill epithelium score of 3, and a kidney tubule score of 9. The gill pillar cell and kidney tubule scores were the highest scores for those cell types among all fishes collected in 1998.

Longnose Skate--One Longnose Skate was collected in zone 1. It was male, weighed 8.25 kg, and was 110 cm long (SL). This skate received a liver hepatocyte score of 1.5 and a kidney tubule score of 6.

Black Cod--Four male Black Cod were collected in zone 3. They ranged from 58 to 70 cm (SL) and from 1.8 to 3.8 kg in weight. Black Cod received CYP1A scores ranging from 1.5 to 3 for liver hepatocytes, 3 for gill epithelium, 1 to 2 for kidney tubules, and 4.5 to 8 for heart endothelium. Each fish had a measurable response (above zero) for each of these cell types. The heart endothelium scores were the highest among all the analyzed species.

Arrowtooth Flounder--Four Arrowtooth Flounder were collected in zone 3 and 5 were collected in zone 2. The fish from zone 3 ranged from 55 to 76 cm (SL) in size and from 1.5 to 4.4 kg in weight. The largest fish was female and the other 3 were male. Two of the fish (both males) received CYP1A scores for kidney tubules of 5. There were no other CYP1A responses (above zero) in these fish. Arrowtooth Flounder from zone 2 ranged from 49 to 80 cm (SL) in size and from 0.8 to 4.4 kg in weight. One of these fish was female (61 cm/2.2 kg) and the rest were male. As found in Arrowtooth Flounder from zone 3, those from zone 2 received CYP1A scores only for kidney tubules. The scores ranged from 1.5 to 4.

Pacific Halibut, zone 1--Twelve Halibut were collected in zone 1. They ranged from 73 to 122 cm (SL) in size and from 3.2 to 20 kg in weight. There were 4 females and 8 males, and the 2 largest fish were both female. These fish received CYP1A scores only for liver hepatocytes, ranging from 0.75 to 1.5. Only 3 of the 12 fish from zone 1 had scores other than zero.

Pacific Halibut, zone 2--Seventeen Halibut were collected in zone 2. They ranged from 77 to 110 cm (SL) in size and from 5 to 18 kg in weight. Five of the fish were female and 12 were male. As in zone 1, the 2 largest fish were both female. These fish received CYP1A scores for both liver hepatocytes and kidney tubules, though only 1 fish had a score other than zero (1.5) for liver hepatocytes, and only 3 fish had scores other than zero (1.25 to 8) for kidney tubules. The score of 8 for kidney tubules was the second highest kidney tubule score in 1998.

Pacific Halibut, zone 3--Twelve Halibut were collected in zone 3. They ranged from 72 to 115 cm (SL) in size and from 4 to 13.6 kg in weight. Four of the fish were female and 8 were male. The largest fish was female. These fish received CYP1A scores only for kidney tubules, and only 1 fish had a score other than zero (3).

Pacific Cod, zone 1--Sixteen Pacific Cod were collected in zone 1. They ranged from 55 to 81 cm (SL) in size and from 1.8 to 5.2 kg in weight. Ten of the fish were female and 6 were male. The 3 largest fish were female. Thirteen of the 16 fish received CYP1A scores for liver hepatocytes that ranged from 1.5 to 3; 4 fish received scores for gill epithelium that ranged from 2 to 3; 10 fish received scores for kidney tubules that ranged from 1 to 4; and 7 fish received scores for heart endothelium that ranged from 0.5 to 5.

Pacific Cod, zone 2--Twenty-nine Pacific Cod were collected in zone 2. They ranged from 55 to 81 cm (SL) in size and from 1.9 to 7.8 kg in weight. Twenty-one of the fish were female and 8 were male. The 7 largest fish were female. These fish received scores for the same cell types as Pacific Cod from zone 1, and for gill pillar cells as well (2 fish had scores other than zero, both scoring 3). Seventeen of the 29 fish received scores for liver hepatocytes, ranging from 1 to 4.5; 15 fish had scores for gill epithelium ranging from 0.5 to 4.5; 5 fish had scores for kidney

tubules ranging from 0.5 to 5; and 15 fish had scores for heart endothelium that ranged from 0.5 to 5.

Pacific Cod, zone 3--Fifteen Pacific Cod were collected in zone 3. They ranged from 55 to 79 cm in size and from 1.9 to 5.5 kg in weight. Eight of the fish were male and 7 were female. Five of the 15 fish received CYP1A scores for liver hepatocytes that ranged from 1.5 to 3; 6 fish received scores for gill epithelium that ranged from 1 to 3; 5 fish received scores for kidney tubules that ranged from 1 to 4; and 4 fish received scores for heart endothelium that ranged from 2 to 6.

CYP1A Response by Organ--The number of responses (greater than zero) per organ (inclusive of all species) was similar among organs; the highest was liver (0.39), followed by kidney (0.32), gill (0.28), and heart (0.26).

CYP1A Response by Species--Considered by species, Halibut had the lowest number of responses (greater than zero) per individual (0.2), followed by Arrowtooth flounder (0.78), Pacific Cod (1.87), Longnose Skate (2), and Black Cod and Aleutian Skate (4).

CYP1A Response by Zone--Without consideration of species caught, zone 1 had the highest number of responses (greater than zero) per fish (1.36 responses/fish), followed by zone 2 (1.24 responses/fish), and zone 3 (1.19 responses/fish). When Halibut collected in 1998 are considered in a statistical analysis as was performed previously for fish collected in 1997 (see above), no significant differences between zones were noted in any of the CYP1A responses (Appendix Table I-40). The same followed for the Student Newman-Keuls test results for the Pacific Cod, i.e., no differences in the CYP1A response between zones. The significance of the low to moderate IHC (CYP1A) scores measured in the fish tissues analyzed in this study is discussed in Section 4 of this report.

3.5 Statistical Results

This section summarizes and provides highlights of the statistical analyses. Full results of statistical analyses are provided in Appendix I. The majority of corresponding figures and tables are also provided in Appendix I of this report.

Surface sediments were collected from 59 locations and examined for 121 chemical and physical parameters as part of the 1997 *Alpha Helix* survey. Sediments from 35 locations, analyzed for 118 chemical and physical parameters, comprised the 1998 statistical analysis data set (Ca, Mn, K, and AVS/SEM were not measured in these sediments, but oil-degrading bacteria were added). Ninety-five organic compounds in each sediment sample were analyzed. Appendix I Table I-1 is a presentation of analyte number and name. While the entire list is necessary for the fingerprinting of specific petroleum sources, combinations and/or ratios of individual analytes can best describe spatial differences. For this reason, and to reduce errors associated with multiple testing, the large organic list was reduced to 23 chemically and biologically important groupings (Appendix I Table I-2). The statistical comparisons presented below were performed using these critical organic compounds plus an additional 26 inorganic sediment measurements (49 analytical values per sediment sample) for the 1997 surface sediments. Twenty-three inorganic and five biological parameters were determined in the 1998 surface sediment, resulting in a total of 51 analytical parameters per sediment sample.

As part of the 1997 survey, replication was varied within and between zones for the purpose of establishing estimates of within station and within zone. Between-zone variability of parameters of interest was modeled using sediments from both the 1997 and 1998 sampling periods in addition to monitoring the variance associated with the years of sampling.

3.5.1 Coefficient of Variation

3.5.1.1 Variability Within Surface Stations

Three stations (Z1R15, Z2R2, and Z3R13) containing 7 field replicate surface grabs collected in 1997 each were used to assess within-station variability. The CV was used to describe the amount of variation of each analyte measured in the 3 zones. The objective of the analysis was to establish a means of comparison between the small-scale distribution of individual analytes at a station with the overall variance of individual analytes in all zones. Appendix I Table I-3 presents the CVs for each of the 49 parameters of interest. Overall the variation was quite low, ranging from 0.22 percent for Fe to a maximum of 8.07 percent for total S/T, suggesting that overall small-scale spatial variance (e.g., within an individual station) is minimal.

3.5.1.2 Variability Within Zones (Surface Stations)

As described in Section 2.1.2, 59 station locations were established and sampled over 4 zones in 1997 (Zones 0, 1, 2, and 3). “Randomness” of location and the number of replicate samples varied within each zone. Zone 0 was dominated by “fixed” stations (8 stations of 3 replicates each), a consequence of bottom sediment type. Zones 1, 2, and 3 contained 14 stations each; 11 possessing 1 replicate, 2 with 3 replicates, and 1 with 7 replicate surface samples. A fourth analysis was conducted on a subcore taken from one sample at each of the “3 replicate stations” (those stations where 3 distinct field replicate samples were taken). This fourth chemical analysis was not considered to be a station replicate due to lack of independence. At best, it could be considered a duplicate, or pseudo-replicate (Hurlbert, 1979). The information contained in these samples is nonetheless important and has been averaged into the values of the source replicate. Coefficient of variation was again used to address variability; however, this analysis included all samples taken within each of the 4 sampling zones in 1997. Appendix I Table I-3 provides the CV on all parameters for each of the 4 zones and a single CV which describes the system variability represented by all zones, stations, and replicates (105 total samples). As expected, variability within zones was greater than within stations.

Coefficient of variation was greatest in zone 0, ranging from 8.52 (Al) to 101.51 (Perylene) percent with only 16 of the 49 analytes having a CV of less than 25 percent. Following in descending order of variability and ascending distance from outermost Cook Inlet: zone 1 had 28 analytes with a CV less than 25 percent (range 4.32 percent Al - 82.36 percent TALK); zone 2 had 31 analytes with a CV lower than 25 percent (range 4.24 percent Al - 107.05 percent sand); and zone 3 had 34 analytes with a CV less than 25 percent (1.88 percent Fe - 114.67 percent sand). The range of CV calculated for all stations ranged from 6.2 percent (Al) to 114.67 percent (sand) and had only 18 analytes with a CV lower than 25 percent.

Figure 3-86 plots in descending order the analyte CV for each of the zones normalized to the overall analyte CV. It is obvious that zone 0 is the most variable and that zones 1, 2, and 3 are quite similar, with zone 3 exhibiting a slightly lower level of variability. The CV ratio depicted in Figure 3-86 is also of interest in that ratios less than 1 indicate that the variability within a zone is less than overall variability for a specific analyte. Variability appears to decrease with

increasing distance from outermost Cook Inlet with 69, 20, 12, and 4 percent of the analytes displaying a CV ratio of greater than 1 in zones 0, 1, 2, and 3 respectively.

3.5.2 Analysis of Variance

3.5.2.1 Between-Zone Comparisons

A General Linear Models (GLM, see Section 2.3.2) analysis was conducted to identify significant between-zone analyte differences ($p \leq 0.05$). Additionally, if the GLM indicated a statistically significant difference between zones, a Student Newman-Keuls multiple range test (SNK, see Section 2.3.2) was run to separate zones at the 0.05 level of significance. Results of the SNK comparisons are generally arranged in descending order of the dependent variable (e.g., zinc), with significant differences between categorical variables (e.g., Zone) identified by a unique letter code (e.g., A,B,C). Categorical variables sharing the same code are not significantly different and can be considered as a group. Categorical variables that share more than one code (e.g., AB) indicate an overlap between groups and/or individual categorical variable. When overlap is noted, only categorical variables with unique codes differ significantly. Table 3-8 provides a summary of the 1997 and 1998 results. Appendix I Tables I-4 through I-8 summarize the GLM/SNK results performed on the surface sediments collected in 1997. Appendix I Tables I-16 through I-23 summarize the GLM/SNK results performed on the surface sediments collected in 1998.

Surface Sediments - 1997. Seventeen metals were examined for significant zone differences. Untransformed data produced significant results for all metals, with the exception of Mn, Ni, Ag, and Tl. In general, zones 0 and 3 are most often different and that zones 1 and 2 regularly overlap with each other and/or with zones 0 and 3. The results of this test are given in Appendix I, Table I-4. When metals data are transformed by dividing by the percent Fe within a sample, all metals are different between zones except As, Mn, Hg, and Ag. Again, zones 0 and 3 are most often identified as unique by the SNK.

Nine chemical/physical sediment parameters measured as percentages of sediment (Al, Ca, clay, Fe, Mg, K, sand, silt, and TOC) were examined and are presented in Appendix I Table I-6. Only Al shows no significant difference between zones. The trend in zone differences differs somewhat from that in the trace metals analyses presented in Appendix I Table I-5. These higher represented analytes tended to group together in pairs, with four of them combining zone 0 with zone 1, and zone 2 with zone 3.

Organic compounds of interest (Appendix I Table I-2) were treated in a manner similar to sediment metals. Two sets of GLM analyses were performed on the 23 organic groupings. The first set of statistical analyses examined untransformed data and the second examined TOC transformed data. Appendix I Tables I-7 and I-8 summarize the statistical results. Fifteen organic groups showed significant difference between zones in the untransformed data set (Table 3-8), while after TOC transformation 18 groupings were indicated as having significant zone differences. Zone 0 was most often unique; however, trends of increasing, or decreasing, concentration with distance from outermost Cook Inlet were less frequent for this group of chemicals than for either the trace metals or the physical sediment parameters.

Surface Sediments - 1998. The GLM/SNK zone analysis was repeated for the 1998 data set on surface sediments measured for 17 metals. Two data sets were evaluated for differences among the defined zones, 1 transformed by dividing each analyte by the percent Fe and 1 non-

transformed. Nine of the 17 metals analyzed showed significant differences between zones using the non-transformed data. In general, zones 0 and 1 were not different from one another on most of the parameters, but different from the other zones (2, 3, and 4) that were grouped together. Following transformation, 6 of 19 metals were shown to have statistical difference between the zones. The differences were less distinct among the zones, but in general, zones 0 and 1 were unique compared with the other zones. The complete analysis results are reported in Appendix I Tables I-16 and I-17.

Six chemical/physical sediment parameters measured as percentages of sediment (Al, clay, Fe, sand, silt, and TOC) were examined and are presented in Appendix I Table I-18. Only Al and Fe showed no significant difference between zones. The groupings were similar to that observed with the trace metals, with the zone 0 and zone 1 sediments paired together and significantly different from the other three zones which were not different from one another. Transformation of the data by the percent iron yielded identical results (Appendix I Table I-19).

The GLM/SNK zone analysis was performed on the same 23 organic groupings measured in 1997, both transformed by TOC and non-transformed. The results are summarized in Table 3-8 (non-transformed data only) and Appendix I Tables I-20 and I-21. Only seven organic groups showed significant difference between zones in the non-transformed data set (Table 3-8 and Appendix Table I-20), while after TOC transformation eight groupings were indicated as having significant zone differences. In general, zone 0 tended to be the most unique, particularly after transformation, with differences attributed mostly due to the concentrations parameters such as the Total PAH and Petrogenic PAH.

As part of the biological analyses, surface sediments were collected to evaluate the RGS-P450 response to corresponding extracts. Significant zone differences for both parameters (TEQ and B[a]PEq) were detected in both the data transformed by TOC and data non-transformed. For each analysis, the response at zone 0 was generally significantly lower than all other zones (1, 2, 3, and 4). The results of this test are given in Appendix I Tables I-22 and I-23. Two new variables were introduced in the 1998 sampling survey, i.e., heterotrophic and crude oil emulsifying bacteria. These were also analyzed for between-zone differences and resulted in no differences, using either transformed or non-transformed data (Table 3-8, Appendix I Tables I-22 and I-23). The mean percent survival for the sediment toxicity tests was also assessed and the results revealed that no significant difference in toxicity exists between zones where sediments were collected (zones 0, 2, and 3). The results for both transformed and non-transformed data are given in Appendix I Tables I-22 and I-23.

Surface Sediments - 1997 and 1998 Combined. A data set consisting of 16 stations, evaluated for 19 metals and 4 physical parameters and sampled during both the 1997 and 1998 surveys (including zones 0, 1, 2, and 3), was constructed to examine the zone differences over the entire sample survey. A GLM model paired with a Bonferroni multiple comparison test was used to establish significant differences ($p < 0.05$) between the zones. Seven metals contained significant differences among zones using the non-transformed data. Many of the zones were grouped together (i.e., two groupings that overlapped one another) and followed the patterns observed with the individual sampling year analyses. Three physical parameters were determined to be significantly different across zones, essentially separating zone 0 from the other zones (1, 2, and 3) or from zone 3. Data transformed by the percent Fe yielded 4 of the metals and 3 physical parameters significantly different across zones, generally isolating zone 0 from the other zones

or zone 3. The complete summary for these analyses is given in Appendix I Tables I-24 and I-25. Only where the GLM determined a significant difference were the data then subjected to the Bonferroni analysis and included in the summary tables.

The GLM/Bonferroni model was also used to establish significant differences among the zones using a data set comprised of the 23 organic groupings measured at the 16 stations. For the non-transformed data set, only 6 of the organic groupings were found to contain significant differences among the zones. As was observed with the results for the surface sediment zone analyses performed separately above, zone 0 was distinct from the other zones mainly due to the lower concentration of parameters such as total and petrogenic PAH, and the sum of the LALK. The same six parameters were determined to be significantly different in the analysis of the transformed data. The results for these data are summarized in Appendix I Tables I-26 and I-27.

The two RGS-P450 biological indicators (TEQ and B[a]PEq) were statistically analyzed for differences across zones using data normalized to TOC and non-transformed data collected at 14 common stations where measurements were performed during each sampling year. Zone 0 was distinctly lower than zone 2 on both biological parameters, with the other zones (1 and 3) no different from either of these two zones using the non-transformed data. After normalization to TOC, the B[a]PEq showed similar differences to the non-transformed data (i.e., zone 0 distinct from zone 2) while the TEQ was not statistically different across the zones. The results for these data are summarized in Appendix I Tables I-26 and I-27.

3.5.2.2 Between-Year Comparison (1997 vs. 1998)

A data set consisting of repeated station sampling for both the 1997 and 1998 surveys was analyzed for differences across the sampling period. The 16 stations were analyzed first using GLM followed by a Bonferroni multiple comparison test to establish whether there were significant differences between the sampling periods. Only where the GLM determined a significant difference were the data then subjected to the Bonferroni analysis and included in the summary tables.

Out of the 19 trace metals analyzed, 3 (Al, Ag, and Sn) exhibited statistical differences during the 2 sampling periods using the non-transformed data and 2 (silt and clay) of the physical parameters showed significant differences. Following transformation, only 2 (Ag and Sn) of the 19 metals and the same 2 physical parameters were found statistically different between the years of sampling. Results for this analysis are summarized in Appendix I Tables I-28 and I-29.

The 23 organic parameters were compiled from the 16 common stations and evaluated using the GLM/Bonferroni model to test for yearly differences. Only 1 of the 23 organic groupings was found to be significantly different between the years of collection (Oleanane/Hopane) using either the transformed or non-transformed data set. A summary of this analysis is given in Appendix I Tables I-30 and I-31.

Differences between years for the two RGS-P450 biological indicators (TEQ and B[a]PEq) were evaluated using data normalized to TOC and non-transformed data that was collected from 14 common stations. There were significant differences between the sampling years for both the transformed and non-transformed data (Appendix I Tables I-30 and I-31).

3.5.3 Pearson's Product-Moment Correlations

3.5.3.1 Sediments

Twenty-Station Sediment Data Analysis. Concurrent measurements for 35 physical/chemical parameters and 2 biological indicators (Appendix I Table I-9) were made at 20 stations during the 1997 sampling survey; 8 in zone 0 and 4 in each of zones 1, 2, and 3. Six stations (zone 1, 7 and 13; zone 2, 1 and 13; zone 3, 11 and 14) had a single field replicate. Three field replicates were taken at the remaining 14 stations. To explore possible correlations between sediment parameters of special interest (amphipod MPS, RGS-P450 toxicity equivalent, AVS concentration, total SEM minus AVS concentration) a Pearson's correlation was performed. Appendix I Table I-10 presents a summary of the results of the processing of untransformed data.

The mean amphipod survival had significant ($z \leq 0.05$) negative correlations with 15 metals, depth, silt, and TOC, but no significant correlation was observed with SEM-AVS. RGS-P450 expressed as TEQ positively correlated with depth, silt, TOC, two metals, and three organic compounds. SEM-AVS correlated negatively with two metals and two organics and had no positive associations. Conversely, AVS positively correlated with three metals and two organic compounds. However, after the percent silt effect was removed, there were few significant differences due to metals or organic contaminants (Table 3-29).

An arc sine square root transformation was applied on all data reported as percents (e.g., amphipod toxicity, clay, and Fe) and the Pearson's correlation was again performed. Appendix I Table I-11 is a summary of this analysis. Amphipod toxicity negatively correlated with the same analytes as with the untransformed data. RGS-P450 positively associated with eight analytes. SEM-AVS and AVS remained unchanged.

Fourteen-Station Sediment Data Analysis. Concurrent measurements for 30 physical/chemical parameters and two biological indicators (Appendix I Table I-32) were made at 14 stations during the 1997 and 1998 sampling surveys; 8 in zone 0 and 2 in each of zones 1, 2, and 3. To explore possible correlations between sediment parameters of special interest (i.e., RGS-P450 toxicity equivalent) a Pearson's correlation was performed. Appendix I Tables I-33 presents a summary of the results for the untransformed data.

The B[a]PEq biological parameter contained significant ($p < 0.05$) positive correlations with 6 metals, 4 organic indices and 2 physical parameters and exhibited a significant negative correlation with the percent sand. The TEQ had significant positive correlations with 4 metals, 2 physical parameters, and 4 organic indices in addition to containing a significant negative correlation with the sand parameter. The complete results for this analysis are given in Appendix I Table I-33. Following normalization, the B[a]PEq was determined to be positively correlated to 2 metals, 1 physical parameter, and 2 organic indices, while containing significant negative correlations with 2 metals and 1 of the organic indices. After normalization, the TEQ data set contained significant positive correlations with 2 organic indices (total PAH and petrogenic PAH) and significant negative correlations with 2 metals (Ni and Cr). The complete results for this analysis are given in Appendix I Table I-34.

Sediment toxicity tests were only performed on seven sediment stations collected in 1998, five of which were repeats of stations that were collected in 1997 (therefore, ten samples are common to both years, with the remaining sediment toxicity test results from nine stations collected in 1997). However the organism used for each year of sampling was different, therefore effectively

eliminating any meaningful correlations between this parameter and the physical/chemical measurements on a set consisting of both years' data.

The seven 1998 stations where sediment toxicity to the amphipod *Ampelisca* was determined were analyzed separately for correlation to the physical/chemical parameters, even though amphipod toxicity can be considered marginal if at all (see Section 3.25). No significant/meaningful correlations were observed between the metals and organic parameters and the mean percent amphipod survival. For example, the only significant correlations, the total PAH ($r=0.81$, $p=0.026$), petrogenic PAH ($r=0.77$, $p=0.041$), percent clay ($r=0.74$, $p=0.036$), and TOC ($r=0.85$, $p=0.016$) were all *positively* correlated with the amphipod survival indicating that mean percent amphipod survival increased with increasing PAH concentrations.

3.5.3.2 Fish Tissue

Tissues - 1997. Sixty-one fish of three species (Black Cod, Arrowtooth Flounder, and Halibut) were collected from zones 0, 2, and 3, at stations F7, 14, and 01, respectively. Tissues from multiple fish within a station and species were composited to generate 13 tissue samples which were processed for 41 organic chemicals, 18 metals, and 2 biological indices (Appendix I Table I-12). A subset of 45 fish was measured for standard length, sexed, and sampled for P450 indicators. Two distinct data sets containing analytical results were generated, one populated with chemical tissue concentrations and the other with length, sex, and P450 indicators. For the purpose of correlative statistics, mean lengths and P450 indicators for unique species and their associated composite were merged into the analytical data set containing analytical chemical results.

The results presented in Appendix I Table I-13 show that very few meaningful, significant correlations between the biological parameters and tissue chemical parameters were obtained.

Tissues - 1998. In 1998, one hundred sixteen individuals from six species (Black Cod, Arrowtooth Flounder, Halibut, Aleutian Skate, Longnose Skate, and Pacific Cod) were collected from zones 1, 2, and 3. Thirty tissue composites were generated and analyzed for 41 organic chemicals, 19 metals, and 2 biological indices. Again, individual tissue responses were averaged in order to correspond to the appropriate chemical/physical measurement performed on the tissue composite. The data sets compiled for Pearson's correlation analysis included all fish regardless of species, a Halibut subset, and a Pacific Cod subset. A summary of the analytes within each data set is given in Appendix I Table I-35.

The review of all significant correlates, both positive and negative, is given in Appendix I Tables I-36 and I-37. Consideration as to the detection limits of both the biological and PAH parameters precludes conclusions regarding the validity of the statistically significant correlations. The response of the biological variables "hepatocyte" and "kidney tubules" contain the most detections across all species (see Table 3-27) and can potentially contain the most reasonable correlations. However, when observing these two variables' significant correlates in the "all fish" data set (Appendix I Table I-36), there are only 3 metals and 2 organic compounds with positive correlations to these response variables. The significant correlations for the two organic compounds (benzo[ghi]perylene and Total PAH) are primarily driven by the same measurement, an exceptionally high value for the benzo[ghi]perylene in one fish composite sample (see Zone 3, Aleutian Skate, in Table 3-24).

Tissues - 1997 and 1998 Combined. Data from both years were combined to determine correlations among the biological parameters with the chemical/physical measurements. Data sets included all fish regardless of species, a Halibut subset and a Pacific Cod subset. The review of all significant correlates, both positive and negative, is given in Appendix I Tables I-38 and I-39. Results are no different than from those discussed for the individual years' data sets, that is, there are very few meaningful correlations between the biological and tissue chemical parameters.

3.5.4 Analysis of Variance/Covariance

Tissues - 1997. Hypothesis tests using the GLM/SNK procedures were applied to both the combined P450/chemical data set and the P450 exclusive data set. The combined data set was examined in a series of three GLM tests; 1) all fish, 2) Halibut only, and 3) Halibut only with length as a covariant. Appendix I Table I-14 summarized the significant results of these analyses. Zones that can be described by the SNK multiple range test possess unique letters (A or B). It is apparent that few of the 68 chemical/biological parameters examined differ significantly with zone.

Appendix I Table I-15 summarizes four GLM processes using only the Halibut tissue measurements, with the P450 indicators as dependent variables, zone as the independent variable and various combinations of sex and length as covariants. The addition of both sex and length appears to refine the analysis and bring into closer focus differences between zones.

Tissues - 1998. Hypothesis tests using the GLM/SNK procedures were applied to the P450 data set, and consisted of fish species that were collected in more than one zone, that is, the Halibut, Pacific Cod, and Arrowtooth Flounder. Each species was investigated separately with 1) no covariate, 2) with sex as a covariate, and 3) with length as a covariate. The results for each species analyzed with no covariate is given in Appendix I Table I-40. Of the significant GLMs, not one resulted in statistical separation using the SNK test. The analysis of covariance yielded identical results, with no difference across the zones for any species.

Tissues - 1997 and 1998. Hypothesis tests using the GLM/SNK procedures were applied to both to a chemical data set and a P450 data set, each consisting of zones where Halibut sampling was repeated during both years, that is zone 2 and zone 3. Analytes for the chemical data set included the individual and total PAH, the individual metals, and the P450-RGS response variables (see Appendix I Table I-35 for complete listing). Analytes for the P450 data set included the cellular biological measures (Appendix I Table I-35). Classification variables in both data sets included year, zone, and the year-zone interaction. Both sex and length were also analyzed as covariates in the biological data GLM. The results for the GLM/SNK analysis for chemical/biological parameters (with no analysis of covariance) are given in Appendix I Tables I-41 and I-42. Very few of the analytical parameters exhibited significant differences across any of the classification variables. Furthermore, any relationships observed among the biologic measures were identical after an analysis of covariance was performed using sex and length as separate covariates (length was noted as an insignificant covariate).

3.6 Quality Control Results

This discussion is intended to provide an evaluation of data quality and usability based on the field and laboratory QC samples collected and analyzed during the first year of this study.

3.6.1 Quality Control in the Field

QC samples were collected in the field to assess overall precision, accuracy, and representativeness of the sampling and analytical efforts. The number of QC samples collected for this effort is based on the total number of field samples as established in the Field Logistics Plans (Arthur D. Little, 1997a; Arthur D. Little, 1998). All results for these samples are presented in Appendix B. Discussion and interpretation of the results are provided in the following sections.

The quality of the sample collection process is evaluated by means of equipment, field, and trip blanks. These sample blanks provide valuable data by monitoring the sampling process for field contaminants and cross-contamination. The trip blank was transported along with the empty sample containers being taken by the sampling team into the field. Equipment and field blanks are used to assess contamination introduced in the field environment and by sampling equipment. When sampling is complete, the blanks are submitted along with the field samples for laboratory analysis. In addition, replicate samples were collected to demonstrate reproducibility and to assess precision.

3.6.1.1 Trip Blank

One trip blank was prepared and shipped along with the station Z0F1 samples in 1997, but its results can be interpreted to assess the potential cross-contamination during transportation of all samples collected for this study. The trip blank was analyzed for PAH, SHC, and S/T. Only one sample shipment was required. Overall, no significant concentrations of relevant analytes were detected in this sample.

For PAH analysis, low molecular weight PAH compounds (i.e., naphthalenes and phenanthrene) were detected at very low concentrations. These were flagged with J and B codes. This demonstrates that values detected were below the detection limits and present on the procedural blanks associated with this sample, and that no cross-contamination occurred during transportation. For SHC analysis, several n-alkanes were detected between 0.026 and 0.14 µg/g. These low concentrations are probably due to the presence of non-SHC compounds at the same elution time or trace laboratory contamination from solvents and/or septa. No analytes were detected for S/T analysis.

3.6.1.2 Equipment Blanks

A total of nine equipment blanks were prepared and submitted for analysis over the entire study period. Three were collected from rinsate of the grab sampling equipment at stations Z0F1, Z0F8, and Z3R13 in 1997, and three similar rinsates were collected at locations Z1R19, Z2R14A, and Z2R23 in 1998. Both the 1997 and the 1998 surveys included an equipment blank collected from rinsate of fish dissection equipment that was used in the on-board laboratory associated with location Z2R14A. One additional equipment blank sample was collected from rinsate of the box core sampling equipment (and core liner) at location Z0F1.

Low molecular weight PAH compounds (i.e., naphthalenes, phenanthrene, and dibenzothiophene) were detected at very low concentrations in the fish dissection and rinsate equipment blanks. These analytes were flagged with J and B codes. This indicates that the values detected were below the detection limits, detected in the procedural blanks associated with these samples, and that no cross-contamination occurred while using the sampling and dissection tools. Low concentrations of midrange n-alkanes were detected (i.e., nC22 through nC31) in the equipment blanks. In the case of samples Z0F1 and Z0R13, concentrations of high-end n-alkanes were also detected. When taking into account the differing volume levels and collection techniques in comparing results from the equipment blanks and field samples, it can be concluded that the potential for cross-contamination from the equipment used to the field samples is negligible. These results are consistent with what is expected in equipment blanks and no further data qualification is required. In addition, these analytes were also observed in procedural blanks at comparable concentration levels. No S/T compounds were detected in the equipment blanks.

3.6.1.3 Field Blanks

Three field blank samples were taken during the collection of sediment samples. One field (deck) blank was collected during sediment sampling in 1997 at location Z1R9 when a forest fire smoke smell was noticed in the air. The other two field blank samples, deck blanks, were collected during sediment sampling at location Z2F1 and location Z2R23, in 1997 and 1998, respectively.

Low molecular weight PAH compounds (i.e., naphthalenes, phenanthrene, and dibenzothiophene) were detected at very low concentrations. These were flagged with J and B codes. This indicates that the values detected were below the detection limits and present in the procedural blanks associated with these samples, and that no contamination can be attributed to ambient sources. Low concentrations of midrange n-alkanes were detected (i.e., nC22 through nC31), probably due to laboratory contamination from solvents and/or septa. The analytes were also observed in the procedural blanks at the same concentration levels. No S/T compounds were detected in the field blanks.

3.6.2 Organics Quality Control

For this program QC measures for organics analysis included evaluation of surrogate compound recoveries and analysis of procedural blank samples, laboratory control spike samples, SRM samples, and control samples.

In addition, ADL participated in the NOAA/NIST intercalibration exercises for organics in 1998, 1999 and 2000. Triplicate analyses of marine and mussel tissue were analyzed for organics (including PAH) as part of these exercises. The results of the ADL analyses were within the top 10% of the more than 30 laboratories participating in the exercises.

3.6.2.1 Surrogate Results

Surrogate compounds were added to all samples including the tissue, sediment, and QC samples. These compounds were added at different concentrations, depending on the matrix, to determine the recovery efficiency during sample extraction, processing, and analysis. Recoveries of the analytes of interest are inferred from the recoveries of the surrogates. The recovery efficiency of all samples collected and analyzed for this study are presented in Table 3-30. In order to simplify the presentation of the surrogate data, only the mean percent recovery, standard deviation, and relative standard deviation were included in the table (percent recovery data for each sample are included in Appendix B). Overall, the surrogate recovery results met the DQO for the project.

3.6.2.2 Laboratory Control Spike Summary

Laboratory control spike (LCS) samples measure the normal concentration bias due to such issues as matrix effects and analytical method errors. For this project, LCS were analyzed on each of the matrices (i.e., sediments, water, oil, and coal), except tissue, as shown in Table 3-31. Fifteen sediment LCS were analyzed for PAH and 17 for SHC. Water LCS were also analyzed, 5 for PAH determination and 5 for SHC. As for the oil and “coal” matrices, only 1 LCS sample was analyzed for both PAH and SHC. Overall, the results are acceptable and demonstrate that the system was in control. Average recoveries were within the range specified in the Work Plan (35 percent to 125 percent). The SD and RSD are all at acceptable levels; the only exceptions are n-Decane for the water SHC LCS analysis with an RSD of 37 and acenaphthylene for the sediment PAH LCS analysis with an RSD of 36 (30 is the limit). The oil and coal matrices LCS recoveries are acceptable for both PAH and SHC analyses.

3.6.2.3 Procedural Blanks

Twenty-nine procedural blanks were analyzed in conjunction with the organics samples. Traces of some PAH target analytes were detected in the blanks at the low ppb concentration and were generally below the reporting limit for the method. Naphthalene and C1-naphthalene were identified in all the blanks, occasionally at concentrations above the reporting limit; however, these compounds are common contaminants associated with the solvents used during extraction and processing. Traces of some SHC target analytes were also detected in the procedural blanks (low ppb). Only in a few cases did the concentrations of any target SHC analyte exceed the reporting limit of the method. S/T target analytes were detected in the low ppb in only one of the procedural blanks analyzed. Overall, the procedural blanks met the DQO in the laboratory QA plan for the program, and do not indicate concentrations of laboratory contamination that will affect the quality or usability of the organics data.

3.6.2.4 Standard Reference Materials

Calibration Solution. SRM 1491 (a solution of certified PAH) was analyzed prior to each GC/MS sequence of samples for PAH analysis. The results of the SRM 1491 analyses are presented in Table 3-32. The difference of the measured values from the certified values is less than the ± 15 percent required in the QA plan, for all samples analyzed.

Sediment. One sediment SRM (SRM 1941a - certified for PAH) was analyzed with each batch of sediment samples. The results of the SRM 1941a analyses are summarized in Table 3-32. The percent difference of the measured values versus the certified values for PAH compounds was within the acceptance criteria (± 35 percent) for all target analytes with a few exceptions. Naphthalene had a mean percent difference of minus 43 percent and minus 51 percent in the 1997 and 1998 analyses, respectively. Fluorene was also below the acceptance criteria at minus 43 percent in 1998 only. These results indicate that the measurement of naphthalene and perhaps

fluorene in the sediments could be biased low due to loss of these more volatile PAH during sample processing. Average recovery of dibenzo[a,h]anthracene exceeded the certified value by 41 percent in 1998, and could indicate a high bias for measurement of this compound in sediments.

Tissue. Four tissue SRM (SRM 1974a - certified for PAH) were analyzed along with the tissue samples. The results of the SRM 1974a analysis are included in Table 3-32. Several analytes (naphthalene, anthracene, and phenanthrene) are outside the acceptance criteria (less than 35 percent difference from the certified value). The high recoveries of naphthalene and phenanthrene are likely the result of laboratory contamination as these analytes were detected in the associated procedural blank. The results for these compounds were qualified in the corresponding tissue samples. The high recovery of anthracene is consistent with the results obtained for this compound in multiple (more than 20 samples) analyses of SRM 1974a over the last three years, and is likely due to the light-sensitive nature of this analyte.

3.6.2.5 Analysis of Control Oils

Cook Inlet crude oil and North Slope crude oil samples were analyzed prior to each batch sequence for PAH, SHC, and S/T analysis. The results of the control oil analyses are compared to the laboratory mean values generated from multiple analyses of the oils. The results of the control oil analyses (Tables 3-33 and 3-34) indicate that accuracy and precision of the analytical methods for PAH, SHC, and S/T analyses are within the acceptance criteria required in the Laboratory QA Plan for the program.

3.6.3 Metals and Total Organic Carbon Quality Control

For this project, QC measures included instrument calibration, standard checks, analysis of standard reference materials (SRM), duplicate sample analysis, method and field blank analysis, and matrix spike analysis for each analyte.

3.6.3.1 Instrument Calibration and Standard Checks

Before instrumental analysis by FAAS, ZGFAAS, CVAAS, ICP/MS or nitrogen-carbon-sulfur analyzer, a three- to five-point calibration was carried out and the linearity of the individual analyte response factors checked. In all instances, the calibration curve for the standards met with the DQO of $r \geq 0.999$. The RSDs between the initial calibration and subsequent calibration checks were <15 percent in all instances.

3.6.3.2 Standard Reference Material Analysis and Intercalibration Exercise

For sediment and coal samples, the accuracy of the digestion and analytical techniques was determined by analyzing SRM BCSS-1, a marine sediment sample issued by the NRC in duplicate with each batch of 40 field samples. A total of 18 SRM BCSS-1 samples were analyzed. Metal concentrations obtained for the SRM BCSS-1 were within the limits specified by the NRC, except for Sb, Sn (1997) and TOC (1998) (Table 3-35). However, Sb, Sn and TOC values obtained for the SRM samples were within 15 percent of the concentrations reported by the NRC (Table 3-35), well within 20 percent of the certified value required by the DQO (Table 2-10). Because SRM BCSS-1 is not certified for Hg, SRM MESS-2, a marine sediment sample issued by the NRC, and SRM 1646a, an estuarine sediment certified by the NIST, were analyzed in duplicate with each batch of 40 field samples. Values obtained for these standards were within the limits certified by the NRC and NIST, respectively (Table 3-35).

To determine the accuracy for the liver and muscle tissue, SRM 1566a, an oyster tissue certified by the NIST, SRM DORM-2, a dogfish muscle, and SRM TORT-2, a lobster hepatopancreas standard, both issued by the NRC, were analyzed in duplicate for every 20 samples. Metal concentrations obtained for SRM 1566a, SRM DORM-2, and SRM TORT-2 are within the limits specified by the NIST (Table 3-36). Because no certified or reference data are available for Ba and Be in SRM 1566a, SRM DORM-2, and SRM TORT-2, a water sample certified by the NIST, SRM 1643d, was used to check the analytical accuracy for these elements and provide additional quality assurance for Sb, Se, and Tl. The metal values obtained for SRM 1643d are within the range of values certified by NIST (Table 3-36) and met the specified DQO (Table 2-10).

Accuracy for suspended solids from the Susitna, Knik, Matanuska and Copper Rivers was determined by the analysis of SRM 2704 (1998), a river sediment, and SRM 1643d (1998), a water sample, both issued by the NIST. Metal values for both SRM are within the certified limits specified by the NIST (Table 3-37). However, no certified reference values are available for Tl, V, and Zn. For the remaining source samples (Cook Inlet crude oil, Cook Inlet produced water, and the Point Woronzof municipal effluent), SRM 1643d (1997), a water sample certified by the NIST, and SRM SLRS-3 (1997), a riverine water sample certified by NRC, were analyzed. Results for these standards are within the limits specified by NIST and NRC, except for As, Ba, Sb, and Se (Table 3-37). Values obtained for these SRM samples are within 12 percent of the concentrations reported by the NIST and NRC (Table 3-37), well within specifications required by the DQO (Table 2-10). Because SRM 1643d and SRM SLRS-3 are not certified for Hg, SRM MESS-2 was digested and analyzed along with the Cook Inlet crude oil sample. Mercury concentrations for this standard are within the limits certified by the NRC (Table 3-37).

Florida Institute of Technology also participated in the 1998 NRC and NOAA intercalibration exercise for trace metals in marine sediments and biological tissues. Two samples of sediment and two samples of tissue were analyzed in quintuplicate for 17 and 13 different metals, respectively. The FIT laboratory was among 13 of 41 laboratories in the intercalibration effort to be rated superior and the only laboratory to report results for 60 sets of data with no values outside the accepted limits (Willie, 1998).

3.6.3.3 Duplicate Sample Analysis

Average analytical precision for the sediment portion of this study (including source material from the Susitna River, Copper River, Homer Harbor, and the coal sample) was determined from analysis of 10 duplicate samples and expressed as average of $[(\text{std. deviation}/\text{mean}) \times 100 \text{ percent}]$. The results are as follows: Ag (12 percent), Al (2 percent), As (6 percent), Ba (2 percent), Be (3 percent), Ca (4 percent), Cd (4 percent), Cr (5 percent), Cu (2 percent), Fe (2 percent), Hg (3 percent); K (0.5 percent), Mg (3 percent), Mn (2 percent), Ni (3 percent), Pb (2 percent), Sb (4 percent), Se (9 percent), Sn (5 percent), Tl (1 percent), V (5 percent), and Zn (5 percent). Results of the duplicates indicate precision is in all cases below the 25 percent required by the DQO (Table 2-10). Analytical precision for fish liver and muscle tissue analyzed in duplicate range from 0 to 18 percent. For the source samples, Cook Inlet crude oil, produced water and Point Woronzof municipal effluent, analytical precision ranges from 0 to 18 percent, except for Pb which, at low levels, averages 28 percent. Analytical precision for the river suspended solids ranges from 0.4 to 14 percent. Thus, results for these samples are well within the DQO (Table 2-10).

3.6.3.4 Method Blank Analysis

Two method blanks were processed and analyzed with each batch of samples to monitor potential contamination resulting from laboratory reagents, glassware, and processing procedures. No contamination from any of these sources was noted and concentrations of analytes in the blanks do not exceed 5 times the MDL.

3.6.3.5 Field Blank Analysis

Six field blanks (2 Van-Veen grab rinses, 1 trip blank, 1 deck blank, 1 fish lab blank, and 1 fish tool rinse) were analyzed for trace metals to monitor potential contamination from field operations. No contamination from any of these possible sources was noted. Concentration of all metal analytes in the blanks was <5 times the MDL.

3.6.3.6 Matrix Spike Analysis

Two matrix spike samples were analyzed with each batch of 40 sediments and/or source materials using the method of standard additions. Results from these analyses provide information on the extent of any signal suppression or enhancement due to the matrix. Spike results for the sediment, and source samples from Susitna River and Copper River, Homer Harbor and the coal samples (Tables 3-35 through 3-37), are within the 80 to 120 percent range specified in the DQO (Table 2-10), except for Ag, Hg (1998), Se, Sn (1998), and V. Even though the recoveries for these metals were <80 percent, no spike corrections were made to the results for these metals.

The percent recovery for the matrix spike samples for the fish liver and muscle samples (Table 3-36) were within the 80 to 120 percent range specified by the DQO for all metals, except Hg and Ni. Spike recovery for Hg averaged 60 percent for the liver-composite samples and 75 percent for the fish flesh samples. This low recovery is commonly observed when organic-rich samples are analyzed by CVAAS. All tissue Hg concentrations reported in Table 3-25, Table 3-26 and Table 3-36 were corrected for their spike recoveries. The Ni values for the liver composite samples were also spike corrected. Recovery of matrix spikes (Table 3-37) in the aqueous and oil source samples also were within the 80 to 120 percent range except for Ag, As (oil), Ba (water), Fe (oil), Ni (water), Se, and V. Nickel values (1998) and all V concentrations were spike corrected. Spike recovery for the river suspended solids (Table 3-37) averaged 97 ± 8 percent, well within the range required by the DQO (Table 2-10).

3.6.4 Toxicity Test Quality Control

During the conduct of the sediment toxicity tests, the established QA/QC measures were performed and monitored to evaluate the validity of the results. The following required QA/QC criteria were met during the performance of these tests and validate the results obtained:

- A 96.5 and 100 percent survival of amphipods in the 'home' control sediment for the *Eohaustorius* and *Ampelisca*, respectively, was greater than the acceptability criteria of 90 percent at the end of the test
- A 91.25 percent survival of amphipods in the 'reference' control sediment was greater than the acceptability criteria of 90 percent at the end of the test
- Salinity, pH, and ammonia in the overlying water were all within the tolerance limits of the test species
- The time-weighted average of daily temperature readings was within $\pm 1^\circ\text{C}$ of the desired temperature and the instantaneous temperature was always within $\pm 3^\circ\text{C}$ of the desired temperature

- Data used in statistical analyses and reported in Tables 3-14 and 3-15 were independently reviewed for accuracy by a second biologist

3.6.5 CYP1A (P4501A) Quality Control

The QC measures for the CYP1A determination included:

- Scoring of samples was performed blind (identities of samples were unknown to scorer)
- The correlation of subjectively determined CYP1A immunohistochemical staining scores with protein immunoblotting of hepatic microsomes, an independent and nonsubjective measurement of CYP1A, has been established at the laboratory in Woods Hole, Massachusetts (Woodin, *et al.*, 1997)

3.6.6 P450 Reporter Gene System Quality Control

1997. From the long-term QC chart, the mean RGS fold induction response to 1 ng/mL TCDD was 100 ± 30 (Figure 3-87). The RGS fold induction responses to TCDD on all assay dates in this study are shown in Table 3-38. These values are within two standard deviations of the running mean, indicating that the tests were acceptable. In addition, the CV of all samples tested, including both sediments ($n = 27$) and tissues ($n = 13$), were < 20 percent, indicating low between-replicate variability. The luminometer was calibrated on August 22, September 22, and October 21, 1997 and yielded linear response curves with an $r^2 = 0.9$, and a detection of 2 pg of luciferase.

1998. The RGS fold induction responses to TCDD on all assay dates in this study are shown in Table 3-38. These values are within two standard deviations of the running mean, indicating that the tests were acceptable. In addition, the percent CV of all samples tested, including both sediments ($n = 27$) and tissues ($n = 12$), were < 20 percent, indicating low between-replicate variability. The luminometer was calibrated on September 17, 1998 as well as January 29, 1999 and yielded linear response curves with an $r^2 = 0.9$, and a detection of 2 pg of luciferase.

3.6.7 Marine Heterotrophs and Crude Oil Emulsifier Quality Control

The QC measures for the enumeration of marine heterotrophs and crude oil emulsifiers included dilution duplicates of each sediment sample. Agreement between the duplicates for the marine heterotrophs was very good, indicating fairly homogeneous samples. The mean relative percent difference (RPD) for the marine heterotrophs counts within a plate (an individual plate was counted at three and five weeks) was 31 percent, while the mean RPD for the duplicate plate analysis per sample was 34 percent. The counts for the hydrocarbon degrader populations were low or barely detected among all samples. Where populations were detected on duplicate plates, the RPD was 51 percent.