35. TRACE ELEMENTS

35.1 Introduction

The trace element studies in the Cook Inlet drainages study area were conducted to acquire baseline data on naturally occurring constituents in upland soil and plants, freshwater river and pond sediment, and freshwater fish, as well as in marine sediments and biota in the Iliamna/Iniskin Estuary. Samples from these media were analyzed for physical and chemical parameters and inorganic constituents; marine samples were additionally analyzed for organic compounds.

The objectives for the trace elements studies were as follows:

- Collect and analyze baseline data on the levels of naturally occurring constituents in surface soil, vegetation, stream and pond sediment, and the tissues of fish from streams.
- Collect and analyze baseline data on the levels of naturally occurring constituents in sediment and biota tissues from the marine environment in the Iliamna/Iniskin Estuary.

Upland soil was sampled in 2004 and 2006 at 11 locations, and 23 species of plants from seven locations were sampled in 2004, 2006, and 2007. During 2004 through 2007, freshwater sediment was sampled at nine locations. Two species of fish were collected from two streams in 2004 and 2005.

In the marine environment in the Iliamna/Iniskin Estuary, intertidal sediments were sampled in 2004, 2005, and 2008 at eight locations. Subtidal sediments from four locations were sampled in 2004 and 2008. Sediments were sampled only at sites classified as soft bottom (silty to sandy) where coring or grab sampling was possible. One plant species, nine invertebrate species, and nine fish species were sampled in 2004, 2005, and 2008.

35.2 Results and Discussion

The upland study of soil and plants demonstrated that concentrations of all 26 elements for which samples were analyzed were detectable in soil samples and most elements also were detectable in plant tissues. Elements varied greatly in concentration across sampling locations and also in their relative abundance in a given location. In soil, aluminum and iron were the most abundant elements, with mean concentrations of 31,000 and 9,900 milligrams per kilogram, respectively. Both diesel-range organics and residual-range organics were detected at respective concentrations of 103 and 1,300 milligrams per kilogram in the single soil sample analyzed for these constituents. Since no development was present in the area where this soil sample was collected, the petroleum-range hydrocarbons detected were assumed to originate from biogenic sources. Total organic carbon was detected at a mean concentration of 15.4 percent.

Differences in elemental concentrations were apparent among plant species and between vegetative tissues and fruit tissues (i.e., berries) within individual species. Among plant groups, shrubs were sampled most often (46 samples) and lichens least often (5 samples). In each of the plant groups (trees, shrubs, forbs, grasses, lichens, mosses, and berries), the essential nutrients calcium, potassium, and magnesium were present in the highest concentrations. There were significant differences in concentrations of metals, anions, and cations between vegetative and fruit tissues. Both crowberry and low bush cranberry shared several of the same elements with significant differences. These included aluminum, barium, calcium, cobalt, magnesium, manganese, potassium, and zinc. Each of these elements, except potassium, had higher concentrations in vegetative tissues than in fruit tissue.

The study of trace elements in freshwater sediment and fish indicated that juvenile or young-of-the-year Dolly Varden and coho salmon contained detectable levels of most elements, cations, and anions. Zinc was present at the highest concentrations in fish tissue; the mean zinc concentration was 151 milligrams per kilogram, which is much higher than the observed concentrations of copper, the next most abundant element, which averaged 6.23 and 7.65 milligrams per kilogram for the two species. These relative concentrations are consistent with the essential nutrient status of zinc, for which fish have active uptake and homeostatic mechanisms in place to handle a wide range of concentrations. The greatest difference in elemental concentrations in fish between the two years was observed for cadmium; the mean cadmium concentration in Dolly Varden from Y Valley Creek in 2005 was more than 16 times higher than that in Dolly Varden from Y Valley Creek in 2004. In addition, the mean cadmium concentration in coho salmon from Y Valley Creek (in 2004) was nearly three times lower than in Dolly Varden from the same creek (in 2005). This is much greater than the range of detected cadmium concentrations in sediment from the two streams from which fish were collected (Y Valley Creek and Unnamed Creek; 0.05 to 0.45 milligrams per kilogram).

Except for zinc, concentrations in sediment were higher than concentrations in fish tissue (e.g., copper concentrations in sediment averaged 42.5 milligrams per kilogram relative to whole fish copper concentrations of 6 to 8 mg/kg). The most abundant elements in sediment were aluminum, calcium, iron, and magnesium, each with mean concentrations of over 4,000 milligrams per kilogram. Mercury was detected at the lowest concentrations in sediment (mean concentration of 0.015 milligrams per kilogram). Concentrations of trace elements in pond sediment were generally lower than concentrations in stream sediment; this pattern was not evident for cations and anions however.

The study of trace elements in marine sediments and biota documented a heterogeneous marine environment in the Iliamna/Iniskin Estuary. For sediments, grain size, as measured by percent fines, varied widely in intertidal sediments (1 to 96 percent) and showed substantial variation in subtidal sediments (25 to 85 percent). Concentrations for total organic carbon also were variable, ranging between 0.1 and 1.3 percent in intertidal sediments and between 0.2 and 0.7 percent in subtidal sediments. Concentrations of inorganic constituents varied by seven orders of magnitude, from mercury at 3 micrograms per kilogram (0.000003 grams per kilogram) to iron at 30 grams per kilogram. Concentrations of organic and inorganic constituents measured in sediment from the Iliamna/Iniskin Estuary agreed moderately well with values in existing literature for previous sediment studies in Cook Inlet. However, differences from previous studies were noted and demonstrate the need for an empirical baseline to document existing environmental conditions in the Iliamna/Iniskin Estuary. Arsenic, copper, nickel, and to a lesser extent, zinc were measured in Iliamna/Iniskin Estuary sediment samples at concentrations greater than concentrations identified with the threshold of biological response. This is an important finding because there has been little development in Iliamna/Iniskin Estuary. The concentrations of "fingerprint" hydrocarbons (i.e., an array of chemicals diagnostic of a likely source) did not rule out any of the three potential sources of low-level petroleum hydrocarbons—biogenic (from biological organisms), petrogenic (from petroleum), or pyrogenic (from combustion)—however, the information from the Pebble Project study provides some support for biogenic and pyrogenic sources.

Trace element concentrations in biotic tissues ranged by over five orders of magnitude from 1 microgram per kilogram for thallium in three fish species to 589,000 micrograms per kilogram for copper in a species of snail. Although there were few available and comparable data sets, concentrations of inorganic constituents measured in tissue samples in Iliamna/Iniskin Estuary compared quite well with values cited in literature for relatively pristine sites.

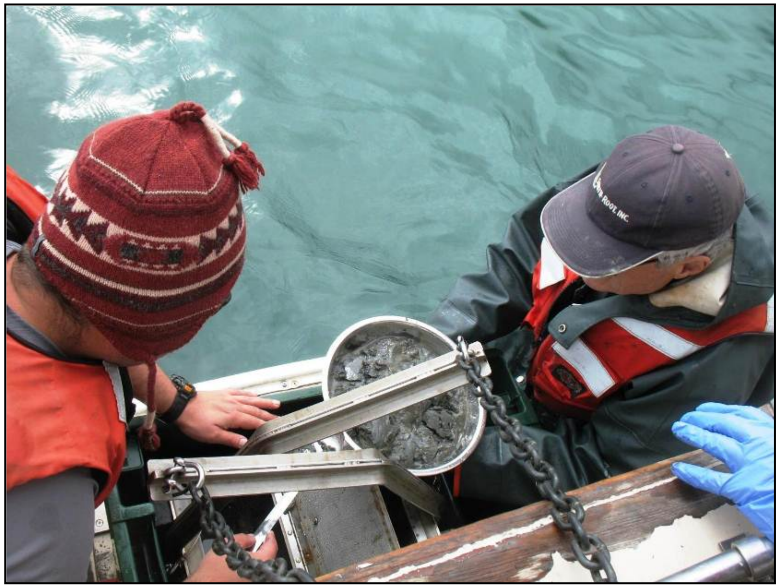
One observation was evident for cadmium. For adult salmonids and for Pacific halibut, the median concentrations were all less than 10 micrograms per kilogram. For juvenile Dolly Varden, starry flounder, and yellow sole, the median concentrations were between 10 and 100 micrograms per kilogram. For mussels, they were greater than 2,000 micrograms per kilogram. Furthermore, cockles and clams had substantially lower concentrations of cadmium than the mussels. On the other hand, the concentrations of cadmium in the habitat of these organisms—intertidal sediment, subtidal sediment, and water (marine water quality is described in Chapter 34)—is quite constant; cadmium was one of the constituents with the least variation. Thus it is clear that different organisms handle cadmium in different ways. Given the niche of mussels as filter feeders, it would appear that the high concentrations in their tissues arise from bioconcentration of cadmium directly from water, a phenomenon not shared by other filter feeders, i.e., clams and cockles—that had lower values for cadmium. However, bioaccumulation apparently does not cause high concentrations of cadmium in top predators such as salmonids.

Similar patterns of distribution among species were observed for boron and to a lesser extent for beryllium, chromium, lead, molybdenum, and thallium in the 2008 samples. One constituent that ran noticeably counter to this pattern was mercury. Median concentrations for mercury were highest in Pacific halibut, while mussels had relatively low concentrations. The data from the Pebble Project study are too limited to establish this observation as a certain case; however, the values from literature do support a pattern of elevated mercury in longer-lived carnivorous fish such as halibut.

Overall, analysis of the trace element data collected from 2004 through 2008 showed low concentrations of constituents as would be expected based on the general known history of the Iliamna/Iniskin Estuary as a marine habitat with virtually no recent development. However, some constituents were detected in samples at concentrations above the most conservative level that may cause a biological response, as reported in the literature. The detected concentrations are ascribed to natural conditions and are documented as existing conditions at the time of the study.

View of sampling location TE23, September 2007.

View of sampling location TE22, September 2007.



Benthic sediment sample collection with a Van Veen bottom sampler, July, 2008

Beach sediment core sampling, July, 2008.

Adult chum salmon sampled for tissue metals at MPS4, August 2004.

Sampling sediments from a mudflat, July 2008.