10. TRACE ELEMENTS

10.1 Introduction

The trace element studies in the Bristol Bay drainages study areas were conducted to acquire baseline data on naturally occurring constituents in upland soil, terrestrial and aquatic plants, freshwater stream and pond sediment, and freshwater fish tissues. Samples of these media from all locations were analyzed for physical and chemical parameters and inorganic constituents; a subset of samples was analyzed for organic compounds as well.

The objectives of the trace element studies were as follows:

- Collect baseline data to provide scientific documentation of the existing levels of trace elements, anions, and cations in surface soil, subsurface soil, fruit (e.g., berries) and/or vegetative (e.g., leaf) tissues from terrestrial plants, aquatic vegetation, stream and pond sediment, and freshwater fish tissues.
- Evaluate the baseline data to identify major factors influencing the distributions of naturally occurring constituents.
- Evaluate naturally occurring biogenic fingerprints in surface soil associated with petroleum-range-hydrocarbon analysis.
- Determine organic content in surface and subsurface soils.

Upland soil was sampled in the summer in 2004 through 2007. Two hundred fifty-three soil samples were collected from 117 locations in the mine study area, including 16 subsurface samples collected at approximately 10 percent of these locations.

Plants also were sampled in the summer in 2004 through 2007. Fifty-one species of plants were sampled from approximately 70 locations in the mine study area; samples from terrestrial plants were collected during two seasons in 2005 through 2007 to represent early vegetative growth and late-season fruit production, while samples were collected only in autumn in 2004. Fruit and vegetative-tissue samples were evaluated separately. Aquatic plants were sampled in autumn in 2005 through 2007. Analyses were completed on 707 vegetative-tissue samples (from terrestrial and aquatic plants) and 80 fruit samples (from terrestrial plants). All plant-sampling locations were collocated with soil- or sediment-sampling locations. Plant species sampled were those known to be used as browse by animals or for subsistence purposes by humans.

Freshwater sediment sampling was conducted annually in 2004 through 2007. In the mine study area during those years, 109 samples were collected from 23 river locations (large drainages), and in 2004, 21 samples were collected from 15 locations identified as minor drainages. In 2005 through 2007, 56 samples were collected from 25 lakes and ponds. Twelve seep samples were collected from nine locations in 2005.

Fish were collected in the mine study area from the North Fork Koktuli River, South Fork Koktuli River, Upper Talarik Creek, and several large lakes. Samples were collected from lakes each year from 2004 through 2008; samples were collected from each of the three rivers in 2004 and 2005, and from a subset of these rivers in 2006 through 2008. In 2004 and 2005, 345 whole-body fish samples were collected from rivers. In 2004 through 2008, 236 muscle and 87 liver samples were collected from lakes and rivers. Six fish species were sampled: coho salmon, Chinook salmon, arctic grayling, northern pike, Dolly Varden, and whitefish.

In the transportation-corridor study area, 17 locations were sampled for soil and vegetation in 2004, and 17 soil samples, 131 vegetative-tissue samples, and 10 fruit-tissue samples were collected. For sediments, in 2004 and 2005, 55 samples were collected from three streams, and 25 samples were collected from 15 locations in five lakes. For fish, 63 whole-body samples were collected from three streams and two species (coho salmon and Dolly Varden).

10.2 Results and Discussion

The study of soil and plants in the mine study area demonstrated that concentrations of all 26 trace elements for which samples were analyzed were above detection limits in soil samples, and most elements were similarly detected in plant tissues. Elements varied widely in concentration across sampling locations and also in their relative abundance in a given location. Both landform type (e.g., talus slope, flood plain) and habitat (e.g., alpine rock, riverine willow scrub) influenced the elemental concentrations in soil and plants. Somewhat stronger relationships were observed between habitat type and chemical concentrations in vegetation than between landforms and chemical concentrations in vegetation, although consistent, significant correlations for a given category and a single chemical were not apparent. In soil, aluminum and iron were the most abundant elements, with mean concentrations of 17,644 and 20,69400 milligrams per kilogram, respectively. Both diesel-range organics and residual-range organics were detected in 13 and all 23 samples analyzed for these constituents, with mean concentrations of 209 and 2,028 milligrams per kilogram, respectively. Since no development was present in the area where these soil samples were collected, the petroleum-range hydrocarbons detected were assumed to originate from biogenic sources, as confirmed by evaluation of the analytical fingerprint. Total organic carbon was detected at an mean concentration of 6.51 percent. It also was noted that cyanide was present at low levels in most samples.

For plants, shrubs were sampled most often (300 samples) and trees least often (17 samples). All of the 26 trace elements for which samples were analyzed were detected in at least some vegetative-tissue samples. Eleven trace elements (aluminum, barium, calcium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, and zinc) were present above minimum detection limits in almost all samples. Differences in elemental concentrations were apparent across plant species and between vegetative and fruit tissues of individual species. One species of moss (green terrestrial moss) had substantially higher mean concentrations of several trace elements than did other plant species. In general, mosses and lichens had higher concentrations than other plant species. It was of interest that naturally occurring cyanide was detected at low levels in 37 percent of vegetative-tissues samples and 25 percent of fruit-tissue samples. The highest concentrations of cyanide occurred in the vegetative tissues of the herb sour dock. There were significant differences in concentrations of metals, anions, and cations between vegetative and fruit tissues. Both crowberry and low bush cranberry samples shared several of the same elements with significant differences. The common elements included barium, copper, manganese, and zinc. Each of these elements, except copper, was found at higher concentrations in vegetative tissues than in fruits.

Overall, 198 sediment samples were collected in ponds, seeps, and minor drainages in the mine study area and were analyzed for trace elements, anions, and cations. All trace elements, anions, and cations for which analyses were done were detected in sediment samples. The most abundant elements in sediment were aluminum, calcium, iron, and magnesium, each with mean concentrations of over 3,500 milligrams per kilogram. Mercury was detected at the lowest concentrations in sediment (mean concentration of 0.040 milligrams per kilogram). A subset of samples from some locations was also analyzed for acid-volatile sulfide, simultaneously extractable metals, and organic constituents, to evaluate bioavailability. Evaluation of the results indicated a wide variability of concentrations in sediment among drainages and different types of waterbodies. For 11 trace elements included in a cross-drainage evaluation (arsenic, barium, cadmium, copper, lead, mercury, manganese, nickel, silver, vanadium, and zinc), concentrations were generally lowest in samples from the North Fork Koktuli River. Concentrations of arsenic, cadmium, copper, lead, manganese, silver, vanadium, and zinc were highest for the South Fork Koktuli drainage, whereas concentrations of barium, mercury, and nickel were highest for the Upper Talarik drainage. Only copper showed significant differences between all three major drainages, likely as a result of differential composition of the base rock across these drainages.

For anions and cations, sediment samples from ponds and minor drainages typically had higher concentrations than samples from other areas in the mine study area. Shallow soils transported by runoff into standing or slow-moving water are more likely to settle out as sediment, thus contributing to this trend. This was exemplified in samples where mean concentrations of cyanide were 17 times higher in samples from minor drainages relative to samples of river, seep, or pond sediments. These results are also consistent with the hypothesis that cyanide is being produced by bacteria in shallow soils. Samples from seeps had lower concentrations of cyanide than other sediment samples. Seep samples represent primarily groundwater, and thus there is no source of cyanide production in these sample locations. The different major drainages, ponds, seeps, and minor drainages had different signatures of natural levels of trace elements and anions.

The freshwater study of fish in the mine study area indicated that samples from all sampled fish species (northern pike, Dolly Varden, arctic grayling, coho and Chinook salmon, and whitefish) contained detectable levels of most of the 14 trace elements for which fish tissues were analyzed, including methyl-mercury. Some fish samples had whole-body analysis (345 samples) while for others only liver (87 samples) and/or muscle (236 samples) tissues were analyzed. Copper and zinc were present at the highest concentrations in whole-body samples across the different drainages. A wide variability of elemental concentrations was apparent over time and among drainages, fish species, and tissue types.

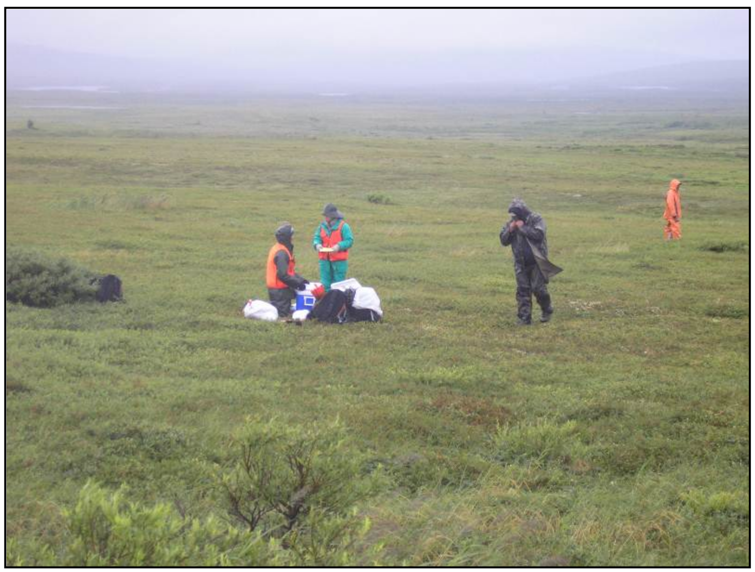
Trace element concentrations in whole-body samples were compared between fish species and between major drainages. Concentrations for various elements differed between species in each river and between rivers for each species. For example, the mean nickel concentrations for fish from the North Fork Koktuli River were higher than the mean concentrations for either the South Fork Koktuli River or Upper Talarik Creek in both 2004 and 2005. The combined 2004-2005 mean nickel concentration for whole-body fish samples from the North Fork Koktuli River (3.63 milligrams per kilogram) was almost five times higher than that for samples from the South Fork Koktuli River (0.76 milligrams per kilogram). Also, the variability of nickel concentrations observed in samples from the North Fork Koktuli River was not evident in samples from the South Fork Koktuli River. Additionally, copper concentrations were significantly higher in coho and Chinook salmon (whole fish) from the South Fork Koktuli River than in salmon from either of the other two major river systems. The higher copper concentrations in the South Fork Koktuli River were expected because copper-rich bedrock is located in the headwaters of that watershed. This copper-rich bedrock results in substrate that is higher in copper than the substrate in other areas. Fish take up the copper through respiration. Since higher concentrations of copper are present in the rock and surface water in this area, more copper is taken up by the fish in these areas. Elemental concentrations were typically higher in liver tissue than in muscle tissue, sometimes substantially. The different major drainages, as well as different fish species, have different signatures of natural levels of trace elements, although element uptake from sediment appears to be generally similar among rivers.

In the transportation-corridor study area, the results of soil, plant, sediment, and fish sampling and analyses were generally consistent with those described above for the mine study area. In sediment, the results indicate that ponds and streams have different signatures of natural levels of some trace elements, anions, and cations. The differences may be related to the constant movement of water in streams compared to the lack of flow in ponds. This lack of flow may allow some naturally occurring constituents to build up in sediments over time, particularly those that bind to particulates and/or are less soluble in water and thus more likely to remain in sediment. This is evident for ammonia (as nitrogen) and selenium, which were present in pond sediment at five and three times greater mean concentrations, respectively, than in rivers and for iron, potassium, manganese, and copper, which had mean concentrations in stream sediments that were more than twice their mean concentrations in ponds. For fish and plants, fewer total samples, and in particular, fewer samples for individual plant and fish species, precludes identification of clear correlations or trends. However, analysis of the data for fish demonstrated that elemental concentrations in fish from Red Creek were often different than concentrations in fish from either Bear Den Creek or Ursa Creek. Since only Dolly Varden were collected in Red Creek and only coho salmon were collected from the other two creeks, it is not possible to establish whether this difference is related to differences between the habitats or to other factors, such as species-specific differences in uptake.

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 Bristol Bay drainages study area as an area 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.

Field sampling site overview, July 2006.

Sampling-location staking with site identification number, July 2006.



Field crew conducting vegetation survey, July 2005.

Organic mat removed, preparing for soil sample collection by removing stones and twigs, July 2006.