

Prepared in cooperation with the National Park Service, Western Arctic National Parklands, Kotzebue, Alaska

Elements in Mud and Snow in the Vicinity of the DeLong Mountain Regional Transportation System Road, Red Dog Mine, and Cape Krusenstern National Monument, Alaska, 2005–06



Scientific Investigations Report 2008–5040

Cover Photograph. Red Dog Mine haul truck on DeLong Mountain Regional Transportation System road near Aufeis Creek, Cape Krusenstern National Monument, Alaska, 2006 (photograph by Miguel Mora, U.S. Geological Survey).

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By William G. Brumbaugh and Thomas W. May

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Conversion Factors and Datum

Multiply	By	To obtain
Length		
micrometer (µm)	0.00003937	inch (in.)
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square centimeter (cm ²)	0.001076	square foot (ft ²)
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
milliliter (mL)	0.03382	ounce, fluid (fl. oz)
liter (L)	0.2642	gallon (gal)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Concentrations of chemical constituents in water are given in micrograms per liter (µg/L).

Concentrations of chemical constituents in solid materials are given in micrograms per gram (µg/g).

Elements in Mud and Snow in the Vicinity of the DeLong Mountain Regional Transportation System Road, Red Dog Mine, and Cape Krusenstern National Monument, Alaska, 2005–06

By William G. Brumbaugh and Thomas W. May

Abstract

A small number of mud, road bed soil, and snow samples were collected in 2005 and 2006 to assess metal concentrations and loadings to areas adjacent to the DeLong Mountain Regional Transportation System (DMTS) road in northwest Alaska. The DMTS road is used by large trucks to transport lead and zinc concentrates from Red Dog Mine to the shipping facility at Red Dog Port; it traverses 32 kilometers of land in Cape Krusenstern National Monument (CAKR). Mud collected in the summer of 2005 from wheel-wells of two passenger vehicles used for transport between Red Dog Mine and the port facility were enriched in cadmium, lead, and zinc by factors of about 200 to 800 as compared with mud collected from a vehicle stationed in Kotzebue, Alaska, whereas DMTS road bed soil samples were enriched by factors of 6 to 12. Thus, as of 2005, dispersal of mine ore wastes or concentrates by vehicles appeared to remain a potential source of metals along the DMTS road.

Compared to snow samples obtained near a gravel road located near Kotzebue, Alaska, metal loadings estimated from individual snow samples collected in CAKR in April 2006 near three creeks, 13 to 50 meters from the road, were greater by factors of 13 to 316 for cadmium, 28 to 589 for lead, and 8 to 195 for zinc. When averaged for all three creek locations, mean loadings of cadmium, lead, and zinc calculated from snow samples collected at a nominal distance of 15 meters to the north of the road were 0.63, 34, and 89 milligrams of metal per square meter, respectively. Variability of particulate and metal loadings between individual samples and the three creek locations probably was affected by localized meteorological conditions and micro-topography on the snow drift and scour patterns, but road orientation on attainable truck speeds also might have been a factor. Results indicated that the “port effect”, previously attributed to fugitive metal-enriched dusts stemming from concentrate transfer operations at the port facility, was not necessarily an important factor affecting

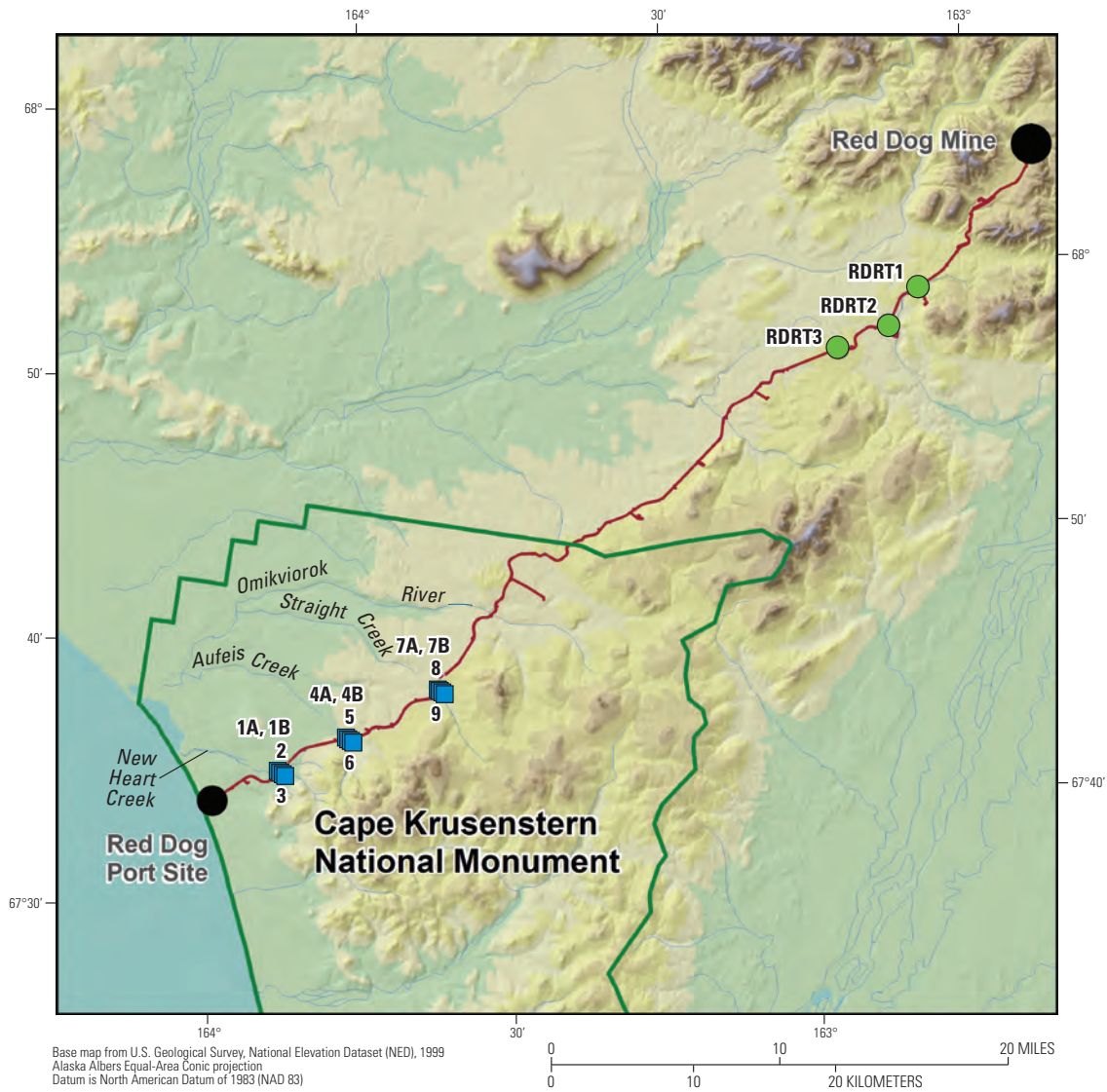
spatial differences of metals deposition in snow along the road in CAKR during winter 2005–06.

The average metal content of particulates in 2005–06 snow samples was slightly less than that of snow samples collected by the U.S. Geological Survey in CAKR at three near-road locations in April 2003. Mean metals concentrations in 2006 snow particulates were about three times greater than in the road bed soils that were sampled in 2005; however, the fraction of annual metals loadings occurring in winter as compared to the remainder of the year was not readily determined by these data. Although procedures have been implemented in recent years to reduce the quantities of metal-enriched fugitive dusts, particulates dispersed near the road during the winter of 2005–06 were enriched in metals and these particulates contributed considerable metal loadings to the nearby terrain.

Introduction

Red Dog Mine, one of the world’s largest producers of lead and zinc concentrates, is situated in northwest Alaska approximately 50 kilometers (km) northeast of the boundary of the Cape Krusenstern National Monument (CAKR; fig.1). The CAKR is one of several National Park Service (NPS) lands managed through the Western Arctic National Parklands (WEAR). Despite the harsh climate of the arctic region, the Red Dog Mine has produced lead and zinc concentrates year-round since operation began in 1989. After milling and flotation concentration at the mine, the powdered ore products are transported 85 km by trucks using the haul road to storage facilities on the Chuckchi Sea, where they await ocean transport during the brief ice-free shipping period from July to September. The haul road is the primary component of the DeLong Mountain Regional Transportation System (DMTS) that also includes the mine and port facilities; it traverses 32 km of CAKR land, for which a 100-year transportation easement was granted by Congressional approval in 1985.

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EXPLANATION

- RDRT3 ● Road bed sample and reference number
- 4A ■ Snow sample and reference number
- DeLong Mountain Regional Transportation System (DMTS) haul road
- Boundary of Cape Krusenstern National Monument

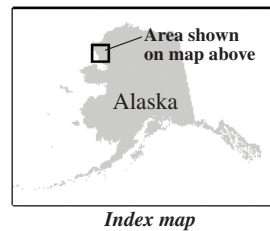


Figure 1. Sampling locations for road bed soil and snow in relation to Red Dog Mine and Port Facility, and Cape Krusenstern National Monument boundary.

In 1999, NPS researchers began sampling moss (*Hylacomium splendens*; henceforth, “moss”) to document patterns of airborne heavy metal deposition on NPS lands from mining operations at Red Dog Mine. The moss sampled along the haul road corridor in 2000 was determined to contain elevated concentrations of cadmium and lead, the source of which was attributed to escapement of ore concentrate from trucks during transport (Ford and Hasselbach, 2001). In 2001, heavy metal concentrations in the moss were measured throughout CAKR (n=226) and geostatistical models were used to predict the extent and pattern of atmospheric deposition of cadmium and lead on NPS lands (Hasselbach and others, 2005). Spatial regression analyses indicated that heavy metal deposition decreased with distance from the haul road and the port site. Analysis of subsurface soil indicated that observed patterns of heavy metal deposition reflected in moss were not attributable to subsurface soils at the sample points. Further, lead concentrations in moss within the northern part of the study area were elevated relative to concentrations previously reported from other Arctic Alaska sites. Collectively, these findings indicated the presence of mine-related heavy metal deposition within the northern part of CAKR.

Large haul trucks apparently have released quantities of finely-powdered mine concentrates from their loads or exterior surfaces while traversing CAKR. In 2001, a new truck fleet with sealable holds was purchased and a washing station was established near the mine to remove concentrates from truck surfaces immediately after loading. In 2003, procedural modifications were incorporated at the port facility to reduce concentrate dust losses during unloading and loading operations (Alaska Department of Environmental Conservation, 2007). Because of the sub-freezing temperatures, truck washing is not routinely implemented for approximately 8 months of the year; consequently, fugitive dusts dispersed along the road during the winter months potentially could constitute a large fraction of the annual loads of metals to the surrounding terrain.

Based on the NPS moss studies, metal bioaccumulation in the CAKR ecosystem resulting from mining activities could be a long-term issue of concern for managing the CAKR ecosystem. Between 2001 and 2004, a mining company contractor (*Exponent*) conducted sampling along the entire DMTS corridor as part of a comprehensive human and ecological risk assessment (ERA). The U.S. Geological Survey (USGS), in cooperation with NPS researchers, initiated studies in 2005 to address data gaps and uncertainties of the ERA that concerned natural resources within CAKR, and to develop strategies for future monitoring. As part of these studies, road soil and vehicular mud was sampled during June 2005, and snow was sampled during April 2006, for elemental analysis. The results of these sample analyses are the focus of this report.

Purpose and Scope

The purpose of this report is to describe results for samples of mud, road bed soil, and snow and to estimate recent (2005–06) loadings of metals from fugitive dusts to regions of CAKR near the DMTS haul road. This assessment includes metal concentration measurements in mud samples collected from mine and haul-road vehicles and in snow pack samples at locations in CAKR where biologic assessments were conducted in summer 2006. Snow was collected in late spring 2006, just before the onset of snowmelt, to qualitatively assess the cumulative winter deposition of fugitive dust and the potential for metal loading to nearby flora and fauna during the initial spring thaw. These data were used to assess the potential for dispersal of ore wastes or mining concentrates by vehicles traversing the DMTS road, and metal loadings to CAKR regions near the DMTS road during the winter months when vehicle washings are less feasible. Potential field and laboratory procedures also are evaluated for future monitoring efforts in this region. The scope of this investigation was limited to comparatively few sampling locations, so it can only be considered a pilot-scale assessment.

Methods

Soil/Mud Sampling

Sampling of DMTS road bed soil and mud samples was conducted on June 16, 2005. Road bed soil and wheel-well mud (henceforth, “vehicle mud”) samples were collected by scraping about 100 to 300 grams (g) of material into a 250-milliliter (mL) polypropylene jar using a combination of the cap and container. The container was pre-cleaned commercially according to U.S. Environmental Protection Agency (USEPA) guidelines for trace metals (U.S. Environmental Protection Agency, 1992). Each jar was sealed and enclosed in a zip-seal plastic bag. Two road bed soil samples were collected from each of three locations along the DMTS road at distances of about 12, 16, and 20 km from Red Dog Mine (fig. 1). At each road location, one subsample was collected from near the center of the road and another from the edge of the road at the top of the shoulder. The road bed soil samples were collected during an initial reconnaissance of the region; additional road soil samples were collected within CAKR in 2006 as part of a separate biological study. Also collected were two samples of dried mud obtained from wheel wells of each of two passenger/work vehicles located at the Red Dog Mine, and two from a vehicle at a reference location. The vehicle mud obtained at the reference location was sampled on June 17, 2005, from a second NPS pickup truck permanently stationed at Kotzebue, Alaska, which is situated on a coastal peninsula about 100 km south/southeast of the DMTS road. The vehicles located at the mine are used periodically for travel to and from the mine

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and port; these included a NPS GMC pickup truck and a mine passenger vehicle.

Snow Sampling

Snow sampling was conducted near the DMTS haul road on April 21, 2006 (fig.1), and near a reference road on the outskirts of Kotzebue on April 24, 2006. Snow sampling was conducted in late spring to qualitatively assess the cumulative winter deposition of fugitive dust and the potential for metal loading to nearby flora and fauna during the initial spring thaw. Four snow samples were collected in each of three drainages (New Heart Creek, Aufeis Creek, and Straight Creek) in CAKR (figs. 1 and 2) that were targeted for biological studies later in 2006. General locations were about 50 meters (m) to the east of the bridge over New Heart Creek, about 50 m to

the west of the bridge over Aufeis Creek, and about 300 m to the east of the bridge over Straight Creek. These sampling locations were not necessarily expected to be fixed stations for future sampling of snow in CAKR. For each drainage, snow was sampled at two locations that were 10 to 50 m apart and each about 15 m north of the road, one location about 50 m north of the road, and the other about 15 m south of the road. Exact distances (indicated later) were measured from the outermost edge of the road berm.

Snow sampling was conducted by a two-person NPS team, and performed according to protocols provided by USGS that generally followed the methods of Ingersoll and others (2002), and Brabets (2004). Pre-cleaned, pre-labeled containers and most sampling equipment were provided by USGS. The team was instructed to locate pre-determined site coordinates using global positioning satellite (GPS) tracking devices, then select nearby representative sampling locations



Figure 2. Snow sampling locations near the DeLong Mountain Regional Transportation System road, Alaska, April 21, 2006. A) Site 1A near New Heart Creek, looking north from road, B) Site 4A, near Aufeis Creek, looking south with road in background, C) Site 7A near Straight Creek, looking south with road in background. Photographs courtesy of L. Jeschke, National Park Service.

at targeted incremental distances from the road where the snow pack was about 0.5 m deep. A pit was dug in the snow and two large plastic rectangular scoops were used to transfer a single column of snow to a 2-liter (L) pre-cleaned bottle. This method was chosen rather than a tube-sampling technique (Clark 2005) to simplify field logistics for the team (including cleaning of sampling equipment) and to facilitate collecting particulates from the surface and within the snow.

At each location, a short trench (about 2 m long) was dug into the snow bank with a conventional aluminum snow shovel. The shoveled snow was piled to one side only, to leave the snow surface on the other side of the trench undisturbed. From the undisturbed side, a 15-centimeter (cm) long x 7.6-cm wide x 5.1-cm deep rectangular plastic scoop was used to remove a vertical section of snow, three scoop-widths wide, to create a small indentation on the undisturbed side of the trench to ensure that the layer originally in contact with the aluminum shovel would not be included in the sample because it might be contaminated by particles from the shovel. Two additional plastic scoops were used to transfer a one scoop-width vertical profile sample from within the trench to represent the full depth of the snow pack. Two scoops were used to facilitate quantitative sampling in case the snow was dry and not easily contained by a single scoop. In the indentation, snow scooping was begun at the top of the snow pack using one scoop as a receiver and the other to scoop snow vertically downward into the receiving scoop. The snow in the sampling and receiving scoops was transferred to a pre-cleaned, pre-labeled 2-L polyethylene bottle. Single scoop-width sampling was continued down through the snow pack until the entire depth was sampled. The bottle was capped and placed into a large zip-seal bag. This sample, which consisted of the vertical section of snow and any associated particulate, was designated replicate 1 for trace metal analysis.

A second sample was collected adjacent to the location just sampled (where the snow surface was still intact) in a similar manner to obtain replicate 2, which was used to determine percent solids and soluble anions. After sampling was completed, each scoop was wiped clean with a lint-free paper towel and stored in a plastic bag until the next use. The trench region was photographed, the GPS coordinates saved and recorded, and the snow was replaced into the trench. Data for each location was recorded on a chain-of-custody sheet, which included: the time and date of sampling, the depth of snow sampled (to nearest 0.1 m), the GPS coordinates (degree, minutes, seconds), and the distance from the edge of the road berm (to nearest 0.5 m). After collection, samples were packed in coolers and kept frozen for shipment to the USGS laboratory in Columbia, Missouri.

Laboratory Procedures for Soil/Mud

All soil and mud samples were lyophilized (freeze-dried) to a constant dry weight, and pulverized with an acid-cleaned glass rod to a coarse, powder-like consistency, during which

pebbles and other particles greater than about two millimeters (mm) in diameter were removed with forceps. Sieving and/or mechanical grinding was considered, but was not performed because most of the sample material was of relatively fine particle size. A 0.25-g sub-sample of the freeze-dried soil or mud was digested with 5.5 mL of 16 molar (M) nitric acid (HNO_3) and 0.5 mL of 12 M hydrochloric acid (HCl) in a tetrafluoroethylene (TFE)-lined vessel. Acids were American Chemical Society reagent grade (Malinkrodt Baker Incorporated, Phillipsburg, New Jersey) further purified by sub-boiling in quartz. Each vessel was sealed and heated to 190 ± 10 degrees Celsius ($^\circ\text{C}$) in a temperature-programmed, laboratory microwave oven. The digestate was transferred to a low-density polyethylene bottle, and diluted to 100 mL with ultra-pure water (18 million ohms per centimeter specific resistivity) to produce a final acid matrix of 0.88 M HNO_3 and 0.12 M HCl. This digestion procedure is essentially the same as USEPA method 3051A, which is termed “total-recoverable” because it is a relatively “aggressive” oxidative procedure, but it does not yield a complete dissolution of all elements, especially those tightly bound within lattices of refractory minerals and silicates (U.S. Environmental Protection Agency, 2007a). Based on information in USEPA method 3051A documentation, as well as results for various certified reference soils and sediments obtained by our laboratory, recovery for this type of method typically is about 90 percent or greater for most of the priority pollutant metals, including cadmium, cobalt, copper, lead, nickel, and zinc.

A second sub-sample of each vehicle mud sample also was prepared using a dilute acid digestion treatment (similar to that used for the snow samples, henceforth referred to as “acid-extractable” in this report) to qualitatively assess the lability of these elements in the mud samples, to allow for a direct comparison with metal concentrations measured in snow particulates, and to assess the effectiveness of this milder digestion treatment for assessing the primary elements of concern. For this, a 0.5-g dried sample was combined with 100 mL of 1.6 M HNO_3 in a 250-mL pre-cleaned high-density polyethylene bottle. The bottle was capped, sealed inside a large zip-seal bag, and then heated for 8 hours in a water bath at 65°C . A 20-mL sub-sample of each extract was filtered for analysis using a fluoroethylene-perfluoropropylene (FEP) sipper straw, an all-polypropylene syringe, and a polypropylene 0.45-micrometer (μm) pore-size filter cartridge. All filtration components were pre-cleaned by drawing and filtering a 20 mL volume of a solution containing 0.8 M HNO_3 and 0.12 M HCl followed by a double rinse with 20 mL of ultra-pure water.

Laboratory Procedures for Snow

Each sample was analyzed as “whole-snow” using an in-bottle, acid-extractable digestion procedure following Hoffman and others (1996). Using this procedure, the potential for laboratory contamination was expected to be minimized

because it requires no transfers or open-vessel evaporative steps. Collecting the separate (adjacent) sample for percent solids and soluble anions ensured that these determinations could be performed without adversely affecting the analysis for trace elements. All 2-L bottles used for snow sampling were purchased as pre-cleaned containers that had been prepared according to USEPA guidelines for trace metals (U.S. Environmental Protection Agency, 1992). Bottles designated for trace metals analyses sample collection (replicate 1) were further cleaned at USGS by treating with hot dilute acid before shipment to NPS-WEAR. For these, 0.5 L of 1.6 M HNO₃ was added to each bottle, which was sealed in a zip-seal plastic bag and heated for 2 hours in a water bath at 65 °C, and then rinsed twice with ultra-pure water. No additional cleaning was performed for bottles designated for collection of replicate-2 snow samples.

Snow samples were stored frozen at the USGS laboratory in Columbia, Missouri, for about 3 months before preparation for analysis. Samples designated for “metals” analysis (replicate 1) were melted at room temperature for 6 hours, then stored refrigerated overnight before preparation. Some samples contained a few milligrams of plant debris, such as grass stems and small leaves, which was removed with acid-cleaned plastic forceps. The liquid snow volume was then determined gravimetrically. High-purity nitric acid was added at a proportion of 10 mL per 100 mL of snow; the bottle was capped, sealed inside a large zip-seal bag, and then heated for 8 hours in a water bath at 65 °C. A 20 mL sub-sample of each digestate was drawn and filtered for analysis using a FEP sipper straw, an all-polypropylene syringe, and a polypropylene 0.45- μ m pore size filter cartridge. All filtration components were pre-cleaned as described previously for the filtration of soil/mud extracts. Final results were corrected for the 10 percent dilution by the nitric acid.

Samples designated for analysis for percent solids and anions (replicate 2) similarly were melted at room temperature for approximately 6 hours and stored refrigerated overnight before preparation. The samples were shaken briefly and allowed to settle for 5 to 10 minutes. A 20-mL liquid sample was drawn from each, filtered through a 0.45- μ m polypropylene filter, and transferred to a polypropylene bottle for anion determination (chloride, nitrate, fluoride and sulfate) by ion chromatography. The remainder of the sample was quantitatively filtered through a pre-weighed, 1.5- μ m pore size glass-fiber filter. The amount of particulate lost during the filtration of each 20-mL sample collected for anions was assumed to be a negligible fraction of the total solids. Plant debris and any sand-sized particles (the latter of which were observed in two samples only) were assumed to be associated with the ground surface and were removed with forceps. The filter was then oven dried and weighed to determine percent solids according to Method 2540A-D (American Public Health Association and others, 1998). Data were corrected for procedural blanks.

Instrumental Analysis and Data Reporting

Analysis of the samples mud and snow trace-element samples was conducted by inductively-coupled plasma mass spectrometry (ICP-MS) using a 62-element semi-quantitative analysis method according to instrument manufacturer guidelines, followed by re-analysis using a fully quantitative method for aluminum (Al), barium (Ba), cadmium (Cd), lead (Pb), and zinc (Zn) according to USEPA quality assurance guidelines (U.S. Environmental Protection Agency, 1996a). The semi-quantitative analysis mode is the more economical and efficient means for obtaining results for several elements. The instrument set-up, analysis time, and data formatting and interpretation are reduced considerably (particularly for quality-assurance measures) for the semi-quantitative analysis as compared with a quantitative analysis for the same number of elements. For example, calibration check standards for semi-quantitative analyses are monitored only at a few selected masses (as opposed to all masses) and fewer quality-assurance samples are analyzed as compared to quantitative methods. Also, reporting limits are conservative estimates based on historical averages (rounded up to reduce the probability of reporting false positives), whereas detection limits for the quantitative analysis are determined for each element based on the instrument performance of specific test samples for each day of sample analyses. Uncertainty limits of the semi-quantitative method are reported by the manufacturer to be ± 30 to 50 percent, depending on element and daily instrumental conditions. Uncertainty generally is greatest for the lightest masses, as well as for iron, because of the potential for interferences. However, the USGS laboratory in Columbia, Missouri, historically has obtained uncertainty limits of about ± 15 percent for most of the determinations performed in this manner, except when concentrations approach detection limits; then relative uncertainty becomes large regardless of the method. For quantitative analyses, calibration for each targeted mass was performed with at least four standards and more frequent and extensive quality-control measures were monitored for each element. Acceptable accuracy limits for quantitative analyses were set at ± 10 percent of true values. If periodic analyses of check standards did not meet this criterion for any analyte, the instrument was re-calibrated and samples were re-analyzed.

For semi-quantitative analyses, each sample digestate was diluted ten-fold by a mechanized auto-diluter as part of the analytical sequence. Calibration was performed with a National Institute of Standards and Technology (NIST) traceable reference solution to which five elements were added for the rare earth region of the mass spectral range. Internal standards used to correct for instrument drift and matrix-induced ionization effects were scandium, rhodium, and bismuth; each added on-line to produce an effective concentrations of 10 micrograms per liter (μ g/L).

Quantitative analysis of acid-extractable treatments of snow and soil/mud samples for aluminum, barium, cadmium, lead, and zinc was also performed with each digestate pre-

diluted 10-fold by the auto-diluter and with on-line addition of scandium, rhodium, and bismuth as internal standards. Atomic masses monitored included ^{27}Al , ^{65}Zn , ^{68}Zn , ^{111}Cd , ^{114}Cd , ^{138}Ba , and $^{206+207+208}\text{Pb}$. The three lead isotopes were summed to correct for local and regional variation in the isotopic composition of that element. Results were reported based on individual masses for cadmium and zinc, depending on quality-assurance sample results and the degree of apparent interferences observed. Minimal differences were observed between final results based on ^{65}Zn or ^{68}Zn , and ^{111}Cd or ^{114}Cd , indicating that either mass could have been used for accurate quantitation for these two elements.

Mercury cannot be determined easily by ICP-MS simultaneously with other elements, so it was determined in soil and mud samples by combustion/amalgamation atomic absorption spectrophotometry (U.S. Environmental Protection Agency, 2007b). Approximately 50 mg of dry sample was used for each determination. The instrument was calibrated using powdered tissue samples that were certified for total mercury content; reference soils were analyzed to assess accuracy.

Road bed soil and vehicle mud sample concentrations are expressed as micrograms per gram ($\mu\text{g/g}$) dry weight on a "total recoverable" basis. Concentrations for the second set of soil/mud sub-samples that were prepared by 1.6 M HNO_3 extraction are expressed as $\mu\text{g/g}$ dry weight and reported as "acid-extractable". Snow results are expressed as acid-extractable elements for melted snow as a liquid concentration ($\mu\text{g/L}$); as a filterable solids concentration ($\mu\text{g/g}$ dry weight); and as a ground surface mass loading in milligrams per square meter (mg/m^2). For the calculation of ground surface loading, the mass of metal measured for each snow pack sample was assumed to be deposited after snowmelt onto a ground surface area of 39 square centimeters (cm^2), based on the 7.6-cm by 5.1-cm dimensions of the sampling scoop base.

Quality-Control Results

For soil/mud samples, quality control (QC) measures incorporated at the digestion stage included blanks, certified reference soils, triplicate sample preparations, and sample spikes. For the digestion of whole snow samples, three blank samples and a blank spike sample were included. Because the entire sample was digested in its collection bottle, laboratory duplicates could not be performed for snow samples; however, duplicate filtrations and analyses were performed on one snow digestate. During each analysis run, blank verification, calibration verification, and standard reference solutions were measured after every 10 samples; duplicates, post-digestion spikes, and interference checks (dilution checks and a synthetic interference solution) also were determined.

Target limits for accuracy during instrumental analysis of calibration verification standards and certified reference solutions were ± 10 percent error for quantitative analyses and ± 30 percent error for semi-quantitative analyses. Target limits

for recovery of pre-digestion spikes and post-digestion spikes were 75 to 125 percent and 85 to 115 percent, respectively. Target limits for precision were ± 10 percent repeatability, expressed as relative percent difference (RPD) or percent relative standard deviation (percent RSD) for instrumental analysis and ± 25 percent repeatability for digestion replicates. For the primary elements of concern (aluminum, barium, cadmium, lead, and zinc), only two individual QC results fell outside of the specified target limits. These included one low spike recovery for barium (61 percent) and one high spike recovery for aluminum (128 percent). Overall, QC results indicated good accuracy and precision for the primary elements of concern as well as most other elements determined by semi-quantitative analyses. In the discussion that follows, QC result summaries are discussed separately for 2005 soil/mud sample total recoverable analyses, 2005 mud sample acid-extractable analyses, and 2006 whole snow sample analyses. Three tables summarizing QC results are included at the back of this report (appendixes A, B, and C). Complete QC results, consisting of 37 data tables, are available from the USGS, 4200 New Haven Road, Columbia, Missouri, 65201.

Soil/Mud, Semi-Quantitative Analysis

Repeated runs ($n=8$) of a reference water during semi-quantitative analysis of total recoverable elements in soil and mud produced mean recoveries of 83 to 105 percent for 32 of the 34 elements present. Lower recoveries were obtained for two elements, including iron which averaged only 70.5 percent, but was still within the targeted accuracy limits. The recovery of gold was only 4 percent, probably because of adsorption losses to the sample delivery system; no corrective action was attempted to remediate the low recovery because gold was not a primary focus of the investigation. Mean recoveries of aluminum, barium, cadmium, lead, and zinc were 96 to 107 percent. Precision of the 8 analyses of the reference water were 0.9 to 9.9 percent RSD for all 34 elements, and 2.3 to 4.7 percent RSD for aluminum, barium, cadmium, lead, and zinc. Semi-quantitative measurement (one analysis) of a mixed set of mixed reference solutions produced recoveries of 97 to 124 percent for 31 elements and 68 percent for iron. Recoveries of aluminum, barium, cadmium, lead, and zinc were 97 to 111 percent. Total recoverable concentrations of cadmium, lead, and zinc, as determined by semi-quantitative analysis in two reference sediments, National Research Council Canada (NRCC) marine sediment and NIST 2704 Buffalo River Sediment, were within 8 percent of certified total ranges (appendix A). Aluminum and barium recovery from those reference sediments was low, but that was expected because the total recoverable procedure does not recover a considerable fraction of aluminum and certain other elements that often are tightly-bound within mineral lattices. Compared to the certified total concentrations, recoveries of cadmium, lead, and zinc from NIST SRM 2709 (San Joaquin Soil) using the total recoverable procedure were 81 to 107 percent.

Also reported by the NIST for SRM 2709 soil are concentrations of selected “leachable” metals that were determined by participating laboratories using variations of USEPA method 3050B (U.S. Environmental Protection Agency, 1996b). Chen and Ma (1998) obtained similar results for many trace elements in soils when comparing USEPA methods 3050B (hot-plate heating) and 3051A (microwave-assisted heating), the latter of which essentially was the total recoverable method used in this study. Total recoverable concentrations of aluminum, barium, lead, and zinc in SRM 2709, as determined by semi-quantitative analysis, were within 13 percent of the reported ranges of leachable metals (appendix A); leachable cadmium was not reported by NIST.

A triplicate total recoverable digestion and semi-quantitative analyses of a road bed soil sample produced relative standard deviations of 15 percent for cadmium, 16 percent for zinc, and ≤ 10 percent for aluminum, barium, and lead (appendix B). Recovery of an aqueous spike of zinc added to a road bed soil sample before digestion was 112 percent, but the amounts spiked for barium, cadmium, and lead were too low to accurately assess recovery (appendix C). Recoveries of 10 other spiked elements were 89 to 134 percent. Blank equivalent concentrations of method (digestion) blanks were below semi-quantitative reporting limits for most elements. One of the three blanks had measurable amounts of aluminum, titanium, chromium, manganese, iron, and barium, but the concentrations were far below the concentrations of those elements in the soil/mud samples, and therefore were not a significant source of error.

Soil/Mud, Total Mercury

Mercury cannot be determined easily by ICP-MS simultaneously with other elements; consequently, separate subsamples of soil and mud were analyzed by USEPA method 7473 (U. S. Environmental Protection Agency, 2007b). The determination was performed in a “fully quantitative” mode. All QC results for mercury were within targeted criteria for quantitative analysis, but details are not discussed because mercury was not an element of primary focus in this investigation.

Soil/Mud, Quantitative Analysis

Repeated runs ($n=10$) of a continuing calibration verification (CCV) solution during quantitative analysis of acid-extractable aluminum, barium, cadmium, lead, and zinc in wheel-well mud produced of 98 to 106 percent recoveries. Quantitative measurement (one analysis each) of two reference solutions produced recoveries of 100 to 104 percent (relative to the upper or lower limits of the certified range) for these five elements. Acid-extractable concentrations measured for cadmium, lead, and zinc were 73 to 88 percent of certified total concentrations (complete dissolution) for NIST 2710 Montana reference soil (appendix A). Aluminum and barium

recovery using the acid-extractable method was low compared to certified total concentrations, but that was expected because that procedure does not recover the fraction of elements that are tightly bound in mineral lattices. Also reported in the certificate of the NIST 2710 soil are concentrations of “leachable” elements, which were determined by participating laboratories using variations of USEPA method 3050B. Concentrations of acid-extractable aluminum, barium, cadmium, lead, and zinc measured for this reference soil were within 13 percent of the ranges of leachable values reported by the NIST (appendix A).

A replicate acid extraction of an individual mud sample was not performed; however, agreement between the three vehicle mud sampling pairs can be compared instead, assuming that the mud collected from the front and back wheel wells of each vehicle were similar in composition. Agreement between the two field sampling pairs obtained from the DMTS vehicles for acid-extractable cadmium, lead, and zinc ranged from 8.2 to 30 percent (appendix B); values that mostly were within the ± 25 percent target of RPDs for laboratory duplicates, despite the fact that they were not actual duplicates. The RPDs were greater for the pair of mud samples obtained from the NPS truck located at the reference site (71, 51, and 64 percent; appendix B), possibly in part because those concentrations were relatively low. The ranges of relative percent difference (RPD) measured for aluminum and barium in all three field pairs of mud samples were 8.9 to 20 percent, and 2.2 to 39 percent, respectively. The RPDs for duplicate analyses of a single mud extract solution were all below 1 percent, indicating that variability attributable to within-run instrumental analysis was small.

Recoveries of elements spiked onto a mud sample before acid extraction (appendix C) were 61 to 110 percent for a “low” spike amount (2 to 200 μg) and 101 to 118 percent for a “high” amount (10 to 1,000 μg). The only spike recovery outside of the 75 to 125 percent target criteria was one barium spike (61 percent); however, that barium spike represented only 20 percent of the amount already present in the sample (spike/sample ratio of 0.2), which probably contributed to the low apparent recovery. When the ratio of amount spiked to the sample amount decreases below 1.0, the apparent spike recovery may become increasingly variable as a result of sample heterogeneity. Recoveries of spikes added to a mud sample after acid extraction were 97 to 103 percent for barium, cadmium, lead, and zinc, and 128 percent for aluminum (appendix C). The reason for the single greater recovery for aluminum is unclear, but precision of aluminum determinations for the ICP-MS method is sometimes poorer than other elements because of its comparatively light mass. Barium, cadmium, lead, and zinc recoveries in an interference check sample that contains extraordinary concentrations of potentially interfering components were 97 to 131 percent. Acid-extractable method blanks produced mean blank equivalent concentrations (BECs) of 1.7, 0.005, 0.001, 0.028, and 0.47 $\mu\text{g/g}$ dry weight for aluminum, barium, cadmium, lead, and zinc, respectively, whereas method detection limits (MDLs) were 0.3, 0.02, 0.01, 0.13,

and 0.60, $\mu\text{g/g}$ dry weight, respectively. Thus, BECs were below method detection limits for barium, cadmium, and lead, and minimally above method detection limits for aluminum. The BECs of all five elements were at least 100-fold lower than the lowest sample concentrations (mud from the NPS truck at Kotzebue) indicating that the accuracy of measured sample concentrations was not significantly affected by laboratory contamination.

Snow, Semi-Quantitative Analysis

Repeated runs ($n=4$) of a reference water during semi-quantitative analysis of elements in snow produced mean recoveries of 75 to 124 percent for 33 of the 34 elements present. Mean recoveries of aluminum, barium, cadmium, lead, and zinc were 94 to 104 percent. Gold was the only element for which the recovery (4.5 percent) was outside of the targeted accuracy limits; however, no corrective action was attempted to remediate or correct for loss of gold because it was not a primary focus of the investigation. Precision, expressed as percent RSDs of the four analyses of the reference water, were 10 percent for aluminum, 1.0 to 2.6 percent for barium, cadmium, lead, and zinc, and 0.5 to 11 percent for the remaining 29 elements.

Snow, Quantitative Analysis

Repeated runs ($n=5$) of a CCV solution during quantitative analysis of acid-extractable aluminum, barium, cadmium, lead, and zinc in whole snow samples produced recoveries of 91 to 109 percent. Quantitative measurement (two analyses each) of two reference solutions produced mean recoveries of 91 to 101 percent (relative to the upper or lower limits of the certified range) for these five elements. Duplicate filtration, dilution, and analysis of a snow sample digestate produced RPDs of 1.3 to 4.3 percent (appendix B). Recoveries of elements spiked onto a blank before acid extraction with snow samples were 99 to 111 percent, whereas recoveries of a spike added to a filtered and diluted snow sample after extraction were 96 to 108 percent (appendix C). The RPDs for duplicate analyses of a snow sample digestate before and after five-fold dilution ranged from -7.2 to +8.2 percent. The mean BECs for dilute acid-extractable aluminum, barium, cadmium, lead, and zinc in method blanks were -2.6, 0.021, 0.025, 0.031, and 1.3 $\mu\text{g/L}$, respectively, and the MDLs were 3.5, 0.9, 0.03, 0.02, and 1.8 $\mu\text{g/L}$, respectively. Thus, the BECs were below method detection limits for aluminum, barium, cadmium, and zinc, and minimally above method detection limits for lead. The BEC for lead was about 40-fold lower than the lowest sample concentrations (the snow sampled near Kotzebue). These results indicate that the accuracy of measured sample concentrations was not affected significantly by laboratory contamination.

Results and Discussion

Soil and Mud Samples

Samples collected in 2005 were analyzed to compare and evaluate concentrations of metals on the haul road to that in mud on vehicles, and to qualitatively assess the potential for metal transport to CAKR by haul trucks or service vehicles tracking through ore wastes or mine concentrates in the mine and port areas. Patterns of metal concentrations in the mud might also be compared to metal concentrations in snow particulates, to qualitatively assess the contribution of mine wastes or concentrates to metal loadings in the snow. Dust originating from road aggregate material was presumed to be the primary source of aluminum; dust originating from mine concentrates and ore wastes was the presumed source of cadmium, lead, and zinc; and dust from the road material and mine wastes were the presumed source of barium. As discussed in the method section, road bed soil samples were collected from three locations (fig. 1), and mud samples were obtained from two vehicles stationed at Red Dog Mine and one vehicle in Kotzebue, Alaska (for reference purposes). Concentrations of 15 elements of potential concern, as determined by a semi-quantitative analysis, are indicated for road bed soils and vehicle muds in table 1. Typical concentrations reported by Teck Cominco for lead and zinc mine concentrates for 14 of these elements (Exponent, 2007) also are indicated.

To facilitate comparisons between road soil and vehicle mud samples, an enrichment factor was calculated by dividing the metal concentration in each sample constituent by the metal concentration in reference site vehicle mud. Hasselbach and others (2005) used aluminum as a reference element to correct for contributions from parent soil dust when calculating enrichment factors for mosses; however, in this study (2005–06), only soils and muds were being compared, so a “simple” enrichment factor (without normalization) was calculated. Notably, Hasselbach and others (2005) reported mean concentrations of cadmium, lead, and zinc for 46 samples of sub-surface soils obtained throughout CAKR as 0.27, 18, and 96 $\mu\text{g/g}$ dry weight, respectively; values that are similar to the concentrations (0.25, 18, 80 $\mu\text{g/g}$ dry weight) measured for the reference mud in this study (table 1). These data indicate that the mud obtained from the vehicle in Kotzebue was a reasonable surrogate of reference soil or mud for CAKR.

Simple enrichment factors for mine concentrates, mine-vehicle muds, and road soils (center and shoulder) are depicted in figure 3. On average, aluminum was 2.2-fold greater and barium was 5-fold greater in the mine-vehicle muds when compared to the reference mud. In contrast, cadmium, lead, and zinc were enriched in the mine-vehicle mud by factors of about 800, 450, and 220, respectively. Enrichment factors in mine-vehicle muds for other metals of potential concern ranged from 10 to 100 for arsenic, antimony, silver, mercury, and thallium. Concentrations of cadmium, lead, and zinc in mine-vehicle muds were about 9, 2, and 5 percent, respec-

Table 1. Concentrations of total recoverable metals of potential concern, as measured by semi-quantitative analysis, in DeLong Mountain Regional Transportation System road bed soil, in mine vehicle wheel-well mud, and in vehicle mud at Kotzebue, Alaska, collected June 2005, as compared with total concentrations of the same metals in Red Dog Mine lead and zinc concentrates.

[All concentrations in micrograms per gram dry weight. Analyses conducted using semi-quantitative method (values rounded to one or two significant figures) except for mercury (USEPA method 7473). For road bed soils, subsample 1 was obtained from road center and subsample 2 from the road shoulder; for wheel-well muds, subsample 1 was obtained from right front well and subsample 2 from right rear well. ID, identification number; DMTS, DeLong Mountain Regional Transportation System; RD, Red Dog; RT, Regional Transportation; NPS, National Park Service; KOTZ, Kotzebue; USGS, U.S. Geological Survey; NR, not reported; <, less than]

Field ID	DMTS road bed soil				Wheel-well mud, Red Dog Mine				Wheel-well mud, Kotzebue				Red Dog Mine concentrates ¹			
	RD RT-1		RD RT-2		RD RT-3		RD Vehicle 8099		RD NPS Truck		KOTZ NPS Truck		1	2	lead concentrate	zinc concentrate
	1	2	1	2	1	2	1	2	1	2	1	2				
Subsample	33842	33843	33844	33845	33846	33847	33848	33849	33850	33851	33852	33853				
Aluminum	22,000	22,000	10,000	12,000	5,000	6,000	19,000	18,000	27,000	30,000	9,000	12,000	1,375	688		
Beryllium	1	0.9	0.5	0.5	0.2	0.3	2	1	1	2	0.1	0.3	NR	NR		
Chromium	30	40	20	20	10	10	70	70	60	60	40	40	677	537		
Nickel	50	40	20	20	10	20	50	50	60	60	30	40	45	16		
Copper	50	50	20	20	10	10	100	100	100	100	20	20	1,400	600		
Zinc	500	600	400	400	300	400	23,000	18,000	16,000	13,000	60	100	108,000	552,000		
Arsenic	0.9	2	0.5	0.4	0.7	0.6	10	10	8	3	0.7	0.8	400	200		
Selenium	0.2	0.2	0.06	0.1	0.09	0.1	1	0.5	0.4	0.6	0.1	0.1	28	3		
Silver	0.3	0.3	0.4	0.3	0.2	0.2	20	20	10	7	0.06	0.1	420	137		
Cadmium	3	4	3	3	2	3	300	300	100	100	0.2	0.3	1,200	3,300		
Antimony	0.3	0.3	0.3	0.3	0.4	0.4	20	20	6	5	<0.04	0.04	1,600	400		
Barium	5,000	5,000	3,000	3,000	2,000	2,000	1,000	1,000	2,000	2,000	300	300	2,400	2,700		
Mercury	0.14	0.18	0.12	0.12	0.1	0.11	4.9	4.9	2.5	2.1	0.01	0.03	18	94		
Thallium	1	1	0.6	0.6	0.5	0.4	20	20	10	8	0.06	0.1	70	19		
Lead	100	100	100	100	80	80	10,000	10,000	4,000	3,000	10	20	580,000	32,000		

¹Typical total concentrations as reported by Teck Cominco (Exponent, 2007).

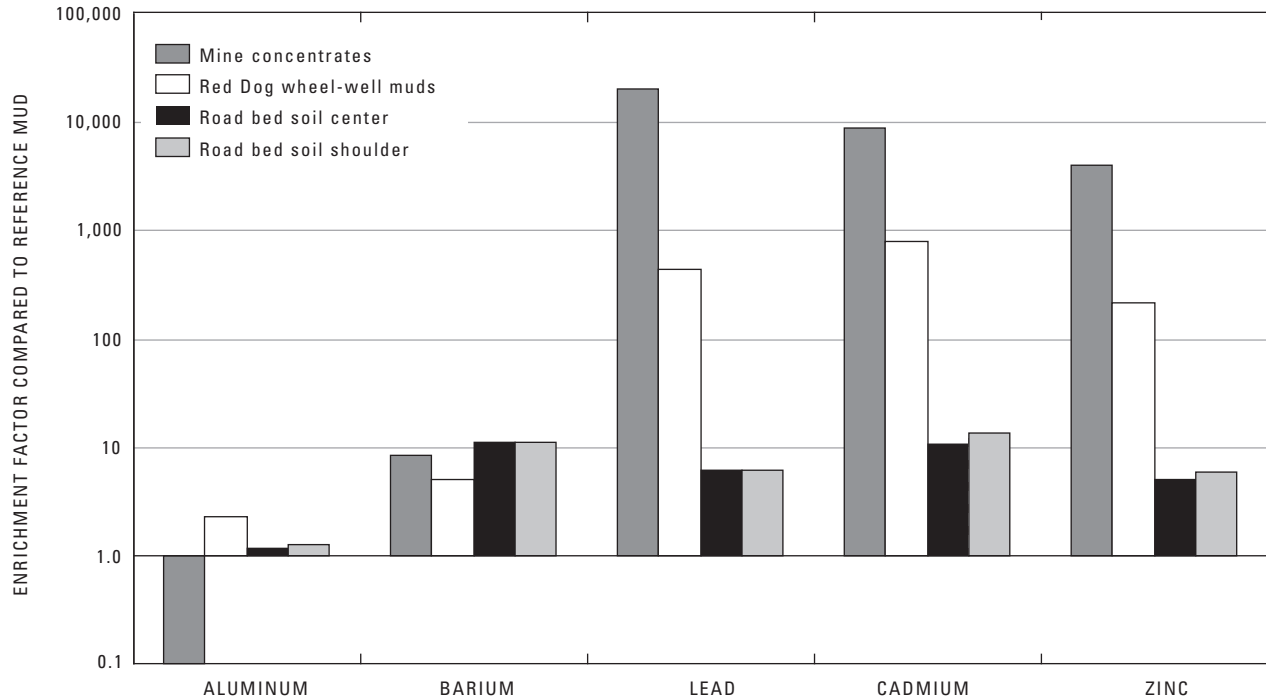


Figure 3. Enrichment of selected metals for Red Dog Mine concentrates, mine vehicle wheel-well muds, and DeLong Mountain Regional Transportation System road bed soil samples, as compared with wheel-well mud obtained from a reference site.

tively, of what would be expected for these three metals in an equal mixture of lead and zinc concentrates based on data reported by Teck Cominco (Exponent, 2007). The greater proportion of cadmium and lower proportion of lead in the vehicle mud is consistent with greater mine production rates reported for the zinc concentrate, which contains about 3-fold greater cadmium concentrations than the lead concentrate (table 1). Thus, these data indicate that in June 2005, mud on vehicles stationed at the mine that were used for traversing the DMTS road had metal concentrations that were about 5 percent of those present in lead and zinc concentrates; therefore, dispersal of mine concentrates and/or ore wastes by these and other vehicles appeared to be a potential source of metals along the DMTS road.

Compared with the reference mud, the DMTS road bed soils were enriched by factors of about 12 for cadmium, 11 for barium, and 6 for lead and zinc. There was little difference between concentrations in the DMTS road center and the road shoulder, but overall, concentrations appeared to be slightly greater in samples from the shoulder (table 1). Road bed soil concentrations were somewhat lower in the samples obtained 20 km from the mine as compared with samples collected 12 km from the mine. Aluminum concentrations were about the same in DMTS road bed soils as in the reference mud, which was not unexpected because mine concentrates contain relatively low concentrations of aluminum. Median concentrations of dust samples collected in 2000 by shaking nearby birch and willow shrubs (Ford and Hasselbach, 2001) were about 11, 400, and 1,500 $\mu\text{g/g}$ dry weight for cadmium,

lead, and zinc, respectively. Thus, road bed soil samples collected in June 2005 (table 1) contained concentrations of these three metals about 3- to 4-fold lower than those reported for the 2000 road dust samples. Improvements in concentrate handling procedures that reportedly have been implemented since 2001 (Alaska Department of Environmental Conservation, 2007) might have helped to reduce metal concentrations in the road soil; however, metal concentrations in the road bed samples might not reflect the extent of metal enrichment in dusts on nearby vegetation. Dust dispersion from the elevated roadbed presumably would be greater during warm, dry, and windy conditions as compared with cooler, calmer, or wetter periods. Consequently, meteorological conditions at the time of each sampling could have affected the concentrations measured in road bed soils as compared with dusts on vegetation. In addition, road bed soil samples collected in 2005 probably included a larger range of particle sizes than the dusts collected in 2000; furthermore, different chemical digestion procedures were used. Data for mosses collected by NPS researchers in 2006 should provide a clearer indication of recent temporal trends of metal concentrations in the dusts on nearby vegetation (Peter Neitlich, National Park Service, written commun., 2007).

Road bed soil and vehicle mud results for other elements (excluding those of potential concern) are presented in table 2. There were no particularly striking differences between sampling locations for these other elements. Calcium concentrations were greatest in the road soils, probably reflecting periodic applications of calcium chloride to the DMTS road

Table 2. Concentrations of total recoverable elements (excluding metals of concern), as measured by semi-quantitative analysis, in DeLong Mountain Regional Transportation System road bed soil, in mine vehicle wheel-well mud, and in vehicle mud at Kotzebue, Alaska, collected June 2005.

[All concentrations in micrograms per gram dry weight. Analyses conducted using semi-quantitative method (values rounded to one or two significant figures). Concentrations of 27 additional elements obtained during the analysis are not reported because they are minimally recovered by the total recoverable digestion method. For road soils, subsample 1 was obtained from road center and subsample 2 from the road shoulder; for wheel-well muds, subsample 1 was obtained from right front well and subsample 2 from right rear well. ID, identification number; DMTS, DeLong Mountain Regional Transportation System; RD, Red Dog; RT, Regional Transportation; NPS, National Park Service; KOTZ, Kotzebue; USGS, U.S. Geological Survey; <, less than]

Field ID	DMTS road bed soil						Wheel-well mud, Red Dog mine						Wheel-well mud, Kotzebue	
	RD RT-1		RD RT-2		RD RT-3		RD Vehicle 8099		RD NPS Truck		RD NPS Truck		KOTZ NPS Truck	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Subsample	33842	33843	33844	33845	33846	33847	33848	33849	33850	33851	33852	33853		
USGS ID														
Element														
Lithium	30	20	10	10	6	8	20	20	30	30	6	10		
Sodium	400	400	200	200	100	200	600	600	800	900	4000	2000		
Magnesium	22,000	27,000	31,000	30,000	38,000	41,000	7,000	5,000	12,000	13,000	12,000	12,000		
Potassium	8,000	8,000	4,000	5,000	2,000	2,000	6,000	6,000	9,000	10,000	1,000	2,000		
Calcium	44,000	58,000	66,000	62,000	79,000	86,000	12,000	10,000	19,000	23,000	48,000	43,000		
Vanadium	60	60	30	30	20	20	100	100	90	100	40	40		
Manganese	800	2,000	400	400	300	300	400	400	800	1,000	200	300		
Iron	15,000	14,000	7,000	7,000	3,000	4,000	22,000	24,000	24,000	23,000	10,000	14,000		
Cobalt	10	10	6	6	3	4	20	20	20	20	7	10		
Gallium	10	10	7	8	3	4	20	20	20	20	6	8		
Germanium	6	9	8	9	3	3	90	70	40	30	5	10		
Rubidium	40	40	20	30	10	10	40	40	50	60	6	10		
Strontium	100	100	100	100	70	80	200	200	100	100	200	100		
Yttrium	9	10	9	9	7	7	9	10	8	8	6	10		
Molybdenum	2	1	0.8	0.6	0.4	0.7	20	10	10	9	1	0.7		
Indium	0.05	0.06	<0.04	<0.04	<0.04	<0.04	0.5	0.6	0.3	0.3	<0.04	<0.04		
Cesium	3	3	2	2	1	1	6	6	6	6	0.3	0.7		
Lanthanum	2	4	4	5	3	4	2	2	1	1	4	8		
Cerium	5	7	6	7	4	4	4	4	3	3	9	20		
Bismuth	0.2	0.1	0.08	0.07	<0.04	<0.04	0.1	0.2	0.3	0.2	<0.04	0.07		
Uranium	1	2	1	1	1	1	20	20	5	4	0.4	0.5		

to reduce dust and ice formation. Slightly greater concentrations of molybdenum, iron, and cobalt were measured in mine vehicle muds as compared to the reference vehicle mud.

Results for acid-extractable metals in vehicle mud samples are indicated in table 3. Acid-extractable concentrations of cadmium, lead, and zinc in vehicle muds were similar to the concentrations measured using the total recoverable procedure (table 1). For example, when comparing means of total recoverable metal concentrations for each of the three pairs of vehicle mud samples to those of acid-extractable metals, the range of RPDs between them were only 2.5 to 5.8 percent, 0.3 to 3.7 percent, and 1.4 to 4.0 percent for cadmium, lead, and zinc, respectively. Although the acid-extractable procedure has no specific relation with any particular geochemical or mineral phase, or with metal bioavailability, it is a much less aggressive treatment than the total recoverable method because the strength of the HNO_3 used to treat the sample is 10-fold less and the temperature nearly 3-fold lower. Based on these data, most of the cadmium, lead, and zinc present in the vehicle mud was readily extracted by the milder dilute nitric acid treatment.

Snow Samples

Snow sampling has been suggested as perhaps the best practical means to measure cumulative dust dispersion during the winter season (mid-September to mid-April), but as yet, no simple method seems to be effective during the remainder of the year. Dust bin collectors, for example, are prone to incur significant losses of sampled material during strong windy conditions that frequently are observed in this region (Clark, 2005). As previously indicated, snow sampling locations along the haul road (fig. 1) were chosen to complement biological sampling sites planned for later that year. For reference

purposes, snow also was sampled near a gravel road located on the outskirts of Kotzebue, Alaska; however, that location has comparatively little vehicular traffic and is not used by large trucks.

Collection information and selected physical data for the snow samples are indicated in table 4. Most notable among these physical data was the quantity of particulates present in the snow pack at various locations. For most DMTS road samples, a layer of dark gray particulates was visible on the snow surface (fig. 2) and at some locations multiple layers of particulates within the snow pack were evident (fig. 2B). Snow samples collected at nominal distances of 15 m north of the DMTS road (n=6) contained an average of 292 mg of particulate, samples collected 50 m north of the road (n=3) had an average of 172 mg, and samples collected 15 m south of the DMTS road (n=3) had an average of 69 mg. In comparison, snow collected near the reference road at 26 and 38 m had a mean of 19 mg of particulates (table 4). Among the snow samples collected on the south of the DMTS road, the one collected at Aufeis Creek (19 m) had the greatest amount of particulates (140 mg). The snow sample collected just south of the road at New Heart Creek contained 47 mg, and the south-side sample collected at Straight Creek contained 21 mg. This latter amount was similar to the reference site samples (table 4). Samples collected on the south side of the road were expected to contain lower amounts of particulates because of the prevailing southerly winds.

Among the three drainages sampled, snow samples collected near Straight Creek generally contained the least amount of particulates and had the least variation among sampling pairs collected at 15-m nominal distances north of the road. For example, snow samples collected from two locations at Straight Creek, each 15 m north of the road, contained 216 and 263 mg of particulates; snow collected from two locations at New Heart Creek, each 15 m north of the road, contained

Table 3. Concentrations of acid-extractable metals, as measured by quantitative analysis, in vehicle mud collected near Red Dog Mine and Kotzebue, Alaska, June 2005.

[All concentrations in micrograms per gram dry weight as extracted with 1.6 molar nitric acid at 65 degrees Celsius. Subsample 1 was obtained from right front well and subsample 2 from right rear well. USGS, U.S. Geological Survey; ID, identification number]

USGS ID	Vehicle ID	Location	Subsample	Aluminum	Zinc	Cadmium	Barium	Lead
33848	Vehicle 8099	Red Dog Mine, Alaska	1	4,810	17,270	221	2,270	9,580
33849			2	4,390	21,150	270	2,210	10,450
33850	NPS Truck	Red Dog Mine, Alaska	1	8,350	15,480	129	6,820	4,880
33851			2	9,210	11,540	102	10,080	3,690
33852	NPS Truck	Kotzebue, Alaska	1	4,690	50	0.16	220	11
33853			2	5,760	98	0.34	246	18

Table 4. Sampling locations and selected physical data for snow samples obtained near the DeLong Mountain Regional Transportation System haul road in Cape Krusenstern National Monument, Alaska, and a reference road near Kotzebue, Alaska, April 2006.

[Liquid volume was at room temperature; total particulates did not include macroscopic particles such as grass blades, stalks, leaves and sand-sized granular particles that were removed before the determination; latitude-longitude as determined by NAD 83. USGS, U.S. Geological Survey; ID, identification number; m, meters; L, liters; mg/L, milligrams per liter; N, north; <, less than; S, south; KOTZ, Kotzebue]

USGS ID	Latitude	Longitude	Location description	Measured distance from road toe (m)	Snow depth (m)	Liquid volume collected (L)	Mass of solids in sample (mg)	Solids concentration (mg/L)	Filterable anion concentration				
									Chloride (mg/L)	Fluoride (mg/L)	Nitrate (mg/L)	Sulfate (mg/L)	
36889	67.60448	-163.94495	1A-2 - New Heart 10m N	15	0.20	0.152	107	704	2.7	<0.08	0.5	2.5	
36890	67.60433	-163.94518	1B-2 - New Heart 10m N	15	0.25	0.160	488	3052	7.6	<0.08	0.4	4.0	
36891	67.60452	-163.94586	2-2 - New Heart 50m N	50	0.30	0.283	210	744	3.3	<0.08	0.5	3.0	
36892	67.60411	-163.94449	3-2 - New Heart 10m S	13	0.40	0.203	47	233	1.7	<0.08	0.3	2.0	
36893	67.63232	-163.84427	4A-2 - Aufeis 10m N	19	0.90	0.642	478	745	3.0	<0.08	0.4	2.2	
36894	67.63239	-163.84421	4B-2 - Aufeis 10m N	20	0.50	0.338	200	591	2.7	<0.08	0.4	2.1	
36895	67.63253	-163.84494	5-2 - Aufeis 50m N	50	0.60	0.498	201	404	2.8	<0.08	0.5	2.1	
36896	67.63200	-163.84344	6-2 - Aufeis 10m S	19	0.90	0.711	140	197	2.2	<0.08	0.4	2.0	
36897	67.67101	-163.70137	7A-2 - Straight 10m N	15	0.70	0.228	216	946	5.2	<0.08	0.4	2.4	
36898	67.67086	-163.70129	7B-2 - Straight 10m N	15	0.70	0.399	263	659	2.2	<0.08	0.4	2.0	
36899	67.67076	-163.70222	8-2 - Straight 50m N	50	0.40	0.160	105	654	2.6	<0.08	0.4	2.1	
36900	67.67098	-163.70033	9-2 - Straight 10m S	15	0.90	0.692	21	30	1.5	<0.08	0.4	<1.6	
36901	66.86425	-162.54565	10A-2 - KOTZ	26	0.50	0.577	15	27	1.3	<0.08	<0.08	<1.6	
36902	66.86449	-162.54521	10B-2 - KOTZ	38	0.60	0.430	23	54	1.5	<0.08	<0.08	<1.6	

107 and 488 mg; and snow samples collected from two locations near Aufeis Creek, 19 and 20 m north of the road, contained 478 and 200 mg of particulates, respectively (table 4). Thus, there were substantial differences in the amounts of particulates in pairs of samples collected from approximately the same distances from the road at each location.

Variation among samples collected at similar distances from the north side of the road was probably caused in part by heterogeneity of particulate deposition patterns. There were rather dramatic depositional “streaks” evident within the snowpack at site 4A and on the snow surface at site 7A (fig. 2). Differences in localized meteorological conditions (such as wind speed and direction) and in micro-topography could be factors contributing to differences in particulate depositions within and between sampling locations. Snowfall in northwest Alaska is highly mobile, and the drifting and scouring can be quite pronounced in windy coastal locations. For example, the snow depth was only about 0.2 m for samples collected near New Heart Creek (fig. 2), which is situated on relatively flat terrain of the coastal plain. Vegetation growth in the arctic tussock tundra can be quite heterogeneous, which also could be a factor in differing amounts of snow and of particulate accumulations at locations just a few meters apart.

Differences in particulate loadings between the three drainages might also be explained in part by the orientation and surface relief of the road and its effects on attainable truck speeds. There is a pronounced curve at each end of the bridge over Straight Creek, but the road follows a straight path over the bridges at Aufeis and New Heart Creeks (fig. 1); consequently, haul trucks and other vehicles can maintain much greater speeds when traveling over Aufeis and New Heart Creeks as compared to Straight Creek. In addition, there is a rather large valley within Aufeis Creek, so haul trucks are likely to approach maximum attainable speeds near the bridge to obtain the momentum needed to ascend the hill on either side of that valley. Presumably, as rates of vehicle speed increase, greater amounts of fugitive dust could be dispersed from truck surfaces and the road surface because of greater wind velocity and vibration.

Concentrations of metals in whole snow closely followed the patterns for particulates. Results for aluminum, barium, cadmium, lead, and zinc in snow are expressed in three ways in table 5: the concentration in the liquid snow (which includes the metal extracted from particulates); the concentration in the particulates (assuming all of metals originated from particulates); and the metal loading (mass of metal per unit surface area, assuming all of the metal in the snow sample would be deposited to the ground surface below, irrespective of the snow depth sampled). When expressed on a snow particulates basis (table 5), cadmium, lead, and zinc concentrations also were greatest for Aufeis Creek and least for Straight Creek, but the mean values for each of the three drainages differed only by factors of 1.3 to 1.4. Thus, the cadmium, lead, and zinc contents of the particulates were fairly consistent among drainages. Arithmetic mean concentrations of cadmium, lead, and zinc in snow particulates for all DMTS road sites com-

bined were 8.0, 450, and 1,090 $\mu\text{g/g}$ dry weight, respectively, whereas mean concentrations of these same metals in the road soils sampled in 2005 (nearer to the mine) were 3.0, 93, and 430 $\mu\text{g/g}$ dry weight, or roughly one-third of concentrations in snow particulates. However, the fraction of annual metals loadings occurring in winter as compared to the remainder of the year is not readily determined by these data.

Compared to the mean of the two reference snow samples, metal loadings estimated from individual snow samples near the DMTS road (table 5) were greater by factors of 1 to 24 for aluminum, 17 to 259 for barium, 13 to 316 for cadmium, 28 to 589 for lead, and 8 to 195 for zinc. Mean loadings of these five elements calculated for each of the three DMTS drainage locations ($n=4$ for each) differed by factors ranging from 3- to 4-fold. Mean loadings of cadmium, lead, and zinc were greatest at Aufeis Creek and least at Straight Creek. When averaged for all three drainages, mean loadings of cadmium, lead, and zinc calculated from snow samples collected at a nominal distance of 15 m to the north of the road were 0.63, 34, and 89 mg of metal per square meter, respectively. Mean loadings for samples collected 15 m to the north of the road were about twice of those collected 50 m to the north and about four times greater than for samples collected 15 m to the south (fig. 4).

As discussed previously, snow drift and scour patterns probably had an effect on the apparent deposition of fugitive dust and the associated metals. Clark (2005) reported that among snow samples collected at three locations near the mine during the winter of 2005, metal concentrations (mass of metal per unit volume of snow) were greater in scour areas, but total loadings were greater in drift areas. Results for the 2006 snow samples collected near New Heart and Aufeis Creeks were consistent with that observation. The average depth of the snow pack for samples collected at New Heart Creek was only about one-third of that for Aufeis Creek snow samples and accordingly, New Heart samples had greater average metal concentrations in the snow (table 5), but Aufeis samples had greater mean metal loadings (fig. 4). Differences in snow pack depths might partly explain the roughly 3- to 4-fold differences in metals loadings between sampling pairs collected at 19 to 20-m distances north near Aufeis Creek. However, the analogous pair of samples collected near New Heart Creek from 15-m distances that exhibited nearly 10-fold differences in metals loadings, did not fit this pattern. New Heart snow sample number 1B-1 had by far the greatest individual metal concentration as well as metal loadings (table 5). Chloride and calcium concentrations also were greatest in that sample (table 4 and table 6, respectively), suggesting a greater affect from road particulates, which presumably would contain elevated quantities of calcium chloride de-icing additive during the winter.

Residue from a historic concentrate spill might have been an additional factor contributing to the increased metal concentrations measured in New Heart Creek sample 1B-1. Through the spring of 2003, five concentrate spills (resulting when haul trucks over-turn) had been documented within

Table 5. Concentrations and estimated loadings of selected metals, as measured by quantitative analysis, in digested whole snow samples obtained near the DeLong Mountain Regional Transportation System haul road in Cape Krusenstern National Monument, Alaska, and a reference road near Kotzebue, Alaska, April 2006.

[Liquid concentrations for whole melted snow after digestion with 1.6 molar nitric acid at 65 degrees Celsius; particulate concentration assumes all extractable metals originated from snow particulates; mass loading assumes all metal in snow sample deposited to a 0.0039 square meter land surface area. USGS, U.S. Geological Survey; ID, identification number; m, meters; µg/L, micrograms per liter; µg/g, micrograms per gram; mg/m², milligrams per square meter]

USGS ID	General location	Site ID	Direction from road	Distance from road (m)	Liquid concentration (µg/L)				
					Aluminum	Zinc	Cadmium	Barium	Lead
36889	New Heart Creek	1A-1	North	15	3,290	356	2.68	929	147
36890	New Heart Creek	1B-1	North	15	25,910	3,780	24.3	7,400	1,240
36891	New Heart Creek	2-1	North	50	4,440	576	4.31	1,580	277
36892	New Heart Creek	3-1	South	13	3,520	433	3.19	963	211
36893	Aufeis Creek	4A-1	North	19	3,090	1,270	9.89	1,780	557
36894	Aufeis Creek	4B-1	North	20	2,070	683	4.91	1,010	315
36895	Aufeis Creek	5-1	North	50	1,640	488	4.01	886	183
36896	Aufeis Creek	6-1	South	19	612	170	1.24	279	56.6
36897	Straight Creek	7A-1	North	15	2,730	332	2.17	526	129
36898	Straight Creek	7B-1	North	15	4,710	737	5.12	714	201
36899	Straight Creek	8-1	North	50	3,360	422	2.96	714	154
36900	Straight Creek	9-1	South	15	283	51	0.39	115	24.6
36901	Kotzebue reference	10-A-1	East	26	332	11	0.04	10	1.1
36902	Kotzebue reference	10-B-1	East	38	356	5	0.04	9	1.2
					Particulate concentration (µg/g)				
36889	New Heart Creek	1A-1	North	15	4,674	506	3.8	1,320	209
36890	New Heart Creek	1B-1	North	15	8,488	1,238	8.0	2,424	406
36891	New Heart Creek	2-1	North	50	5,970	774	5.8	2,124	372
36892	New Heart Creek	3-1	South	13	15,080	1,855	13.7	4,126	904
36893	Aufeis Creek	4A-1	North	19	4,147	1,705	13.3	2,389	748
36894	Aufeis Creek	4B-1	North	20	3,504	1,156	8.3	1,710	533
36895	Aufeis Creek	5-1	North	50	4,059	1,208	9.9	2,193	453
36896	Aufeis Creek	6-1	South	19	3,114	865	6.3	1,420	288
36897	Straight Creek	7A-1	North	15	2,886	351	2.3	556	136

Table 5. Concentrations and estimated loadings of selected metals, as measured by quantitative analysis, in digested whole snow samples obtained near the DeLong Mountain Regional Transportation System haul road in Cape Krusenstern National Monument, Alaska, and a reference road near Kotzebue, Alaska, April 2006. —Continued

[Liquid concentrations for whole melted snow after digestion with 1.6 molar nitric acid at 65 degrees Celsius; particulate concentration assumes all extractable metals originated from snow particulates; mass loading assumes all metal in snow sample deposited to a 0.0039 square meter land surface area. USGS, U.S. Geological Survey; ID, identification number; m, meters; µg/L, micrograms per liter; µg/g, micrograms per gram; mg/m², milligrams per square meter]

USGS ID	General location	Site ID	Direction from road	Distance from road (m)	Aluminum	Zinc	Cadmium	Barium	Lead	
										Particulate concentration (µg/g)—Continued
36898	Straight Creek	7B-1	North	15	7,142	1,118	7.8	1,083	305	
36899	Straight Creek	8-1	North	50	5,140	646	4.5	1,092	236	
36900	Straight Creek	9-1	South	15	9,378	1,683	12.9	3,811	815	
36901	Kotzebue reference	10-A-1	East	26	12,372	414	1.6	354	41	
36902	Kotzebue reference	10-B-1	East	38	6,561	84	0.7	157	22	
Mass loading / surface area (mg/m ²)										
36889	New Heart Creek	1A-1	North	15	128	14	0.10	36.2	5.7	
36890	New Heart Creek	1B-1	North	15	1,063	155	1.00	304.	50.9	
36891	New Heart Creek	2-1	North	50	322	42	0.31	115.	20.1	
36892	New Heart Creek	3-1	South	13	183	23	0.17	50.1	11.0	
36893	Aufeis Creek	4A-1	North	19	509	209	1.60	293.	91.7	
36894	Aufeis Creek	4B-1	North	20	179	59	0.43	87.5	27.3	
36895	Aufeis Creek	5-1	North	50	209	62	0.51	113.	23.4	
36896	Aufeis Creek	6-1	South	19	112	31	0.23	50.9	10.3	
36897	Straight Creek	7A-1	North	15	160	19	0.13	30.8	7.5	
36898	Straight Creek	7B-1	North	15	482	75	0.52	73.0	20.6	
36899	Straight Creek	8-1	North	50	138	17	0.12	29.3	6.3	
36900	Straight Creek	9-1	South	15	50	9	0.069	20.4	4.4	
36901	Kotzebue reference	10-A-1	East	26	49	2	0.006	1.4	0.2	
36902	Kotzebue reference	10-B-1	East	38	39	1	0.004	0.9	0.1	

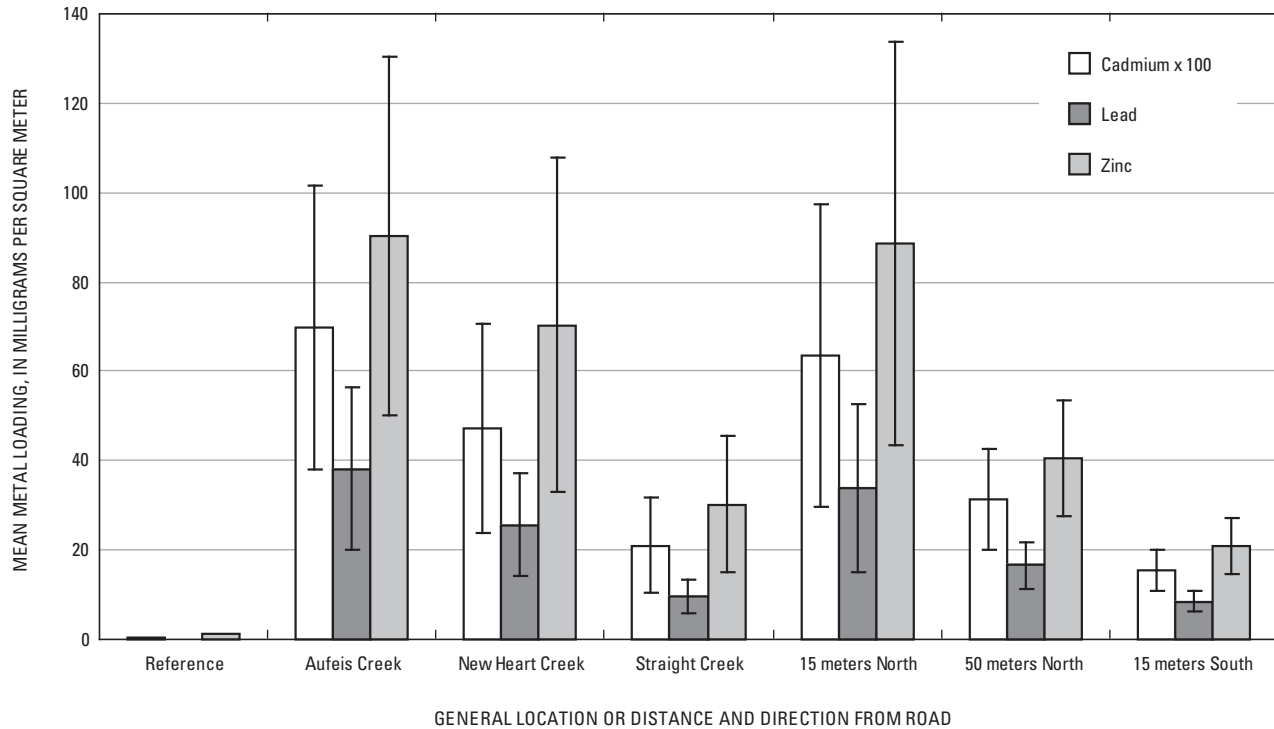


Figure 4. Comparison of cadmium, lead, and zinc loadings from 2006 snow samples categorized by drainage and distance from the DeLong Mountain Regional Transportation System road. Note: error bars are plus or minus one standard error.

CAKR boundaries between 1990 and 1999 (Turner, 2003). Two of those spills occurred near the 2006 snow sampling locations at New Heart Creek. A field survey of historic spill sites conducted during the summer of 2002 revealed that a substantial amount of zinc concentrate remained at those two spill sites near New Heart Creek (Turner, 2003). Although most of the remaining spilled concentrate was to be removed in 2003 (Turner, 2003), perhaps remobilization of residue from one of those two historic spills contributed to the higher metal concentrations in sample number 1B-1. This possibility might seem unlikely for most typical snow samples, but in this instance it is more plausible because of the shallow snow depth (0.2 m) sampled at the 1B-1 location.

Comparison to Recent Studies

Two other reports describe recent (2003–05) snow samplings in this region, which can be compared to these 2005–06 samples. Clark (2005) collected snow samples from three locations near Red Dog Mine in April 2005, and as might be expected, those samples contained considerably greater amounts of metals than did 2005–06 near-road samples in CAKR. For example, a downwind “snow drift” sample collected by Clark that was about 0.9 km west/northwest of the mine/mill gyrator crusher, contained mean loadings of cadmium, lead, and zinc that were about 80 to 160 times greater than the overall mean of metal loadings in snow from 2006 CAKR north road sites.

Brabets (2004) reported metal concentrations of particulates in snow collected in April 2003, but not loadings. The sampling design of that study was based on a grid system that included one sample collected near the center of each of 28, 10 square kilometer (km^2) cells. Only three of those 2003 samples were obtained near the DMTS road; one location west of New Heart Creek, one west of Omikviorok River, and one at the northern boundary of CAKR. The 2003 snow sample collected by the road near New Heart Creek contained particulate concentrations of cadmium, lead, and zinc that were roughly twice that of the mean of the samples collected at New Heart Creek in 2006. The greater metal concentrations in particulates of the 2003 snow sample collected near New Heart Creek might be attributed in part to the fact that it was collected about 0.5 km nearer to the port than the 2006 sample, and because it was sampled before measures to reduce fugitive concentrate losses were implemented at the port in the summer of 2003 (Alaska Department of Environmental Conservation, 2007). Mean metals concentrations in particulates of all three of the near-road snow samples collected in 2003 by Brabets (2004) were about 11, 490, and 1,800 $\mu\text{g/g}$ for cadmium, lead, and zinc, respectively. Those values are similar to the concentrations reported for dusts collected from vegetation adjacent to the road in the summer of 2000 (Ford and Hasselbach, 2001), and slightly greater than the mean metal concentrations measured in particulates of the 2006 snow samples (fig. 5). Notably, concentrations of these metals in surficial soil samples collected from 10 m north of the road in 2003 as part of three transect

characterizations (TT2, TT3, TT8; Exponent, 2007) were of a similar magnitude (fig. 5).

Based on this rather limited data set, particulates that were dispersed into snow along the road during winter 2005–06 appeared to have slightly less cadmium, lead, and zinc concentrations as compared to 2002–03; however, absolute metal loadings could not be evaluated from the 2003 samples. Presumably, total annual metal loadings being dispersed to CAKR lands have been reduced somewhat in recent years. Depending on the mobility, fate, and cumulative deposition of metal-enriched particulates, it remains uncertain if decreases in annual loadings will result in concomitant decreases in CAKR ecosystem media concentrations.

Within CAKR, lead and other metal concentrations in roadside vegetation collected in 2001 tended to be greatest near the port site, the so-called “port effect” (Hasselbach and others, 2005). Apparently, this was as a result of losses and dispersion of concentrates during transfer operations at the port in addition to that which occurred during transport on the DMTS road. Elevated metal concentrations were measured in soils within port-site boundaries in the late 1990s, but in 2003 most of the contaminated port-site soil was removed, and concentrate loss-control measures were implemented (Alaska Department of Environmental Conservation, 2007). Based

on empirical models derived from the 2001 sample data, lead concentrations in moss near the road in CAKR were predicted to exceed 400 $\mu\text{g/g}$ out to about 9 km east/northeast from the port-site management boundary (Hasselbach and others, 2005). These regions of greatest lead concentrations included the haul road areas near New Heart and Aufeis Creeks, but not at Straight Creek.

Results from the limited number of snow samples of this study indicate that for the three drainages sampled, the “port effect” was not necessarily an important factor affecting east-west spatial differences of metals deposition during the 2005–06 winter. Metal loadings were, in fact, the lowest in the drainage furthest from the port (Straight Creek), but samples near Aufeis Creek, which is about 10 km from the port, had greater metal loadings than those collected near New Heart Creek, only about 5 km away. Presumably, dispersion of metal-enriched fugitive dusts near the port has been greatly reduced after cleanup of port soil and implementation of concentrate loss-control procedures in 2003 (Alaska Department of Environmental Conservation, 2007). In addition, cessation of port shipping operations from early fall through early summer might result in a decreased ‘port effect’ for snow samples obtained in early spring when compared with dusts or vegetation collected in mid-to late summer. The absence of

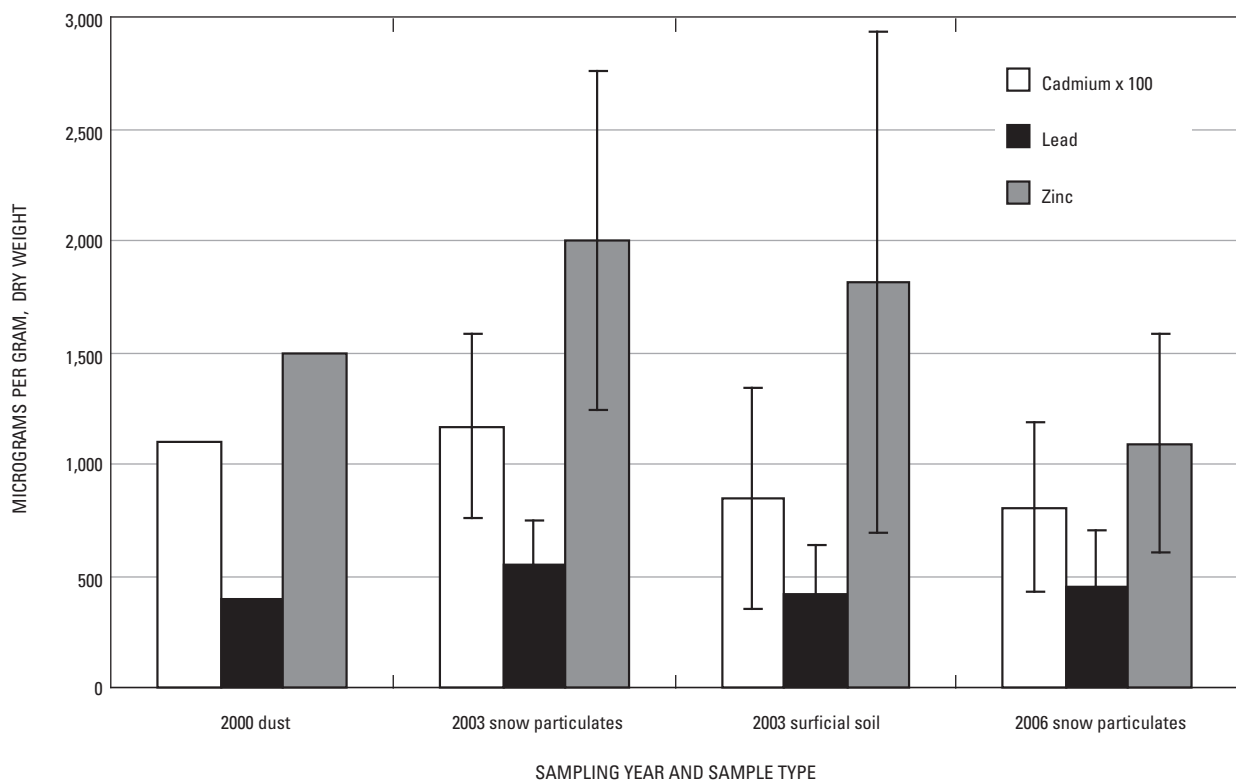


Figure 5. Comparison of cadmium, lead, and zinc concentrations in selected samples of dust, snow particulates, and surficial soils collected adjacent to the DeLong Mountain Regional Transportation System road in Cape Krusenstern National Monument between 2000 and 2006. Concentrations are means with error bars represented by plus or minus one standard deviation except for 2000 dust, which are median values. Sources: 2000 dust (Ford and Hasselbach, 2001); 2003 snow particulates (Brabets, 2004); 2003 soil (Exponent, 2007); 2006 snow particulates (this study).

Table 6. Concentrations of acid-extractable elements, as measured by semi-quantitative analysis, in snow samples collected near the DeLong Mountain Regional Transportation System haul road in Cape Krusenstern National Monument, Alaska, and a reference road near Kotzebue, Alaska, April 2006. —Continued

[All concentrations in micrograms per liter of whole melted snow after digestion with 1.6 molar nitric acid at 65 degrees Celsius. Analyses conducted using semi-quantitative method and rounded to one or two significant figures. Concentrations of twenty seven additional elements obtained during the analysis are not reported because they are minimally recovered by the dilute acid extraction method. USGS, U.S. Geological Survey; ID, identification number; m, meters; N, north; S, south; KOTZ, Kotzebue; <, less than]

USGS ID	36875	36876	36877	36878	36879	36880	36881	36882	36883	36884	36885	36886	36887	36888
Site and field ID	New Heart 10m N (A) 1A-1	New Heart 10m N (B) 1B-1	New Heart 50m N 2-1	New Heart 10m S 3-1	Aufeis 10m N (A) 4A-1	Aufeis 10m N (B) 4B-1	Aufeis 50m N 5-1	Aufeis 10m S 6-1	Straight 10m N (A) 7A-1	Straight 10m N (B) 7B-1	Straight 50m N 8-1	Straight 10m S 9-1	KOTZ (A) 10A-1	KOTZ (B) 10B-1
Lithium	10	60	10	10	9	5	4	1	6	10	8	0.8	0.5	0.5
Beryllium	0.4	1	0.4	0.3	0.3	0.1	0.1	<0.1	0.2	0.2	0.3	<0.1	<0.1	<0.1
Sodium	300	800	400	300	500	400	600	400	700	400	400	300	1,000	1,000
Magnesium	50,000	300,000	50,000	50,000	100,000	50,000	40,000	10,000	20,000	30,000	20,000	2000	1,000	1,000
Aluminum	3,000	17,000	4,000	3,000	3,000	2,000	1,000	700	2,000	4,000	3,000	300	400	400
Potassium	700	2,000	1,000	800	1,000	600	700	400	700	700	900	200	200	200
Calcium	90,000	500,000	80,000	80,000	200,000	80,000	60,000	20,000	30,000	60,000	40,000	4,000	2,000	3,000
Vanadium	10	60	10	9	10	7	6	2	5	10	7	0.6	0.8	0.9
Chromium	9	50	10	8	10	10	6	3	6	10	7	2	2	2
Manganese	200	2,000	300	300	500	200	300	60	200	400	300	30	50	40
Iron	4,000	33,000	5,000	4,000	4,000	2,000	2,000	700	4,000	7,000	4,000	500	600	600
Cobalt	4	30	5	4	7	3	3	0.9	3	6	7	0.4	0.4	0.5
Nickel	10	100	20	20	20	10	8	3	9	20	10	1	<1	1
Copper	6	50	9	6	20	7	5	1	4	9	6	<1	<1	<1
Zinc	300	3,000	500	400	1,000	600	500	100	300	700	400	40	6	<1
Gallium	2	10	2	2	2	1	0.9	0.3	1	2	2	0.2	0.2	0.2
Germanium	<0.1	0.7	0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	0.2	0.1	<0.1	<0.1	<0.1
Rubidium	7	30	9	8	10	5	4	2	6	7	7	1	0.6	0.7
Strontium	80	800	100	80	200	70	60	20	50	90	70	7	5	6
Yttrium	9	90	9	8	20	8	6	2	4	20	5	0.5	0.4	0.4
Molybdenum	0.2	2	0.3	0.2	0.5	0.2	0.2	<0.1	0.2	0.2	0.2	0.1	<0.1	<0.1
Silver	<0.1	1	0.3	0.2	0.7	0.2	0.2	<0.1	0.1	0.3	0.2	<0.1	<0.1	<0.1

Table 6. Concentrations of acid-extractable elements, as measured by semi-quantitative analysis, in snow samples collected near the DeLong Mountain Regional Transportation System haul road in Cape Krusenstern National Monument, Alaska, and a reference road near Kotzebue, Alaska, April 2006. —Continued

[All concentrations in micrograms per liter of whole melted snow after digestion with 1.6 molar nitric acid at 65 degrees Celsius. Analyses conducted using semi-quantitative method and rounded to one or two significant figures. Concentrations of twenty seven additional elements obtained during the analysis are not reported because they are minimally recovered by the dilute acid extraction method. USGS, U.S. Geological Survey; ID, identification number; m, meters; N, north; S, south; KOTZ, Kotzebue; <, less than]

USGS ID	36875	36876	36877	36878	36879	36880	36881	36882	36883	36884	36885	36886	36887	36888
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Cadmium	2	20	4	3	10	5	4	1	2	5	3	0.4	<0.1	<0.1
Indium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Antimony	0.5	3	0.8	0.6	2	0.8	0.6	0.2	0.5	0.7	0.6	0.1	<0.1	<0.1
Cesium	1	8	2	2	2	1	1	0.3	1	2	1	0.2	<0.1	<0.1
Barium	700	6,000	1,000	800	1,000	800	700	300	500	700	700	100	10	9
Lanthanum	3	30	3	3	6	3	2	0.7	1	5	1	0.1	0.3	0.4
Cerium	3	30	4	3	6	3	2	1	2	8	2	0.3	0.8	0.6
Thallium	<0.1	0.8	0.2	0.1	0.3	0.1	0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	<0.1
Lead	100	800	300	200	600	300	200	50	100	200	100	20	1	1
Bismuth	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Uranium	1	10	1	1	2	1	0.9	0.3	0.5	2	0.7	<0.1	<0.1	<0.1

an obvious port effect indicates that unloading concentrates from haul trucks at the port, which occurs year-round, was not a primary factor contributing to metals concentrations in 2006 snow samples. If not, elevated concentrations of metals in the snow samples probably resulted mostly from dispersion of mine ore wastes or concentrates from haul trucks and other vehicles traversing the road during the winter of 2005–06, and possibly in part from remobilization of previously dispersed particulates. Accordingly, particulate and metal loadings in the snow at each location might have been affected by the local topography, meteorological conditions, and the road orientation because of those effects on wind speed and direction, and possibly on attainable truck speeds.

Dissolved metals concentrations of in the melted snow were not measured in this 2005–06 study. Dissolved concentrations in snowmelt were presumed to be important primarily for assessing risks to aquatic organisms, and cumulative information through 2006 indicates that risks to aquatic biota within CAKR are moderate to low (Exponent, 2007). Furthermore, dissolved concentrations as measured by liquefaction of snow in the laboratory might poorly reflect the conditions and interactions of melting snow with the vegetation during spring in the arctic tundra. Consequently, a more detailed field study that specifically targets the snowmelt would be needed to adequately address potential concerns in regard to the dissolution of metals into melting snow. Brabets (2004) reported dissolved elemental concentrations for snow samples collected in CAKR during April 2003 and not surprisingly, the three near-road samples of snow collected during that study had among the greatest concentrations of dissolved metals. For those three near-road snow samples, dissolved metal concentration ranges (in $\mu\text{g/L}$) were reported as: cadmium, 0.34 to 1.0; lead, 0.6 to 5.6; and zinc, 5.8 to 43.2. The sample from the New Heart Creek near-road location had the greatest overall concentration of zinc, and the second greatest concentration of lead and cadmium. For comparison, the USEPA recommends the following concentrations as criteria for the protection of aquatic life based on a continuous chronic concentration (CCC) at a water hardness of 100 mg/L; cadmium, 0.25 $\mu\text{g/L}$; lead, 2.5 $\mu\text{g/L}$, and zinc, 120 $\mu\text{g/L}$ (U. S. Environmental Protection Agency, 2006). Thus, some of the dissolved metal concentrations in snow for the near-road locations reported by Brabets were greater than recommended CCC aquatic life criteria for cadmium and lead, but not for zinc. Because of dilution from upstream flows, near-road stream-water metals concentrations probably were considerably less than concentrations in the snowmelt. Dissolved metal concentrations in stream-water samples collected during open-water season in 2002 from New Heart Creek about 15 m downstream of the road (Brabets, 2004) were in fact well below the USEPA, CCC criteria; however, stream-bed sediments collected from 26 sites within CAKR as part of that same study were most elevated in cadmium, lead, and zinc for sampling locations in New Heart Creek, and some of those samples exceeded probable effects concentrations suggested for sediments (MacDonald and others, 2000). In any event, monitoring during the spring snow-

melt would better address any potential adverse effects to the aquatic environment, as well as the terrestrial biota, stemming from a possible “pulse” of dissolved metals that might occur during that season.

Methodology Assessment

For sampling and chemical preparation of snow, the in-bottle digestion using dilute (1.6 M) nitric acid was selected to simplify procedures and potentially reduce laboratory contamination because no transfers or open-vessel evaporative steps are required. For vehicle mud samples, the same in-bottle, acid-extractable method produced similar concentrations of cadmium, lead, and zinc as compared with the more aggressive total recoverable digestion; concentrations were within 87 to 100 percent of the leachable ranges reported for aluminum, barium, cadmium, lead, and zinc in a standard reference soil (appendix A). Therefore, this simpler in-bottle digestion appears to be suitable to monitor metals concentrations in soils, dusts, or snow samples, but additional laboratory and field replication is recommended to better characterize the repeatability of the method.

Variability of metals measured between pairs of individual snow samples collected at 15-m nominal distances north of the road was considerable, probably in part because of effects of micro-topography on the snow drift and scour patterns, as well as the dust deposition. Noting such factors while collecting several evenly-spaced samples at similar distances from the north side of the road (15–20 m, for example) at each location should improve data comparability for future trend analysis. Additional sampling from the south side of the road and/or from greater distances could be useful, but these would be of a lower priority if resources are limited. Compositing of samples might be performed if analytical budgets were limited, but analyses of individual samples could provide useful information for assessing sampling variability.

Variation of snow sampling technique also might have been a factor in the variability of results. To simplify field logistics, plastic scoops were used for sampling and pre-cleaned 2-L bottles were used for collection, similar to that described by Ingersoll and others (2002). Snow at least 0.5 m deep was expected to be available for sampling, but at the New Heart Creek locations, snow only 0.2 to 0.4 m deep was encountered. Consequently, the volume of those samples only amounted to about 20 to 30 percent of the capacity of the 2-L collection bottle. For that location, two or three vertical grabs could have been combined to provide a volume more similar to other locations where at least 0.5-m sections were sampled. Alternately, use of a tubular device, such as that typically used for sampling from deep snow banks might be considered. Examples include the commercially-available “Adirondock” snow tube sampler (made of fiberglass) or one fashioned from poly-vinyl chloride pipe (Hansen, 2003). These types of devices might allow for collection of a more consistent surface area in a manner that is less dependent on technique, which in

turn could provide more accurate loading estimates. Depending on weather conditions and the physical characteristics of the snow pack (hardness of crust and amount of particulates, for example), uniform collection and transfer of particulates and subsequent decontamination might be more problematic with a tube sampler as compared to a scoop. For this pilot study, the simplicity of using the plastic scoops was judged to outweigh any potential advantages of conventional snow tube sampling apparatus.

A separate (adjacent) snow sample was collected to determine percent solids as a means to minimize the risk of bias of metal determinations potentially caused by laboratory manipulation and contamination. Otherwise, the particulates must be isolated from the snow by washing and filtration, followed by drying and weighing before digestion, and the resultant filtered liquid sample analyzed separately or recombined with the particulate before digestion. The disadvantage of the separate sample approach is that the amount of particulates present in adjacent pairs of samples might vary, thereby contributing to variation of metals concentrations when calculated based on particulates. This approach primarily was chosen with consideration of the reference location snow samples because minimal concentrations were anticipated. However, if only DMTS near-road monitoring was to be conducted, performing particulate and acid-extractable metal measurements from a single sample might be preferable because any contamination resulting from the additional laboratory processing would likely be insignificant compared with concentrations near the DMTS road. Actually, measuring particulates in the snow might not be necessary at all because the determination of metal loadings will be of primary importance, and that can be determined without assessing particulate loadings.

Summary and Conclusions

In this investigation, a small number of mud, soil, and snow samples were collected in 2005 and 2006 to assess metal concentrations and loadings in areas adjacent to the DeLong Mountain Regional Transportation System (DMTS) road. Mud collected in summer 2005 from the wheel-wells of two passenger vehicles used for transport between Red Dog Mine and the port facility were enriched in cadmium, lead, and zinc by factors of about 800, 450, and 220, respectively, as compared with mud collected from a vehicle stationed in Kotzebue, Alaska. Thus, as of 2005, dispersal of mine ore wastes or concentrates by vehicles appeared to remain a potential source of metals along the DMTS road. Compared with a reference mud, samples of DMTS road bed soils obtained at locations that were 12 to 20 kilometers from the mine were enriched by factors of about 12 for cadmium, 11 for barium, and 6 for lead and zinc. Concentrations of metals in the 2005 road bed soils were about 3-fold lower than in dust samples collected from vegetation adjacent to the road by National Park Service (NPS) researchers in 2000; however, differences in sampling

conditions and sample particle sizes might have been factors contributing to the apparent temporal differences.

Snow sampling has been suggested as perhaps the best practical means to measure dust and metals accumulation near the DMTS road during the winter (roughly mid-September to mid-April). Compared to snow samples obtained near a gravel road located on the outskirts of Kotzebue, Alaska, metal loadings estimated from individual snow samples collected in April 2006 near three creeks in Cape Krusenstern National Monument (CAKR), 13 to 50 meters (m) from the road, were greater by factors of 13 to 316 for cadmium, 28 to 589 for lead, and 8 to 195 for zinc. When averaged across all three creek locations, mean loadings of cadmium, lead, and zinc calculated from snow samples collected at a nominal distance of 15 m to the north of the road were 0.63, 34, and 89 milligrams of metal per square meter, respectively. Mean loadings for samples collected 15 m to the north of the road were about twice of those collected 50 m to the north, and about four times greater than for samples collected 15 m to the south.

Among the three drainages sampled, cadmium, lead, and zinc loadings were greatest at Aufeis Creek, least at Straight Creek (furthest from the port), and intermediate at New Heart Creek (nearest to the port). These results indicate that the “port effect”, previously attributed to fugitive metal-enriched dusts stemming from concentrate transfer operations at the port facility, was not necessarily an important factor affecting spatial differences of metals deposition into snow along the road during winter 2005–06. Removing contaminated soil and improving concentrate handling procedures at the port facility in 2003 might help explain these observations, as well as the cessation of port shipping operations between early fall and early summer. Differences in particulate and metal loadings in snow among the three creek locations probably were affected by localized meteorological conditions and micro-topography on the snow drift and scour patterns, but road orientation on attainable truck speeds also might have been a factor. More intensive sampling is needed to substantiate these conclusions.

Compared with snow samples collected by the USGS at three near-road locations in April 2003, the metal content of particulates that accumulated in the snow during 2005–06 seemed to decrease slightly, but absolute metal loadings could not be compared because loadings cannot be determined from the 2003 data. Mean metals concentrations in 2006 snow particulates were roughly three times greater than in the road bed soils that were sampled nearer to the mine in June 2005; however, the fraction of annual metals loadings occurring in winter as compared to the remainder of the year was not readily determined by these data. Although procedures have been implemented in recent years to reduce the quantities of metal-enriched fugitive dusts, particulates dispersed near the road during winter 2005–06 were enriched in metals, and these particulates contributed considerable metal loadings to the nearby terrain. Presumably, total annual metal loadings being dispersed to CAKR lands have been reduced in recent years. Depending on the mobility, fate, and cumulative deposition of these metal-enriched particulates, it remains uncertain

if decreased annual metal loadings will result in concomitant decreases in CAKR ecosystem media concentrations.

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Appendixes A–C

28 Elements in Mud and Snow in the Vicinity of DMTS Road, Red Dog Mine, and Cape Krusenstern Monument, Alaska

Appendix A. Quality-control summary for certified reference materials.

[Concentrations in micrograms per gram dry weight. Certified total concentrations are based on a complete dissolution of all mineral phases. Reported leachable concentrations are based on results of several laboratories using variations of United States Environmental Protection Agency total recoverable digestion method 3050B. Recovery = 100% if measured value is in certified or reported range, otherwise recovery calculated from upper or lower limit of certified/reported range. NRCC, National Research Council of Canada; PACS-1, supplier identification code (meaning unknown); ±, plus or minus; nr, not reported; --, not applicable; nc, not certified; NIST, National Institute of Standards and Technology (USA)]

Standard reference material	Element	Certified total concentration	Reported leachable concentration	Preparation method	Analysis method	Measured concentration	Recovery of total (percent)	Recovery of leachable (percent)
NRCC PACS-1 marine sediment	Aluminum	64700 ± 1200	nr	total recoverable	semi-quantitative	23,700	37	--
	Barium	nc	nr			438	--	--
	Cadmium	2.38 ± 0.2	nr			2.60	101	--
	Lead	404 ± 20	nr			391	100	--
	Zinc	824 ± 22	nr			843	100	--
NIST 2704 Buffalo River sediment	Aluminum	61100 ± 1600	nr	total recoverable	semi-quantitative	28,100	47	--
	Barium	414 ± 12	nr			179	45	--
	Cadmium	3.45 ± 0.22	nr			3.46	100	--
	Lead	161 ± 17	nr			178	100	--
	Zinc	438 ± 12	nr			488	108	--
NIST 2709 San Joaquin soil	Aluminum	75000 ± 600	20,000–31,000	total recoverable	semi-quantitative	35,300	47	113
	Barium	968 ± 40	392–400			450	48	112
	Cadmium	0.38 ± 0.01	nr			0.33	89	--
	Lead	18.9 ± 0.5	12–18			14.9	81	100
	Zinc	106 ± 3	87–120			117	107	100
NIST 2710 Montana soil	Aluminum	64400 ± 800	12,000–26,000	acid-extractable	quantitative	10,490	17	87
	Barium	707 ± 51	300–400			322	49	100
	Cadmium	21.8 ± 0.2	13–26			19.0	88	100
	Lead	5532 ± 80	4,300–7,000			4,737	87	100
	Zinc	6952 ± 91	5,200–6,900			4,985	73	96

Appendix B. Quality-control summary for replicated samples.

[ID, identification number; RPD; relative percent difference between duplicates; RSD, relative standard deviation for triplicates (in percent); RD, Red Dog; RT, Regional Transportation; --, not applicable; NPS, National Park Service]

Sample type	Sample ID	Replicate type	Preparation method	Analysis method	Element	RPD	RSD
Road soil	RD RT-2	lab digestion & analysis	total recoverable	semi-quantitative	Aluminum	--	7.0
					Barium	--	5.1
					Cadmium	--	15.1
					Lead	--	9.8
					Zinc	--	16.2
Mud	Mine vehicle 8099	field pair	total recoverable	semi-quantitative	Aluminum	2.6	--
					Barium	4.5	--
					Cadmium	2.6	--
					Lead	0.2	--
					Zinc	22	--
Mud	NPS truck at mine	field pair	total recoverable	semi-quantitative	Aluminum	10.3	--
					Barium	21.5	--
					Cadmium	24.3	--
					Lead	20.1	--
					Zinc	15.2	--
Mud	NPS truck at reference	field pair	total recoverable	semi-quantitative	Aluminum	29.1	--
					Barium	0.25	--
					Cadmium	50.1	--
					Lead	48.4	--
					Zinc	60.7	--
Mud	Mine vehicle 8099	field pair	acid-extractable	quantitative	Aluminum	8.9	--
					Barium	2.2	--
					Cadmium	20	--
					Lead	8.2	--
					Zinc	20	--
Mud	NPS truck at mine	field pair	acid-extractable	quantitative	Aluminum	9.8	--
					Barium	39	--
					Cadmium	23	--
					Lead	28	--
					Zinc	30	--
Mud	NPS truck at reference	field pair	acid-extractable	quantitative	Aluminum	20	--
					Barium	11	--
					Cadmium	71	--
					Lead	51	--
					Zinc	64	--
Whole snow	New Heart 1A-1	filtration & analysis	acid-extractable	quantitative	Aluminum	2.1	--
					Barium	2.8	--
					Cadmium	1.7	--
					Lead	1.3	--
					Zinc	4.3	--

30 Elements in Mud and Snow in the Vicinity of DMTS Road, Red Dog Mine, and Cape Krusenstern Monument, Alaska

Appendix C. Quality-control summary for spiked samples.

[--, amount spiked was too low for valid recovery assessment]

Spike type	Spiked sample type	Preparation method	Analysis method	Element	Recovery (percent)
Pre-digestion	road soil	total recoverable	semi-quantitative	Aluminum	112
				Barium	--
				Cadmium	--
				Lead	--
				Zinc	--
Pre-extraction	mud	acid-extractable	quantitative	Aluminum	109
				Barium	61
				Cadmium	109
				Lead	110
				Zinc	98
Pre-extraction	mud	acid-extractable	quantitative	Aluminum	118
				Barium	102
				Cadmium	106
				Lead	103
				Zinc	101
Post-extraction	mud	acid-extractable	quantitative	Aluminum	128
				Barium	97
				Cadmium	103
				Lead	100
				Zinc	101
Post-extraction	snow	acid-extractable	semi-quantitative	Aluminum	124
				Barium	104
				Cadmium	102
				Lead	100
				Zinc	112
Pre-extraction	blank (with snow)	acid-extractable	quantitative	Aluminum	111
				Barium	102
				Cadmium	101
				Lead	99
				Zinc	111
Post-extraction	snow	acid-extractable	quantitative	Aluminum	108
				Barium	106
				Cadmium	100
				Lead	104
				Zinc	96

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