CADMIUM GEOCHEMISTRY OF SOILS AND WILLOW IN A METAMORPHIC BEDROCK TERRAIN AND ITS POSSIBLE RELATION TO MOOSE HEALTH, SEWARD PENINSULA, ALASKA

Larry P. Gough¹, Paul J. Lamothe², Richard F. Sanzolone², Larry J. Drew¹, Julie A. K. Maier³, and John H. Schuenemeyer⁴

¹U.S. Geological Survey, National Center, MS 954, Reston, Virginia 20192; ²U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225; ³University of Alaska, P.O. Box 756720, Fairbanks, Alaska 99775; ⁴Southwest Statistical Consulting, LLC, 960 Sligo St, Cortez, Colorado 81321, USA.

ABSTRACT: The regional geochemistry of soil and willow over Paleozoic metamorphic rocks in the Seward Peninsula, Alaska is potentially high in cadmium (Cd), and willow, a preferred browse of moose, bioaccumulates Cd. Local moose show clinical signs of tooth wear and breakage and have been declining in population for unknown reasons. Willow leaves (all variants of *Salix pulchra*) and A-, B-, and C-horizon soils were sampled near 2 mining prospects suspected to be high in Cd. Although Al, Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn were examined, our focus in this exploratory study was on the level of Cd in the 3 soil horizons and willow between and within the 2 prospects and their vicinity. We used an unbalanced, one-way, hierarchical analysis of variance (ANOVA) to investigate the geochemistry of soils and willow at various distance scales across the 2 prospect areas that were separated by ~80 km; sites within a location were approximately 0.5 km apart and replicate samples were separated by ~0.05 km. Cd concentration was significantly different in willow between and within sites, and within sites for all soil horizons. Specifically, this exploratory study identified highly elevated levels of Cd in willow growing over Paleozoic bedrock in the Seward Peninsula at both prospects and over the Paleozoic geologic unit in general. Potential negative effects for moose are discussed.

ALCES VOL. 49: 99-111 (2013)

Key words: Alaska, *Alces alces*, cadmium, health, mineralized soil, moose, plasma-mass spectrometry, willow.

INTRODUCTION

In 2002 the United States Geological Survey (USGS) initially studied the relationship between regional geology and the geochemistry of soils and vegetation that occur in specific geologic terrains. Specifically, how soil geochemistry and the uptake and bioaccumulation of toxic trace elements by native vegetation might ultimately affect the health of grazing herbivores (Eisler 1985, Brazil and Ferguson 1989, Gough et al. 2009); this relationship is increasingly important if animal health is threatened (Glooschenko et al. 1988). Moose (*Alces* *alces*) are an essential cultural and economic resource in northern regions, thus their health and numbers are a primary management focus of resource agencies (Maier et al. 2005, Schmidt et al. 2008). Local accounts of excessive tooth breakage (all moose \geq 7 years old had broken incisiform teeth) and enamel defects in a declining moose population on the Seward Peninsula, Alaska raise special concern (Smith 1992, Rozell 2003, Stimmelmayr et al. 2006), yet the etiology of enamel defects are unclear.

We propose that a possible explanation for this local moose issue is elevated

concentrations of Cd in their preferred willow (Salix spp.) browse, because high willow consumption can expose moose to elevated concentrations of Cd (Gough et al. 2002). In excess, Cd has numerous adverse physiological effects on mammals (Arnold et al. 2006, Kabata-Pendias 2011) including tooth and bone construction, uterus and general mammary gland development, growth inhibition, and renal tubular dysfunction (Eisler 1985, Larison et al. 2000). Excess Cd also competes with Cu, Zn, and Ca for active sites on enzymes, phytochelatins, and cysteine-rich metal-binding proteins (metallothioneins).

In general, there is a direct linear relationship between Cd concentration in plant material and soils (Kabata-Pendias 2011). Uptake in plants is affected by soil pH, carbonate and clay content, and Cd in plants is associated with its affinity for sulfhydryl groups and other side chains of proteins (Kabata-Pendias 2011). Uptake by plants is also affected by a number of physical and chemical soil features; as soil pH decreases, uptake increases (Hough et al. 2003), and uptake generally increases as the total amount in soil increases. Low microbial soil activity in soils, as in the study area, oxic soil conditions enhances which enhances uptake; conversely, permafrost and low soil temperatures reduce uptake. However, we reported previously that Cd is bio-accumulated in willow at levels several times higher than that in other native vegetation, up to $10-100 \times$ greater at the same location (Larison et al. 2000, Gough et al. 2002, 2006). In areas of Alaska that lack diversity of winter forage species like the Seward Peninsula, moose consume willow almost exclusively and are known to remove >55% of the current annual twig growth (Bowyer and Neville 2003).

We hypothesize that bioaccumulation of Cd by willow in areas of Alaska naturally high in Cd may be detrimental to the health of moose (Gough et al. 2002) either by being directly toxic (nephropathy or poor bone construction) and/or by inducing Cu deficiency (Frank et al. 2000). The purpose of this pilot study was to describe the biogeochemistry of Cd in soil and willow in an area with documented physical abnormalities in moose and regionally elevated graphite and Cd concentrations in bedrock (J. Slack, USGS, pers. comm.).

STUDY AREA

The study occurred on the Seward Peninsula, Alaska at 2 locations, the Quarry Prospect and Big Hurrah transects (Fig. 1); both locations have a long history of placer gold mining (Collier et al. 1908, Kaufman 1986, Read and Meinert 1986). The 2 locations were separated by ~80 km, collection sites within each location were approximately 0.5 km apart, and within a site near replicate soil samples were collected ~0.05 km apart. The A-, B-, and C-horizon soil and willow leaf samples were collected from 21 sites combined.

Location 1 (Quarry Prospect transect) had 10 sampling sites located northeast of the Teller Road between the Sinuk and Cripple Rivers at approximately 64° 42' N latitude and 165° 45' W longitude (Fig. 1). The area of Arctic tundra/shrub tundra was at \sim 230 m elevation and extended from the Quarry Prospect (an excavated pit with abundant sulfide mineralization) northeast for 3 km. Bedrock geology of the area is composed of Paleozoic metamorphic rocks (Till et al. 1986, Till et al. 2011), and based on the map of Bundtzen et al. (1994), is within both the massive marble and the graphitic schist and quartzite members, the latter described as either carbonaceous, finegrained mudstones or mylonites. These units are known to be potentially high in Cd (Werdon et al. 2005b).

Location 2 (Big Hurrah transect) with 11 sites was east of the Council Road in an area



Fig. 1. Simplified geology of the southern Seward Peninsula, Alaska, the study area and transect locations within (geology and base map after Till et al. 2011).

of Arctic tundra/shrub tundra at elevation of ~120-150 m. The sampling transect circumnavigated a low hill (identified on USGS C-5 quadrangle map as hill 596) and was in the southern half of section 33 at approximately 64° 40' N latitude and 164° 15' W longitude. Bedrock geology of the area is defined as Ordovician to Precambrian graphitic schist and quartzite on the north, west, and south sides of the hill, and Ordovician to Precambrian schist on the east; both units are part of the Mixed Unit as identified by Till et al. (1986, 2011) and Werdon et al. (2005a, b). Like location 1, these geologic units are known to be potentially high in Cd (Werdon et al. 2005b).

METHODS

Soil Samples

In general, soils of the Seward Peninsula ecoregion (Nowacki et al. 2002), sometimes referred to as the Norton Sound Highlands, are classified as Pergelic Cryaquepts to Pergelic Cryorthents (Rieger et al. 1979). These soils belong to the soil orders Inceptisol and Entisol, respectively, are both poorly- and well-drained, underlain by permafrost, and commonly form in gravely colluvium. Depth to permafrost varies depending on aspect (slope orientation) and elevation and was between 15–90 cm. Soil sample pits were dug to a depth that included the C-horizon.

Each sample was a mixture of soil that originated most commonly from the weathering of colluvium, bedrock, and loess. A-, B-, and C-horizon materials were collected, rocks were removed, and approximately 0.5 kg of the material was put into paper soil bags. Soil samples were dried under forced air at ambient temperature. The air-dried samples were disaggregated in a mechanical mortar and pestle and sieved at 2 mm (10 mesh), and the minus-2-mm fraction was saved for



Fig. 2. This female moose is foraging in a stand of *Salix pulchra* (tealeaf willow) near the shore of Norton Sound; *S. pulchra* is common throughout the southern Seward Peninsula, Alaska.

further analysis. A split of the minus-2-mm material was ground to pass through a 0.15mm sieve, using an agate shatter box. This material was subjected to chemical analysis using inductively coupled plasma-mass spectrometry (ICP-MS) following a 4-acid digestion protocol (Crock et al. 1999, Briggs and Meier 2002). A subset of A-, B-, and C-horizon soils was examined by quantitative x-ray diffraction (XRD) for their bulk mineralogical composition (Gough et al. 2008).

Plant Samples

Plant sampling was limited to the leaf material of the ubiquitous willow of the region, *Salix pulchra* (tealeaf willow; Fig. 2). Although many willows are not considered preferred browse species because of the presence of tannins and alkaloids (Hans-

Joachim et al. 1979), S. pulchra contains relatively low amounts of these 2 substances and is actually preferred by moose. This species is quite common in areas throughout Alaska and Canada occurring within forests, at and above tree line, and in Arctic tundra with adaptability and propensity to form hybrids (Hultén 1968). It is easy to identify in the field, even without flowers or seeds, because of its broad, diamond-shaped to elliptical leaves and its tendency to retain the previous year's leaves and stipules; the latter trait makes the shrubs quite easy to identify at a distance. It is obvious from field observations that moose browsed on both leaves and twigs. The leaf material from at least 3 adjacent shrubs (in a radius ~ 5 m from a soil pit) was composited, placed in cloth sample bags, and allowed to air dry.

In the laboratory leaf material was placed in Teflon® beakers, submerged and rinsed in deionized water, and drained; this process was repeated 3 times. The material was then rinsed briefly with deionized water and allowed to drip drain, and forced air was used to dry the material at ambient room temperature. Samples were ground in a Wiley® mill to pass a 2-mm sieve, ashed in an oven at 450–500 °C for 18 h, digested using the same 4-acid protocol as the soil samples, and analyzed using ICP-MS (Briggs and Meier 2002).

Statistics

The study design was constructed to investigate differences in levels of Cd in willow and soil geochemistry between and within locations. An unbalanced, one-way, performed hierarchical ANOVA was (SYSTAT 11, SYSTAT® Software, Inc.) to assess possible significance where Cd was the response variable. The analyses were performed on the log base 10-transformed data because of the right-skewed nature of the data (Miesch 1976). Because the prospect locations and samples within locations were purposefully selected, this is considered a 'fixed effects' model procedure. This statistical design allows the partitioning of the total measured natural variation into its component parts, Level 1 and Level 2. Level 1 is the comparison of means between locations (the Quarry Prospect and Big Hurrah areas) and Level 2 compares the means within locations; the nearby samples are used to estimate the error term. All samples were analyzed in a random sequence to help negate any systematic errors that might occur in either sampling or analysis.

Factor analysis is a multivariate statistical procedure designed to describe variability by partitioning it into some smaller number of common factors and a component unique to each variable (Schuenemeyer and Drew 2011). It was used as an exploratory tool to examine possible correlations among the element concentrations. The goals were to 1) determine if the factors can be interpreted according to some geochemical association, and 2) determine if factors vary within and between willow leaves and soil horizons.

RESULTS

Soil Analysis

Although the soils sampled in the Seward Peninsula (mostly Pergelic Cryaquepts to Pergelic Cryorthents, Rieger et al. 1979) contain transported loess material, they are predominantly residual, organic in nature, and composed of weathered metamorphic bedrock and loess. The samples were analyzed for numerous elements (Gough et al. 2008); however, here we focus on the biogeochemistry of Cd and 8 other metals. The Quarry Prospect and Big Hurrah transects had 10 Cd samples in 7 levels (sample locations) and 11 Cd samples in 8 levels, respectively, for the A-, B-, and C-horizon soils. There were 13 Cd willow samples in 9 levels in Quarry Prospect and 8 samples in 6 levels in Big Hurrah. The bulk mineralogical composition of selected soil samples determined by quantitative XRD is presented in Table 1.

The hierarchical ANOVA using log base 10 values (Table 2) indicated that Cd concentrations in all 3 soil horizons were similar at the Level 1 effect (between locations); conversely, the Level 2 (within locations) effect was significant (P < 0.05; Table 2). We caution that sample sizes were small.

Summary statistics for the concentration of elements in willow and the A-, B-, and Chorizon soils at the Quarry Prospect and Big Hurrah transects are presented in Table 3. The main purpose of this table and units (log base 10) is to provide descriptive analysis (mean, standard deviation) and comparison among the elements and soil horizons.

CADMIUM AND MOOSE HEALTH – GOUGH ET AL.

loess, Sew [Opet, Pre	vard Peni scambrian	nsula. 1 mixed 1	unit of the	Nome Gr	oup (chlorite	-rich schist and	d marble);				:			
Opesq, O	rdovician	to Preca	ambrian mi	xed unit o	of the Nome	Group (graphit	tic schist a	und quartzite	i); —, mineral	was not	observed].			
		•					1	Veight percer	ıt					
Sample identifier	Soil horizon	Rock unit	Loss on ignition	Quartz	Potassium feldspar	Plagioclase	Calcite	Dolomite	Amphibole	Pyrite	Goethite	Apatite	Rutile	Peat
05AK011A	V	Opet	8.8	39	0.4	2.3					1.3	0.1	0.6	9.8
05AK011B	В		3.5	36	0.8	1.5		0.1	I		2.3	0.6	0.5	3.5
05AK011C	С		4.2	35	0.4	1.3					3.7		0.7	5.1
05AK021A	Α	Opet	41	19	1.1	1.6		0.2		0.1	2.3	0.2	0.1	39
05AK021B	В		3.5	44	2.5	2.1	0.2				3.2	0.3	0.1	6.2
05AK021C	С		3.5	46	1.8	2.1	0.2		I		3.7	0.3	0.1	6.5
05AK131A	А	Opesq	10	45	1.6	2.1		I	I		2.4	I	0.2	17
05AK131B	В		8.8	47	2	2.2		I	I	0.1	2.3	0.1		13
05AK131C	C		8.8	48	1.8	2.2					2.5	0.2		12

Table 1. Bulk mineralogy (quantitive XRD; Gough et al., 2008) for representative samples of A-, B-, and C-horizon tundra soils developed from bedrock and

This comparison is best made when data are in log units since 1 or 2 observations can skew the mean and/or standard deviation (SD). The following is a descriptive analysis based upon inspection of means and SD and is not based on the results of statistical tests. These data (Table 3) are useful as preliminary geochemical baseline values for the 2 locations.

Sample means for Cd concentration among the soil horizons were higher in the Big Hurrah than Quarry Prospect, but not significantly different (P > 0.05); the same pattern occurred for Cu, Fe, Mo, and Ni concentrations. Conversely, sample means for Al, Co, Pb, and Zn were higher at Quarry Prospect in all soil horizons.

Willow Analysis

The ANOVA for Cd concentrations in willow leaves and soils is presented in Table 2; both the Level 1 and the Level 2 (Level 1) effects were highly significant (P < 0.001). The mean concentrations of Cd, Fe, Ni, and Zn from the horizon samples were consistent between the 2 transect locations (Table 3).

Factor Analysis

For the A-, B-, and C-horizon soils, the variables were logarithmically-transformed element concentrations expressed in parts per million (ppm). The choice of 3 common factors was made after examining the data, and a varimax (orthogonal) rotation was used. Since all concentrations are in log base 10 of ppm, factor analysis was performed on the covariance matrix. The factor analysis with the willow data was performed similarly except that Mo and Pb were omitted Table 2. Results of a hierarchical ANOVA of cadmium (Cd) concentration (n = 21; data are in log base 10) measured in 3 soil horizons and willow leaves in the Quarry Prospect and Big Hurrah regions, Seward Peninsula, Alaska, USA.

Source	Sum of squares	Degrees of freedom	Mean squares	F-ratio	p-value
		A-Horizon Soil			
Level 1	0.029	1	0.029	0.517	0.499
Level 2(Level 1)	3.266	13	4.487	4.487	0.038*
Error	0.336	6	0.015		
Total sum of squares	3.631				
		B-Horizon Soil			
Level 1	0.098	1	0.098	2.285	0.181
Level 2(Level 1)	4.849	13	0.373	8.700	0.007*
Error	0.257	6	0.043		
Total sum of squares	5.204				
		C-Horizon Soil			
Level 1	0.128	1	0.128	1.978	0.209
Level 2(Level 1)	4.604	13	0.354	5.489	0.023*
Error	0.387	6	0.065		
Total sum of squares	5.119				
		Willow			
Level 1	1.622	1	1.622	150.362	0.0001*
Level 2(Level 1)	4.333	13	0.333	21.648	0.001*
Error	0.092	6	0.015		
Total sum of squares	6.047				

*, significant at the 0.05 probability level.

because of the presence of censored data (less than the detection limit).

The factor analysis is presented in Table 4 with the largest absolute values highlighted in each row. The numbers under the factor column headings are loadings (weights) of a chemical element on a factor. Element loadings may be considered to be the correlation between an element and a factor. For example, in the A-horizon, Cd loads heavily (0.778) on Factor 1 (i.e., Cd and Factor 1 are strongly associated), and lightly on Factors 2 (0.126) and 3 (0.198), and has a unique component of 0.339; the unique component usually contains error which is difficult to isolate. In total, the factor loading patterns were consistent across the 3 soil horizons.

This is illustrated by Factor 1 in the A-horizon and Factor 2 in the B- and C-horizons loading heavily on Cd, Pb, and Zn, Factor 2 in the A-horizon and Factor 3 in the Band C-horizons loading heavily on Co and Fe, and Factor 3 in the A-horizon and Factor 1 in the B- and C-horizons loading heavily on Cu, Mo, and Ni (Table 4). Note that the variability accounted for by Factors 1 and 2 is approximately the same, so the fact that the pattern appeared in Factor 1 in the A-horizon and Factor 2 in the B- and C-horizons is not important. Unfortunately, there is no clear factor pattern in willow and the data set was too small to justify a specification of more than 3 factors.

		Willow		A	A-horizon soil		Η	3-horizon soil		(C-horizon soil	
	Mean	Std dev	Detection	Mean	Std dev	Detection	Mean	Std dev	Detection	Mean	Std dev	Detection
Element	log base 10	log base 10	ratio	log base 10	log base 10	ratio	log base 10	log base 10	ratio	log base 10	log base 10	ratio
						Quarry Pros	pect Transect					
Al, ppm	1.818	0.185	10:10	4.729	0.172	10:10	4.822	0.153	10:10	4.819	0.153	10:10
Cd, ppm	0.478	0.553	10:10	0.080	0.546	10:10	-0.099	0.653	10:10	-0.050	0.637	10:10
Co, ppm	-0.578	0.390	10:10	1.040	0.135	10:10	1.092	0.146	10:10	1.163	0.145	10:10
Cu, ppm	0.935	0.167	10:10	1.341	0.099	10:10	1.341	0.135	10:10	1.356	0.105	10:10
Fe, ppm	1.992	0.130	10:10	4.550	0.083	10:10	4.628	0.091	10:10	4.674	0.114	10:10
Mo, ppm	_	_	6:10	-0.207	0.172	10:10	-0.258	0.204	10:10	-0.272	0.146	10:10
Ni, ppm	0.072	0.228	10:10	1.346	0.168	10:10	1.399	0.185	10:10	1.467	0.146	10:10
Pb, ppm	_	_	2:10	1.608	0.676	10:10	1.641	0.676	10:10	1.653	0.661	10:10
Zn, ppm	2.390	0.243	10:10	2.445	0.537	10:10	2.433	0.602	10:10	2.448	0.601	10:10
						Big Hurra	h Transect					
Al, ppm	1.868	0.208	10:11	4.665	0.159	11:11	4.749	0.138	11:11	4.754	0.117	11:11
Cd, ppm	1.187	0.231	11:11	0.133	0.303	11:11	0.005	0.357	11:11	0.073	0.365	11:11
Co, ppm	0.358	0.335	11:11	0.908	0.323	11:11	1.019	0.353	11:11	1.101	0.295	11:11
Cu, ppm	0.826	0.100	11:11	1.702	0.203	11:11	1.813	0.171	11:11	1.878	0.190	11:11
Fe, ppm	2.022	0.159	11:11	4.560	0.253	11:11	4.673	0.238	11:11	4.697	0.222	11:11
Mo, ppm	—	—	7:11	1.083	0.219	11:11	1.134	0.186	11:11	1.155	0.209	11:11
Ni, ppm	0.810	0.200	11:11	1.683	0.239	11:11	1.782	0.229	11:11	1.832	0.193	11:11
Pb, ppm	_	_	0:11	1.166	0.214	11:11	1.241	0.169	11:11	1.266	0.150	11:11
Zn, ppm	2.211	0.137	11:11	2.173	0.172	11:11	2.268	0.202	11:11	2.310	0.195	11:11

Table 3. Summary statistics for the concentration of selected elements measured in willow leaves and A-, B-, and C-horizon soils in the Quarry Prospect and Big Hurrah regions, Seward Peninsula, Alaska, USA. Cadmium (Cd) results are highlighted; "—" = not determined due to the presence of values below the detection limit. The detection ratio expresses the number of values above the detection limit to the total number of analyses.

Table 4. Factor analysis of the concentration values (n = 21; data are in log base 10) for Al, Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn measured in 3 soil horizons and willow leaves in the Quarry Prospect and Big Hurrah regions, Seward Peninsula, Alaska, USA. The symbol "—" indicates not calculated because of the presence of censored data; also not used in the cumulative variance calculation (see text).

Element	Factor 1	Factor 2	Factor 3	Unique component
	Factor	loadings for the A-h	orizon	
Al, ppm	0.352	0.568		0.545
Cd, ppm	0.778	0.126	0.198	0.339
Co, ppm	0.200	0.975		0.005
Cu, ppm		0.263	0.902	0.118
Fe, ppm	0.120	0.831	0.246	0.234
Mo, ppm	-0.112	-0.257	0.921	0.073
Ni, ppm		0.510	0.791	0.110
Pb, ppm	0.871	0.199	-0.210	0.158
Zn. ppm	0.968	0.217	-0.108	0.005
Cumulative variance	0.277	0.551	0.824	
	Factor	loadings for the B-h	orizon	
Al, ppm	-0.121	0.296	0.474	0.673
Cd, ppm	0.318	0.800	0.238	0.202
Co, ppm		0.171	0.982	0.005
Cu, ppm	0.967		0.173	0.026
Fe, ppm	0.300	0.128	0.858	0.157
Mo, ppm	0.901	-0.177	-0.267	0.085
Ni, ppm	0.789		0.457	0.160
Pb, ppm	-0.215	0.890	0.157	0.138
Zn. ppm		0.984	0.164	0.005
Cumulative variance	0.291	0.578	0.839	
	Factor	loadings for the C-h	orizon	
Al, ppm		0.333	0.599	0.523
Cd, ppm	0.329	0.792	0.276	0.188
Co, ppm		0.203	0.976	0.005
Cu, ppm	0.958			0.069
Fe, ppm	0.212	0.159	0.875	0.164
Mo, ppm	0.929	-0.110	-0.218	0.076
Ni, ppm	0.847		0.359	0.143
Pb, ppm	-0.225	0.866	0.223	0.150
Zn. Ppm		0.979	0.189	0.005
Cumulative variance	0.302	0.584	0.853	

D1	F (1		T ()	T T '
Element	Factor 1	Factor 2	Factor 3	Unique component
	F	Factor loadings for Will	low	
Al, ppm	0.103		0.992	0.005
Cd, ppm	0.993			0.005
Co, ppm	0.656	0.688		0.096
Cu, ppm	-0.551			0.693
Fe, ppm			0.608	0.623
Mo, ppm				—
Ni, ppm	0.659	0.711	0.235	0.005
Pb, ppm				—
Zn. Ppm	0.172	-0.726	0.126	0.428
Cumulative variance	0.314	0.530	0.735	

Table 4. continued

DISCUSSION

In order to assess the scale of spatial variability in the concentration of Cd and other elements in soils and willow across the landscape, sampling occurred at 2 mineralized prospects separated by 80 km. The greatest difference in Cd concentration in soils occurred within locations across all soil horizons and not between the locations, indicating general uniformity in landscape geochemistry. For willow, an important proportion of the total biogeochemical variability of Cd occurred between and within locations. When one examines the distribution of Cd, these trends may be due to variation in soil mineralogy, especially in the amount of amorphous graphite present because it has been associated with Cd. Unfortunately, because the graphite in soils is amorphous, it is not detectable in the quantitative XRD procedure. Differences in the transition metals Cd, Co, Ni, and Zn may be explained by variability in the amount of graphite in the bedrock because in this terrain high graphite content correlates with high levels of transition metals (J. Slack, USGS, pers. commun.). For these elements, the geochemistry of the bedrock appears to affect the biogeochemistry of the willow. Together, these trace element data show consistency among the soil horizons whereas,

because of the too small data set, the pattern for willow could not be characterized.

This exploratory study identified elevated levels of bioavailable Cd in soils developed over Paleozoic metamorphic bedrock and local willow leaves on the Seward Peninsula, Alaska. Typical Cd content across a variety of plant foodstuffs (grasses, grains, vegetables, fruits) ranges from 0.005-1.3 ppm dry weight (Kabata-Pendias 2011), whereas in this study we found much higher levels of 0.65-42.0 ppm Cd in willow; the location means were 3.0 and 15.0 ppm. This corresponds to previous reports of high Cd concentrations in willow in Colorado (Larison et al. 2000) and Alaska (Gough et al. 2002). However, the levels from the Seward Peninsula are higher than those reported for willow in the Colorado ore belt (Larison et al. 2000). Because willow can bioaccumulate Cd, its role in the health of the local moose population is of concern given the endemic tooth breakage and negative physiological effects associated with elevated Cd in mammals. A direct moose tissue analysis was not performed, but would be warranted in the area.

ACKNOWLEDGEMENTS

The authors thank personnel of the Bering Straits Native Corporation, and especially I. Anderson of the Land and Resources Department for anecdotal historical moose information and allowing us access to native corporation lands. The bulk mineralogy for soils was provided by D. Eberl, USGS, Boulder. We also thank A. Till, geologist with the USGS in Anchorage, for providing the geologic base used in our figures and for her guidance in the field.

REFERENCES

- ARNOLD, S. M., R. L. ZARNKE, V. L. TRACEY, M-A. CHIMONAS, and A. FRANK. 2006. Public health evaluation of cadmium concentrations in liver and kidney of moose (*Alces alces*) from four areas of Alaska. Science of the Total Environment 357: 103–111.
- Bowyer, R. T., and J. T. NEVILLE. 2003. Effects of browsing history by Alaskan moose on regrowth and quality of feltleaf willow. Alces 39: 193–202.
- BRAZIL, J., and S. FERGUSON. 1989. Cadmium concentrations in Newfoundland moose. Alces 25: 52–57.
- BRIGGS, P. H., and A. L. MEIER. 2002. The determination of forty-two elements in geological materials by inductively coupled plasma-mass spectrometry. Chapter I *in* J. E. Taggart, editor. Analytical Methods for Chemical Analysis of Geologic and Other Materials. U. S. Geological Survey Open-File Report 02-223. U. S. Geological Survey, Denver, Colorado, USA.
- BUNDTZEN, T. K., R. D. REGER, G. M. LAIRD, D. S. PINNEY, K. H. CLAUTICE, S. A. LISS, and G. R. CRUSE. 1994. Preliminary geologic map of the Nome mining district. State of Alaska Division of Geology and Geophysical Surveys, Public-Data File 94-39. Alaska Division of Geological & Geophysical Surveys, Fairbanks, Alaska, USA.
- COLLIER, A. J., F. L. HESS, P. S. SMITH, and A. H. BROOKS. 1908. The gold placers of parts of Seward Peninsula, Alaska, including the Nome, Council, Kougarok,

Port Clarence, and Goodhope precincts. U. S. Geological Survey Bulletin 328.

- CROCK, J. G., B. F. ARBOGAST, and P. J. LAMOTHE. 1999. Laboratory methods for the analysis of environmental samples. Pages 265–287 *in* G. S. Plumlee and M. J. Logsdon, editors. Reviews in Economic Geology Volume 6A, The Environmental Geochemistry of Mineral Deposits, Part A, Processes, Techniques, and Health Issues. Society of Economic Geologists, Inc., Littleton, Colorado, USA.
- EISLER, R. 1985. Cadmium hazards to fish, wildlife, and invertebrates - a synoptic review. U. S. Fish and Wildlife Service Biological Report 85 (1.2). U. S. Fish and Wildlife Service, Laurel, Maryland, USA.
- FRANK, A., R. DANIELSSON, and B. JONES. 2000. The 'mysterious' disease in Swedish moose. Concentrations of trace elements in liver and kidneys and clinical chemistry. Comparison with experimental molybdenosis and copper deficiency in the goat. The Science of the Total Environment 249: 107–122.
- GLOOSCHENKO, V., C. DOWNES, R. FRANK, H. E. BRAUN, E. M. ADDISON, and J. HICKIE. 1988. Cadmium levels in Ontario moose and deer in relation to soil sensitivity to acid precipitation. Science of the Total Environment 71: 173–186.
- GOUGH, L. P., J. G. CROCK, and W. C. DAY. 2002. Cadmium accumulation in browse vegetation, Alaska - implication for animal health. Pages 77–78 *in* H. C. W. Skinner and A. Berger, editors. Geology and Health - Closing the Gap. Oxford University Press, New York, New York, USA.
 - ——, ——, B. WANG, W. C. DAY, D. D. EBERL, R. F. SANZOLONE, and P. J. LAMOTHE. 2008. Substrate geochemistry and soil development in boreal forest and tundra ecosystems in the Yukon-Tanana Upland and Seward Peninsula, Alaska. U. S. Geological Survey Scientific

Investigations Report 2008-5010. U. S. Geological Survey, Reston, Virginia, USA.

- , R. EPPINGER, P. H. BRIGGS, and S. GILES. 2006. Biogeochemical characterization of an undisturbed highly acidic, metal-rich bryophyte habitat, east-central Alaska. Arctic, Antarctic, and Alpine Research 38: 522–529.
- —, P. J. LAMOTHE, R. F. SANZOLONE, L. J. DREW, and J. A. K. MAIER. 2009. The regional geochemistry of soils and willow in a metamorphic bedrock terrain, Seward Peninsula, Alaska, 2005, and its possible relation to moose. U.S. Geological Survey Open-File Report 2009–1124. U.S. Geological Survey, Reston, Virginia, USA.
- HANS-JOACHIM, G. J., G. O. BATZLI, and D. S. SEIGLER. 1979. Patterns in the phytochemistry of Arctic plants. Biochemical Systematics and Ecology 7: 203–209.
- HOUGH, R. L., S. D. YOUNG, and N. M. CROUT. 2003. Modeling of Cd, Cu, Ni, Pb and Zn uptake, by winter wheat and forage maize, from a sewage disposal farm. Soil Use and Management 19: 19–27.
- HULTÉN, E. 1968. Flora of Alaska and Neighboring Territories. Stanford University Press, Stanford, California, USA.
- KABATA-PENDIAS, A. 2011. Trace Elements in Soils and Plants, 4th Edition. CRC Press, Boca Raton, Florida, USA.
- KAUFMAN, D. S. 1986. Surficial geologic map of the Solomon, Bendeleben, and southern part of the Kotzebue quadrangles, western Alaska. U.S. Geological Survey Miscellaneous Field Studies Map MF01838-A.
- LARISON, J. R., G. E. LIKENS, J. W. FITZPATRICK, and J. G. CROCK. 2000. Cadmium toxicity among wildlife in the Colorado Rocky Mountains. Nature 406: 181–183.
- MAIER, J. A. K., J. M. VER HOEF, A. D. MCGUIRE, R. T. BOWYER, L. SAPERSTEIN, and H. A. MAIER. 2005. Distribution and density of moose in relation to landscape characteristics - effects of scale.

Canadian Journal of Forestry Research 35: 2233–2243.

- MIESCH, A. T. 1976. Geochemical survey of Missouri - methods of sampling, laboratory analysis, and statistical reduction of data. U.S. Geological Survey Professional Paper 954-A. U. S. Government Printing Office, Washington, D. C., USA.
- NOWACKI, G., P. SPENCER, M. FLEMING, T. BROCK, and M. T. JORGENSON. 2002. Unified Ecoregions of Alaska 2001. U. S. Geological Survey Open-File Report 02-297. http://agdc.usgs.gov/data/projects/fhm> (accessed October 2012).
- READ, J. J., and L. D. MEINERT. 1986. Goldbearing quartz vein mineralization at the Big Hurrah mine, Seward Peninsula, Alaska. Economic Geology 81: 1760– 1774.
- RIEGER, S., D. B. SCHOEPHORSTER, and C. E. FURBUSH. 1979. Exploratory Soil Survey of Alaska. U.S. Department of Agriculture, Soil Conservation Service, Washington, D. C., USA.
- ROZELL, N. 2003. The mystery of the broken moose teeth. Alaska Science Forum Article 1669. University of Alaska-Fairbanks, Fairbanks, Alaska, USA.
- SCHMIDT, J. I., K. J. HUNDERTMARK, R. T. BOWYER, and K. G. MCCRACKEN. 2008. Population structure and genetic diversity of moose in Alaska. Journal of Heredity Advance Access. http://jhered.oxfordjournals.org/cgi/content/ full/esn076v1 (accessed October 2012).
- SCHUENEMEYER, J. H., and L. J. DREW. 2011. Statistics for Earth and Environmental Scientists. John Wiley & Sons, Hoboken, New Jersey, USA.
- SMITH, T. E. 1992. Incidence of incisiform tooth breakage among moose from the Seward Peninsula, Alaska, USA. Alces Supplement 1: 207–212.
- STIMMELMAYR, R., J. A. K. MAIER, K. PERSON, and J. BATTIG. 2006. Incisor tooth breakage, enamel defects, and periodontitis in a declining Alaskan moose population. Alces 42: 65–74.

TILL, A. B., J. A. DUMOULIN, B. M. GAMBLE, D. S. KAUFMAN, and P. I. CARROLL. 1986. Preliminary geologic map and fossil data, Solomon, Bendeleben, and southern Kotzebue Quadrangles, Seward Peninsula, Alaska. U.S. Geological Survey Open-File Report 86-276. http:// pubs.er.usgs.gov/> (accessed October 2012).

, —, M. B. WERDON, and H. A. BLEICK. 2011. Bedrock geologic map of the Seward Peninsula, Alaska: U.S. Geological Survey Scientific Investigations Map 3131, scale 1:500,000. <<u>http://</u> pubs.usgs.gov/sim/3131/> (accessed October 2012).

WERDON, M. B., R. J. NEWBERRY, D. J. SZU-MIGALA, J. E. ATHEY, and S. A. HICKS. 2005a. Bedrock geologic map of the Big Hurrah area, northern half of the Solomon C-5 quadrangle, Seward Peninsula, Alaska. Report of Investigations 2005-1b. State of Alaska Division of Geological and Geophysical Surveys, Fairbanks, Alaska, USA.

, D. S. P. STEVENS, R. J. NEWBERRY, D. J. SZUMIGALA, J. E. ATHEY, and S. A. HICKS. 2005b. Explanatory booklet to accompany geologic, bedrock, and surficial maps of the Big Hurrah and Council areas, Seward Peninsula, Alaska. Report of Investigations 2005-1a. State of Alaska Division of Geological and Geophysical Surveys, Fairbanks, Alaska, USA.