Chapter 4—Biogeochemical and Biochemical Pathway Investigations of Cadmium in Subarctic Ecosystems Using a Cadmium Accumulator Species (Willow)

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BACKGROUND

This study focuses on a portion of the Fortymile River and Goodpaster River watersheds (fig. 1) in the Eagle and Big Delta 1:250,000-scale quadrangles, respectively. The study area comprising these two watersheds lies within the Interior Highlands Ecoregion of Alaska (Gallant and others, 1995) and is a patchwork of State, Federal, private, and Alaska Native lands. The resource management of the region is complex because of the diverse land ownership and the many land-use options. In 1980, the Fortymile River and its major tributaries were designated a Wild and Scenic Corridor by the Alaska National Interest Lands Conservation Act (ANILCA). Jurisdiction of the land bordering the river continues to resides with the U.S. Bureau of Land Management. The Alaska Department of Natural Resources has jurisdiction over the management of the recreation uses of the rivers (rafting, canoeing, and fishing) and mining. The U.S. Environmental Protection Agency monitors mining discharges into these watersheds as required by the National Pollutant Discharge Elimination System (NPDES) of the Clean Water Act. Finally, both sport and subsistence hunting are important in the region and are managed by Federal and State agencies.

Placer gold was first discovered in the Fortymile Mining District in 1886 and has been mined there ever since. Yeend (1996) summarizes the mining history of the gold placers of the Fortymile River region and provides details of the Tertiary and Quaternary deposits that support those placers. Within the past 3 or 4 years there has been a dramatic increase in exploration and claim-staking activity in this region of Alaska (Swainbank and others, 2000). This renewed interest is due mainly to the discovery of highly Au-mineralized quartz bodies, several hundred meters below the surface, on the Pogo property in the Goodpaster River watershed (fig. 1; Smith and others, 1999). It is this discovery, and the likelihood of additional ones, that is a major driver for the regional environmental geochemical studies currently being conducted within the U.S. Geological Survey Mineral Resources Program.

ECOSYSTEM PROCESSES AND LANDSCAPE SETTING

A conceptual framework for this work is taken from the state-factor model as detailed by Van Cleve and others (1991; see fig. 2). This approach assumes that the processes by which energy, nutrients, and trace elements flow through the ecosystems of the region are controlled by five “exogenous” conditions (state-factors): regional climate, biota (microbes, plants, and animals), topography, soil parent material, and time. Ideally, in order to study ecosystem perturbations (either natural or human-caused), only one of these state-factors should be varied while the other four are kept as constant as possible. Unfortunately, these factors may or may not be independent of each other and may be difficult to isolate (for example, time); however, as Van Cleve and others (1991) explain, subarctic boreal forest ecosystems are both extreme (cold, dry climate) and simple (low number and diversity of biotic species) compared to ecosystems in more temperate regions. By directing our work over geologic terrain that is well defined in areal extent, structure, and chemistry we hope to control the parent-material factor while keeping the other factors relatively constant. Understanding the parent-material factor, in turn, is important for understanding the ecosystem processes affecting the regional soils. Further, by understanding the physical and chemical characteristics of the soils we hope to better define the trace-element reservoirs and their geoavailability and bioavailability.

Terrain, Vegetation, and Hydrology

The Interior Highlands Ecoregion (also known as the Yukon-Tanana Upland) is characterized by vegetated, rounded, low mountains with scattered, sparsely vegetated to barren high peaks (up to a maximum elevation of about 2,200 m). The vegetation of the region is classified by Viereck and Little (1972) as closed spruce-hardwood forest containing tall to moderately tall white and black spruce (*Picea glauca* and *P. mariana*, respectively), paper birch (*Betula papyrifera*), aspen (*Populus tremuloides*), and balsam poplar (*Populus balsamifera*). Fires are common, due mainly to lightning strikes, and most of the study area shows evidence of past fire disturbance. The area has a continental climate, and the weather station at the village of Eagle (70 km north of the study area) records the following average annual weather values for the period 1949-2000: precipitation, 302 mm (12 in.); minimum mean annual temperature, -10.9°C (12.7°F); maximum mean annual temperature, 2.1°C (36°F); snowfall, 142 cm (55.3 in.).

The Fortymile and Goodpaster Rivers drain mostly subarctic boreal forest, tundra, and muskeg having discontinuous permafrost. Even soils not underlain by permafrost are commonly frozen to various depths for much of the growing season. Over the year, discharge by the Fortymile River and its tributaries is highly variable (Kostohrys and others, 1999) because of (1) a rapid spring ice-break-up period (April-June), (2) runoff from storm events (the frozen nature of the terrain accentuates the runoff potential), (3) summer dry periods, and (4) freeze-up (October-November).

Maximum flow on the mainstem of the river in May can exceed 340 $m^3 s^{-1}$ (1 $m^3 s^{-1}$ = 35.31 $ft^3 s^{-1}$), and base flow during January, February, and March is <1 $m^3 s^{-1}$. There is usually some flow on the mainstem in midwinter from groundwater sources. Breakup usually occurs in late April. The rivers and streams of this region are dark ("black-water") because of dissolved organic matter. The water is, however, low in conductivity (~90-220 $\mu S\ cm^{-1}$), has pH values that are commonly above 7.3, and has turbidity values that seldom exceed 2 ntu (Crock and others, 1999, 2000; Wanty and others, 2000).

Geology

Bedrock and associated surficial deposits control the primary minerals and chemical elements that are available for weathering and that ultimately enter hydrologic and biologic systems. Therefore, understanding the geologic framework of the area is important to assessing the geoavailability and bioavailability of metals in the area.

In a complementary project, new geologic maps have been compiled of both watersheds (Day and others, 2000; see fig. 3). These build on the previous geologic mapping of Foster (1976), Foster and others (1994), and Dusel-Bacon and others (1995). This new effort was conducted to address two specific needs: (1) the structural characterization of regional lithologic units that underlie the study area; and (2) the definition of any possible mineralized and (or) altered zones that might occur in the study area. This detail of information is critical to the assessment of both the subsurface hydrologic flow patterns and the chemistry of surface and subsurface water, soils, and vegetation.

In general, the bedrock of the region is composed of metamorphosed supracrustal rocks intruded by various types of granitoids and ultramafic rocks. The supracrustal rocks are biotite schist, biotite-amphibole schist, quartzite, marble, sulfide-rich biotite schist, and pelite. The protoliths for these supracrustal rocks are, respectively, graywacke, mafic volcanic and compositionally equivalent intrusive rocks, quartz-rich sandstone, limestone, sulfide-rich siliciclastic sediments, and pelitic sediments. Late metamorphic sulfide-bearing quartz veins cut all of the supracrustal rocks. The supracrustal rocks are interpreted to have been originally deposited on a continental margin and (or) distal to an island-arc complex in a back-arc basin.

Intruding the metamorphic supracrustal rocks are three main granitoid suites. The Steele Creek Dome Tonalite (Day and others, 2000) is a composite body of foliated biotite-hornblende tonalitic orthogneiss containing country-rock rafts of paragneiss. Two mica±garnet-bearing leucogranite bodies locally invade the supracrustal rocks.

In addition to the geologic studies already published on the Fortymile River watershed (Day and others, 2000; Gamble and others, 2001), we are completing a detailed geologic map of a portion of the Goodpaster watershed that surrounds the Pogo property. These efforts are being conducted in cooperation with the Alaska State Department of Natural Resources, Teck Cominco, Ltd., and WGM Exploration, Inc.

Soils

An understanding of soil genesis and composition is critical to the interpretation of the geochemical data. We are particularly interested in understanding the mobility of metals and their uptake by plants within a well-defined geologic/pedologic context. Soils at the study sites are classified as Cryaquepts (Inceptisols) having variable amounts of undecomposed (fresh) and decomposed organic matter in the A horizon. Van Cleve and others (1983) estimate that about 78 percent of the land area of Alaska is occupied by Inceptisols. More than 70 percent of sites examined in this study thus far have been near saturation, and permafrost was commonly encountered 15 to 50 cm below the surface. Most sites have silty-loam to fine-sandy-loam A soil horizons with abundant root penetration. The A horizon is usually less than 10 cm thick and light brown in color. Several of the sites have ash/charcoal layers (usually less than 2 cm thick) within the A horizon, indicating past fire disturbance. The B horizon is usually about as thick as the A horizon, lighter in color, and contains moderate root volume. The deepest soils (C soil horizons) commonly extend to depths greater than 20 to 40 cm and consist of fine- to coarse-sand-textured material with small blocks of angular bedrock and few roots. Because of the low temperatures, these soils experience limited chemical and biological weathering; therefore, the clay content and cation exchange capacity are low. Nevertheless, slow organic matter decomposition and nitrification does produce slightly acid soil conditions in the mature forest ecosystem (Gough and others, 2001).

The presence of silt (micaceous glacial loess) in the upper horizons is ubiquitous, and we are finding that it has an important influence on overall soil chemistry. Foster and others (1979) state that in the Big Delta 1:63360 quadrangle, silt and sand from the Tanana River flood plain to the south dominate the composition and texture of soils within about 50 km of the river. Silt-loam-textured soils are common in interior Alaska and are derived from loess laid down during the Holocene (Daniel Muhs, oral commun., 2000) and during the last glacial maximum (Van Cleve and others, 1983).

CADMIUM PATHWAYS, BIOAVAILABILITY, AND RESEARCH ISSUES

Although both reconnaissance and detailed studies on the distribution of Cd in stream sediments and lithologic units have been conducted throughout Alaska , there have been no studies on the bioavailability of Cd and its biological transport mechanisms. This section describes the U.S. Geological Survey Mineral Resources Program's present and planned research that attempts to fill this gap.

Distribution, Concentration, and Speciation of Cadmium

Biogeochemical investigations will be conducted on the pathways that control Cd transport and uptake by vegetation. The occurrence of Cd in eolian-dominated subarctic soils developed over major rock units will be examined, as well as its relative bioaccumulation in willow. The bioaccumulation of Cd by willow (*Salix* spp.) has been recognized for some time (Gough and others, 1991); however, it was Shacklette (1972) that presented some of the earliest data for Cd in willow and compared these data with other deciduous tree species. The connection of high levels of Cd in willow to adverse animal health, under natural (geogenic) conditions, has only recently been demonstrated (Larison and others, 2000).

We now have Cd data (fig. 4) for three soil horizons and for the leaf and twig material of *Salix glauca* L. (grayleaf willow) collected at sites within defined rock units of both watersheds. Gough and others (2001) present regional geochemical baselines for Cd and As in plants and soils. These values present a "snapshot" for the material sampled during this Fortymile River watershed study. In general, the soil Cd concentrations are slightly higher (two to three times) in our study area when compared to values from material collected elsewhere in Alaska (Gough and others, 1988), whereas Cd concentrations in plant material are similar (Gough and others, 1991). All geochemical data for the Fortymile River watershed available to date are published in Crock and others (1999, 2000) and include data from rock, bottom sediment, water, soil, and vegetation samples.

New studies that will be initiated in 2002 have three major objectives: (1) define the cycling of Cd and its bioaccumulation in willow and compare concentrations in willow to those in different rock types and soil horizons in mineralized and non-mineralized areas; (2) define the transient (and permanent) reservoirs for Cd (using soils and vegetation) and the probable transfer processes between these reservoirs; and (3) with the assistance of an Alaska state veterinary toxicologist assess the relative importance of Cd concentrations in willow to the health of browsing animals (moose and ptarmigan). The importance of willow to moose is demonstrated by feeding studies that have developed the following order of browse preference: willow >> aspen > birch > alder > cottonwood (K. Hundertmark, Alaska Department of Fish and Game, oral commun., 2001).

Processes That Mobilize and Redistribute Cadmium

Cadmium in soils within the study area is derived from the weathering of loess and of the primary metasedimentary and metavolcanic bedrock. In these soils, Cd is commonly adsorbed by various clay minerals and by calcium and magnesium carbonates. Cadmium does not form highly stable complexes with organic matter. In addition, in these cold boreal forest soils, where microbial decomposition rates are low, the Cd that is tied up in organic matter probably remains immobile for some time. Cadmium can form many compounds of low solubility by precipitation as carbonates, hydroxides, and phosphates. This process is less important, however, in the moderately low pH, generally low-carbonate soils of the study area. Cadmium is readily leached from soils at pH values below about 5.0, especially if the soils have a sandy texture. Soils so far examined in the Fortymile watershed range in pH from 4.8 to 6.2. The oxic, slightly acidic soils of the region may permit a large amount of Cd to be absorbed and translocated by plants. Zinc has close geochemical similarities with Cd and competes for exchange sites in soil. However, these soils are not particularly high in Zn, and therefore Zn probably has a minimal adverse influence on Cd bioavailability.

Cadmium Impacts on Biota and Processes That Influence Its Bioavailability

In general, Cd is considered a heavy metal of major environmental concern because of its high mobility and the small concentration at which it can adversely affect plant (Das and others, 1997; Hale and others, 2001) and animal (Larison and others, 2000) metabolism. In addition, there is growing concern over the increase in environmental Cd (mainly from industrial emissions) and its adverse impact on soil biological activity (Kabata-Pendias, 2001). Cadmium is a nonessential heavy metal and a powerful enzyme inhibitor. In a recent study of white-tailed ptarmigan in Colorado, Larison and others (2000) found that a diet of willow buds, with mean Cd concentrations as low as 2.1 ppm (dry weight basis), resulted in renal tubular damage and increased chick mortality. In addition, these authors hypothesized that Cd poisoning may be more widespread than previously suspected among other willow-feeding herbivores (for example, hare, beaver, and moose) in areas with high Cd in browse species.

A major unknown in this project is whether the levels of Cd in the accumulator willow species in our study area have a measurable impact on the health of browsing animals. We are, however, recording Cd concentrations comparable to those in Colorado that have been shown to be detrimental to animal health. This fact has aroused the interest of both game managers and public health workers in Alaska. In a recent study by the Alaska State Department of Health and Social Services, soil, sediment, fish, and berries from the Red Dog Mine area in northwest Alaska were examined for unusually high heavy metal levels (State of Alaska, 2001). This study did not find metal levels in these foods to be excessive. In addition, the State wishes to know the level of Cd in moose muscle, liver, and kidney tissue, because these are consumed by subsistence hunters in rural Alaska (tissue samples may be available for analysis from the State's archive and through cooperation with native hunters). Very high levels of Cd in moose liver and kidney tissue have recently been reported as a concern for human consumption in Vermont (K. Hundertmark, Alaska Department of Fish and Game, oral commun., 2001).

In addition to the U.S. Bureau of Land Management (with which the U.S. Geological Survey has a Memorandum of Understanding in place), initial activities of the project will concentrate on arranging formal working agreements with the Alaska Department of Fish and Game (ADF&G), Alaska Native groups, and industry. ADF&G has a major project examining the accumulation of trace elements in important subsistence fish species. In preliminary discussions, ADF&G has expressed an interest in our involvement in a companion study that would focus on the cycling of trace elements in regional terrestrial ecosystems.

Initial discussions with the U.S. Geological Survey's Biological Resources Discipline revealed that they currently have no personnel in the northwest with a specific interest in the general field of trace-element toxicity and epidemiology.

Major Knowledge Gaps and Needed New Research Directions

From a review of the literature, the actual biochemical form (speciation) of Cd in willow tissue has not been defined. We plan to use X-ray absorption spectroscopy (XAS, Stanford University Synchrotron) and gas chromatography mass spectrometry to define the mode of occurrence of Cd within willow tissue (possibly phytochelatins and related peptides as well as metalothionines). In addition, we need a better understanding of the form of Cd in the soil. Investigations using X-ray diffraction will help define the mineralogy of both the loess and bedrock parent materials of the soils (primary and secondary mineral reservoirs). Sequential extractants will be used to define loosely vs. strongly adsorbed Cd in soil. Specifically, we will define the Cd reservoir that is readily dissolved with distilled water, Cd adsorbed onto organic matter, Cd coprecipitated with metal oxides, and Cd coprecipitated with crystalline iron (oxyhydroxides). We have yet to define the exact soil extractants to be used.

The Alaska Department of Fish and Game has expressed an interest in examining the possible impact of elevated Cd, Pb, and Zn levels in willow shrubs on the health of willow ptarmigan in northwest Alaska (P. Weber-Scannell, oral commun., 2001). We are currently developing a cooperative effort with several State agencies to examine the health of these birds in areas of high soil Cd, such as near the sedimentary exhalative Zn-Pb-Ag mineralized terrain surrounding the Red Dog deposit (fig. 1).

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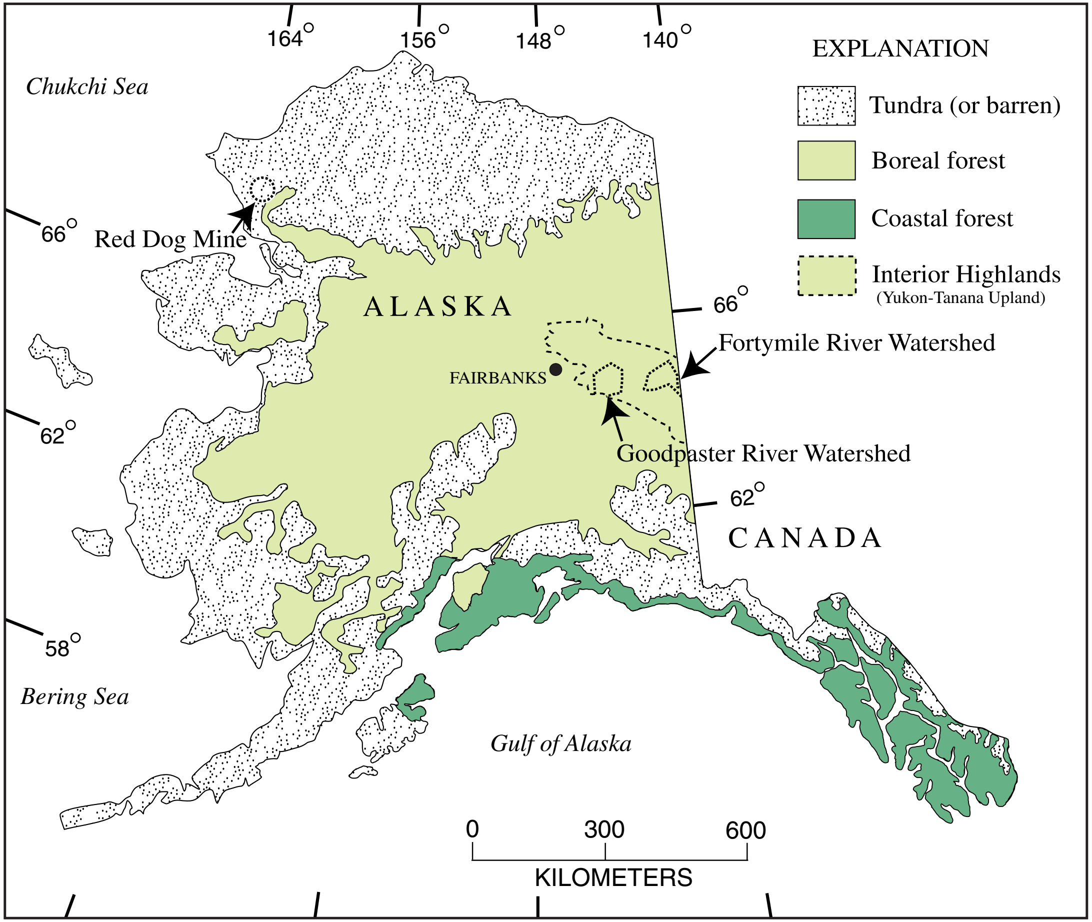

Figure 1. Location within Alaska of the Fortymile and Goodpaster River study areas relative to the three generalized major vegetation types. Future work may include Cd mobility studies in and near the highly mineralized terrain that surrounds the exhalative Zn-Pb-Ag deposit at Red Dog Mine.

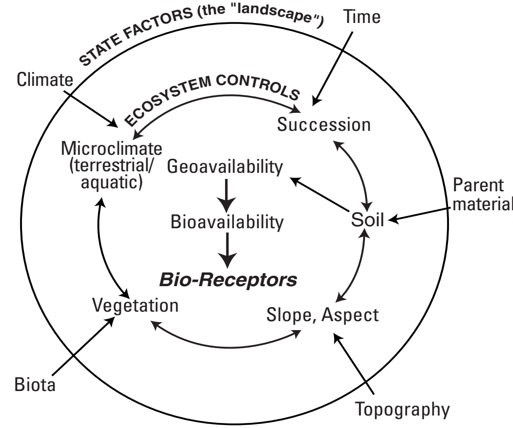

Figure 2. State factors and major ecosystem controls of trace element cycling, subarctic boreal forest, east-central Alaska (after Van Cleve and others, 1991).

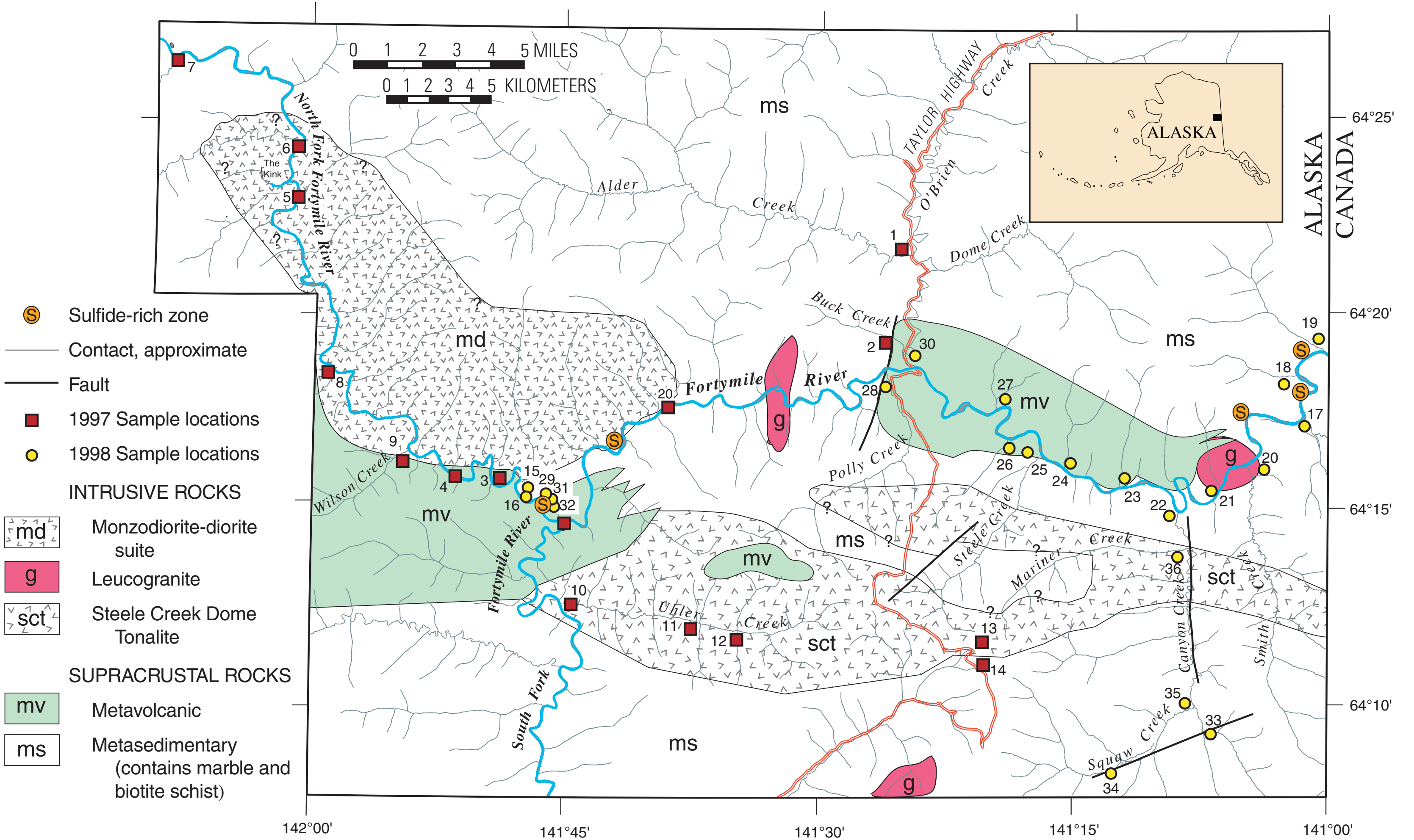

Figure 3. Generalized geology of a recently completed study within the Fortymile River watershed (from Day and others, 2000). The 1997 and 1998 sample locations are for water, bed sediment, soil, and vegetation collections (Gough and others, 2001).

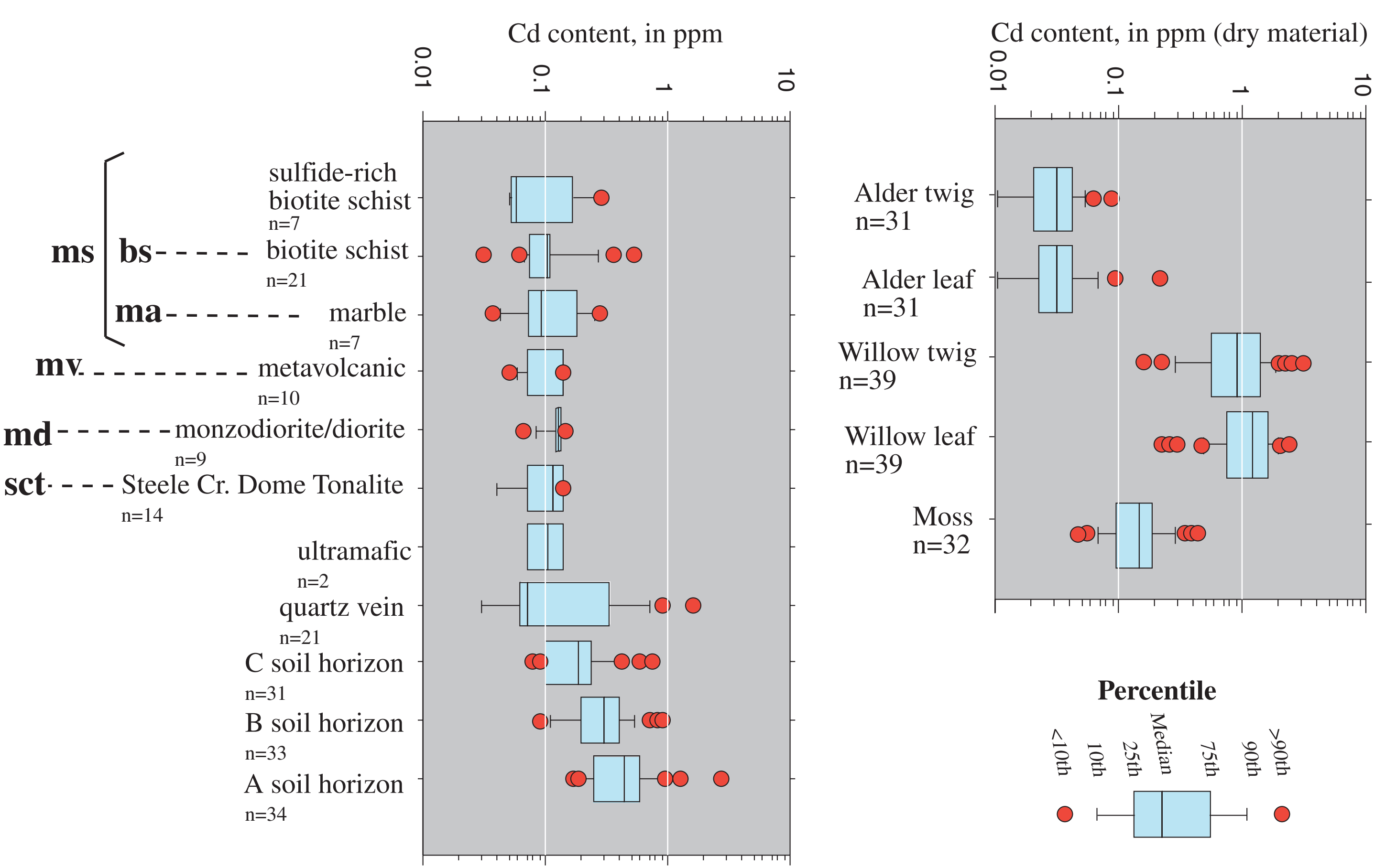

Figure 4. Concentration of Cd in rock, soil, and vegetation samples from the Fortymile River watershed, east-central Alaska. Rock-unit abbreviations are keyed to figure 3. Percentile classes for the sample groups are defined in the percentile key. Red dots are individual sample values having percentile values >90 or <10 in their groups.