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Selenium in soils of western Colorado

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ABSTRACT

Seleniferous soils are host to a diverse and unique community of plants, animals, and microorganisms. Often, studies of these organisms, if they report selenium at all, only report the total selenium content of the soil. We conducted a field survey of soils to determine a) whether total selenium is a reliable proxy for bioavailable selenium, and b) the general characteristics of typical seleniferous soils. We analyzed soils from 32 seleniferous and nearby non-seleniferous habitats across western Colorado. In normal, low-selenium soils, the relationship between total and bioavailable selenium is roughly linear. In seleniferous soils however (total Se > 2 mg/kg), there is no relationship between total and bioavailable selenium. Also, these soils can be broadly characterized by two principal axes: a metals-rich axis likely explained by the mineralogy and depositional environment of the parent rock, and a soluble, salt-rich axis likely explained by soil weathering and hydrology. There is considerably more variation along the former axis, which also appears to predict primary productivity, but selenium content, particularly bioavailable selenium, is influenced by the latter. Researchers in seleniferous environments must recognize that seleniferous soils are heterogeneous, and may be shaped by current environmental factors as much as by the geological past.

1. Introduction

Selenium is both an essential nutrient and an acute toxin and environmental pollutant. In the arid west, selenium generally occurs in two forms, the non-available elemental form, and the highly bioavailable selenate form (Oldfield, 2002). One might expect that biotic and abiotic processes would keep these two forms in dynamic equilibrium, and so many studies of organisms from seleniferous ecosystems (if they report soil selenium at all – some do not (e.g. Cowgill and Landenberger, 1992; Somer and Çaliskan, 2007; Galeas et al., 2008)) only report total soil selenium or are ambiguous about whether they are reporting total or bioavailable selenium (e.g. Galeas et al., 2007; Freeman et al., 2009; Sors et al., 2009).

Seleniferous soils in the western United States have been of scientific interest at least since the 1890s, when researchers were trying to determine the cause of a mysterious illness affecting grazing cattle, known at the time as “alkali disease” (Trelease, 1942). Also called “blind staggers”, the disease caused gastrointestinal pain, listlessness, aimless wandering, paralysis, and death. It was eventually discovered that certain plants growing on seleniferous soils were also very high in selenium, and could cause the disease if fed to cattle in controlled settings (Beath et al., 1934). Feeding a sheep with as little as 1.3 g/kg of these plants was sufficient to cause death in just a few hours (Beath et al., 1934). These “indicator plants” were frequently found to have more than 1000 mg/kg selenium in their aboveground tissues, and were noted to be indicative of seleniferous sedimentary formations (Trelease and Trelease, 1937; Beath et al., 1939a). While normal soils generally contain less than 2 mg/kg of selenium (Mayland et al., 1989; Oldfield, 2002) these seleniferous formations often contain more than 10 mg/kg of selenium, and have been reported to contain up to 1200 mg/kg in rare instances (Mayland et al., 1989).

Some of the plants that inhabit these soils are now referred to as hyperaccumulators, because of their ability to take up trace elements at hundreds or thousands of times background levels, without apparent harm (Brooks et al., 1977; Boyd, 2007). The most well known selenium accumulators are in the genera *Astragalus* (Fabaceae) and *Stanleya* (Brassicaceae) (Freeman et al., 2006; van der Ent et al., 2013), although at least 20 taxa from 7 families have been demonstrated to hyperaccumulate the element (Krämer, 2010). However, even in the state of Colorado alone, many of the known selenium hyperaccumulators are tracked as rare or

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threatened, including *Astragalus debequaeus*, *A. eastwoodiae*, *A. linifolius*, *A. nelsonianus, A. oocalycis*, *A. osterhoutii*, and *A. rafaelensis* (CNHP, 1997+). This is due in part to habitat degradation from uranium and natural gas extraction, because these resources often coincide with seleniferous formations (Beath, 1943; Presser, 1994). In fact, one of the collections in this survey was at a former population of *A. debequaeus* that had been extirpated by a well pad, and another was collected from the disturbed soil covering a recently buried pipeline. However, the rarity of these species is most likely attributable to the limited extent and discontinuous nature of seleniferous soils to begin with. Thus, our understanding of the form and distribution of seleniferous soils can help inform the conservation of these species and their ecological partners.

Selenium, like its elemental neighbor, sulfur, is quite volatile in its liquid and gaseous forms, and thus tends to be reduced in intrusive igneous rocks, and marginally enriched in extrusive rocks, particularly basalt and ash (Malisa, 2001). However, because selenium strongly adsorbs to clay minerals and may be bioenriched by aquatic organisms, it is typically found at some of its highest levels in clay-rich sedimentary rocks, including mudstones and shales - particularly those that were deposited during periods with high levels of volcanism (Byers et al., 1936; Beath et al., 1939a; Mayland et al., 1989). Such conditions were not uncommon during the Cretaceous and early Paleogene periods, when the Sevier and Laramide orogenies caused substantial volcanism in the western US, and the Western Interior Seaway covered much of what is now the Rocky Mountains, creating an ideal depositional environment for mudstones and shales. Indeed, many Cretaceous and Paleocene sediments of the western US are dangerously enriched in selenium content (Beath et al., 1939a,b; Kulp and Pratt, 2004).

However, mineralogy is not the only factor affecting selenium levels in the environment. The ionic forms of selenium in particular are highly soluble, and can be easily leached from or deposited in soils by water (Kulp and Pratt, 2004; Tuttle et al., 2014b). The southeastern United States, for example, has soils that are generally deficient in selenium, due to high levels of rainfall and leaching (Mayland et al., 1989). Likewise, high levels of precipitation, among other factors, causes certain parts of the Tibetan Plateau to have soil so deficient in selenium that it causes chronic nutrient deficiency in humans who live in the area (Wang et al., 2013). On the other hand, in acidic, poorly drained soils, precipitation is positively associated with total selenium, but negatively associated with bioavailable selenium, because highly insoluble ferric selenite forms and is sequestered (Byers et al., 1936; Oldfield, 2002).

Because the biotic and abiotic cycling of selenium may disproportionately deplete or enrich only certain chemical forms of the element, the ratio between total and bioavailable selenium may not be predictable. If that ratio is not consistent, researchers could potentially mischaracterize seleniferous and non-seleniferous areas by conflating the two. Herein we tested the implicit hypothesis that total selenium is a reasonable proxy for bioavailable selenium. We also sought to better characterize the soils of seleniferous habitats in order to improve the success of biodiversity conservation efforts in these areas.

2. Methods

2.1. Soil collection

We collected soil samples from 32 sites across western Colorado, where selenium hyperaccumulators in the genus *Astragalus* occur in close proximity to congeneric non-accumulators based on protected occurrence data from the Colorado Natural Heritage Program (CNHP). At each site, we collected soil at CNHP-provided GPS coordinates. If there were positively identified *Astragalus* plants present, we collected at the one that was closest to those coordinates. If not, we collected at those coordinates, as precisely as possible. We sampled the top ~10 cm of soil from four microsites, located 0.5 m from the sampling center in the cardinal directions, and homogenized the samples.

Our collections were taken in two primary areas: in and around the town of DeBeque, and along seleniferous formations ringing the Uncompahgre Plateau. Seleniferous collections near DeBeque were largely soils derived from the Atwell Gulch member of the Wasatch Formation. The Atwell Gulch member is a known seleniferous stratum that is mud-dominated and straddles the Paleocene-Eocene boundary. (Beath et al., 1939a,b). Seleniferous collections around the Uncompahgre Plateau were primarily from soils derived from the Morrison formation, another known seleniferous stratum, which was deposited during the late Cretaceous (Beath et al., 1939a,b). Although the formation is broadly seleniferous, the Salt Wash member is particularly so (Beath, 1943). Non-seleniferous collections were of soils derived from neighboring strata, which have similar present-day characteristics (Fig. 1).

All soils were shallow (sometimes <10 cm to bedrock), dry, azonal, and rocky, and were most likely either Orthents or perhaps Argids, based on our field observations. They appeared to be mostly composed of recently eroded parent rock, as they were generally collected on or near talus slopes, alluvial washes, or braided arroyos. Most sites were adjacent to cliffs or badlands. Although the

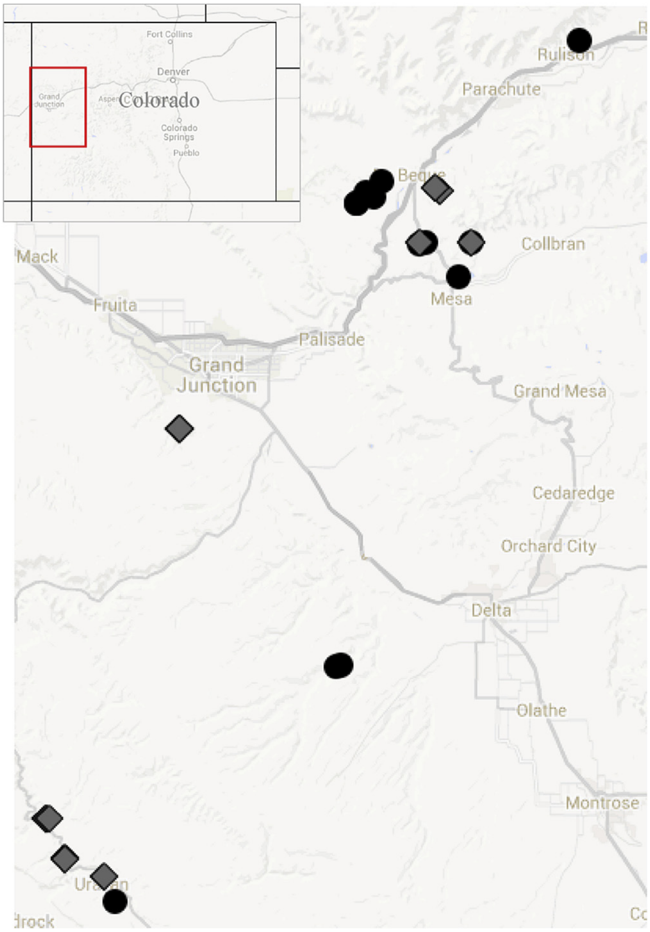

Fig. 1. Map of soil collection sites in Western Colorado (inset). Sites were chosen for having seleniferous plants growing in close proximity to non-seleniferous plants. Sites which had high total selenium (>2 mg/kg) are depicted as grey diamonds, while those with low total selenium (<2 mg/kg) are depicted as black circles.