



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.

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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. rafaensis* (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

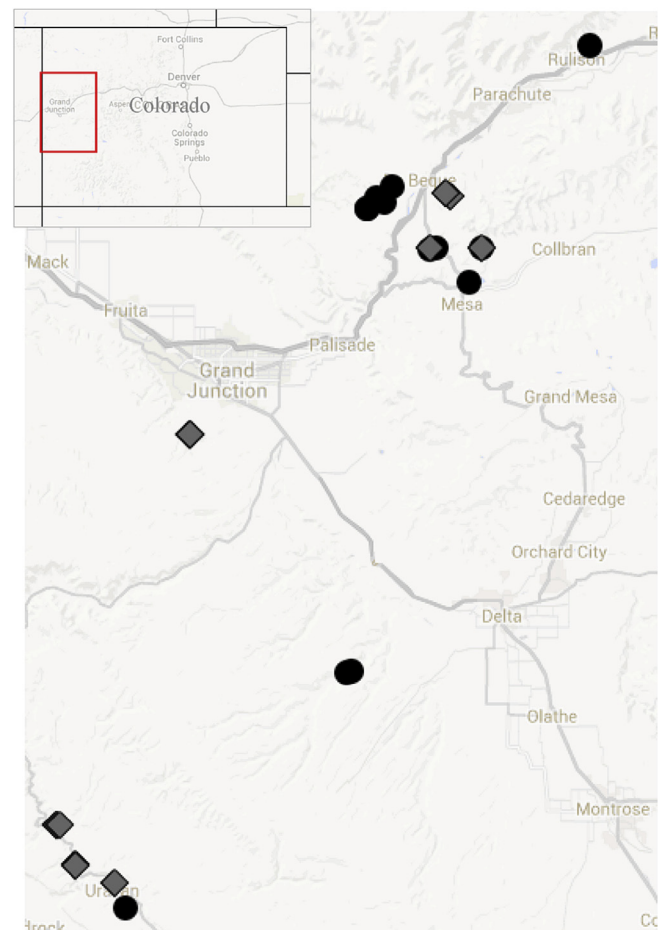


Fig. 1. Map of soil collection sites in Western Colorado (inset). Sites were chosen for having seleniferous plants growing in close proximity to non-seleniferous plants. Sites which had high total selenium (>2 mg/kg) are depicted as grey diamonds, while those with low total selenium (<2 mg/kg) are depicted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

NRCS Web Soil Survey (2016) does not have sufficient resolution to determine the soil types at our sites with any certainty, the database corroborates our field assessment. The vast majority of our sites mapped onto Orthent soil series, typically Ustic Torriorthents or Lithic Ustic Torriorthents, with a few Torrertic Ustorthents. These series were often next to or complexed with rock outcrops or badlands. A few of our sites mapped to Argid soil series, such as Ustic Haplargids or Ustic Calciargids, although these series were all very near to or complexed with Orthents.

The sites were sparsely vegetated, with an abundance of bare ground at every site. Piñon-juniper woodland and/or sagebrush scrub were the dominant plant communities at all of the sites. Known seleniferous areas typically also hosted selenium accumulator species, including *Astragalus* and *Stanleya* species.

2.2. Soil analysis

Soils were analyzed via the standard testing panel plus total and bioavailable selenium tests by the Soil, Water and Plant Testing Laboratory at Colorado State University. Bioavailable essential nutrients were determined via AB-DTPA extraction. Total and plant available selenium were determined with ICP-AES. Conductivity and pH were determined with the 1:1 soil:water method. Lime content (CaCO_3) and texture were estimated categorically. Site precipitation data were taken from the PRISM climate group 30-year normals (1981–2010), based on the 800 m spatial resolution (<http://www.prism.oregonstate.edu/>).

2.3. Statistical analysis

All data sets were analyzed via JMP Pro v11. We tested the relationship between total Se and bioavailable Se using both log-transformed and untransformed data using standard linear regression. In order to characterize the general properties of the soils we collected, we performed several exploratory univariate and multivariate analyses. Because soil texture and lime content were reported categorically, the relationship between these variables was tested via chi square test. For other analyses of soil texture or lime content, the variables were assigned arbitrary ordinal numerals and analyzed non-parametrically. Soil textures were ranked in order of clay content (sandy clay loam = 1, sandy clay = 2, clay = 3), and lime content was ranked in order of increasing lime (low (<1%) = 1, medium (1–2%) = 2, high (2–3%) = 3, very high (>3%) = 4). For univariate comparisons of either clay or lime and another soil variable, we used the non-parametric rank-order Spearman's rho test. We used untransformed and rank-order data for our PCA, as it does not assume normality.

3. Results

The ability of total selenium to predict bioavailable selenium was mixed (Fig. 2, Fig. S1). In normal soils (<2 ppm total Se), log-transformed total selenium was a strong predictor of log-transformed bioavailable selenium ($P < 0.001$, $n = 16$, r^2 adj. = 0.52). Even still, the bioavailable portion averaged 35% of total selenium, but ranged between 0.1% and 82%. In seleniferous soils (>2 mg/kg total Se), there was no relationship between log-transformed total and log-transformed bioavailable selenium ($P = 0.65$, $n = 16$, r^2 adj. = -0.05). Untransformed data produced qualitatively similar results for both normal soils ($P < 0.01$, $n = 16$, r^2 adj. = 0.46) and seleniferous soils ($P = 0.35$, $n = 16$, r^2 adj. = -0.01) (Fig. S1). Soil texture was not a significant predictor of total or bioavailable selenium (Spearman $\rho = -0.27$, $P = 0.13$; Spearman $\rho = -0.18$, $P = 0.32$; respectively).

A PCA of continuous soil variables revealed two main groups of

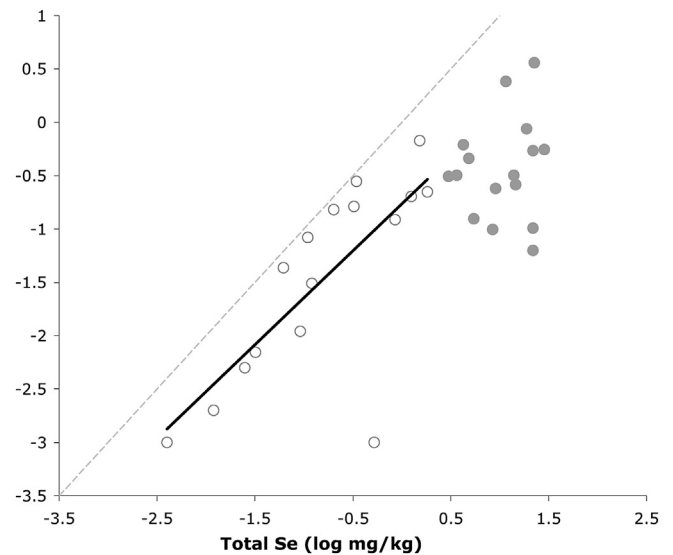


Fig. 2. Log-transformed total soil selenium versus log-transformed bioavailable soil selenium. Unfilled circles represent normal soils, i.e. those with <2 mg/kg total Se. The solid line represents the best fit line for normal soils. The filled circles represent seleniferous soils (>2 mg/kg total Se). There is no trendline for seleniferous soils because the relationship is not significant. The dashed light grey line represents the identity line, i.e. a 1:1 bioavailable fraction.

vectors (Fig. 3). The first grouping, which is largely oriented along PC1, contains vectors for the metals copper, zinc, and iron, as well as for texture, phosphorus, and % organic matter. Mean annual precipitation, when included, aligns with PC1, but the eigenvector loading was very weak, so we excluded it from the analysis, and its inclusion or exclusion does not affect the loading of other variables. The second grouping is orthogonal to the first, and is largely oriented along PC2. It contains the vectors for nitrate, bioavailable selenium, potassium, and conductivity. Manganese, total Se, lime, and pH are intermediate between these axes. Manganese is positively correlated with both sets of vectors, while lime, pH, and total Se are positive for the second group of vectors, but negative for the first (Fig. 3a). If we exclude non-seleniferous soils (<2 mg/kg total Se) from the analysis, we see nearly identical results (Fig. 3b).

Although total Se was weakly associated with both PC1 and PC2 (Fig. 3), there was no significant difference between low total Se soils and high total Se soils in terms of any of soil variables we measured, except for bioavailable selenium, which was only marginally different ($P < 0.05$, $n = 32$, $r^2 = 0.15$). All of the soils, both low and high total Se, shared broad similarities (Table 1). Sand and clay dominated the samples, with 53% of samples being sandy clay loam, 28% being sandy clay, and 18% being clay. Soil texture was not statistically associated with lime content ($\chi^2 = 0.38$, $n = 32$, $df = 6$), which ranged from <1% to >3% (with a majority of samples being >3%), and was moderately associated with pH, with more lime leading to a more basic soil (Spearman $\rho = 0.40$, $P < 0.05$). Soil texture was also associated with pH, with more clay-rich soils being more basic (Spearman $\rho = 0.61$, $P < 0.001$). The pH range was approximately normally distributed, from weakly acidic to weakly basic. Organic matter content was low in all samples, with a maximum of just 1.2%.

4. Discussion

It is clear from our results that while total selenium may be a fairly reasonable proxy for bioavailable selenium in “normal” soils (although it only explains ~50% of the variance), it is a poor proxy for bioavailable selenium in geologically seleniferous soils. In arid

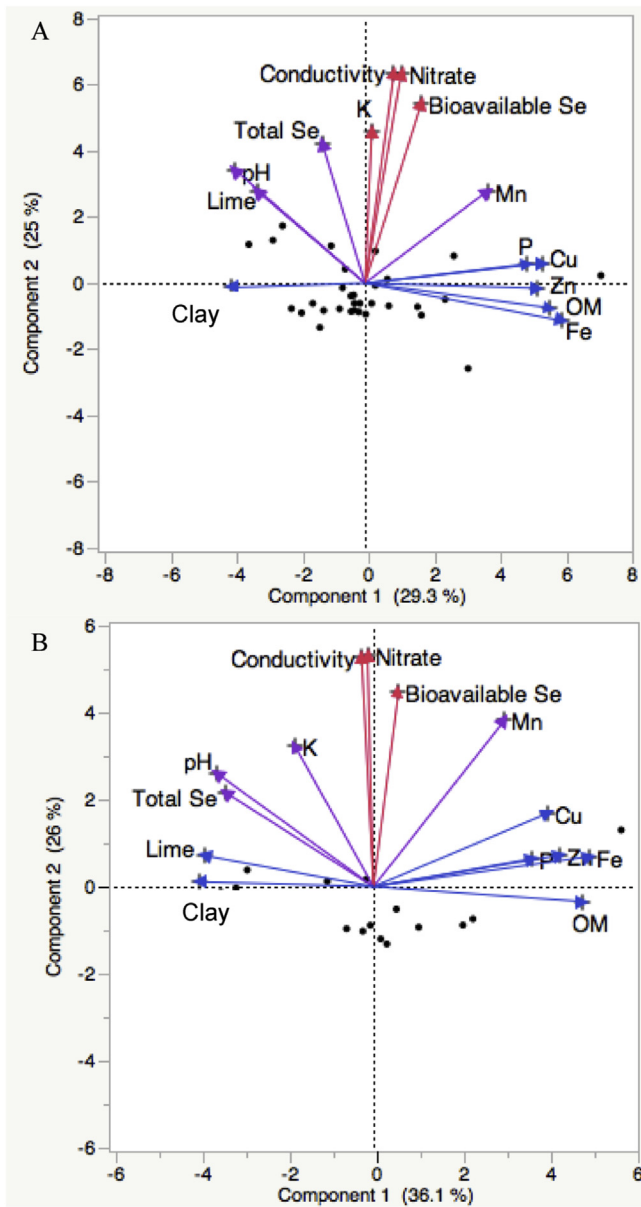


Fig. 3. PCA biplot of soil variables for all soils collected (A) and only seleniferous soils (>2 mg/kg total Se) (B). Blue vectors are those which orient primarily along PC1, red vectors align primarily along PC2, and purple vectors are intermediate between the two axes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

soils, selenium typically occurs as either elemental selenium, which is both biologically unavailable and poorly soluble, or selenate, which is both highly bioavailable and highly soluble (Oldfield, 2002). It seems possible that the breakdown in correlation between total and bioavailable selenium above 2 mg/kg is because the rate of replenishment for selenate is exceeded. In other words, when levels of selenium are low and precipitation depletes the selenate portion, the rate of chemical and biological oxidation of elemental selenium to selenate, although slow (Oldfield, 2002), is likely sufficient to replenish bioavailable selenium fairly rapidly. On the other hand, if total selenium is high, the slow rate of oxidation may not be sufficient to replenish selenate, particularly when precipitation events are relatively frequent or severe, and/or where soils are well drained.

Under ideal conditions, plants (both hyperaccumulators and non-accumulators) take up selenium roughly proportionally to

Table 1

Table of average soil variables across all 32 sites. Most variables were substantially right skewed, so we report both mean and median below. Conductivity is reported in mmhos/cm. All nutrients are reported as mg/kg. Annual precipitation data were estimated with the PRISM climate model, and are reported in mm.

Variable	Mean \pm SD	Median	Interquartile range
pH	7.65 \pm 0.47	7.65	7.40–7.88
Conductivity	2.78 \pm 12.18	0.40	0.30–0.70
% Organic	0.65 \pm 0.25	0.60	0.43–0.80
Nitrate	8.38 \pm 32.69	1.95	1.13–2.92
Phosphorus	1.65 \pm 2.15	1.00	0.40–1.85
Potassium	243.4 \pm 109.6	208.0	168.0–303.8
Zinc	0.420 \pm 0.495	0.314	0.240–0.422
Iron	3.52 \pm 1.61	3.35	2.68–3.98
Manganese	2.82 \pm 1.45	2.47	1.73–3.17
Copper	1.80 \pm 1.04	1.65	1.34–2.15
Total Selenium	6.94 \pm 8.77	2.41	0.14–13.38
Bioavailable Selenium	0.40 \pm 0.74	0.18	0.05–0.42
Annual Precipitation	332.9 \pm 32.3	328.6	308.2–345.5

bioavailable supply, although this proportion can vary tremendously between species or even within species under different climatic and ecological conditions (Wang et al., 2013; Statwick et al., 2016). Studies of seleniferous habitats should take care to report bioavailable selenium content, not necessarily total selenium. Inferences about plant behavior or plant communities made from total selenium alone may lead to erroneous conclusions. Also, although selenium is known to adsorb strongly to the clay fraction in soils (Goldberg, 2014), we found no significant relationship between clay content and either total or bioavailable selenium, meaning that this relationship is likely much more dynamic in field settings.

Based on our PCA, the soils of the western slope of Colorado can be described by two major axes (Fig. 3). We suggest the first of these axes largely represents the depositional environment and mineralogy of the parent rock. Soils more positive in PC1 are sandier, lower in lime, more acidic, and higher in available mafic metals. Since mafic metals, particularly iron, are also associated with higher phosphorus content in rocks (Porder and Ramachandran, 2012), we were not surprised to see phosphorus also align with PC1. The combination of larger grain size (implying shorter transport distance and/or higher turbidity), less lime (from deepwater organisms), and more metals (from nearby volcanic sources) leads us to speculate that soils that are more positive along PC1 are derived from sedimentary rocks that were originally deposited in terrestrially or in relatively shallow water, perhaps during periods of sea level regression or on topographically higher areas (Sluijs et al., 2008). Soils that are negative on PC1 are thus perhaps derived from sediments deposited in deeper water, during periods of transgression, or in topographically lower areas.

There are certainly other factors that can influence these variables on relatively short timescales; in particular, texture can be modified by erosion, while lime can be deposited through wind or pedogenesis. While we cannot rule out the possibility that PC1 also describes some of these Quaternary processes, we think that their effects are likely minimal. Firstly, one would predict that erosion would reduce lime content, grain size, and metal content together. Instead, we see soils with smaller grain size and lower metal content have more lime, not less. Second, because soils were generally Orthents collected immediately downslope from their parent rocks and in an arid climate, we expect that weathering and pedogenesis would have little time or distance to modify the soils. Finally, while wind almost certainly modifies these arid soils, we suspect that the effects of wind are essentially random, and would not systematically modify some soils more than others.

PC2, on the other hand, is made up of vectors representing highly soluble compounds like selenate, nitrate, potassium, and others that influence conductivity, so it likely describes soil hydrology. Soils that are highly positive on PC2 may be those in shallow, depressed, or poorly drained areas in which evaporation is dominant, and soluble compounds are concentrated near the surface. Soils that are highly negative along PC2 are those in which leaching is dominant, and soluble compounds are removed from the soil. Soluble selenium ions are very rapidly depleted by precipitation, and although precipitation is rare in arid regions, when it does occur, the high efflux of selenium from soil into surface and groundwater can be acutely toxic (Presser, 1994; Kulp and Pratt, 2004; Kuisi and Abdel-Fattah, 2010; Mast et al., 2014; Tabein et al., 2014a,b; Tuttle et al., 2014a,b; Tamoto et al., 2015). We were thus not surprised to find bioavailable selenium aligned strongly with PC2. It is worth noting that although total selenium seemed to be marginally influenced by both axes, bioavailable selenium was entirely unrelated to the mineralogy of the parent rock, and influenced solely by hydrology.

While one might expect phosphorus to align with PC2, phosphorus is relatively insoluble, and soils within a given climatic region have been shown to have a phosphorus level that correlates much more strongly with parent rock composition than with soil weathering (Porder and Ramachandran, 2012). Weathering eventually does deplete soil phosphorus, but only substantially so on the time span hundreds of thousands of years, even in very wet climates (Porder and Ramachandran, 2012; Newman and Hart, 2015).

We admit that it seems counterintuitive for organic matter to be loaded on PC1 rather than PC2. However, given a median phosphorus concentration of 1 mg/kg, this ecosystem appears to be primarily phosphorus limited, rather than nitrogen limited. This is perhaps not surprising, given that 1) carbonate rocks and sandstones are low in phosphorus to begin with (Porder and Ramachandran, 2012), 2) the arid climate likely minimizes phosphorus inputs from weathering, and 3) nitrate inputs may be high because of increasing anthropogenic atmospheric nitrate deposition in the arid west (Fenn et al., 2012) and/or nitrogen fixation from *Astragalus* hyperaccumulators (Alford et al., 2012).

In short, the seleniferous soils of western Colorado not substantially different than other arid soils, which is to say that they are relatively inhospitable, even without taking the toxic levels of selenium into account. Their phosphorus limitation, low moisture, low organic matter, and lack of developed structure make them challenging for all but the most well adapted plants to survive. Despite seleniferous communities generally being associated with seleniferous strata, the amount of bioavailable selenium in those soils can range from toxic to nearly deficient. Selenium availability is dictated in large part by hydrology, meaning that soils high in bioavailable selenium may also be saline or nitrate enriched, possibly making them more susceptible to desertification or exotic species invasion (Dukes and Mooney, 1999; Singh, 2009). Since these habitats are already limited in extent and many seleniferous species are obligate endemics, seleniferous communities might be especially prone to extirpation or extinction.

When planning restoration or revegetation projects for seleniferous species, scientists and land managers should take care to consider the hydrology of a site, as well as its geology, in order to best select sites that are actually enriched in bioavailable selenium. By considering total selenium alone, one might infer differences between habitats where none really exist, or even where the differences are the opposite of what was expected. For example, one of our “seleniferous” sites had more than 14 times the total selenium of one of our non-seleniferous site, but only 10% of the bioavailable selenium. A survey that included these two sites and categorized them based on total selenium would yield results that were

inconclusive at best. Similarly, choosing a potential site for a revegetation project based on these numbers could lead to unexpected failure. Thus, it is crucial to measure and report the concentration of bioavailable selenium in the soil when surveying seleniferous habitats, as well as to consider the factors that will promote the stability of the bioavailable selenium supply in the long term.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jaridenv.2016.10.006>.

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