Plants as Biomonitors

Indicators for Heavy Metals in the Terrestrial Environment

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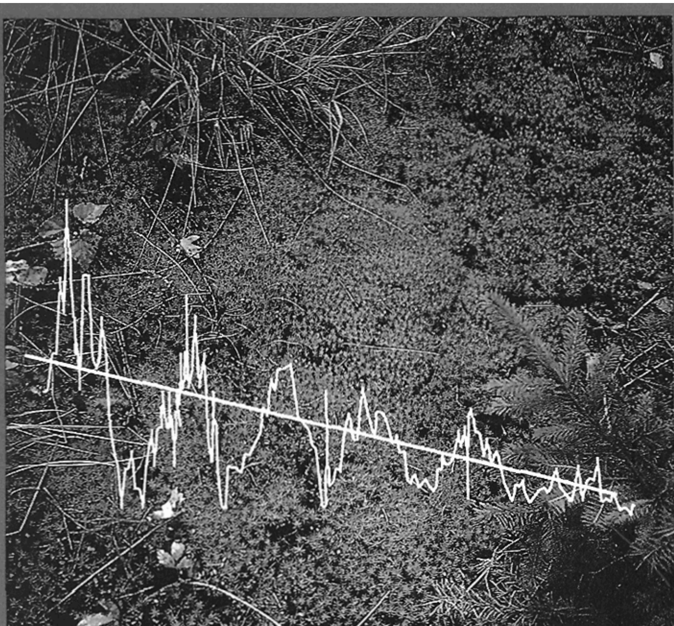

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8 Serpentine Endemics as Biological Indicators of Soil Elemental Concentrations

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8.1 Introduction

8.1.1 Serpentine Plants and Soil Mineral Resources

Serpentine soils of California, as well as other areas of the world, are closely associated with significant deposits of a variety of minerals, most notably nickel, chromite, cobalt and asbestos [1]. For this reason there has been considerable interest in the possible role of serpentine plants as bioindicators of such deposits [2, 3]. This interest has led us to pose two experimental questions: a) Are there variations in mean soil elemental concentrations between individual serpentine deposits? b) Can foliar concentrations of serpentine plants be used to predict soil concentrations of valuable trace metals? In this chapter we report on investigations to resolve these questions, using field data collected at a series of California serpentine sites from Del Norte to Santa Barbara Counties.

8.1.2 What Are Serpentine Soils?

Serpentine soils, in the context utilized by most plant ecologists, consist of a loosely defined series of soils weathered from ultramafic parent materials which are high in concentrations of magnesium and iron (i.e., ferromagnesium minerals). These basic serpentine minerals or serpentites (antigionite and chrysotile) are hydrous magnesium silicates, represented by the chemical formula $Mg_3Si_2O_5(OH)_4$, derived from the weathering of olivines and pyroxenes [4]. Iron oxides, chromite, and biotite are common accessory minerals.

The terms serpentine and ultramafic are commonly used interchangeably to describe soils of this type [4], but this utilization has led to some lack of precision in definitions relevant to questions of the mineral composition of serpentine soils. Ultramafic soils in the broad sense, often termed ophiolites [5], may include a variety of mineral assemblages beyond the basic hydrous magnesium silicates. Trace metals such as nickel, chromium and cobalt are commonly present in relatively high concentrations. These accumulations result from ionic substitution of nickel, cobalt and iron for magnesium in the crystal structure of the serpentine minerals [4]. These characteristic trace metal occurrences, together with low calcium/magnesium ratios resulting from the enrichment in the latter cation, are commonly associated with serpentine soils. However, serpentine-type soils may also be derived from the alteration of magnesium-rich rocks such as metamorphized dolomites [6]. Such soils have the characteristic low ratio of calcium to magnesium, but lack high concentrations of trace metals.

8.1.3 Serpentine Soils as Plant Habitats

While serpentine soils commonly share common types of parent material, the weathering processes of soil formation are highly dependent on variations in climatic regime, age, topographic relief, and biological activity [7]. As a result it is difficult to make generalizations about the nutritional characteristics of a typical serpentine soil. Commonly, but not invariably, serpentines share the traits of high trace metal concentrations and relatively low calcium/magnesium ratios as described above. In addition, these ultramafic soils commonly are characterized by relatively low concentrations of a number of important plant nuturients (potassium, phosphate, and molybdenum) and low cation exchange capacities [4]. Thus plant populations growing on serpentine soils face potential problems of both mineral deficencies and toxicities, as well as an unfavorable ratio of calcium to magnesium for normal plant growth.

Problems of plant growth on serpentine soils relate not only to nutritional conditions of mineral concentrations, but to physical properties of these soils [4, 6]. Outside of tropical climates, serpentine soils are commonly shallow and stoney, and thus have limited water holding capacities and limited volume for root growth. Their dark color, furthermore, subjects them to relatively greater extremes of soil temperature than most non-serpentine soils.

8.1.4 Physiology of Serpentine Growth

The sparse plant cover and low scrubby growth associated with vegetation on most temperate serpentine soils has led to a variety of explanations for the *serpentine factor* which negatively impacts plant growth [4]. A large literature of studies exists, as well as a series of sometimes contradictory hypotheses, to explain the apparent low levels of primary production in these soils. These hypotheses can be divided into problems of toxicities, mineral deficiencies, and calcium/magnesium balance [4, 6, 9].

8.1.4.1 Mineral Toxicities of Serpentine Soils

Nickel, chromium and cobalt all occur in unusually high concentrations in many, but not all serpentine soils and have been implicated as possible causes of mineral toxicities. Particular attention has been given to nickel in this respect because of its relatively high solubility. Nickel may be directly toxic itself to plants, or indirectly toxic through an induced iron deficiency resulting from competition between these two elements [4]. While non-serpentine plants commonly exhibit leaf concentrations of $0.1-5\ \mu g\ g^{-1}$ dry weight for nickel, serpentine species are reported to contain $20-100\ \mu g\ g^{-1}$ [4, 10]. A number of serpentine endemics, however, have been shown to be remarkable hyperaccumulators of nickel. *Sebertia acuminata* (Flacourtiaceae), a forest tree from New Caledonia, has a sap with up to $25000\ \mu g\ g^{-1}$ nickel by weight [11, 12].

While such an example is extreme, a number of cases of nickel hyperaccumulation have been found in plant species from serpentine soils in many parts of the world. For this reason there has been considerable interest in the use of endemics as bioindicators of metal deposits [2]. Despite these occurrences, however, hyperaccumulation of nickel is a relatively rare response to serpentine soils [12]. It is largely limited to tropical woody species in the Flacourtiaceae and Violaceae, and to genera of herbaceous Brassicaceae in the temperate zone.

Chromium concentrations in serpentine soils are commonly $10-250$ times those present in non-serpentine soils [4]. The distribution of chromium within the serpentine soils, however, is much more inhomogeneous than nickel because of the scattered occurrence of chromite minerals. It has been suggested that because of its low solubility, chromium represents far less problems of toxicity for plants than nickel [4, 9]. The majority of studies of chromium concentrations in leaves of serpentine plants have found relatively low concentrations [13, 14], suggesting that this element is largely unavailable or excluded from uptake.

Cobalt levels of serpentine soils may be 20 times those of non-serpentine soils, and this may likewise lead to toxicities for nonadapted plant species. Although hyperaccumulators of cobalt have been described [15], none of these are known to be present on serpentine soils. While typical levels of cobalt in the leaves of serpentine plants are about 10 times those of non-serpentine species, the absolute concentrations, nevertheless, are only about $10\ \mu g\ g^{-1}$ in most species [4]. These low levels suggest exclusion of this element rather than accumulation. Cobalt concentrations of more than $100\ \mu g\ g^{-1}$ leaf tissue, nevertheless, have been reported from *Calochortus* in California from both serpentine and non-serpentine soils [16].

8.1.4.2 Mineral Deficiencies

If slow growth of serpentine endemics is not due entirely to trace metal toxicities, nutrient deficiencies may be of considerable importance. Soil levels of such macronutrients as nitrogen, phosphorus, and potassium are characteristically low [4], and molybdenum deficiencies may also be important [17]. Despite a large number of studies, the significance of these deficiencies in serpentines relative to other stress factors has not been clearly resolved.

8.1.4.3 Calcium/Magnesium Balance

Absolute and relative concentrations of calcium and magnesium in serpentine soils may be an important factor in the fertility of these habitats. High levels of tissue magnesium are known to limit plant growth [8], and serpentine endemics characteristically are more tolerant of high levels of magnesium than their non-serpentine congeners [18, 19]. Low concentrations of calcium may also be a second factor in serpentine infertility. This effect is thought to result less from a direct deficiency, but rather from increased levels of toxicity for nickel and other heavy metals when low amounts of calcium are present in leaf tissues [20]. While the full nature of calcium metabolism in serpentine endemics remains uncertain, a number of studies have established that calcium fertilization does increase the fertility of serpentine soils [4]. Finally, the ratio of calcium to magnesium in plant tissues may also be a significant factor in plant growth on serpentines. A number of authors have suggested that ratios less than 1.0 may be detrimental to the growth of non-serpentine plants [see 4].

8.2 California Serpentine Soils

8.2.1 Distribution and Geological Origin

Outcrops of ultramafic rock are widely distributed in California, most notably in two broad bands of outcrops which extend from southeast to northwest along both sides of the Central Valley (Fig. 1). The western and more extensive of these bands extends along the Coast Ranges from Santa Barbara County to the south to the northwestern area of the state in Del Norte County where extensive deposits continue northward into Oregon. Within this band, serpentine outcrops occur over a wide diversity of terrain types from low foothills to the tops of mountain peaks as high as 2755 m. Mineralogically, the serpentines of the Coast Ranges in California are largely serpentinites derived from ultramafic igneous intrusives within the complex of Franciscan sedimentary rocks of Mesozoic age [21]. Outcropping of these minerals are generally associated with fault zones associated crustal tectonic movements of oceanic and continental plates along the Pacific Coast of North America.

The second band of ultramafic outcrops in California, distributed along the foothills of the Sierra Nevada from Tulare County northward to Plumas County, is much less extensive and topographically diverse. Here, serpentite is associated with igneous and sedimentary rocks that predate the granite baserock of the Sierra Nevada. As in the Coast Ranges, these serpentine outcrops represent intrusives along crustal fault lines.

While a large portion of the serpentine formations in California date from the late Cretaceous or early Tertiary, overlying marine and igneous deposits largely protected these minerals from erosional weathering at the surface until the Late Pliocene or early Quaternary [22]. This relatively late date for serpentine exposure is of considerable evolutionary significance since it suggests that most of the woody plant endemics of serpentine soils today were already present in the California flora at this time, occupying other mineral substrates.

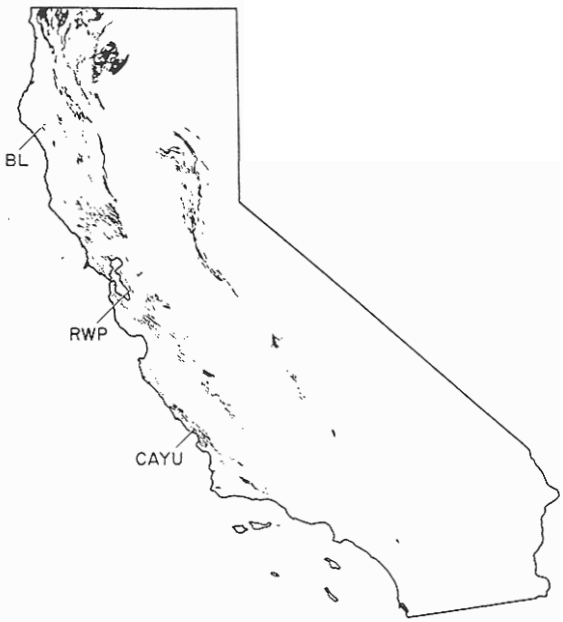

Fig. 1. Geographic distribution of serpentine outcrops in California [1]. Field study sites are indicated for Blue Lake (BL), Redwood Park (RWP), and Cayoucos (CAYU).

8.2.2 Chemical Composition of California Serpentine Soils

While there have been numerous studies investigating the chemical nature of California serpentine soils [see 9 for a review], these have largely focused on specific soil types or elements and have not been comparative between sites. It is well known that soils weathered from ultramafic parent materials reflect the elemental concentrations of the parent material, as well as the subsequent biotic and abiotic history of profle development. Most sepentine soils in California are residual or colluvial in nature, having been formed *in situ* over their parent materials. Such soils characteristically are shallow and rocky. Some serpentine soils in California, however, are alluvial in origin, and thus may have deeper profiles and a significant proportion of clay sediments. Kruckeberg has recently described the diversity of soil series derived from serpentine parent materials in California [9]. His listing includes series within three soil groups – haploxerolls, argixerolls and xerochrepts.

Are California serpentine soils relatively homogeneous in chemical characteristics, given their geographic and historical variation in origin? The answer to this question is clearly no, as illustrated in Fig. 2 which compares nutrient concentrations in three serpentine soils from California with soil chemical data for a typical agricultural and "normal" soil. We have used our analyses to determine mean elemental concentrations

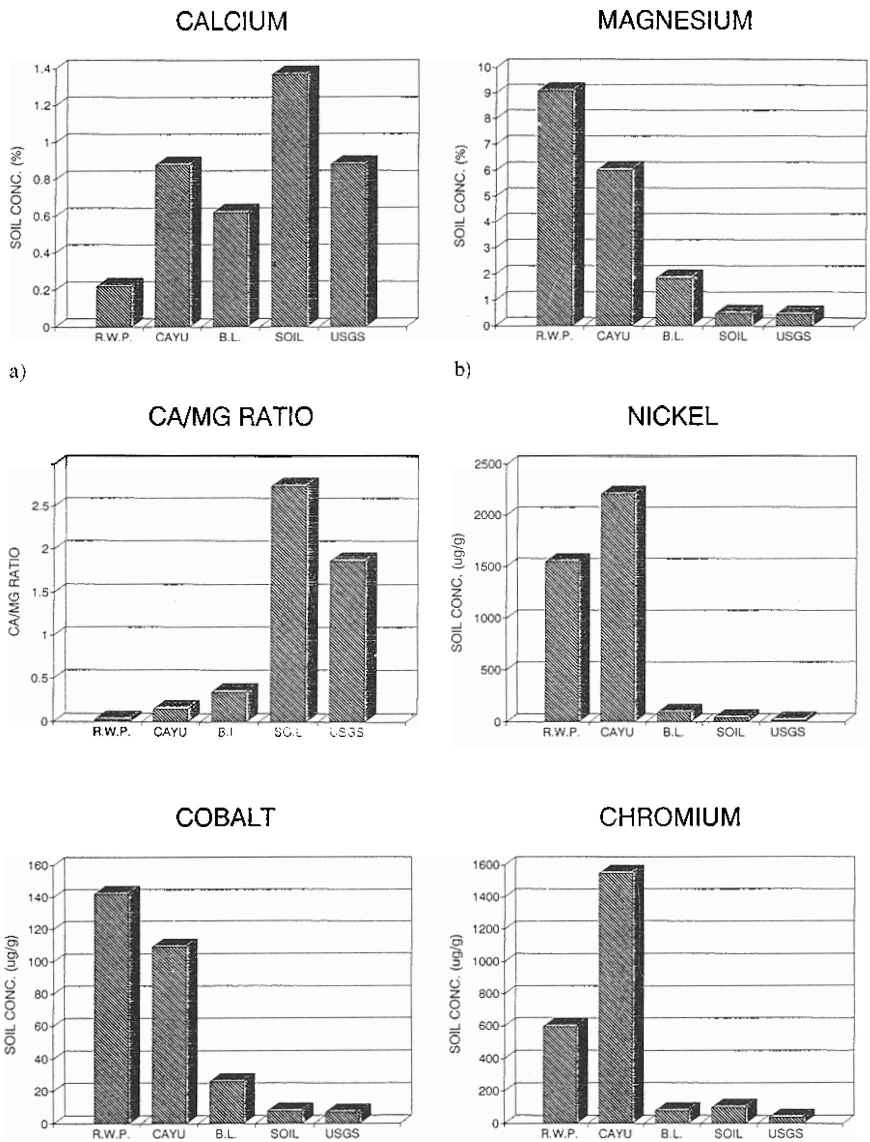

Fig. 2a–f. Mean elemental concentrations of surface soils at three California serpentine outcrops (BL, RWP, CAYU) compared to agricultural (SOIL) and typical surficial (USGS) soils [23, 24]; all concentration data in $\mu g\ g^{-1}$.

for mineral soils at 2–8 cm depth at five positions within eight serpentine sites. We report data here on three of these sites which represent the range of mineral concentrations present, as well as northern, central, and southern geographical positions within the state. These sites are Blue Lake in Humboldt County, Redwood Park in Alameda County, and Cayoucos in San Luis Obispo County. Soil analyses were carried out using ICP facilities at the Laboratory of Biomedical and Environmental Sciences, UCLA. Our data are compared to nutrient concentrations reported in the literature for general agricultural soils [23] and USGS typical soil [24].

While total soil calcium concentrations were relatively low at Redwood Park, soils from the other two serpentine site were not significantly different from those of the typical USGS soil (Fig. 2a). Soil magnesium levels, however, were notably high in all of the serpentine sites, with values ranging from three times agricultural soil levels at Blue Lake to nearly 20 times these levels at Redwood Park (Fig. 2b). The serpentine characteristic of low calcium to magnesium ratio was notable in all of the serpentine soils, with values for weight ratio varying from 0.02–0.34 in the soils compared to 1.9–2.7 in the agricultural and USGS soils (Fig. 2c).

Trace metal patterns in the serpentine soils were not as consistent as the Ca/Mg ratio data. For nickel, the Redwood Park and Cayoucos soils showed high concentrations, while the Blue Lake Soils were only slightly higher than the control soils (Fig. 2d). Cobalt concentrations showed a similar pattern of high concentrations at Redwood Park and Cayoucos, but with intermediate values at Blue Lake (Fig. 2e). Concentrations for chromium demonstrated another variant on this pattern. Redwood Park, with the highest concentrations of nickel and cobalt, had only 40% of the concentrations of chromium present at Cayoucos. Both of these sites were nevertheless much richer in chromium than Blue Lake whose concentrations were not significantly different from those of the control soils (Fig. 2f).

8.3 Nutrient and Trace Metal Accumulation in Serpentine Endemics

If serpentine plants are to have value as bioindicators of soil nutrient condition and/or metal occurrence, it is important to understand the fidelity of individual species to serpentine soils and the the relationship between soil and plant tissue levels of metals. This approach can be best investigated by looking at serpentine endemics whose range is at least regionally indicative of ultramafic soil conditions.

8.3.1 California Serpentine Endemics

While early California geologists mapped the occurrence of serpentine outcrops in California as early as 1826 [see 21], the linkage between serpentine soils and vegetation was not made until the early 20th century. Bradley [25] clearly described the relationship between these soils and a characteristic sparseness of growth in the corresponding vegetation in 1918, but the evolutionary significance of the unique serpentine flora of California was not fully appreciated before the pioneering work on edaphic endemism by Mason in 1946 [26, 27].

No other serpentine area in the temperate regions of the world have as rich a flora of serpentine endemics as California. Kruckeberg has documented 152 species (215 taxa including subspecies) of vascular plants in California which are endemic to serpentine soils [9]. Another 146 species in California are regional indicators of serpentine soils, but may occur on other specialized substrates elsewhere in the range. The endemics include ferns (2 species), conifers (2 species), monocots (22 species), and dicots (126 species). This group of species is largely composed of herbaceous taxa, with the Asteraceae, Liliaceae, Brassicaceae and Polygonaceae contributing nearly half of the total. Two genera of woody, evergreen shrubs are important, however, *Arctostaphylos* (5 taxa) and *Ceanothus* (4 taxa).

Floristically, serpentine endemics make up about 10% of the endemic flora of California [22], a remarkable figure considering that serpentine soils comprise only 1% of the land area of the state [9]. Biogeographically, however, the distribution of serpentine endemics over the range of these soils in California is not even. The northwestern coastal region of the state supports the richest number of such species despite the more mesic climate conditions which might be expected to reduce the edaphic stresses present on serpentine soils.

8.3.2 Trace Metal Accumulation in California Serpentine Endemics

Trace metal accumulation, most notably for nickel, has been noted for a number of species of California serpentine endemics and serpentine tolerant herbs. These species include nickel concentrations of $5000-10000\ \mu g\ g^{-1}$ in two genera of herbaceous Brassicaceae from California, *Thlaspi* and *Streptanthus*, and moderately high concentration (up to $664\ \mu g\ g^{-1}$) in one species of *Viola* [10]. High concentrations of zinc (above $1000\ \mu g\ g^{-1}$) were also found in *Thlaspi*. Moderately high concentrations of nickel and relatively high concentrations of cobalt and copper have been reported in localized species of *Calochortus* including both serpentine and non-serpentine soils [16].

Calcium/magnesium ratios of California serpentine plants have not been described in any systematic manner. If leaf tissues of the serpentine flora are reflecting cation concentrations of their ultramafic soils, such ratios would be expected to be 1.0 or below. At these levels, non-serpentine plants would generally exhibit nutritional problems.

Despite the notable levels of hyperaccumulation of nickel and zinc that have been reported for a few serpentine taxa in California, the vast majority of California serpentine endemics do not have unusual concentrations of trace metals in their leaf tissues. We have surveyed more than 90% of these taxa without identifying other hyperaccumulators in either herbaceous or woody species. Our data for serpentine tolerant or endemic woody taxa is shown in Table 1. Nickel concentrations in populations of these taxa never exceeded 40 μg g^{-1}, and were generally less than 10 μg g^{-1}. Chromium concentrations averaged only about 2 μg g^{-1}, with a high level of 12 μg g^{-1}. Zinc concentrations were also low and cobalt levels were always below our lower limit of analysis at > 1.5 μg g^{-1}. While concentrations of these trace elements may be elevated over levels found in leaf tissues of related taxa growing on non-serpentine soils, the levels present are not sufficiently high to expect any toxicity problems. Instead, these modestly elevated concentrations of trace metals reflect an inefficiency in the process of physiologically excluding uptake of the elements.

Calcium/magnesium ratios in our woody taxa ranged from 2.1 for *Ceanothus*, 3.3 in *Arctostaphylos*, and 2.7 for *Quercus durata*. These values are not notably different from those present in chaparral shrubs growing on non-serpentine substrates. Our findings of an absence of any unusual tolerance of low Ca/Mg ratios

Tab. 1. Leaf concentrations of Trace Metals (Nickel, Chromium and Cobalt), Calcium and Magnesium in Serpentine Populations of Three Genera of Woody Chaparral Shrubs.
All values are in μg g^{-1} dry weight. Calcium/magnesium ratios were calculated on a weight basis. *Sample size is based on three analyses each times the number of field samples.*

Species	County	Ni	Cr	Co	Ca	Mg	Ca/Mg	n
Ceanothus pumilus	Oregon	12.0	4.4	< 1.5	15900	3690	4.31	9
C. pumilus	Del Norte	38.6	12.5	< 1.5	11200	3440	3.26	9
C. ferrisae	Santa Clara	5.1	0.5	< 1.5	7750	3960	1.96	31
C. jepsonii	Lake	9.0	1.6	< 1.5	7590	2280	3.33	9
C. jepsonii	Mendocino	9.4	3.7	< 1.5	4820	3300	1.46	3
C. jepsonii	Marin	7.6	0.5	< 1.5	7530	3000	2.51	14
C. jepsonii	Sonoma	10.8	0.7	< 1.5	2600	6000	0.58	6
C. jepsonii	Napa	5.2	2.4	< 1.5	4130	3107	1.33	3
C. jepsonii var. albiflorus	Lake	1.0	0.6	< 1.5	11700	3050	3.84	3
C. jepsonii x C. ramulosus	Marin	9.6	0.4	< 1.5	3930	4830	0.81	3
C. jepsonii x C. conjugans	Sonoma	8.3	1.2	< 1.5	6760	3000	2.25	3
Ceanothus mean		11.0	2.6	< 1.5	7583	3540	2.14	
Arctostaphylos nispidula	Sonoma	7.0	5.4	< 1.5	5350	1550	3.45	3
A. obispoensis	San Luis Obispo	3.3	2.4	< 1.5	9890	2350	4.21	15
A. benitoensis	San Benito	1.7	5.7	< 1.5	9620	3110	3.09	21
A. franciscana	San Francisco	2.2	0.2	< 1.5	8090	2310	3.50	6
A. stanfordiana	Mendocino	3.8	2.1	< 1.5	7500	1570	0.48	6
A. stanfordiana	Lake	0.5	0.7	< 1.5	3780	4310	0.88	3
A. stanfordiana	Trinity	0.6	0.3	< 1.5	13600	1160	11.7	3
A. stanfordiana	Sonoma	6.2	5.6	< 1.5	7480	2670	2.80	3
A. stanfordiana	Mendocino/Lake	1.7	1.4	< 1.5	3620	1250	2.90	3
A. manzanita var. bakeri	Sonoma	2.4	2.6	< 1.5	4540	2220	2.04	12
Arctostaphylos mean		2.5	2.6	< 1.5	7340	2250	3.26	
Quercus durata	Marin	14.2	2.6	< 1.5	6130	2460	2.49	3
Q. durata	San Benito	0.3	0.7	< 1.5	8540	3140	2.72	3
Q. durata	San Luis Obispo	0.8	0.1	< 1.5	5530	1050	5.27	3
Q. durata mean		5.1	1.2	< 1.5	6730	2220	3.03	

in the leaves of serpentine species parallels the findings of other workers. Krause [8] measured such ratios for the above-ground tissues of 326 species of serpentine plants and reported a mean weight ratio of 3.1. These data suggest that serpentine plants maintain a normal balance between calcium and magnesium by regulating their relative uptake of these cations.

8.4 Conclusions

Serpentine soils vary in their degree of serpentiness. Trace metal concentrations and Ca/Mg ratios are variables that may differ greatly between and within serpentine areas. These soil chemical characteristics are furthermore not dependent variables, and may change independently both between and within sites.

The great majority of temperate serpentine plants, both herbs and woody taxa, use avoidance of toxicity and/or mineral stress rather than tolerance to maintain their survival on these soils. Tolerance through hyperaccumulation of trace metals is rare, and the presence of plant leaf tissues with unusally low ratios of Ca/Mg is uncommon. Avoidance of trace metal uptake, however, is certainly not a process with 100% efficency. Thus it is not surprising to find elevated concentrations of time metals in serpentine species, compared to plants growing on non-serpentine soils. These concentrations are not sufficiently high, however, to cause toxicity problems. In the same manner, if such trace metal concentrations are to be be used in predicting high levels of soil trace metals, these small differences in tissue concentration must be identified.

8.5 References

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