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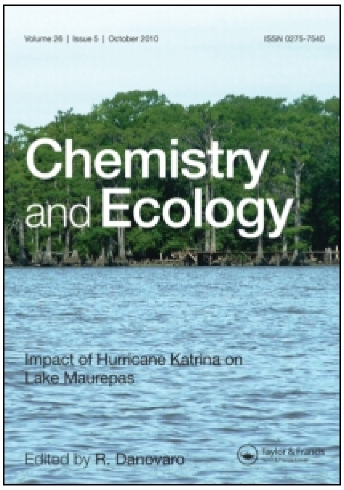

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PLANT UPTAKE OF TRACE METAL OXOIONS FROM TWO CONTRASTING ACID SOILS

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Uptake of arsenic, molybdenum, uranium and vanadium by species of natural vegetation (*Agrostis capillaris*, *Betula pendula*, *Calluna vulgaris*, and *Deschampsia flexuosa*) on two contrasting, highly acid soils (pH of soil solution 4.2–4.3), differing in natural abundance of these elements, was compared. The soil developed from alum shale was rich in these elements, the soil from a gneiss moraine was poor in these elements. Leaf/above ground biomass concentrations were positively related to soil concentrations of the elements, but least closely for uranium, and vanadium tended to be excluded by the plants, compared to arsenic, and especially to molybdenum. The relationships between soil and plant concentrations were broadly similar whether nitric acid-digestible or the much lower DTPA extractable soil fractions were considered. Leaf concentrations of plants from the shale and the gneiss soil, respectively, ranged 1.41–2.76 and 0.30–0.58 nmol g^{-1} dry weight for arsenic, 14–140 and 0.5–9.6 for molybdenum, 0.031–0.069 and 0.013–0.030 for uranium, 2.3–6.4 and 0.75–3.3 for vanadium.

Keywords: Arsenic; molybdenum; plant; uptake; uranium; vanadium

INTRODUCTION

Little is known about uptake of trace metal oxoions by natural – seminatural vegetation on very acid soils. Concentrations of these elements (As, Mo, U and V) are typically low. Most abundant is vanadium (2–3 micromol g^{-1} in the earth's crust), whereas arsenic (ca. 0.02 micromol g^{-1}), molybdenum and uranium (ca. 0.01 micromol g^{-1})

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are rare elements (Greenwood and Earnshaw, 1984). Higher natural concentrations of these elements, however, are found in some rocks, notably the partly biogenic alum shales. Being an essential micronutrient, most attention has been paid to the availability and chemical properties of soil molybdenum. The three other elements have mainly been studied in a context of anthropogenic pollution, largely under conditions deviating from the natural soil pools of these elements.

Except in the primary minerals, soil molybdenum and arsenic are present as oxoanions (molybdate and arsenate) with a high/fairly high affinity for positively charged constituents. In acid soils, oxides/hydroxides of iron and aluminium provide positively charged sorption sites for molybdenum, whereas molybdenum at high soil pH is thought to be associated with calcium (Sims, 1996). Soluble arsenic in well-drained soils is mainly the arsenate species ($HAsO_4^{2-}$, $H_2AsO_4^-$) and iron oxides/hydroxides are involved in arsenate adsorption (Sadiq, 1997). Arsenic and (to some extent) molybdenum have several properties resembling those of phosphorus. In particular arsenic, at elevated concentrations, may reduce uptake and metabolic activity of this macronutrient. Arsenic and molybdenum may also be incorporated into organic compounds synthesized by organisms. Some organisms are capable of converting inorganic arsenic to methylated arsines, and molybdenum is an important constituent of the enzymes nitrate reductase and nitrogenase.

On the contrary, uranium in secondary forms occurs in soils mainly as oxocations (UO^{2+}, UO_2^{2+}, UO_2OH^+). In soil solutions of a low pH, it would be present as uranium oxide. At a higher pH this ion forms negatively charged complexes with carbonate, which may be relatively mobile (Harmsen and DeHaan, 1980). It also forms complexes or chelates with negatively charged organic soil constituents. Exudation by organisms of some low-molecular weight organic acids, notably citric acid, may dissolve sorbed and precipitated uranium in the form of uranyl citrate in soils (Ebbs-Stephen *et al.*, 1998).

Vanadium mainly occurs as the vanadyl ion (VO^{2+}) in soils, though the anionic vanadate is known from natural waters and might also be found in some soils. The vanadyl ion is unusually stable and retains its identity throughout a wide variety of reactions, forming many complexes with humic acids and other organic compounds (McBride, 1978; Wehrli and Stumm, 1989; Branca *et al.*, 1990). In acid mineral soils, vanadyl oxide is partly associated with iron oxides and Fe–Mg minerals from which it is released by weathering and resorbed by, *e.g.*, clay minerals (Berrow *et al.*, 1978).

The objectives of this study are to compare soil concentrations and uptake of oxoion trace metals in natural vegetation on two contrasting, highly acid soils differing in chemical properties and natural abundance of these elements. It is hypothesized that uptake of these elements in above-ground biomass of four quantitively important vascular plant species is positively related both to total and extractable soil concentrations of these elements.

MATERIALS AND METHODS

The two soils/sites selected for the study were one natural podzol developed from Archaean-gneiss moraine, and one soil developed from Cambrian alum shale, deposited 150–350 years ago as heaps of finely crushed shale from early industrial alum production and spontaneously colonized by acidicolous native vegetation. Both are located in central Scania, south Sweden. The gneiss soil is low, the shale soil rather high in the oxoion metal elements considered. Both soils are highly acid, pH (0.1 M $BaCl_2$) of the gneiss soil being 3.6 ± 0.2, of the shale soil 3.7 ± 0.1, which corresponds to pH ca 4.2–4.3 in the soil solution. Organic matter content of the two soils differed, being $13.0 \pm 1.9\%$ in the gneiss soil and $7.2 \pm 0.5\%$ in the shale soil.

Soils (0–10 cm depth) and plant biomass were sampled in August 1999 using ten plots ($5\,m^2$) per site having all four species selected for the study in common. Every soil sample was made up of 3 subsamples, each $385\,cm^3$. About 20 g (fresh weight) of plant biomass was sampled in all plots: green leaves of *Agrostis capillaris* L., *Deschampsia flexuosa* (L.) Trin. and *Betula pendula* Roth (the latter from 0.5–1 m tall plants), and entire annual long shoots of *Calluna vulgaris* (L.) Hull. The four species were quantitatively important in the vegetation of both sites.

Soils were pretreated by shifting through a plastic net (mesh 6 mm) with careful mixing, material > 6 mm being discarded. Water content was determined gravimetrically (80°C) on a subsample, also used for determining organic matter % (loss on ignition 550°C, 2 h) and nitric acid digestible concentrations of metals. Extraction of 20 g soil at field moisture was performed with 100 ml 5 mM DTPA (20 min; filtration 10 min) for metal analysis, extraction of 10 g soil at field moisture with 50 ml 0.1 M barium chloride (1 h) for electrometric pH determination. Digestion of 0.5 g dried (80°C) and finely ground soil was carried out using 15 ml conc. nitric acid (3 d, ca. 80°C), followed by evaporation of excess acid to ca. 2 ml, and dilution (H_2O) to 25 ml, for metal analysis.

Biomass samples were pretreated in the following way: within 2.5 h of sampling, washed by vigorous shaking with water, 30 sec, and dried to constant weight at 60°C. Complete digestion of 1 g dried material was carried out using 20 ml conc. nitric acid, excess acid evaporated to ca. 2 ml, and samples diluted (H_2O) to 50 ml. Soil and plant extracts/digests were analysed for arsenic, molybdenum, uranium, and vanadium by ICP-MS (Perkin Elmer ELAN-6000), calibrated against standards prepared in the pertinent matrix. 'Nitric acid digestible' soil concentrations of 13 other elements were also determined by ICP-ES (Perkin Elmer Optima 3000 XL) or ICP-MS for characterization of the soils (Tab. I).

TABLE I Nitric acid digestible concentrations of elements, micromol (g dry weight)$^{-1}$, in the two soils studied; means ± S.E. ($n = 10$). Elements (Al, Ca, Fe, K, Mg, Mn, P, and S) were determined by ICP-ES, all other elements by ICP-MS

	Shale soil	*Gneiss soil*	*Ratio shale soil/gneiss soil*
Aluminium	1600 ± 110	285 ± 19	5.6
Arsenic	0.173 ± 0.019	0.029 ± 0.005	6.0
Calcium	16.6 ± 0.4	73 ± 5	0.23
Cobalt	0.150 ± 0.007	0.059 ± 0.007	2.5
Copper	1.48 ± 0.04	0.146 ± 0.016	10.1
Iron	890 ± 30	271 ± 16	3.3
Magnesium	66 ± 4	56 ± 7	1.2
Manganese	1.54 ± 0.06	5.4 ± 0.3	0.29
Molybdenum	0.95 ± 0.02	0.012 ± 0.001	79
Phosphorus	16.3 ± 0.6	12.3 ± 0.7	1.3
Potassium	460 ± 24	22 ± 2	21
Selenium	0.023 ± 0.002	0.005 ± 0.001	4.6
Sulphur	124 ± 14	12.2 ± 2.4	10.2
Thorium	0.049 ± 0.001	0.019 ± 0.003	2.6
Uranium	0.078 ± 0.003	0.003 ± 0.000	26
Vanadium	10.9 ± 0.5	0.63 ± 0.02	17.3
Zinc	0.89 ± 0.03	0.54 ± 0.02	1.6

Metals in both soils and plants were calculated as nanomol or micromol (g dry weight)$^{-1}$.

RESULTS

Nitric acid digestible concentrations of the elements considered were between 6 times (As) and 79 times (Mo) higher in the alum shale soil than in the gneiss soil (Tab. I). Several other elements were also higher in the shale soil, including aluminium, copper, potassium, selenium, and sulphur. Not much different were magnesium, phosphorus, and zinc, whereas calcium and manganese were lower in the shale soil. The fractions released from finely ground soils by hot concentrated nitric acid treatment is a substantial part of the total contents, though not really the total.

DTPA extractable concentrations were only a small fraction of the nitric acid digestible, the relatively largest proportion (ca. 1%) being released of arsenic (Fig. 1). The lowest proportion (0.1 – 0.3%) was released in molybdenum, the relative release of uranium and vanadium being intermediate. The DTPA release of molybdenum and uranium, calculated as % of the nitric acid digestible amount, tended to be higher in the alum shale than in the gneiss soil. However, an overall positive linear relationship, on a log–log basis, between soil concentrations measured by the two extraction methods is apparent.

Biomass concentrations of molybdenum were 13–29 times higher, according to species, in plants from the alum shale soil than in plants from the gneiss soil (Tab. II). Biomass concentrations of the other three elements were only 1 – 5 times those of plants from the gneiss soil. *A. capillaris* was particularly rich in molybdenum, leaves from the alum shale soil having a mean concentration of 140 nanomol (g dry weight)$^{-1}$ (or 13.4 ug g^{-1}). The highest concentrations of uranium and vanadium were measured in *C. vulgaris* from the shale soil, whereas *D. flexuosa* from the gneiss soil was particularly low in these elements.

The concentrations of all four elements in plant biomass were positively related to soil concentrations, both soils compared, irrespective of method of soil extraction. However, only for arsenic was the relative difference between soils in biomass concentrations similar

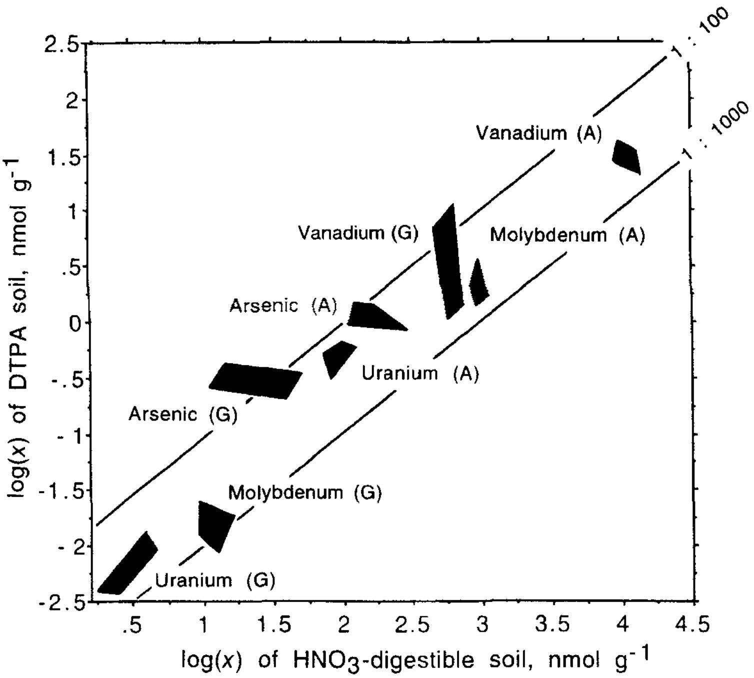

FIGURE 1 Relations (log–log transformed data) between DTPA extractable and nitric acid digestible concentrations of arsenic, molybdenum, uranium and vanadium in the alum shale (A) and the gneiss (G) soil. Variability of replicates ($n = 10$) indicated as black fields (outermost four replicates connected).

TABLE II Concentrations of arsenic, molybdenum, uranium and vanadium (nanomol g^{-1} dry weight; means ± S.E.; $n = 10$) in plants from the alum shale (A) and the gneiss (G) site, and the concentration ratio A/G

Species	*Soil*	*As*	*Mo*	*U*	*V*
A. capillaris	A	2.76 ± 0.81	140 ± 20	0.032 ± 0.003	2.3 ± 0.3
	G	0.58 ± 0.07	9.6 ± 0.5	0.030 ± 0.002	3.3 ± 0.3
B. pendula	A	1.45 ± 0.31	13.6 ± 4.0	0.031 ± 0.006	2.3 ± 0.4
	G	0.30 ± 0.02	0.48 ± 0.05	0.019 ± 0.001	1.5 ± 0.1
C. vulgaris	A	1.94 ± 0.12	29.5 ± 4.8	0.069 ± 0.015	6.4 ± 1.0
	G	0.55 ± 0.02	2.2 ± 0.5	0.018 ± 0.002	2.6 ± 0.5
D. flexuosa	A	1.41 ± 0.22	89 ± 8.4	0.035 ± 0.004	2.7 ± 0.4
	G	0.31 ± 0.04	3.1 ± 0.2	0.013 ± 0.001	0.75 ± 0.06
A. capillaris	A/G	4.8	14.6	1.1	0.7
B. pendula	A/G	4.8	28.3	1.6	2.2
C. vulgaris	A/G	1.7	13.4	3.8	2.5
D. flexuosa	A/G	4.5	28.7	2.7	3.6

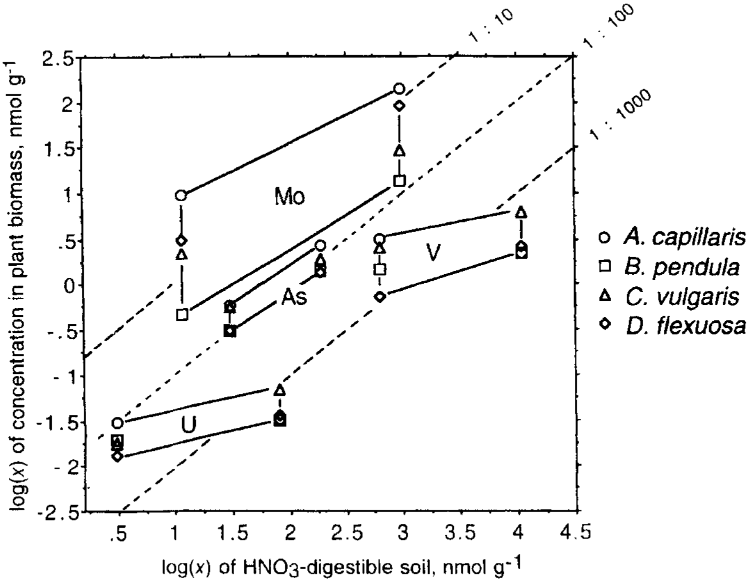

FIGURE 2 Relations (log–log transformed data) between mean concentrations of arsenic, molybdenum, uranium and vanadium in leaves/long shoots of the species studied and mean nitric acid digestible soil concentrations of the same elements.

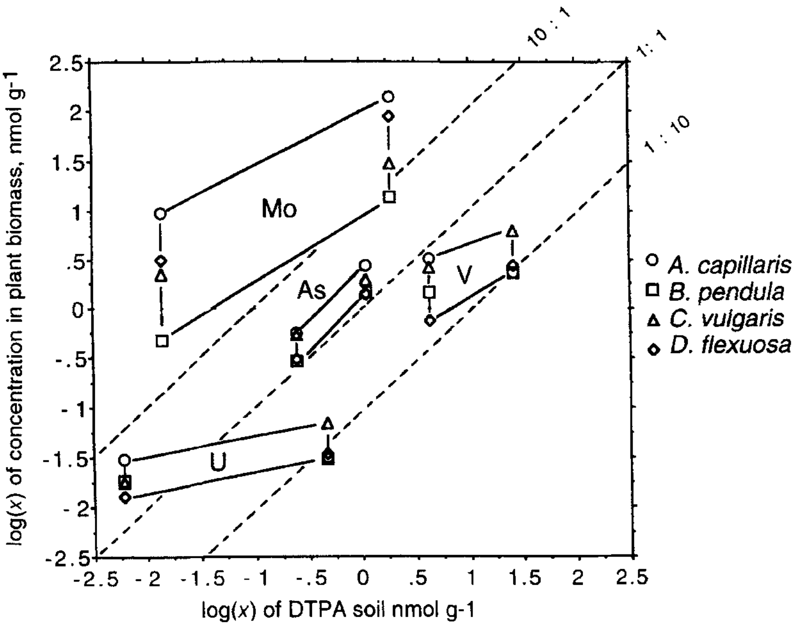

FIGURE 3 Relations (log–log transformed data) between mean concentrations of arsenic, molybdenum, uranium and vanadium in leaves/long shoots of the species studied and mean DTPA extractable soil concentrations of the same elements.

to the relative difference in soil concentrations (Figs. 2, 3). In the three other elements, especially uranium, differences in plant biomass concentration between soils did not amount to the difference in soil concentration. Compared to the two other elements, uranium and vanadium tended to be 'excluded' by the plants. Biomass concentrations of the essential micronutrient molybdenum were highest, compared to concentrations in both soils, whereas biomass concentrations of uranium were the lowest also in this comparison. The relative position of elements in Figures 2 and 3 are closely similar, thus being independent of soil fraction used in the comparisons.

DISCUSSION

Knowledge about availability and uptake mechanisms of these oxo-ionic elements in plants is limited. Availability to plants of molybdenum is highly dependent on soil pH, considered much lower under acid than under neutral or alkaline soil conditions and positively influenced by liming (Black, 1968; Dreesen *et al.*, 1982), whereas liming had no great effect on concentrations of arsenic in crops (Andersson and Siman, 1991). No specific uptake system of molybdenum is known for plants, but uptake of molybdate could be mediated unspecifically by one of the sulphate transporters (Zimmer and Mendel, 1999). Arsenate is considered a strongly competitive physiological analogue of phosphate in higher plants (Ullrich *et al.*, 1989) and is taken up by the same transport system as phosphate, at least in the grass *Holcus lanatus* and related species (Meharg and Macnair, 1991, 1992). Mechanisms controlling plant uptake and transport of the two other elements are little studied or unknown. Uptake of uranium seems competitively depressed by calcium (Mortvedt, 1994).

By far the lowest biomass concentrations were measured in uranium, ranging 0.031–0.069 nmol g^{-1} in plants from the shale soil and 0.013–0.030 nmol g^{-1} in plants from the gneiss soil. Reported values for crops (timothy, wheat straw and soybean leaves) ranged 0.08–0.21 nmol g^{-1} (Mortvedt, 1994), for beet leaves ca. 0.10–0.17 nmol g^{-1} (Tracy *et al.*, 1983). Reports on biomass concentrations of vanadium differ largely according to age of the report, old data usually being rather high and probably overestimations due to failing analytical technique. More recent findings usually range $1-10\,\text{nmol g}^{-1}$ dry weight, according to several studies. Mean concentrations reported for a large number of samples from Slovakia were ca. $4\,\text{nanomol g}^{-1}$ in 2 yr old needles of *Picea abies* and ca. $6\,\text{nmol g}^{-1}$ in leaves of *Fagus sylvatica* (Mankovska, 1997). Mean arsenic concentrations of the same materials were ca.3.0 and $3.6\,\text{nmol g}^{-1}$, respectively. These concentrations are slightly higher (in arsenic distinctly higher, compared to concentrations in plants from the gneiss soil) than those of the present study. Surface contamination from ambient air pollution in Slovakia might have contributed to some extent, as proposed by Mankovska (1997).

Molybdenum concentrations in biomass varied about one order of magnitude among plants from the same soil but differed even more between the soils. The two grass species (*A. capillaris* and *D. flexuosa*) were particularly rich in molybdenum, whereas *B. pendula* was low. High concentrations of molybdenum in wild-growing grasses, compared to other plants, were also reported by Markert and Haderlie (1996). Otherwise, leguminous plants are known to take up comparatively much molybdenum, and also to concentrate this in their seeds (Tyler and Zohlen, 1998), probably a function of the demand for molybdenum in the nitrogenase of their *Rhizobium*. Mechanisms accounting for the high molybdenum levels in grasses are less apparent but might be related to an efficient nitrate reductase system demanding this element.

CONCLUSIONS

Oxoion trace metal concentrations in leaves/long shoots of four species studied were higher in plants from the alum shale soil, which was relatively richer in these elements, than in plants from the gneiss soil. Whether plant concentrations were compared with the nitric acid digestible or the much lower DTPA extractable soil fractions of the elements was of little importance to these relationships. Least flexible compared to soil concentrations were plant concentrations of uranium, an element which tended to be excluded from uptake.

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