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As and Se in soils and plants from abandoned mining areas of the Salamanca province, Spain

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Abstract

Four mining zones were chosen for this study. The Morille, Montejo and Saucelle mining zones which produce tin and tungsten ores with sulphides hosted in shales. The Cabaco mining zone which produces tungsten ore with pyrite and arsenopyrite hosted in granites.

In the Salamanca province, the arsenic background is less than 10 ppm in soils formed from granite and shales. Anomalous soils contain more than 10 ppm and range from 10 to > 1000 ppm, due to arsenopyrite alteration in mining areas.

High and very high arsenic content in plants (99–40669 ppb, some of them probably phytotoxic) were collected in these mining zones.

The arsenic content in *Vulpia bromoides* (L) SF Gray, show a correlation with the arsenic content in the soils; nevertheless for *Agrostis castellana* Bois & Rent, other pedological factors (such as pH) must have a greater effect than the arsenic content in the soil.

Dactylis glomerata L. has a higher degree of arsenic accumulation than *Ag. castellana* and *Cynosurus echinatus* L. in the same As-anomalous soil.

On the other hand, the selenium contents in plants are low, with most of the data showing values lower than 50 ppb (which is considered to be deficient for animal nutrition) and ranging from 2 to 260. These values are in agreement with other data obtained previously in the Salamanca province. *V. bromoides* contain higher selenium levels than *Ag. castellana* in most of the soils studied.

Introduction

There are about 200 occurrences of mineralized zones in the Salamanca province, Spain, most of which are mined and smelted until very recently. Sn and W in arsenical ores, mainly arsenopyrite, are the most occurring minerals. The mining activities in these zones have led to contamination of the agricultural land, with total soil As values as high as 1000–2000 ppm due to weathering of Arsenopyrite to Scorodite. In contrast, the average soil concentration of As worldwide, is 6 ppm, with a typical range of 0.1 to 40 ppm (Bowen, 1979).

Once Arsenopyrite oxidation ceases, scorodite dissolves incongruently to iron hydroxide and arsenate ion solutions (Dove & Rimstidt, 1985). Pasture herbage growing in contaminated soils in Cornwall (UK) contained up to five times more As than herbage from control sites elsewhere (Davies, 1980). In general, the amounts of As in grass increase with increasing As content in the soil, but the As uptake by plants is greatly dependent on other pedological factors (pH, OM, clay content, Fe and Mn oxides content, etc.).

Plant toxicity due to As is often reached prior to the accumulation of toxic levels for the wildlife which ingest the plants (Tamaki & Frankenberger, 1992). However, some individual plant species on high As soil have shown to accumulate As to extreme levels which could cause physiological disfunctions or poisoning in grazing livestock. Also, the poisoning could be caused by ingestion of As-rich soils or mine waste.

Selenium behaves in on of two ways depending on its concentration and chemical form. Selenium can be an essential element or a toxin to plants, livestock and

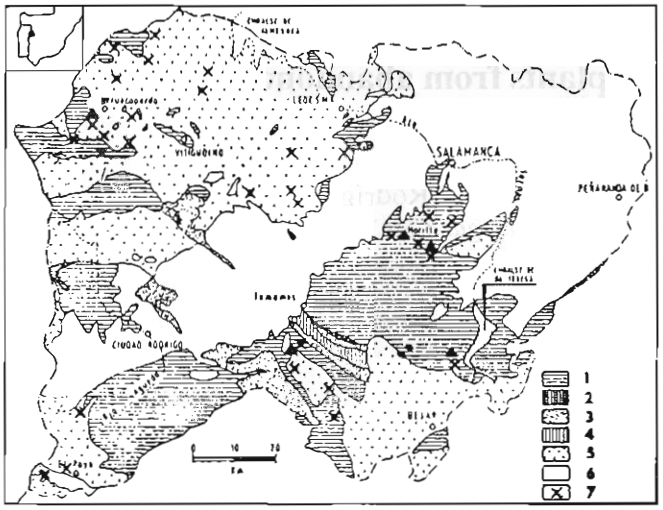

Fig. 1. Study areas (triangles) in the Salamanca province and geological sketch (Carcía Sánchez *et al.*, 1980). 1 – Schists grau wake complex (Precambric-cambric. 2 – Limestones (Cambric). 3 – Quarzites (Arenig). 4 – Shales. 5 – Granites. 6 – Terciary Cover. 7 – As anomalies.

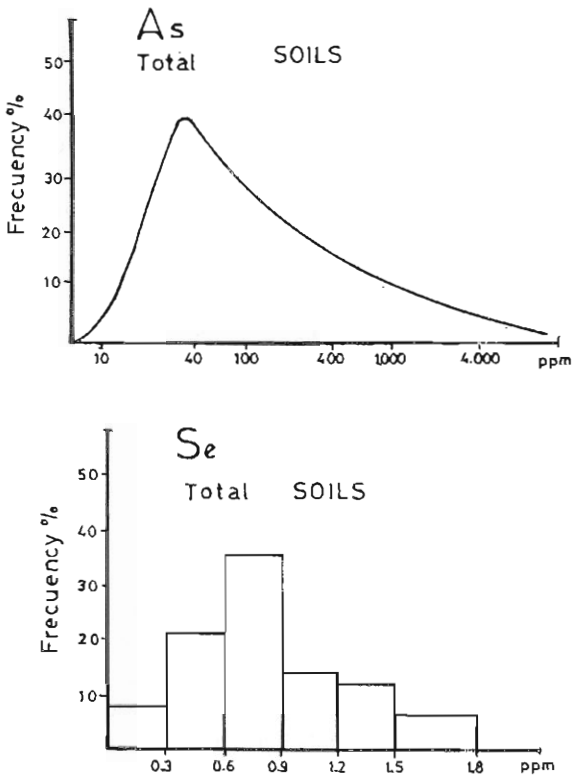

Fig. 2. Frequency distribution of As and Se contents in soils.

humans. Selenium toxicity in livestock is known in a few areas around the world, but Se deficiency has turned out to be much more common than Se toxicity.

The desirable Se level in forages and cereals is > 50 ppb (Gissel-Nielsen *et al.*, 1984) and to avoid symptoms of deficiency, Se levels in grain and ley vegetation should be > 100 ppb, (Frank *et al.*, 1986). More than 450 ppb Se is the minimum concentration required in soils if feed crops are to provide animals with adequate amounts of Se (Whatkinson, 1963). Although the Se concentration in most soils is not specially low, on neutral to acid mineral-soils with relatively high contents of Fe and O.M., it is fixed strongly in the soil making its availability to plants very low.

Material and methods

Soils were sampled from 0–15 cm topsoil, from the following topologies: *district cambisol*, *humic cambisol*, *district leptosol*, *humic leptosol* with the selected characteristics as shown in Table 1. The situation of samples are given in Fig. 1

The plants were sampled in June 1994 and the following species were selected: *Aira cariophyllea*, *Agrostis castellana*, *Bromus mollis*, *Cynosurus echinatus*, *Dactylis glomerata*, *Taeniatherum caput-medusae*, *Hordeum murinum*, *Senecio jacobaea*, *Vulpia bromoides*.

Table 1.

Sample N°	Coarse Sand %	Fine Sand %	Silt %	Clay %	pH	C %	O.M. %
28598	21.5	31.5	28.5	15.9	5.54	2.03	3.49
28599	25.0	34.5	21.3	15.5	5.75	1.81	3.12
28600	19.0	38.0	21.5	13.1	5.57	2.96	5.10
28601	24.5	26.0	21.0	20.3	5.14	2.81	4.85
28602	16.5	42.0	23.9	11.8	4.97	3.15	5.43
28603	14.0	50.5	13.5	19.4	4.94	1.76	3.03
28604	17.0	58.0	9.5	13.8	5.80	0.64	1.10
28605	22.5	40.5	12.5	18.5	4.43	2.51	4.83
28606	32.0	51.5	6.5	9.2	5.02	0.75	1.29
28607	22.5	49.5	12.2	10.8	5.13	0.51	0.87
28608	33.5	48.0	4.6	15.0	5.87	0.45	0.78
28609	12.0	63.0	10.7	13.4	5.20	2.93	5.04
28610	7.5	64.5	12.3	11.0	4.11	1.97	3.40
28611	26.5	56.5	6.6	11.4	6.67	0.32	0.55
28612	63.0	22.5	6.8	9.2	5.39	1.09	1.87
28613	19.5	60.0	8.7	8.2	5.15	0.47	0.81
28614	35.5	32.5	14.3	13.4	6.08	1.59	2.74

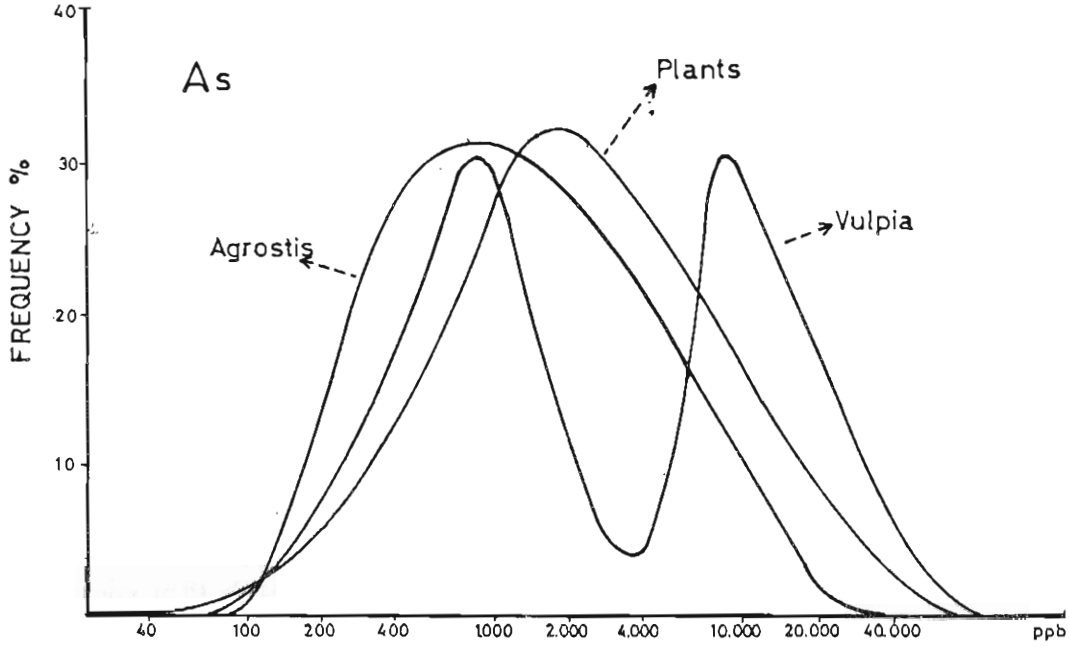

Fig. 3. Frequency distributions of As in plants (all species pooled), Vulpia and Agrostis.

Chemical analysis

Arsenic and Se in plants, and Se in soils were determined by hidride generation and AA spectrophotometry in a flow system (FIA, HG-AAS) and a standard addition method. The detection limits were: 0.8 ppb for As and 1 ppb for Se. As in soil was determined by

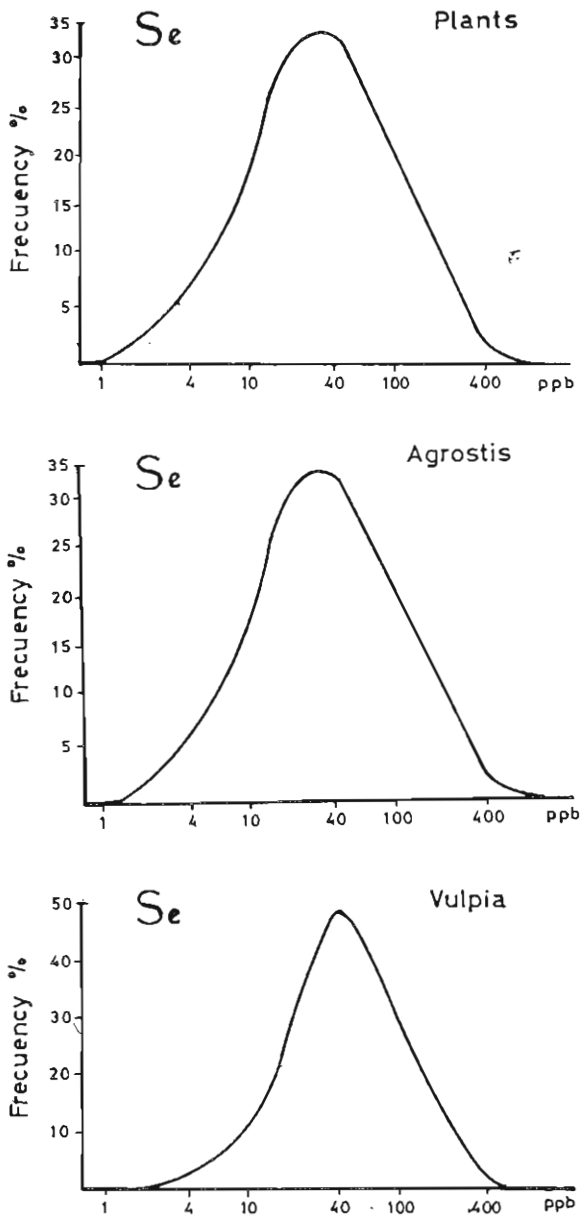

Fig. 4. Frequency distributions of Se in plants.

X-ray fluorescence spectrometry. The detection limit was 5 ppm.

Results

The chemical analysis of soils and plants are presented as histograms in Figs. 2, 3 and 4.

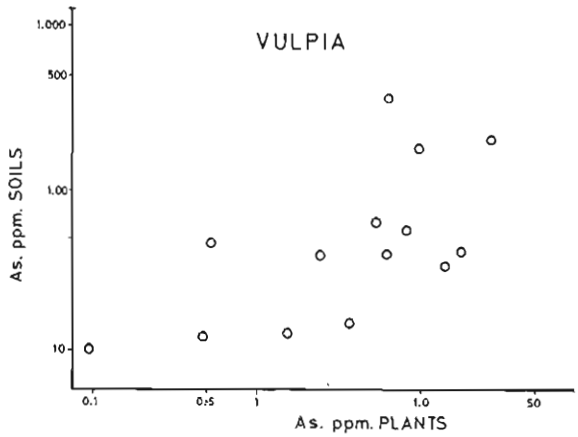

Fig. 5. Correlation between total As in soils with plant As.

Discussion

The total As ranges in herbage are very wide (99–40699 ppb). *Agrostis* shows a distribution lognormal with mode around 1000 ppb, and in *Vulpia* is bimodal with modes of 1000 and 10000 ppb. For some plants the As contents are probably phytotoxic (Sheppard, 1992) and thus act in protecting livestock. The As contents in herbage are similar to those in other mining zones, e.g. Cornwall (Davies, 1980).

Only *Vulpia* shows some correlation between its As contents and total As concentrations in soils (Fig. 5).

Soil pH seems to act as a regulator of As accumulation in *Agrostis* (Fig. 6), although the correlation is rather poor.

The degree of As accumulation in plants occurs in the following sequence: *Aira* > *Cynosurus* > *Elymus* > *Dactylis* > *Vulpia* > *Senecio* > *Agrostis*.

Physiological disfunctions in livestock may be due to ingestion of As-rich soil or mine waste more than to the amounts of As in the herbage.

The variation in the range of Se contents in plants is narrow (2–260 ppb) with a lognormal distribution and modes around 30–40 ppb. These values are too low to be considered deficient for animal nutrition (Frank *et al.*, 1986). The findings for the Se contents are similar to other previous data collected for the Salamanca province (Montalvo *et al.*, 1983) and corresponds to the data obtained for wheat and maize in thirty countries as reported by Sillanpää & Jansson, (1992).

The degree of Se uptake in the studied plants occurs in the following sequence: *Vulpia* > *Elymus* = *Agrostis* > *Senecio* > *Cynosurus*

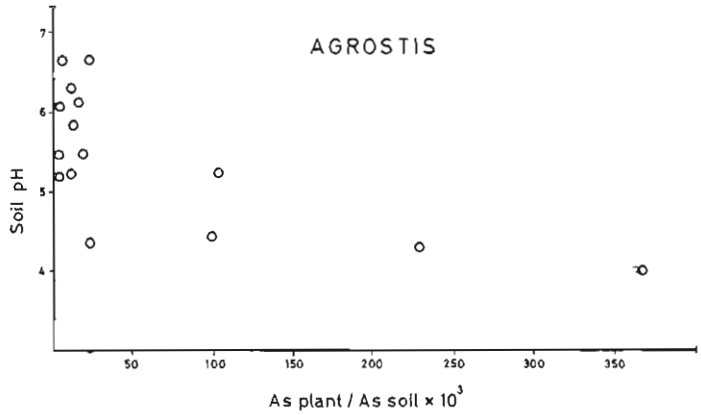

Fig. 6. Correlation between soil pH with As accumulation degree in Agrostis.

Senecio *jacobaea* shows the following distribution in the different organs:

Se: leaves > flowers > roots > branches

As: leaves > roots > flowers > branches

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