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# Elevated Lead and Zinc Contents in Remote Alpine Soils of the Swiss National Park

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#### ABSTRACT

Weathering of bedrock and pedogenic processes can result in elevated heavy metal concentrations in the soil. Small-scale variations in bedrock composition can therefore cause local variations in the metal content of the soil. Such a case was found in the remote alpine area of the Swiss National Park. Soil profiles were sampled at an altitude of about 2400 m, representing soils developed above different bedrocks. The concentration of lead in the profiles was found to be strongly dependent on the metal content in the bedrock underlying the soil and was strongly enriched in the top 10 cm. The dolomitic bedrock in the study area contains elevated lead concentrations compared with other dolomites. Dissolution of dolomite and accumulation of weathering residues during soil formation resulted in high lead concentrations throughout the soil profile. The enrichment of lead in the topsoil, however, is largely attributed to atmospheric input. The isotopic signature of the lead clearly indicates that it is mainly of natural origin and that atmospheric deposition of anthropogenic lead contributed to about 20 to 40% to the lead concentration in the topsoil on the bedrock with elevated lead concentrations. In the soils on bedrock with normal lead concentrations, the anthropogenic contribution is estimated to be about 75%. Also, zinc was very strongly enriched in the topsoil. This enrichment was closely correlated with the organic matter distribution in the profiles, suggesting that recycling through plant uptake and litter deposition was a dominant process in the long-term retention of this metal in the soil.

The major external source of heavy metals in soils is usually pollution caused by anthropogenic activities, such as metal mining, smelting, and processing. Additionally, diffuse pollution by wet and dry deposition has resulted in the long-term accumulation of heavy metals all over the world, for example in Greenland ice (Rosman et al., 1993), Scandinavian soils (Bindler et al., 1999; Rosman et al., 1998), or peat bogs (Weiss et al., 1999). While this is true for most contaminated soils, some high metal concentrations in soils are of natural origin, resulting from weathering of the underlying bed-

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rock. Soils in the Mendip region in Great Britain, for example, are highly enriched in lead, zinc, and cadmium due to the high concentrations of these metals in the bedrock and the presence of mineralized veins (Fuge et al., 1991). This area has a long history of mining and smelting. Soils developed on serpentinite are highly enriched in nickel and chromium and sustain a specialized plant community composed of Ni-tolerant species (Proctor and Baker, 1994). These soils are restricted to small areas and are easily recognized by their special plant community.

Weathering of bedrock with only slightly elevated metal concentrations may result in an enrichment of metals by pedogenic processes (Fleige and Hindel, 1987; Blaser et al., 2000). Therefore, soils in areas that are not known to have elevated metal concentrations in the bedrock may also show naturally elevated metal concentrations.

In the course of the implementation of the Swiss National Soil Monitoring Network, unexpectedly high HNO<sub>3</sub>-extractable lead concentrations of up to 140 mg kg<sup>-1</sup> were found in the topsoil of a remote site (Munt la Schera) in the Swiss National Park at an altitude of 2400 m above sea level, far away from industry and major traffic routes (Federal Office of Environment, Forests and Landscape, 1993). These high contents fall far outside the normal ranges given in the literature for lead in soils not exposed to direct air pollution, for example 10 to 30 mg kg<sup>-1</sup> (Alloway, 1990) or 2 to 60 mg kg<sup>-1</sup> (Scheffer and Schachtschabel, 1992). They clearly exceed the guide value of 50 mg  $kg^{-1}$  for lead given by the Swiss Ordinance Relating on Burdens in Soil (Schweizerischer Bundesrat, 1998). In addition, the zinc concentrations at the Munt la Schera site, averaging around 100 mg kg<sup>-1</sup> in the topsoil, are beyond the normal range for unpolluted soils.

Given the remote location of the Swiss National Park, which had been kept free from direct human impacts, except for hiking on a few trails since the beginning of the century, speculations were raised that the high metal contents may have resulted from the deposition of aerosols originating from the industrial centers of Northern Italy (Scheurer et al., 1993). Investigations of Steinnes et al. (1989) in southern Norway showed that atmospheric long-distance transport may indeed lead to heavy metal pollution of areas located far away from large industrial

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and urban centers. The lead concentrations in the topsoil observed in these two areas is similar in extent to that observed in the Swiss National Park.

However, if long-range transported air pollution were the primary source of the lead found in the topsoil, the spatial variation of this metal should not depend on the type of bedrock. To check the hypothesis about the origin of the high lead concentrations at the Munt la Schera, we analyzed the distribution of lead in soil profiles at locations with similar exposure to climatic and edaphic factors on three different bedrock formations. In addition, the isotopic composition of the lead was analyzed at one site. Soil contamination by anthropogenic lead generally can be recognized by a shift of the Pb isotope ratios towards less radiogenic values from unpolluted to polluted parts of the soil (Chow et al., 1975; Bacon et al., 1996).

### **MATERIALS AND METHODS**

#### **Sampling Sites**

The study area is situated on the southern aspect of the Munt La Schera, a mountain south of the Pass dal Fuorn





crossing the Swiss National Park. The Munt La Schera belongs to the inner alpine chains in the southeastern part of Switzerland, characterized by the East Alpine Sediments. On the basis of the geological map of Dössegger (1987) we chose three pairs of sampling sites. Each pair of sites represented one of the following stratigraphical members of the Engadine Dolomites from the Trias as described by Dössegger and Müller (1976): Raibl rauhwacke, Vallatscha dolomite, and Fuorn sandstone. Figure 1 shows the geological situation of the area with the six sampling sites marked in the Fuorn, Raibl, and Vallatscha formation. All sampling sites were within a distance of 1 km of each other on south-facing slopes of comparable inclination at altitudes between 2300 and 2450 m above sea level. With respect to the local relief, one profile of each pair was situated at a slight elevation (topographical convexity) and the other in a slight depression (topographical concavity). The vegetation of the study area consists of a sedgedominated alpine turf (plant community: caricetum firmae; Campell and Trepp, 1968). The yearly precipitation is about 1000 mm, the average temperature -0.2°C (Fries, 1985).

#### Soil Sampling and Analysis

In order to comply with the National Park regulations, disturbances had to be kept at a minimum. An additional constraint was that all material had to be carried by backpack to the next access road, which severely restricted the sample weights. All profiles were sampled in a single campaign within 2 d under dry weather conditions. At each sampling location, soil samples were taken at depth intervals of 0 to 5 and 5 to 10 cm, and below that at 10-cm intervals down to the bedrock, from which a sample was also taken. No organic horizons were present in the sampled profiles, except for the Fuorn 2 profile, which had a very thin (<2 cm) and discontinuing organic toplayer. All samples were taken within the mineral horizons, the organic layer of the Fuorn 2 profile was not sampled. The term topsoil is used here for the uppermost mineral horizon characterized by accumulated organic matter (A horizon). The profile pits were refilled immediately after sampling. In the laboratory, soil samples were dried at 40°C for 48 h and then passed through a 2-mm nylon sieve. Rock samples were first ground using an agate disk mill and then dried for 90 min at 100°C.

The HNO<sub>3</sub>-extractable heavy metals, designated as total heavy metal concentration, were determined by digesting 5-g subsamples in 50 mL of 2 M HNO<sub>3</sub> for 2 h at 100°C, following the procedure used by the Swiss National Soil Monitoring Network (Federal Office of Environment, Forests and Landscape, 1987). The extracts were analyzed by flame atomic absorption spectroscopy (AAS). Each of these extractions and analyses were performed in duplicate. Soil samples from a round robin test (Swiss Federal Research Station for Agroecology and Agriculture, 1989a) were included and an agreement with the certified values for lead within 15% was found. The standard deviation for three samples with 7 to 13 measurements was between 7 and 10%.

Ammonium-acetate/EDTA-extractable heavy metal concentrations of the two Vallatscha and the two Raibl profiles were determined using the method of Lakanen and Erviö (1971). Triplicate extracts of each sample were prepared by shaking subsamples suspended in a solution of 0.5 M NH<sub>4</sub>acetate and 0.02 M EDTA for 1 h at 20°C and then analyzed by inductively coupled plasma (ICP) spectrometry.

Soil pH was measured in  $0.01 M \text{ CaCl}_2$  at a soil to solution ratio of 10 g per 25 mL. Carbonate contents were determined using the pressure calcimeter method of the Swiss Agricultural Research Stations (Swiss Federal Research Station for Agro-

	Situation	Soil ty	pe by	Lithic contact (depth to bedrock)	Type of bedrock
Site		U.S. classification (Soil Survey Staff, 1997)	FAO classification (FAO-UNESCO, 1990)		
				m	
Fuorn 1	local elevation	Typic Cryopsamment	Umbric Regosol	0.7	sandstone
Fuorn 2	local depression	Typic Cryumbrept	Umbric Regosol	0.6	sandstone
Raibl 1	local elevation	Cryic Rendoll	Calcaric Regosol	>0.8	rauhwacke
Raibl 2	local depression	Lithic Crypsamment	Rendzic Leptosol	0.2-0.4	rauhwacke
Vallatscha 1	local elevation	Lithic Cryoorthent	Rendzic Leptosol	0.2	dolomite
Vallatscha 2	local depression	Typic Cryorthent	Dystric Regosol	0.5	dolomite

Table 1.	Soil	types	of the	six	study	sites.
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ecology and Agriculture, 1989b). Organic carbon contents were determined according to the Walkley–Black dichromate procedure (Nelson and Sommers, 1982).

In addition to the other analyses, lead was separated by a cation exchange procedure from aliquots of the HNO<sub>3</sub> extracts of the Vallatscha 2 profile and the isotopic composition determined by thermal ionization mass spectrometry (TIMS). The analytical details are given by Hansmann and Köppel (2000).

#### **Plant Sampling and Analysis**

At each site, plants were collected at two areas of  $0.25 \text{ m}^2$  close to the profile pit. All plants were cut above the soil surface and collected without distinction between dead and living material. The plants were dried for 72 h at 40°C and weighed. They were milled in a tungsten-carbide disk mill. Plant material (200 mg) was digested in a microwave with 3 mL HNO<sub>3</sub> and 1 mL H<sub>2</sub>O<sub>2</sub>. Zinc was measured by flame atomic absorption spectroscopy and Pb by graphite tube (GT)–AAS. Each sample was digested in duplicate.

#### RESULTS

The soil profiles of the study area exhibited considerable morphological differences not only between but also within the three geological units (Table 1). The texture was loamy sand or sandy loam in the profiles Fuorn 1 and Raibl 2, but was silt loam in the other four profiles. At the time of sampling, the two Fuorn soils were found to be clearly drier than the other profiles.

As shown by Fig. 2, the fine earth of the two Fuorn sites and Vallatscha 2 was carbonate free and had a pH of 4.0 to 4.5 (Fuorn 2) and 5.5 to 6.5 (Fuorn 1, Vallatscha 2). The two Raibl profiles and Vallatscha 1 were characterized by a high carbonate content and a pH of 7.5, with a general increase with depth. A sharp decrease in the carbonate content toward the topsoil can be observed for these three soils. The organic carbon content in the topsoil was varying between 8 and 10%. The differences in soil properties reflect the variations of the parent material and the relief depending factors of soil formation (e.g., different snowcover and snowmelt, erosion, and accumulation) within a few hundred meters.

The Raibl 1 profile contains elevated organic matter concentrations at the 40- to 50-cm depth. This corresponds to a darker color observed at this depth in the profile. This layer is very likely the original surface of a buried soil. The profile Vallatscha 2 was situated in a slight depression. It has a very thick topsoil of about 30 cm, which is much thicker than all other profiles, where the topsoils are about 10 cm thick. This profile is most likely characterized by an accumulation of eroded topsoil in the depression.



Fig. 2. pH, carbonate, and organic matter content of the six profiles.

	Bed	rock	Plants	
Site	Pb	Zn	Pb	Zn
	mg kg <sup>-1</sup>			
Fuorn 1	12.0	7.2	3.6	59.6
Fuorn 2	5.0	2.3	2.5	44.8
Raibl 1	36.0	9.6	2.5	32.6
Raibl 2	35.9	9.6	3.0	26.8
Vallatscha 1	35.8	17.3	5.2	30.3
Vallatscha 2	nd†	nd	1.2	47.4

 

 Table 2. Mean concentrations of Pb and Zn in the bedrock and in plants collected at the sites.

#### † nd, not determined.

Table 2 gives the results of the chemical analysis of the bedrock samples. The measured  $HNO_3$ -extractable lead concentrations of the Raibl rauhwacke and the Vallatscha dolomite bedrock samples were consistent at 36 mg kg<sup>-1</sup>, which is five to seven times higher than average values given by Tuchschmid (1995) for Swiss rauhwacke and dolomite, while the zinc concentrations were in the normal range of the two rock types (10–17 mg kg<sup>-1</sup>). The lead and zinc concentrations of the Fuorn samples were both low and were within the range of values given by Tuchschmid (1995) for sandstone formations in Switzerland.

The total lead concentrations of the soil samples varied according to lead concentrations of the bedrock samples (Fig. 3). Soils developed on Fuorn sandstone with 5 to 12 mg kg<sup>-1</sup> lead had much lower lead concentrations through the whole profile than the soils developed on dolomite (Raibl, Vallatscha) with about 36 mg kg<sup>-1</sup> lead. This not only applied to the subsoil, which shows a good consistency between bedrock and soil content, but also for the topsoil. The maximum lead concentration found in this study (76 mg kg<sup>-1</sup>) does not reach the reported maximum of 140 mg kg<sup>-1</sup> for this area (Federal Office of Environment, Forests and Landscape, 1993). The zinc concentrations did not show a large variation between the six sampling sites (Fig. 4).

Both metals were enriched at the surface as compared with the soil beneath. The lead concentration at the 5-cm depth is between 9 and 22 mg kg<sup>-1</sup> higher than in the 10- to 20-cm depth. Only the profile Vallatscha 2, characterized by the much deeper topsoil, contains 33 mg kg<sup>-1</sup> more lead in the topsoil. Zinc was even



Fig. 3. Comparison of the lead content of the bedrock and of the soil at the 10- to 20-cm depth.

more strongly enriched than lead in the topmost 5 cm of all profiles. Below the surface layer, the concentrations tended to decrease rapidly to background levels. In the Raibl 1 profile, a slight enrichment of zinc between 30 and 60 cm was observed, accompanied by a similar pattern of organic carbon content. There is a strong positive correlation between the total zinc concentration and the organic carbon content (Fig. 5). The  $R^2$  value for all six profiles is 0.79.

Much lower lead concentrations were extracted by ammonium-acetate/EDTA than by the HNO<sub>3</sub> procedure (Fig. 4). The ammonium-acetate/EDTA procedure generally yielded less than 10% of the HNO<sub>3</sub>-extractable lead, except for the profile Vallatscha 2, where it consistently exceeded 15% and reached up to 26%. Relative to the soil below, ammonium-acetate/EDTAextractable lead was more strongly enriched at the soil surface than HNO<sub>3</sub>-extractable lead. Furthermore, higher ammonium-acetate/EDTA-extractable lead was found in the subsoil between the 20- and 60-cm depth of the Raibl 1 profile, accompanied by increased zinc concentrations. Apart from the relative enrichments, the concentration profiles of ammonium-acetate/EDTAextractable lead were comparable in shape with the HNO<sub>3</sub>-extractable concentration profiles.

Table 2 shows the results of the chemical analysis of the plants collected at the six sites. The values for lead are in the range from 1.2 to 5.2 mg g<sup>-1</sup>, for zinc from 27 to 60 mg g<sup>-1</sup>. We found neither a correlation between lead and zinc in the topsoil and in the plants ( $R^2 = 0.054$  and 0.080, respectively), nor between ammonium-acetate/EDTA-extractable and plant lead ( $R^2 = 0.0005$ ).

The results of the lead isotope analyses of the Vallatscha 2 profile are given in Table 3. The lead isotopic ratios show weak trends toward more radiogenic compositions from the topsoil to a depth of 20 cm.

#### DISCUSSION

The results demonstrate a considerable spatial variability of lead and zinc concentrations in the soils of the study area. This variability was not restricted to metal concentrations in the subsoil, but was also found to a similar extent in the topsoil. The differences of the heavy metal concentration profiles of the six soils were clearly related to the geological parent material and not to the local topography. As there was also no indication for different exposure of the sampling sites toward atmospheric deposition, we conclude that parent material was the principal factor for this variability. Lead-zinc mineralizations in Mid-Triassic dolomites are known in this area (Kellerhals, 1962) and thus origin from weakly mineralized bedrocks could explain the lead enrichment in the soils. The low plant availability of lead and the absence of any correlation between soil and plant lead content at the study site is typical for the lithogenic origin of this metal (Filipinski, 1989).

The bedrock under the two Fuorn soils has very low carbonate content whereas under the other soils it is composed of dolomite. The carbonate content decreases from the bedrock to the topsoil because of dolomite



Fig. 4. Total lead, ammonium-acetate/EDTA-extractable lead, and total zinc of the six profiles.

weathering. Dissolution of the carbonate has enriched the insoluble fraction with the bound heavy metals (Fleige and Hindel, 1987; Filipinski and Grupe, 1990). This process should result in an even distribution of the metal through the soil profile (Filipinski, 1989; Filipinski and Grupe, 1990).

The soils of our study contain between 9 and 22 mg kg<sup>-1</sup> more lead in the top 5 cm than in the 10- to 20-cm depth irrespective of the varying total amount of lead in the soil. Assuming that this increase in lead concentration is caused by atmospheric input of anthropogenic lead that is concentrated in the top 10 cm, a lead input of 0.7 to 1.8 g m<sup>-2</sup> can be calculated for the profiles of our study. Shotyk et al. (2000) report a cumulative anthropogenic lead input of 1.1 g m<sup>-2</sup> for a peat bog located about 30 km to the southwest of our study area at an altitude of 1800 m. This value compares very well with our estimate. The anthropogenic fraction of lead in the topsoils of our study area is therefore between



Fig. 5. Relationship between the zinc concentration and the organic matter content of all samples from the six study sites.

20 and 75% of total lead. Anthropogenic lead has the largest influence on the two Fuorn profiles (about 75%), which have low lead concentrations in the subsoil, and the lowest influence on the Raibl and Vallatscha profiles, which have high lead concentrations in the subsoil.

Soils of the Swiss lowlands, which are contaminated by lead from anthropogenic sources, contain about 20 to 30 mg kg<sup>-1</sup> more lead in the top 10 cm than in the subsoil (Blaser and Zimmermann, 1993). This additional lead in the topsoil is almost entirely extractable by ammonium-acetate/EDTA, whereas the lithogenic lead in the subsoil is characterized by a low extractability by ammonium-acetate/EDTA (Blaser and Zimmermann, 1993). The soils in our study area contain between 4 and 16 mg kg<sup>-1</sup> more ammonium-acetate/EDTA-extractable lead in the top 10 cm than in the 10- to 20-cm depth. This value compares again very well with the before-mentioned increase of 9 to 22 mg kg<sup>-1</sup> total lead, which can be attributed to atmospheric input.

This result is further supported by the analysis of the lead isotopes. The lead isotopic ratios (Table 3) from the samples of the upper part of the Vallatscha 2 profile show similar trends, which are indicative of contamination. On a three-isotope diagram (<sup>206</sup>Pb/<sup>204</sup>Pb vs. <sup>208</sup>Pb/<sup>204</sup>Pb), the isotopic data of this profile (filled circles) fall into one group well separated from other lead signatures (Fig. 6). They fall into the area of lead isotopic signature

Table 3. Lead isotopic ratios of the profile Vallatscha 2.

	1	1		
Depth	Concentration	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>204</sup> Pb	<sup>206</sup> Pb/ <sup>207</sup> Pb
cm	mg kg <sup>-1</sup>			
0-5	68.2	18.936	38.465	1.207
5-10	56.6	19.067	38.535	1.215
10-20	35.2	19.117	38.543	1.218
20-30	31.9	19.453	38.650	1.238
30-40	26.9	19.379	38.678	1.233
40-50	23.0	19.347	38.669	1.232

Pb/Zn ratio



Fig. 6. <sup>208</sup>Pb/<sup>204</sup>Pb versus <sup>206</sup>Pb/<sup>204</sup>Pb diagram showing the data of profile Vallatscha 2 (filled circles) and some potential anthropogenic pollutants. The data of pollutants represented by squares are from Hansmann and Köppel (2000) and from Grousset et al. (1994). The fields for Triassic galenas and sediments are based on data of Köppel and Schroll (1985). The line labeled SK represents the terrestrial lead evolution curve of Stacey and Kramers (1975).

of Triassic sediments from the Eastern Alps (Köppel and Schroll, 1985). Saharan dust (Grousset et al., 1994) might also be a possible contaminant at this site. However, due to the low lead content of only 7 mg kg<sup>-1</sup> in the Saharan dust, the observed lead enrichment in the topsoil of this profile cannot be explained by air fall deposition of Saharan dust.

It can be postulated that the lead in the topsoil of the Vallatscha 2 profile is composed of a three-component mixture of 40% lead from background material, 20% from Triassic mineralized material (e.g., galena) and 40% of the long-term integrated aerosol ISA-20 (Hansmann and Köppel, 2000). The 40% anthropogenic contribution would correspond to a deposition of 2.05 g m<sup>-2</sup> lead. The use of ISA-20 (integrated Swiss aerosol of the 20th century) for the lead pollution ratio may underestimate the anthropogenic contribution since it does not include pre-1900 emissions. Taking into account also this contribution, the lead isotopic composition would be slightly more radiogenic than ISA-20. This would result in a higher calculated percentage of anthropogenic lead in the topsoil.

It has been argued previously that the observed lead enrichment in the Swiss National Park could result from air-borne lead from the industrial and urban centers of the Po plain in Northern Italy (Scheurer et al., 1993). Our study shows that only the increase in the lead concentration in the topsoil is anthropogenic, whereas the high concentrations in the subsoil of the Vallatscha and Raibl profiles cannot be attributed to anthropogenic lead input.

On all three bedrocks, the soils are also characterized by significant zinc enrichment in the topsoil, although the zinc concentrations of the bedrock itself are not elevated. Such a behavior of a heavy metal has usually been attributed to an aerosol-derived anthropogenic input (Filipinski, 1989; Filipinski and Grupe, 1990), but was not found for zinc in Swiss soils in industrialized areas (Federal Office of Environment, Forests and



Fig. 7. Lead to zinc ratio of the Raibl and Vallatscha profiles as a function of organic matter content.

Landscape, 1993). It is therefore unlikely that anthropogenic input is responsible for the zinc enrichment in our study area. A mechanism that could be responsible for this enrichment of zinc in the topsoil is vegetation recycling. Increased metal concentrations in the topsoil by vegetation recycling have been found in particular in forests (Martin and Bullock, 1994; Johnson and Petras, 1998; Blaser et al., 2000). The fact that the relative enrichment was found to be stronger for zinc than for lead is consistent with the fact that plant uptake of the non-essential element lead is in general much lower than of the essential micronutrient zinc. As Table 2 shows, the zinc content in the plants at the study sites was 6 to 40 times higher than the lead content. One of the plants identified at the site was Minuartia verna L., which is known to be a metallophyte plant growing on heavy-metal (zinc and lead) contaminated mining spoils (Brooks, 1998).

The different behavior of lead and zinc is also recorded in the lead to zinc ratio, which changes with depth. In the bedrock, the Pb to Zn ratio was between 2 and 3.8. The Pb to Zn ratio decreased with increasing organic matter content, which means that zinc was preferentially enriched (Fig. 7). The preferential enrichment of zinc is clearly related to the distribution of organic matter in the soil profile. The strong correlation between zinc and organic matter is particularly evident in the Raibl 1 profile (Fig. 2 and 4), where increased organic carbon concentration between 30 and 60 cm corresponded with elevated zinc concentrations at the same depth.

Interestingly, the Raibl 1 profile does not only contain elevated zinc concentrations between the 30- to 60-cm depth, but also elevated ammonium-acetate/EDTA-extractable lead (Fig. 4). The elevated ammonium-acetate/ EDTA-extractable lead can either be the remnant of lead in the buried topsoil or lead that has been transported through the soil profile and adsorbed onto the organic matter in this layer. Figure 8 shows that there is a perfect relationship between the ammonium-acetate/ EDTA-extractable lead and total zinc ( $R^2 = 0.94$ ) in the profiles at four of the sites for which ammoniumacetate/EDTA data are available. Total lead, on the



Ammonium-acetate/EDTA-extractable Pb (mg kg<sup>-1</sup>)

Fig. 8. Ammonium-acetate/EDTA-extractable lead vs. total zinc in the Fuorn 1, Raibl 1, and the two Vallatscha profiles. The inset shows total lead vs. total zinc for the same samples.

other hand, does not correlate with total zinc (inset to Fig. 7). Whether this also indicates a contribution of plant recycling to lead transfer in these soils is a speculation that seems unlikely, but on the other hand cannot be completely excluded.

Zinc is normally considered to be quite mobile in soils (McBride, 1989), although soil organic matter is known to have a high potential in storing heavy metals (Schulin et al., 1995). Zinc enrichment in the topsoil is usually not found to this extent in soils in industrialized areas of Switzerland (Federal Office of Environment, Forests and Landscape, 1993). Atteia (1994), on the other hand, has reported a very strong zinc enrichment in the top 5 cm with an almost complete depletion at the 5- to 20-cm depth for a podzol at 2000 m altitude developed over gneiss. The soils of our study area are situated at a comparable altitude of 2400 m. These soils are governed by quite different climatic conditions than the soils investigated in most studies, which are forest or agricultural soils. Further studies about the behavior of heavy metals in alpine soils are needed to understand this behavior and the differences with soils at lower elevations.

## **CONCLUSIONS**

The results of this study show that the heavy metal concentrations in the soils strongly reflect those of the underlying bedrock. Enrichment of lead in the soils may have resulted by accumulation of immobile heavy metal compounds during dolomite dissolution. Lead isotope data suggest that an anthropogenic component is present and comprises about 20 to 75% of total lead. Lead in the contaminated part of the profile selected for isotope analysis seems to be composed of lead from several sources, namely from background lead in the dolomite

and from anthropogenic aerosols. Zinc is recycled by plants and highly enriched in the topsoil.

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