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Transport of major and trace elements in soils and aquifers of different ecosystems of Switzerland

OLIVIER ATTEIA¹

Key words: Trace elements, soil, aquifer, bulk precipitation, transport, weathering, Switzerland

ABSTRACT

The input of major and trace elements to alpine aquifers of western Switzerland is investigated. In addition, trace element dynamics within different soils are compared. The concentrations of pollutants in bulk precipitation at the studied sites is rather low compared to other European rural regions like Sweden or Germany. Water fluxes are modelled in the cambisol and estimated on the other sites. The three soil types are very different in a pedogenesis point of view. The studied cambisol presents a low exchange capacity and low saturation down to 1.5 m depth, with atmospheric input neutralised in the first soil layers. Iron mobilisation in the top layers and fixation in amorphous form at depth is significant in the podzol. Soils on carbonated rocks neutralise the solution close to the soil surface. Comparison of different soils and aquifers shows distinct elements' dynamics as follows:

- Cu and Pb are retained by soil and aquifer on every site. The most important retention is realised in organic soil layers.
- K, V, Rb and Cr are slowly released in soil solution independent of soil pH. K is released in gneissic aquifer and Cr in the deeper part of the cambisol. Si, B and Ba dynamics are independent of soil type but depend on soil hydraulic status.
- Mn and Zn are released only for a soil pH below 5. Fe behaviour is typical of pedogenetic evolution: stopped in calcareous soils, released in cambisol and redistributed from surface to spodic layers in podzol. Ni and Co behaviour can be related to some extent to the behaviour of Fe.
- Ca, Mg and Sr generally originate from aquifers on acid sites, but are commonly released by soil on carbonated sites. Evaporites release SO₄, Sr and Mg. The studied gneissic aquifer, apart K, Na and Si, produces typical trace elements i.e. As, Mo and U.

The importance and the limits of the chemical criterion for differentiation of the previously cited groups is shown and the potential harmful effects of pollution are deduced from the trace elements dynamics.

RESUME

L'apport d'éléments traces par l'atmosphère et leur transfert dans les sols et les aquifères sont étudiés et mis en relation avec la dynamique des éléments majeurs et les types de sol. Les apports de polluants atmosphériques sont relativement faibles dans le contexte européen. Les flux d'eau dans les sols sont soit estimés par les lysimètres, soit calculés par un modèle de bilan hydrique pour le sol brun. Dans celui-ci, malgré le faible taux de saturation jusqu'à la profondeur de 1,5 m les polluants atmosphériques sont retenus dans les horizons de surface jusqu'aux horizons spodiques. La dynamique des solutions est simplifiée dans les sols carbonatés en raison de la précipitation dès l'augmentation du pH au contact de la roche. La comparaison de différents écosystèmes permet de différencier plusieurs groupes d'éléments:

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- Cu et Pb sont fixés à tous les étages de l'écosystème, la rétention la plus importante étant réalisée par la matière organique des sols.
- K, V, Rb et Cr sont lixiviés lentement sans influence du pH, K est libéré par les aquifères gneissiques et Cr dans la partie profonde du sol brun. Les dynamiques des Si, B et Ba ne dépendent pas du type de sol mais plutôt du régime hydrique.
- Mn et Zn sont libérés dans le sol seulement en dessous de pH 5. Les dynamiques de Al et Fe sont liées à la pédogénèse: fixés en milieu carbonaté, lixiviés dans le sol brun et redistribués dans le podzol. Le comportement de Ni et Co peut être rapproché de celui de Fe.
- Ca, Mg et Sr proviennent des aquifères en milieu acide et des sols en milieu carbonaté, les évaporites libèrent SO₄, Sr et Mg. L'aquifère gneissique étudié libère, mis à part K, Na et Si, des traces spécifiques telles que As, Mo et U.

L'importance et les limites des critères chimiques dans la différenciation des groupes cités sont discutées et les conséquences de la pollution actuelle sont déduites des dynamiques des différents éléments traces.

Introduction

In a context of increasing pollution and global climate change, the understanding of elements' cycling through the ecosystems is a primordial one. Soil plays a key role in element fluxes because it is the interface between atmosphere, biosphere and lithosphere. During cycling through soil and vegetation, trace elements play an ubiquitous role: they are necessary as micronutrients but can be toxic at higher concentrations.

The first studies of trace element behaviour emerged in mining. In this field, the commonly called trace elements are concentrated in specific and often rare minerals or rocks. To understand the occurrence of the minerals, numerous theoretical studies were done on trace element geochemistry (Wedepohl 1979). Nevertheless, the physical conditions (T°, pressure) prevailing in the liquid-solid interaction during rock formation are quite different from the soil conditions.

In soil science, important advances in the field of trace elements analysis began with the soil contamination and acid rain studies (Oden 1976, Heinrichs & Mayer 1977). The focus was on the soil adsorption characteristics of the pollutants. Numerous papers during the last two decades deal with laboratory pollutants adsorption equilibrium on clay or organic matter (Schmitt & Sticher 1990). Major element soil geochemistry is well known (Drever 1985), but few papers deal with geochemistry of trace elements in soils (Tardy 1969, Mosser 1980, Pedro 1969). Therefore, studies of their cycling in field conditions is necessary to evaluate direct and induced effects of anthropic contamination.

Biogeochemical studies of pollutants (Heinrichs 1980, Turner 1983, Bergkvist 1987) are generally based on the comparison of fluxes and reservoirs of pollutants at different levels of the ecosystem. We adopted the same approach but we studied many trace elements in very different soil types.

First we try to determine fluxes of trace elements in natural, low contaminated, ecosystems. An ecosystem is considered as the sum of the vegetation, soils and aquifers. We then compared these fluxes and tried to understand the difference between different sites and between elements. This analysis is based on the elements' chemistry and some characteristics of the studied soils such as pH, organic matter content, or concentrations of the elements in the solid. A priori we did not focus our study on specific elements. During the first sampling stage, the concentrations of all elements were measured and we selected elements with concentrations in excess of 1µg/l. This selection is similar to the list

of elements existing at concentrations higher than 10 mg/kg in the continental crust (Puchelt 1992). This selection excludes Cd and Be which can be pollutants even at concentrations lower than a $\mu\text{g/l}$.

Sites, Materials and Methods

Sites

In a network studying aquifer typology (Parriaux 1990), composed of 17 sites spread over a 8,000 km² region in the French part of Switzerland, we have collected data for several years. These sites include major alpine lithologies. They are overlain by typical soils of the temperate climate zone (Pedro 1968): calcic cambisol, acid cambisol, podzol (FAO soil classification). For the soil study, we selected 7 sites in the whole network (Fig. 1). The results of the three most important sites: Calc, Camb and Podz are presented. The other sites, including few soil solution samples, are used to determine the background atmospheric input. Main soil characteristics are presented in Table 1. The Calc site is located in the Swiss Jura and includes two calcic cambisols, one under forest and the other on extensive pasture. They are both thin soils with high organic matter content and near neutral pH. Camb site is 20 km north of Lausanne, it is a small watershed covered by a spruce forest with a deep acid cambisol on a homogeneous sandy burdigalian molasse. Podz site is in France near Chamonix at 2,000 m altitude. The soil is totally covered by rhododendron and a few small larches near the site. The soil is a typical podzol developed on a recent gneiss moraine (Dambrine 1985).

Hydrological limits of the watersheds are estimated with different techniques like topography analysis, tracers (Parriaux 1990) and isotopes (Dubois 1986). A soil survey tested the homogeneity of each watershed, and defined the number of sites to be set up on

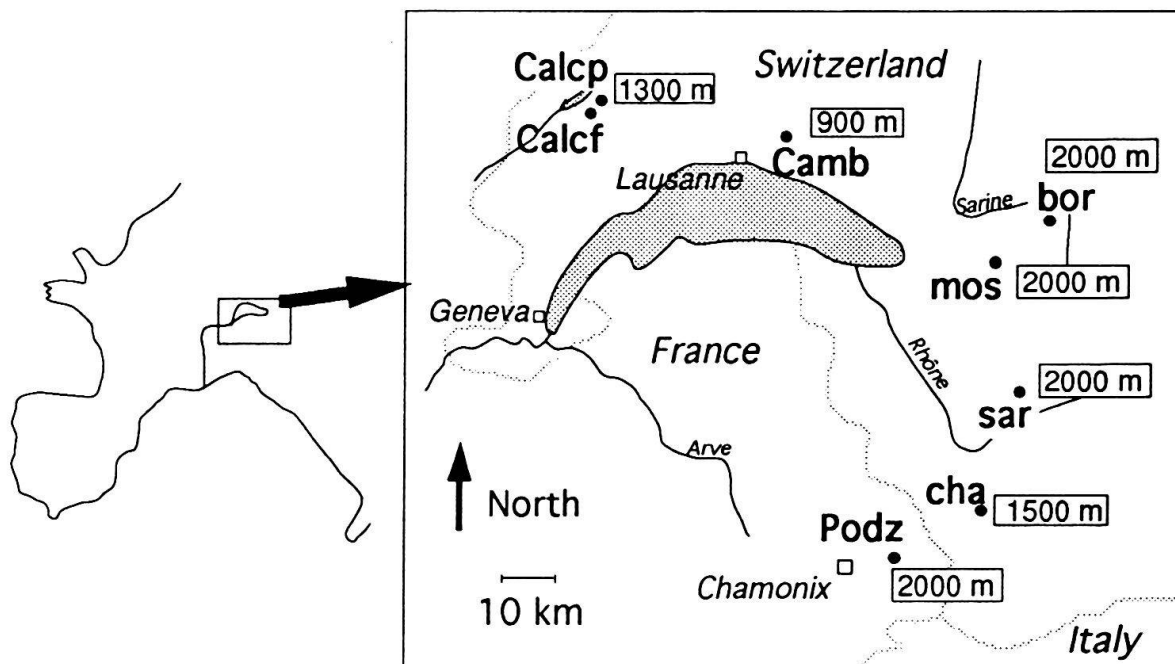


Fig. 1. Location of the studied sites.

each watershed according to the existing soil units. Only Calc is equipped with two neighbouring sites, one in the forest and another on pasture, because of different soil types corresponding to different land use (Atteia 1992). On each site, precipitation, the soil and soil solutions, and spring waters have been investigated.

Material

To collect soil solution, lysimeters (tension and/or free tension on) have been placed near the contact between soil and geological substratum. In Podz and Camb soils another lysimeter series is installed below the A2 and B1 layer respectively (Tab. 2). The lysimeter type is chosen according to soil texture and structure. The 0-tension lysimeters, made

Site	Altitude m	Spring m	Prec. mm/y	Int. mm/y	ET mm/y	Size km ²	Underlying rock
Camb	885	880	1200	150	420	0.02	Burdigalian molasse
Podz	2000	≈1200	1700		350	?	Gneissic moraine
Calc	1330	970	1600	300	250	20	Malm Limestone

Tab. 1. Main characteristics of the sites

Altitude: altitude of the soil station, spring: altitude of the spring, Prec.: precipitation, amount Int.: interception by forest canopy, ET: Evapotranspiration, size: estimated size of the watershed.

Layer	Depth cm	pH	O.M. %	T még/100g	S/T %
Camb					
A1	0-8	3.7	24.3	13.9	19
B1	8-20	4.3	8	7.4	5
B1 *	20-40	4.5	5.6	4.5	7
	40-60	4.5	3.8	3.65	10
B2 *	60-80	4.6	3.6	3.15	8
	80-100	4.6	3	3.04	11
	100-120	4.7	2.7	3.2	9
BC	120-140	4.7	2.7	3.5	9
	140-170	4.9	2.3	5.25	26
Podz					
A0	0-5	3.7	86.4	31.1	63
A1	5-9	3.8	56.7	16.9	40
A2 *	9-15	4	6	6	12
Bh	15-20	4.1	20.9	18.9	6
Bhs	20-30	4.6	14	9.5	5
Bs *	30-55	4.9	4.5	2.8	9
BC	55-75	5.6			
CalcF					
	0-5	5.6	25.3	41	100
A1	10-20	7	19.4	49.1	100
*	20-30	7.7	24.9	36.4	100
CalcP					
A1	0-10	5.4		24.7	100
(B)	10-20	6.5	19.2	32.5	100
BC *	20-25	6.9	16.8	35.2	100

Tab. 2. Main characteristics of the soils

pH: pH in water extract 1:5, T: total exchange capacity, S: exchangeable cations, *: location of one lysimeter series at the bottom of the layer, for Calc, F: Forest and P: pasture, O. M.: organic matter content.

of polypropylene (PP) gutters, are inserted by force into the soil in a soil pit. They are inserted in a direction parallel to the soil slope. The soil pit is refilled with care after lysimeter insertion. To decrease natural variability of soil solution (Radulovitch 1987) 6 lysimeters are installed at the same depth leading to a total surface of 0.12 m² and are connected to the same PP collector. Water balance has been approximated by comparing cumulative chloride fluxes in rainfall and soil solution (Atteia 1992). Only Camb site is equipped with porous cups. On this site, the known hydraulic pressure determines the suction to apply to porous cups. The chemistry of the porous cups solutions is compared using two types of lysimeters (Atteia 1992).

Bulk precipitation is collected with polyethylene (PE) funnels and throughfall is obtained with three PE gutters placed under the canopy. All the materials were tested and showed no contamination of trace elements. Prior to installation, all materials were rinsed with nitric acid and deionized water. After every sample collection, collectors were washed with distilled water.

Spring waters were collected directly from the spring in 1 l PE bottles.

Analysis

Solutions have been collected from January 1990 to November 1991. Collected waters (rain, snow, soil solutions and spring water) were analysed for major anions and cations and trace elements. Before analysis all the samples are filtered by 0.45 µm sieves. One part of the sample is stored at -20°C for anion analysis and another part is acidified with 0.5% of suprapure HNO₃ and stored at 4°C.

Major cations concentrations were determined with a DCP-AES (ARL, Spectraspan II) with LiCl modifier to decrease differences between alkaline and alkaline-earth elements. Sulphates are analysed with ICP (Jobin-Yvon 38) in S form and with ion chromatography (Sykam) the results agree well with a difference lower than 10%. Other anions are determined by an automated colorimeter technique (Technicon). ICP-MS (VG Plasmaquad) acquisition allowed the simultaneous determination of all trace element concentrations. Nevertheless, for routine analysis we only analyse elements with a concentration greater than 1 µg/l. This arbitrary limit is chosen to avoid contamination effects. Considering this limitation B, V, Cr, Ni, Fe, Mn, Cu, Zn, Pb, Ba and Sr are analysed at trace level.

To determine the total content of major elements, the soil is ground, dried and fused at 1200°C with Sr metaborate and then dissolved with HNO₃ 2%. This technique gives less than 1% error on international standards. The analysed layers are cited in Table 1. To determine the total content of trace elements content, X-ray fluorescence is performed on discs of ground soil mixed with a binding material, this technique also agrees well with international standards values. Cu concentrations were too low to be detected by using this technique. To eliminate the effect of the dilution of mineral soil in organic matter, we normalise all the concentrations to Zr, assuming Zr as a stable element in these profiles. This technique is common in weathering studies (Cramer & Nesbitt 1983) and gave, in our study, concentration profiles showing weathering and accumulation patterns consistent for the considered soil type. On the Camb and Podz site we have calculated the total amount of one element lost in the root zone, with reference to bedrock, assuming Zr as a stable element. The depletion is compared to fluxes of the same element

in solution at the same depth (80 cm for Camb and 50 cm for Podz). The ratio of depletion to flux equals the thime to reach the actual depletion with the actual flux in solution. This ratio allows a comparison of the actual lixiviation velocity to the historical one.

For extractable elements we used two techniques: a pH 4.65 Ammonium-Acetate EDTA mixture (NH_4EDTA) with 1:10 ratio soil-solution for determination of "mobile" elements (Lake 1984) and a pH 3 oxalate-oxalic acid mixture (Tamm reactant) with a 1:40 soil-solution ratio for dissolution of amorphous oxides (Jeanroy 1983, Cavallaro 1984). These extracts do not separate every form of elements in solids, but few extracts were used because: (i) use of ICP-MS prohibit extracts containing Cl if high precision is required, (ii) few extracts can be obtained with high purity and (iii) extracts' reactions with some trace elements are not known. Therefore these extraction procedures are used for comparison of the different profiles. On the Camb soil samples, water extracts with a ratio of soil to solution 1:10 have been performed.

Flux calculation

Precise calculation of water fluxes in soil requires numerous measurements in the field and good computer codes (DeCoursey 1988). In many trace element budget studies, concentrations are obtained with a fairly high accuracy but estimates of water fluxes are very poor. Assuming that the hydraulic functioning of the lysimeters and rain gauge are self consistent around the year, we can take the average concentration weighted with volume, as an estimate of element concentration. The average annual fluxes is equal to:

$$P_{\text{moy.}} \cdot V_{\text{tot.}} \cdot \sum C_i/V_i$$

with $P_{\text{moy.}}$: mean yearly precipitation obtained from climatic map, C_i concentration of the element for the i event, V_i : the volume obtained for the i event and $V_{\text{tot.}}$: the total volume. We took into account the evapotranspiration effect which reduces the water fluxes between atmosphere and top soil layers. This was done by using our water balance calculation and literature data (Atteia 1992), the results are summarised in Table 1. It is evident that such fluxes are imprecise but we will only consider the large differences in fluxes in the next sections.

Results

Atmospheric deposition

The study of atmospheric deposition of trace elements over the region is described elsewhere (Atteia 1992). We used enrichment factors to assess the origin of the elements. Fe, Ni, V, Rb and Cr concentrations are low, and are derived from the continental crust. For Mg, Cl and Na, sea sprays are the main contributors to the concentrations existing in bulk precipitation. All these elements present statistically similar concentrations over the whole zone. Cu, Pb, Zn and B like SO_4 and NO_3 clearly originate from human activities. The concentrations of these pollutants are similar on every site, even those at 2,000 m altitude, suggesting long range transport. Sr, Ba and K concentrations in rainfall seem to increase in the neighbourhood of bare rocks. Mn concentrations could be influenced by human activities or the presence of forest in some sites. Compiling existing literature

showed that the measured fluxes of major acidifiers are typical of low values for rural Europe. Concerning trace elements, fluxes of heavy metals in our study are similar, for Mn, Cu and Zn, and lower, for V, Ni and Pb, than the fluxes measured in other studies applied to rural sites of Sweden and Germany (Bergkvist 1986) or United States (Galloway 1982). Concerning snow, the levels of Cu and Zn concentrations obtained by Batifol Bouteron (1984) on the "Mont Blanc" are lower than ours whereas Pb and Mn ones are similar.

The effect of forest on trace element concentration is described in Atteia & Dambrine (1993). Heavy metal concentrations in throughfall are similar to the ones in bulk precipitation. Sr is enriched by approximately 30% and Ba more than 100%, Fe and B are retained by vegetation. Mn and Rb show important biological cycling, throughfall concentrations being an order of magnitude higher than precipitation ones.

Concentrations in soil solutions, site comparison

The average concentrations of major and trace elements in the different sites and different media are listed in Table 3. For comparison of the soil solution concentrations, statistically different group obtained by ANOVA are presented. The elements can be divided into three groups: (i) Mn, Zn and Fe which can reach concentrations greater than 50 µg/l in some sites, (ii) Ba, Sr, B and Cu whose concentrations are between 1 and 20 µg/l and (iii) Ni, Pb, V, Cr and Rb generally around 1 µg/l. Ba, Rb, Pb and Cr do not present any statistical differentiation between sites. For the other elements we can distinguish different patterns: Mn, Zn, Cu and Ni concentrations are much higher in Camb than in the two other sites. Sr, B and V show similar concentrations at Camb and Calc but lower concentrations at Podz. Only Fe shows much higher concentrations at Podz than at the two other sites.

A comparison of concentrations of some heavy metals in soil solutions of different ecosystem studies is shown in Table 4. Concentrations at the Solling site are higher than

mg/l	pH	Ca	Si	Mg	K	Na	Al	Cl	N	S
Podz	4.88 ^a	0.59	1.75	0.11	0.17	0.37	0.34	0.43	0.21	0.46
Calc	7.66 ^c	33.7	5.86	0.38	0.16	0.49	0.09	1.42	1.71	0.93
Camb	5.62 ^b	2.79	4.94	1.59	0.37	0.93	0.41	1.41	0.33	2.85

µg/l	Mn	Zn	Fe	Ba	Sr	B	Cu	Ni	Rb	Pb	V	Cr
Podz	4.62 ^a	11.5 ^a	69.4 ^b	12.1 ^a	1.85 ^a	3.39 ^a	1.48 ^a	1.08 ^a	1.08 ^a	0.88 ^a	0.08 ^a	0.02 ^a
Calc	1.09 ^a	13.9 ^a	17.2 ^a	18.8 ^a	11.9 ^b	9.64 ^b	2.42 ^a	0.79 ^a	0.4 ^a	0.25 ^a	0.72 ^b	0.23 ^a
Camb	158 ^b	130 ^b	20.6 ^a	16 ^a	12.7 ^b	12.4 ^b	5.68 ^b	2.04 ^b	0.69 ^a	0.83 ^a	1.11 ^b	0.21 ^a

Tab. 3. Average weighted concentrations of elements in soil solutions.

Concentrations are for the period of March 1990 to November 1991. Concentrations are weighted with volume of water. For trace elements, letters a and b characterize statistically different groups of data. N: nitrogen in nitrate form, S: sulfur in sulfate form.

$\mu\text{g/l}$	Zn	Cu	Ni	Pb	Cr
Solling	520	9	15	2	0.6-1.2
Spanbeck	540	9.6		4	
Varsjo (A)	34	4	0.9		1.2
" (B1)	65	2	2.2		1.7
" (B2)	151	1.4	4.1		0.8
Gardsjon (A)	38	4.1	1.8	19.5	2.3
" (B1)	55	0.7	2.5	2.5	1.2
" (B2)	75	0.7	3.6	1	1.3

Tab. 4. Average concentrations of some heavy metals in soil solutions obtained in other studies:

Source of data:

Solling, Spanbeck (Germany): Schultz (1987) and Heinrichs and Mayer (1980). Varsjo and Gardsjon (Sweden): Bergkvist (1987): A layer: 15 cm, B1 layer: 35 cm and B2 layer: 55 cm.

ours, but this site is known to be highly polluted and acidified. The two Swedish sites present soil solution concentrations of Cu, Zn and Ni similar, but slightly lower, than the Camb levels. These concentrations are higher than the ones existing in Calc and Podz. Pb and Cr concentrations in solutions of the cited Swedish soils are higher than the ones in our sites. Keller (1991) found Cu concentrations between Camb and Calc values for a cambisol and a podzol in the same region of Switzerland. The studied sites show low concentrations of heavy metals for Podz and Calc whereas Camb seems to show intermediate values. B, Ba, Rb, V and Sr concentrations in soil solutions in literature are too scarce to make any comparison.

Element concentration on the water way through the ecosystem

Figure 2 describes the fluxes of each element for the different levels of the ecosystem (atmosphere, soil and spring). Spring water composition at the Podz site may be imprecise because it is a calculated average of concentrations from different fractures having very different compositions in one tunnel.

At all sites, fluxes of Pb and Cu decrease from atmosphere to spring, this decrease being sharper for Pb than for Cu.

V, Cr and Rb fluxes are low in the atmosphere and remain fairly similar in soils and springs. B presents the same behaviour but with higher fluxes. Some exceptions exist for B and Cr in spring water.

Ba fluxes increase from atmosphere to soil at all sites. In B2 and Bh layers, two patterns exist: increase of flux at the Camb site and decrease at Podz. Fluxes of Ba at spring level decrease down to a level equivalent to atmospheric ones. Behaviour of Ni is similar to Ba despite a much smaller increase between atmosphere and soil solution. Therefore Ni can be considered as intermediate between Ba and the previous group of elements.

Fe levels are fairly stable from atmosphere to soil solution and become null in spring waters at Calc and Camb. On the other hand, the A2 layer of Podz releases a large amount of Fe compared to other sites, nevertheless the Fe concentrations remain at trace level.

At Calc and Podz site, Zn fluxes decrease along the water way and Mn levels remain very low. For Camb site, the scheme is totally different with a significant release of Mn and Zn in B layer. Mn fluxes are much higher in throughfall than in precipitation and top soil. This pattern is characteristic of biological cycling as cited by different authors (Hofken 1986, Godt 1986). Nevertheless Mn and Zn net release are clear between B1 and B2 layers.

BP: Bulk Precipitation, Tf: throughfall, Soil 1: A2 layer at Podz and B1 at Camb, Soil 2: Bs layer at Podz and B2 at Camb (see Table II for depth), Sp: Spring.

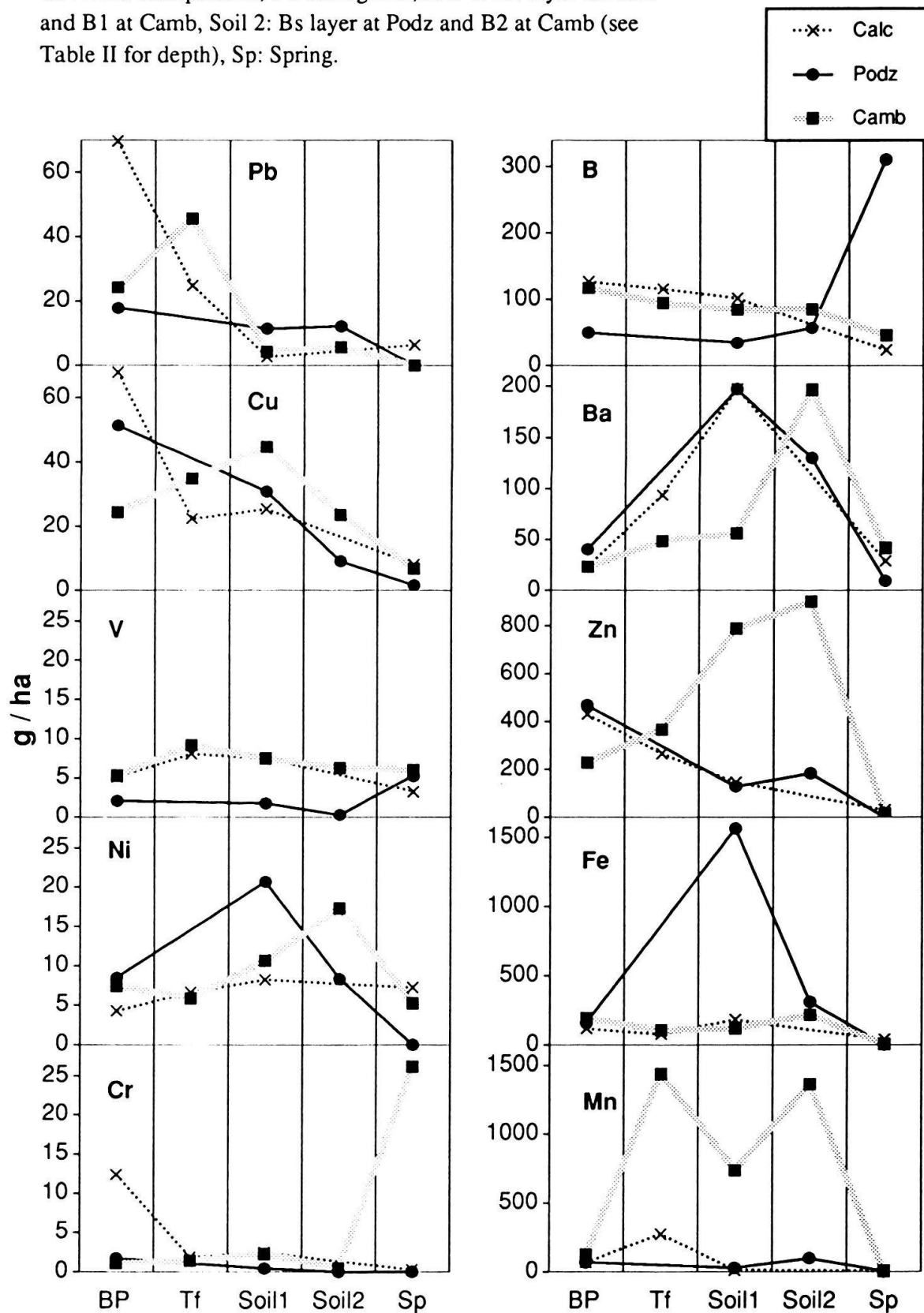


Fig. 2. Fluxes of trace elements in rainfall, soil solutions and springwater (g/ha).

The site showing the more specific features for trace elements dynamics is Camb where not only levels but also the vertical evolution of concentrations are different from the other sites, for many elements. It is surprising to notice that the most different sites from the pedogenetic point of view present similar behaviour concerning trace elements dynamics.

Discussion

In this section we try to relate the observed concentrations and calculated fluxes of elements to the soil properties and chemical characteristics of the elements. We then try to deduce the influence of different factors on the trace elements dynamics.

Ni - V - Cr

Concentrations of these elements in the *soil solution* are similar in the three sites, apart for low V concentrations at Podz. As with V, the soil Cr budget (output flux less input flux) is close to equilibrium while that of Ni is negative, all the soils releasing Ni. Concerning the total concentration in *soils* the Ni/Fe, Cr/Fe and V/Fe ratios are similar for all layers in the same soil and, except for Cr, very similar in different soils (Fig. 3). This suggests that the dynamics of these elements are close to that of Fe. These associations have long been established in mineralogy (Wedepohl 1979); the fact that they exist in soils suggests that the elements belong to the same minerals in all soils and that they pass the same evolution during the weathering process. Concerning the mobility (flux/stock) or fluxes of these elements, a similar sequence is found in all soils: Ni > Cr > V. This sequence exists also in the soil extract: more than a half of total Ni is in amorphous Fe-Mn oxide phase, and less than 1% of V can be extracted with the same reactant (cf. Tab. 5). Theoretical Eh-pH diagrams of these elements in water (Garrels 1968, Davies 1980) predict Ni in soluble form and V and Cr in particulate form in the conditions prevailing in soils.

For major elements, a calculation of the time to reach soil depletion with the current fluxes is presented in Figure 4 and gives a time close to the soil age (8 to 10,000 years). This suggests that the current fluxes are similar to the historical ones which could be interpreted as a constant dissolution rate for these elements, this rate being independent of soil pH. This is the case for feldspar dissolution (Lindsay 1979), minerals which mainly contribute to the fluxes of the cited elements. For Ni, the same calculation gives the same time as for the major elements at Camb site. We conclude that Ni can originate from pH-independent dissolution at our sites contrary to Bergkvist's conclusions (Bergkvist 1987).

For V, calculations have not been attempted for the Camb site because measurement errors are higher than V depletion because of the low level of V in soil solutions. Comparison for Cr shows a very long time for achieving current depletion. But Cr being in particulate form at these pH levels (Bergback 1989), soil solution concentrations underestimate the total annual flux. Figure 4 shows that the same kind of results is found for V and Cr at the Podz site. For this site Ni calculations could be inaccurate because of the accumulation of this element by organic matter in top layers.

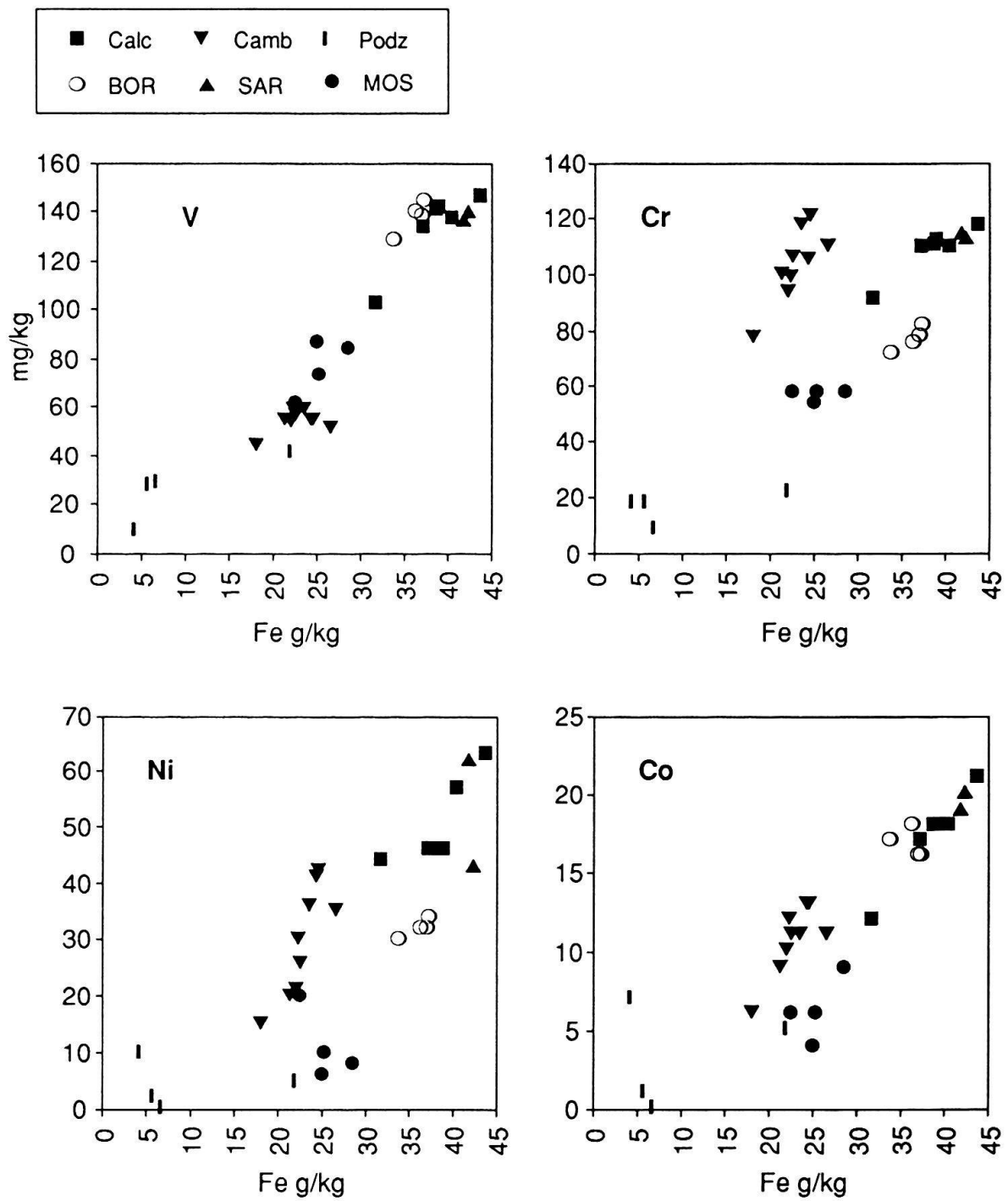


Fig. 3. Total concentrations of Ni, V, Cr and Co in soils plotted against Fe ones. MOS, BOR and SAR are three other sites of the study (cf. Fig. 1).

Mn and Zn

These elements are only released in Camb soil (Acid cambisol), concentrations at this site being 5 to 12 times higher than those at Podz. Following the same calculation of total depletion time as the one done for major elements and Ni in the previous section, Figure 4

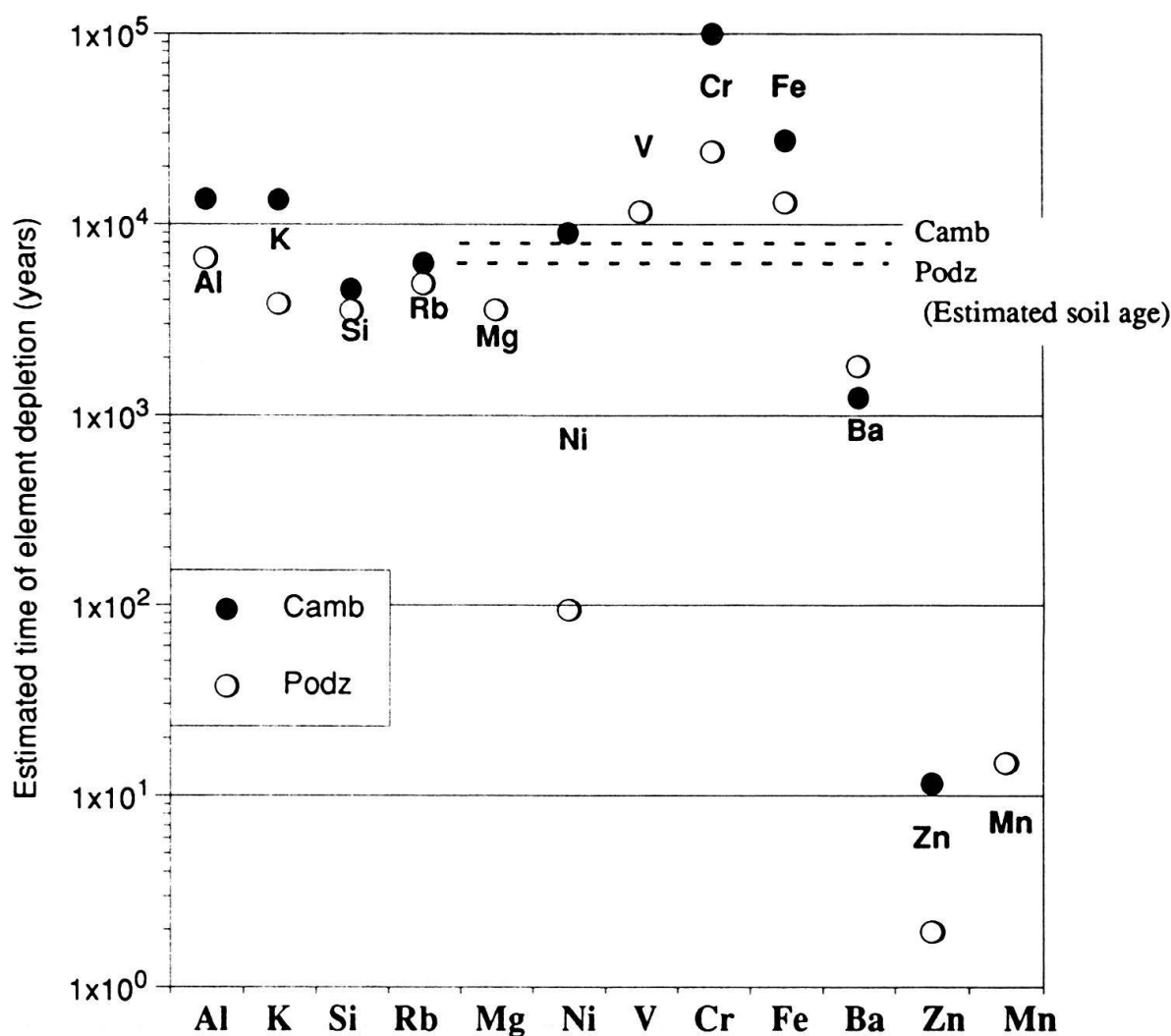


Fig. 4. Estimated time of element depletion with current fluxes for site Camb and site Podz i.e. the total soil depletion for one element divided by the current annual flux. It corresponds to years. Total depletion is calculated with reference to bedrock concentrations and Zr invariant. Annual flux equal the flux at 80 cm depth at Camb, or below A2 layer at Podz, minus atmospheric flux.

shows that actual Mn and Zn fluxes are high compared to the historical depletion. Release of Mn and Zn at the Camb site have increased tremendously recently. Moreover, Figure 5 indicates that concentrations of these elements in water extract of Camb soil increase dramatically when soil pH drops below five. Recent Mn and Zn release in soil solution seems to be related to recent soil acidification. This behaviour is similar to that of Al during soil acidification (Driscoll et al. 1985); it has been forecasted by soil acidification models (DeVries 1989) and verified by laboratory experiments (Tyler 1981) and ecosystem studies (Schutz 1987).

At Podz, Mn and Zn concentrations are much lower while soil pH is slightly more acidic than that of Camb. The low value of Zn concentrations can be interpreted as a mass action's law effect because Zn has been almost totally depleted from the A2 and Bh layers (Tab. 5). Concerning Mn, biological cycling existing at the Camb site (Atteia & Dambrine 1993) cannot explain the flux increase in solution in the B layer. The role of

mg/kg	Mn	Ox	Ac	Ba	Pb	Pb	Ox	Ac	Rb	Sr	Cr	OxAc	Ni	Ox	Ac	Zn	V	OxAc	Co	
calcf3	1010	39	19	36	29	5	5	5	95	64	110	1	0	57	14	1	137	3	0	18
calcf15	1030	42	13	111	24	3	3	3	93	73	118	1	0	63	13	0	146	3	0	21
calcf25	740	45	6	63	8	7	4	4	69	112	91	2	0	44	18	0	103	4	0	12
calcp5	1120	46	0	110	31	8	0	0	102	66	111	1	0	46	23	0	141	4	0	18
calcp15	1130	45	9	85	16	13	4	4	99	63	110	1	0	46	22	0	134	4	0	17
calcp25	1210	43	9	140	21	4	3	3	109	70	112	1	0	46	21	0	142	3	0	18
calcRM	110			3	6				10	218	26			9			4			2
Camb4	440	38	12	126	46	83	42	42	72	65	77	6	2	15	100	0	44	10	1	6
Camb14	660	53	4	232	10	100	41	41	89	73	100	5	0	20	100	7	55	7	0	9
Camb30	940	57	2	197	4	100	51	51	88	71	94	5	0	21	98	2	54	7	0	10
Camb50	840	50	3	315	6	100	19	19	103	77	106	3	0	26	52	1	56	5	0	11
Camb70	750	52	2	288	5	100	16	16	102	78	99	4	0	30	54	1	59	5	0	12
Camb90	680	38	1	280	3	100	15	15	100	78	118	3	0	36	24	0	59	3	0	11
Camb110	620	38	1	246	4	100	10	10	96	76	105	3	0	41	18	0	55	3	0	13
Camb130	500	29	1	296	5	88	7	7	99	77	121	3	0	42	16	0	55	3	0	13
Camb150	790	48	5	265	1.				95	75	110	1	0	35	14	0	51	2	0	11
CambRM	570			341	1.				91	138	122			55			53			10
Podza0	50	15	8	1.	51	21	62	62	33	37	18	0	0	10	92	73	9	11	6	7
Podza1	110	2	1	1.	3	100	100	100	69	57	18	1	0	2	100	100	28	2	1	1
Podze	190	0	0	256	14	100	39	39	129	79	9	2	0	0	100	100	29	4	0	0
Podzbh	250	100	45	206	20	100	19	19	107	78	30	14	1	n			92	15	1	15
Podzbhs	340	100	30	318	12	100	16	16	122	93	32	13	2	n			56	8	0	12
Podzbs	420	1	2	427	12	72	15	15	151	121	22	5	0	5	100	17	41	2	0	5
PodzRM	420			481	13				173	105	26			7			44			5

Tab. 5. Total concentrations of elements in soils and % extractable.
Ox is the % extract by Ammonium Oxalate – Oxalic acid, Ac: extract by Acetate Ammonium EDTA pH 4.65.

RM: Bedrock, l: below detection limit, n: no measurement.

For Calc and Camb, numbers following the identification are the average depth of the soil layer in cm.
For Podz, the letters following the identification indicate the name of the soil layers.

redox potential seems to be insignificant because variations of Mn concentration in soil solution are not related to the water table level. On the other hand, up to 50% of Mn is extractable with Tamm reactant in Camb soil mineral layers whereas this value is less than 5% at Podz. Hence Mn is much less accessible in Podzol than in the acid cambisol. This could be explained by existence of Ferro-magnesian minerals at the Camb site. Thus

pH is not the only factor governing Mn and Zn releases; existing mineralogy also plays a significant role. Moreover, water flows much slower in Camb soil than in Podz soil, which could increase the concentration of Fe and Mn (Luxmoore 1990) in soil solution.

Fe

Fe is an important metal in pedogenesis studies (Duchaufour 1983), in fact in this study Fe shows a different behaviour in each of the three sites (Fig. 2). Profiles of total Fe in soil show high depletions in the A2 layer of the Podzol and in the top 50 cm of the cambisol. These high depletions are not compatible with the current dissolved fluxes (Fig. 4) because Fe, like Cr, is mainly in particulate form (Stumm 1970).

Fe shows an original and well known behaviour in Podzol (Tonkogonov 1987, Sanborn 1989, Farmer 1982) with a higher depletion in the A2 layer than in the acid cambisol compared to Al for instance. Accumulation of Fe in amorphous form in the spodic layer leads to a total content twice as high as that of the bedrock. Lateral movements of solutions in the top layers amplify this accumulation (Dambrine 1985, Atteia 1992).

The ratios between V, Cr and Fe are the same for the accumulation in the spodic layers as for the depletion in the other soils. On the other hand, Ni is eliminated from these layers. As V is known to precipitate with newly formed Fe oxides (Bloomfield 1981) it could suggest that Fe, V, Ni and Cr are released separately from the A2 layer and that Fe, V and Cr form new precipitates in the spodic layers.

Rb

Rb concentrations are generally low in soil solutions and do not statistically differ between the three studied soils. For Camb and Podz soil, total Rb depletion is consistent with actual fluxes (Fig. 5). This fact could be explained by a pH independent dissolution of minerals containing Rb such as feldspars.

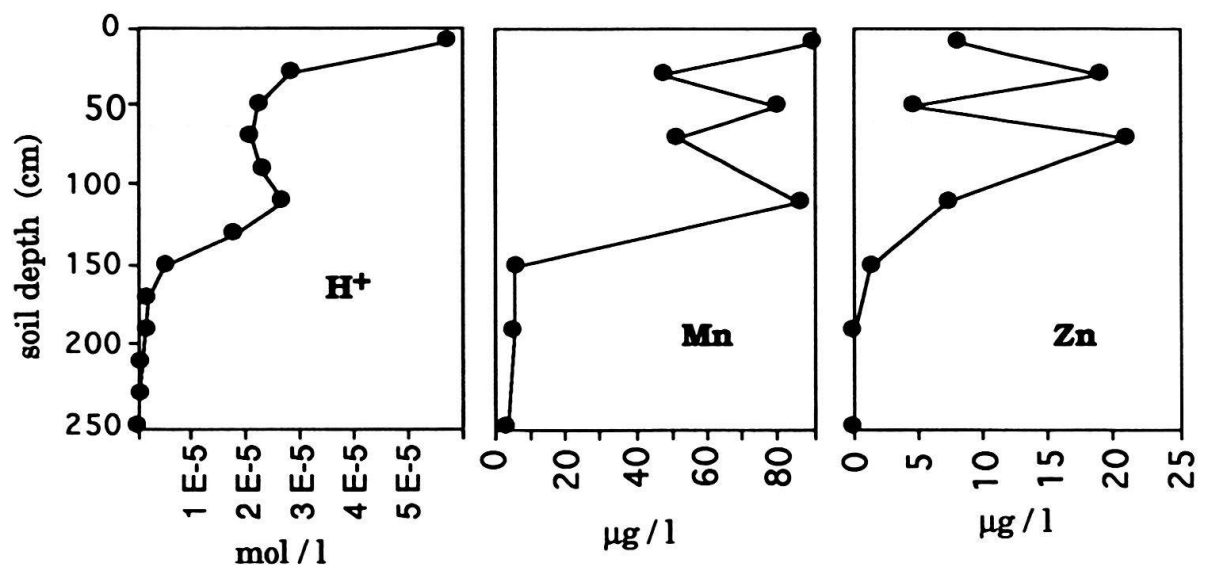


Fig. 5. Mn, Zn and H⁺ concentrations in water extracts (1:10) of Camb soil according to depth.

In minerals, Rb substitutes K because of similar radius and charge (Mahan 1977) with a ratio of 160 to 300 for K/Rb (Wedepohl 1979). The correlation between K and Rb is clear in throughfall composition (Atteia 1993) showing the same behaviour in vegetation. In soil solutions this relationship is less clear certainly because concentrations of both elements are low and near detection limits ($R^2 = 0.57$ at Camb and 0.68 at Podz). At the Camb site, K/Rb equals 228 in bedrock, 180 in top soil layer and 333 in soil solution. For Podz, this ratio equals 166 in bedrock, 105 in the top soil layer and 196 in soil solution. These ratios are fairly close for such different situations and media, which shows that Rb behaviour is close to that of K. Nevertheless the ratio decreases from soil bottom to top and is higher in soil solution than in soil; this proves that Rb is more resistant to weathering than K. All ratios are higher for Camb than for Podz, so the composition of soil solution of different soils reflects the difference of the original mineral composition. Finally, the Rb concentrations or the value of the K/Rb ratio in soil solution are related to the composition of the original material and to the weathering rate. We think that the calculation of this ratio in soil solutions and soils can be a very useful tool for weathering studies.

Sr

Sr is the only trace element to be released from all soils and aquifers to solutions. In almost all solutions, Sr concentrations are correlated to those of Ca. In carbonated soils the Sr/Ca ratio is equal to that of the underlying rock, proving that Sr originates from calcareous gravel existing in soils. Sr concentrations in these soils are lower than the spring one because equilibrium with calcite and Sr-CO₃ is not fulfilled in soils due to the low contact time between calcareous gravel and solutions in soils.

At the Camb site, we calculated the amount of Ca and Sr released in solutions between 0 to 30 cm and 30 to 80 cm depth. In this amount, the ratio of Ca/Sr (120) is higher than that of the total soil (50) which suggests that Sr is more retained than Ca by this soil. This is also sustained by the fact that Ca/Sr ratio is lower in soil (50) than in bedrock (204). For Podz site, the evolution of Ca and Sr concentrations through the profile are too low to do any calculation, mainly because the minerals containing Ca are almost entirely weathered. As K/Rb ratio, Ca/Sr ones can be useful in weathering or cation exchange studies.

Cu and Pb

Cu and Pb originate from human activities; their fluxes decrease along all the water course while their total concentration in solids increases from the bottom to the top soil layers. This pattern is particular to elements retained in the top soil, and has also been observed for Cu and Pb by different authors (Bergkvist 1987, Schultz 1987, Stahr 1987).

In the two acid soils, the total content of Pb is directly proportional to organic matter content (Fig. 6). The slope of the linear regression is different for the two soils because Podz contains much more organic matter for a similar Pb content. The concentrations of Pb in solution is statistically equal in the three soils though the soil and soil solution pH are totally different from one site to another. In other studies (Bourg & Vedy 1986), it can be seen that even in more acidic soils Pb is retained with organic matter in the top of mineral layers. While Pb is almost entirely oxalate-extractable in mineral layers, this is

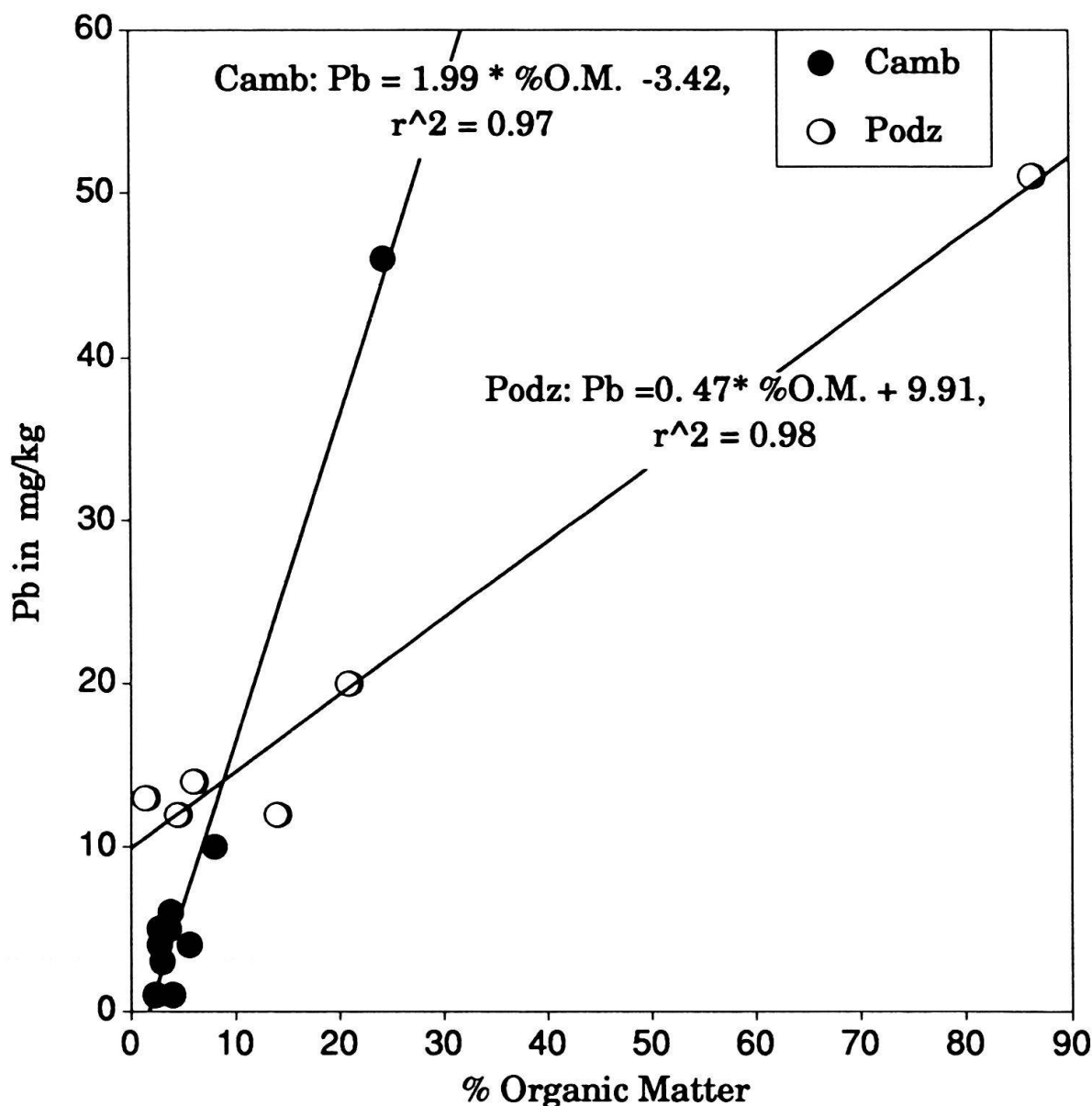


Fig. 6. Relationship between total Pb content of soils and organic matter content.

not the case in organic layers (e.g. A0 of Podz in Tab. 3), suggesting that some organic sites resist to extractant attack. These three remarks suggest that Pb is strongly bounded to organic matter and remains bounded whatever the chemical conditions are. This is also described by Tyler (1981) and Berggren (1989). It is then important to study the origin and movement of organic matter and particularly its relationship with hydraulic factors like quick snowmelt on podzols.

Concerning Cu, Xray fluorescence detection limits (approx. 4 mg/kg) are too high to measure Cu levels in the different soils. Nevertheless extractable quantities are of some mg/kg, near FX detection limits, suggesting that the major part of Cu is extractable. Cu concentrations in soil solution are similar in soils with pH varying from 4 to 8, this behaviour could be explained by strong Cu complexing with organic matter as cited

by Berggren (1989), Buffle (1989) or Keller (1991). The average ratio between the concentration of the element in soil solution ($\mu\text{g/l}$) and the “mobile” amount (NH_4EDTA -extractible in mg/kg) is equal to 0.42 for Pb and of 26 for Cu which shows that Pb is much more strongly bounded to “exchange sites” (organic matter) than Cu.

B and Ba

B and Ba can be compared because their concentrations in soils solutions do not depend on soil type. Average Ba concentrations in soil solution are similar in the three soils and are higher in soil solutions than in precipitation. Profiles of total concentrations of Ba in soils show a significant depletion certainly due to weathering in the top layers (Tab. 3). Exchangeable Ba constitute less than 1% of total Ba. Therefore the concentration of Ba in soil solutions seems to be related to feldspar weathering, as Ba generally lies in feldspars (Wedephol 1979). None of the possible equilibrium of Ba with some Ba mineral is fulfilled. The precise location of Ba in soil minerals should be studied.

In precipitation, B has clearly an anthropogenic source (Meybeck 1986) and concentrations in soil solutions are similar to those of precipitation. While this pattern is true for average concentrations, it is not verified for each event, concentrations being higher in summer-fall than in winter-spring. The temporal evolution of the B concentrations is close to that of Si and seems to be related to variation in soil hydraulic status. Co-evolution of B and Si concentrations can be explained by similar chemical properties: they are both metalloids and undissociated weak acids at the soil solution pH. Their existence in clay interlayers could explain a behaviour related to water status. There also exists a correlation between B and Ba in soil solutions which cannot be explained by classical chemical properties of these elements, as they are very different.

Behaviour of the elements in the aquifers

We already pointed out that almost all the elements released by soils (Mn, Zn, Ba, Ni, Fe) are absent in springs and therefore seem to be fixed in the aquifers. This can be explained by different chemical reactions such as precipitation in the form of carbonate and hydroxides or adsorption on clays existing in rock fissures. Considering the pH of spring water each of these reactions are likely to occur and we have no means of specifying the prominent one as the aquifers were considered to be black boxes. The relative importance of each reaction is determined by differences in kinetics of the reactions.

Sr can be considered to be a major element in specific springs (concentration of several mg/l), containing evaporites (Mandia 1990) and come from the high solubility of celestine (SrSO_4). On other sites, Sr mainly comes from SrCO_3 dissolution, its behaviour being close to that of Ca.

Cr presents high concentrations at Camb spring, and considering the solution pH, it should be in $\text{Cr}_2\text{O}_7^{2-}$ form (Stumm 1970). As in soil, Cr is in Cr^{3+} form (Bartlett 1976) it has undergone an oxidation between soil and spring. This phenomenon is rather surprising because of the water table's existence but it has been observed by Bartlett (1979) who associates this oxidation with Mn reduction at specific redox potential.

Only the Podz spring contains elements which do not exist in soil solution: As, Mo and U. These three elements are sensitive to Redox variations. These elements are re-

leased with sulphates and could therefore originate from old reduced zones which are now undergoing oxidation (Dubois 1992).

Conclusion

The first task of this study was to define the respective roles of the atmosphere, soils and aquifers in the release of trace elements in springs. For each of the three studied sites, almost all elements are more concentrated in the atmosphere and soil solutions than in the spring. They seem to accumulate in deep soil layers or aquifers due to the pH increase and retention of organic matter in the top soil layers. The preferential role of the soil feature can be explained by the fact that the studied soils are derived from the underlying rock but present a much higher specific area which is directly in contact with acid atmospheric water. The aquifer role is important when chemical reactions different from those of soil occur in that zone i.e.: current or historical differences in redox potential (Cr, As, Mo, U and eventually Se) or existence of highly soluble minerals (mainly evaporite releasing Sr and Ga).

The studied springs are currently free of trace contamination, but the three types of ecosystems will react differently if the current scenario of atmospheric inputs continues.

- On carbonated rocks, all trace metals are fixed in the first meters of the aquifer. The size of the aquifer protects them against trace elements contamination. This fact does not exclude nitrate or organic pollution.
- On Podzol, organic matter carries a large amount of heavy metals but its fixation in spodic layers leads to fixation of trace metals in this layer. A problem can arise when organic matter passes directly to spring or rivers as in the thin soil – aquifer system in Scandinavia. In this case, rivers and lakes can be highly polluted.
- Acid cambisol releases high levels of pollutants (Mn, Zn) which mainly originate from soil acidification rather than atmospheric deposition. For the Camb example the scenario is simple: when the decarbonation wave reaches the spring level, water composition will be above the legal values for drinkable water. On equivalent substratum, existence of preferential flow could lead to the contamination of aquifers even now or in the near future.

Comparison of three very different sites allows us to suggest the role played by different factors and processes in real conditions. The role of pH is of little importance when we deal with very different geology and soil types. On one specific soil however, acidification plays a significant role, particularly on Mn and Zn concentrations in soil solutions. Organic matter is a buffer and a vector for many elements, particularly Cu and Pb; its movement is related to physical processes which need further investigation. The podzolisation process induces significant releases of V and Cr (like Fe) from the A2 layer, these elements being stable in other soils. Weathering processes play a significant role on Ni, Rb, Sr, Ba and Mn. In this case, the mineral composition of parent material can be decisive for differences in soil solutions composition. The hydraulic status of the soil induces temporal evolution of B and Ba concentrations. The role of biological cycling, redox potential and exchange have not been studied enough to give relevant conclusions.

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