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International Journal of Mass Spectrometry 242 (2005) 243–250

www.elsevier.com/locate/ijms

ICP-MS-based tracing of metal sources and mobility in a soil depth profile via the isotopic variation of Sr and Pb

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Received 11 November 2004; accepted 30 November 2004

Abstract

The isotopic compositions of lead and strontium and the total concentration of 11 elements (Rb, Sr, Ca, Ba, Cu, Zn, Mn, Fe, Pb, Cr, Cd) in NH_4NO_3 extracts (reflecting the mobile, bioavailable fraction) and total digests of soil fractions along a soil depth profile were analyzed using sectorfield ICP-MS. This information allows distinguishing between recent external (atmospheric deposition) and primary geogenic sources. Both isotopic systems indicate a clear difference between the surface composition and the composition of lower geogenic levels within the investigated soil profile. An increase of the $^{87}Sr/^{86}Sr$ isotope ratio can be observed in the total digest down to a depth of about 120 cm for Sr, whereas Pb shows a stable isotopic composition starting from a depth of about 60 cm. We found increased isotopic ratios of $^{87}Sr/^{86}Sr$ in the mobile fraction of the topsoil compared to the subsoil and to the total digest in the topsoil. This observation and the increased Sr levels in the mobile fraction of the topsoil are an indicator for recent deposition of Sr along with the dust derived from the paving of the forest roads in the study area. The significant change of the $^{87}Sr/^{86}Sr$ ratios in the total digest at 120 cm depth can be related to a variation in the lithology of this layer, which was confirmed by a concomitant change of the conventionally applied Ti/Zr ratio. This lithogenic inhomogeneity was not apparent from the fairly homogenous distribution of total Sr in the soil profile. Similarly, we were able to distinguish the accumulation of anthroponic heavy metal sources and their recent mobilization within the topsoil from long-term leaching of geogenic sources in deeper soil layers.

Keywords: Inductively coupled plasma mass spectrometry; Isotope ratios; Soil science; Metals

1. Introduction

Anthropogenic contamination in soils represents a significant risk to human health due to a possible mobilization into drinking water and plants via the food chain [1,2]. Moreover, stable systems are required in order to make a clear relation of heavy metal contamination to their sources of origin for risk assessment and risk management at contaminated sites. Several possibilities in order to estimate metal mobilization have been applied. The application of sequential extraction procedures reveals the amount of elements with high and low mobility within the soil [1]. Continuous methods like percolation are give additional information on the mobility in various soil compartments [3]. Chipley et al. combined an on-line leaching of soils to an ICP-MS in order to obtain real-time leaching data [4].

The isotopic composition of different elements is widely used as a clear indicator for different sources of origin [5]. Lead is an element of major importance in isotopic composition studies, since the data allow to determine sources of atmospheric lead [6,7] and to monitor the change of the source of origin in soils with respect to deposition time [8] or to the geological horizon [9]. Analysis of strontium isotopic ratios is a powerful tool in provenance studies and has been

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doi:10.1016/j.ijms.2004.11.028

applied successfully on inorganic [10] and organic samples [11], as well.

Secondary deposition of heavy metals on soil surfaces are mainly of anthropogenic origin [1]. The deposited material displays the isotope composition of the original ores before its conversion to raw or end products and its release to the environment. After emission into the atmosphere, transboundary air pollution by convective mixing processes over long distance leads to final deposition during precipitation events. After deposition on soil, heavy metals are mobilized to deeper layers and the measurement of enrichment and the isotopic composition along a soil profile can now be used to track anthropogenic versus natural sources and to assess possible effects of anthropogenic pollution in soils and further effects to drinking water or the food chain.

Inductively coupled plasma mass spectrometry (ICP-MS) has become the method of choice for isotope abundance ratio measurements in a variety of applications due to its ease of operation, high sample throughput and widespread availability. Limited precision is obtained by single collector instruments compared to multi-collector devices or thermal ionization mass spectrometer [12,13]. Nevertheless, single collector instruments allow a fast screening of both the isotopic composition and the ultra trace multielement composition. Total combined uncertainties of better than 0.1% make single collector ICP-MS suitable for a number of applications [9,14,15].

This paper presents the application of isotope ratio measurements of Sr and Pb in soil science for tracing metal sources and mobilization along a soil profile and can be seen as extension of our prior work in this field [9].

2. Experimental

2.1. Instrumentation and analytical performance

All analytical data were acquired by using a Finnigan MAT Element magnetic sector field ICP-mass spectrometer (Finnigan MAT, Bremen, Germany) operated in low resolution mode ($m/\Delta m = 400$) for analyzing both the isotopic composition of Pb and Sr and the concentration of Sr, Rb, Ba, Pb, Cd, Ti and Zr. The medium resolution mode settings were applied in order to analyze Ca, Fe, Zn, Mn, Cu and Cr due to possible spectral interferences especially in the complex soil matrix.

The torch is equipped with a Pt-guard electrode (CD1, Finnigan MAT, Bremen, Germany). A PFA nebulizer in combination with a double-pass Scott type spray chamber cooled to 4 °C was used as nebulizing system and sample transport to the nebulizer was established by a peristaltic pump (Perimax, Spetec, Vienna, Austria). In order to obtain maximum precision for isotope abundance ratio measurements and to enable quasi-simultaneous measurement conditions, parameters like sampling time, settling time of the magnet, segment duration, number of samples, mass window, and total scan duration were optimized according to previous studies [15]. The optimized instrumental parameters established for isotope ratio measurements are summarized in Table 1. Isotope ratios of Pb and Sr were corrected for deadtime and mass bias. External mass bias correction was accomplished by using an external standard, certified for the isotopic composition, which was analyzed every fifth sample. Isotope ratios were calculated from six independent runs per sample. The multiplicative correction factor was calculated from the quotient of the certified value divided by the measured value. Total combined uncertainties of isotope ratios were calculated according to Eurachem and GUM guidelines. Total combined uncertainties were 0.08% for the Pb isotope ratios and 0.07% for Sr isotope ratios.

Table 1
Operating parameter settings of the Finnigan MAT element and optimized instrumental parameters for isotope ratio analysis

General instrumental parameter	
RF power (W)	1250
Sample gas flow rate (L min^{-1})	1.0
Cooling gas flow rate (L min^{-1})	13.2
Auxiliary gas flow rate (L min^{-1})	1.5
Isotope ratio conditions	
Acquisition mode	Electrostatic scanning (E-scan)
Number of isotopes	^{87}Sr/^{86}Sr and ^{207}Pb/^{206}Pb
Mass window (%)	10
Settling time of magnet (s)	0.05/0.001
Sample time (ms)	5
Number of samples	10
Segment duration (ms)	50
Runs/passes	1 × 1000
Analysis time (min)	2.5
Replicate measurements	5
Deadtime (ns)	20

2.2. Chemicals and reagents

Mass bias correction for Pb was performed using a solution (2 ng g^{-1} in 1% (w/w) HNO_3) of the NIST SRM 981 Lead (NIST, Gaithersburg, MD, USA). Mass bias correction for Sr was performed using a solution (2 ng g^{-1} in 1% (w/w) HNO_3) of the SRM 987 reference material (NIST, Gaithersburg, MD, USA).

Calibration standards were prepared by gravimetrically diluting 1000 μg mL^{-1} single element ICP-MS standard solutions (Merck, Darmstadt, Germany) to a final nitric acid concentration of 1% HNO_3. The concentration in μg g^{-1} was calculated by using the according densities at 20 °C of the single standard solutions as given on the solution bottles. The stock solutions were pipetted into PE bottles on a balance at a temperature of 20 ± 1 °C and further diluted gravimetrically. The solutions were stored in polyethylene bottles at 4 °C prior to analysis. Quantification of the elemental concentration was performed using external calibration and internal standardization using ^{115}In and ^{187}Re (all at a concentration of 1 ng g^{-1} in the final solution) as internal standards.

Calibration standards were selected for each element according to the expected concentration range as derived from semi-quantitative measurements prior to the final quantification. A certified reference water solution (TM27, Canadian National Research Lab., Vancouver, Canada) was used for quality control of the external aqueous calibration. A certified reference soil (GBW07403, Institute of Environmental Chemistry Academia Sinica, China) was used for the quality control of the final quantification of elemental concentration of both the soil digests and extracts. The final results of the analysis of the certified soil were in the certified range for all measured elements.

In all analytical work, analytical reagent grade nitric acid (Janssen Chimica, Geel, Belgium) was additionally cleaned by subboiling in an ultrapure quartz apparatus (Milestone MLS GmbH, Leutenkirch, Germany). Reagent I grade water (18 MΩ) was additionally purified by subboiling.

The latter HNO_3, $H_2O_2$30% pro analysi (Merck, Darmstadt, Germany), additionally subboiled HCl pro analysi (Merck), H_3BO_3 pro analysi (Merck) and HF 48% pro analysi (Fluka, Buchs, Switzerland) were used for digestion.

2.3. Rb/Sr separation by ion batch ion exchange

Due to the high Rb content in both the total digest and the NH_4NO_3 extract, a quantitative Rb/Sr separation was a prerequisite for accurate Sr isotope ratio measurements. Therefore we applied a method, which we successfully evaluated for quantitative Rb/Sr separation for Sr isotope ratio measurements [16]. Moreover, the applied method removes Ca, as well, in order to minimize any effects of possible Ca based interferences [17]. The further evaluation of the Rb/Sr separation showed that Rb can be separated from Sr quantitatively up to a Rb:Sr ratio of 1000:1. At higher ratios, the solution has to pass the resin repeatedly.

The resin (EIChroM Industries, Inc., Darien, IL, USA) consists of a crown ether (bis-*t*-butyl-*cis*-dicyclohexano-18-crown-6) adsorbed on an inert substrate [18,19]. The resin was dispersed and washed in ultrapure water and finally conditioned in 3 mol L^{-1} HNO_3. 0.3 mL dispersed resin were packed in a polyethylene column and conditioned with 1 mL of 3 mol L^{-1} nitric acid. 2 mL of the samples were loaded onto the resin in all experiments. The column was washed three times with 0.5 mL of 3 mol L^{-1} nitric acid and Sr was eluted with 2 mL ultrapure water. HNO_3 concentration was added to all samples prior to Rb/Sr separation to a concentration of 3 mol L^{-1} nitric acid. The solution was diluted to 1% (w/w) HNO_3 after passing the resin in order to obtain an approximate Sr concentration of 2 ng g^{-1} for isotope ratio analysis. The analysis of ^{85}Rb in the mass spectrum together with Sr isotopes at mass 86 and 87 was used to monitor the quantitative separation of the interfering isotope ^{87}Rb in all samples.

Table 2
Characteristics of the investigated soil profile (Dystric Cambisol) [9]

Depth (cm)	Horizon	CEC (mmol$_c$ kg^{-1})	BS (%)	pH (0.01 M $CaCl_2$)
0–2	AEh	156	37	3.00
5–10	Bhs	134	14	3.50
60	Bw1	47	26	4.10
120	Bw2	37	30	4.10
220	BCw	40	29	4.00

2.4. Soil characterization [9]

Soil samples were collected in the Günser Mountains, Eastern Austria from a soil profile according to the pedogenetic horizons. The soil was classified as Dystric Cambisol developed on periglacial slope deposits derived from phyllite and schist. The study area is located in a periglacial landscape formed by the easternmost outcrops of the European Alps. The region has never been affected by the Alpine glaciation during the Pleistocene. This has resulted in profiles of deep weathering and acidification, and relatively large amounts of low-order clay minerals such as kaolinite in the soils. These minerals are an indicator of the advanced stage of weathering.

Samples were air-dried and passed through a 2 mm sieve. Common soil characteristics were measured according to standard procedures [20]: pH (0.01 M $CaCl_2$), cation exchange capacity (CEC—calculated as the sum of exchangeable cations in 0.01 M $BaCl_2$), base saturation (BS—calculated as the percentage of the sum of Ca, Mg, K, and Na relative to CEC). The latter soil characteristics are summarized in Table 2. An aliquot of the sieved and air-dried soil samples was ground using an agate ball mill for total digestion.

2.5. Sample preparation

Digestion of ground soil samples was performed by microwave assisted digestion (MLS-1200, Milestone, Leutkirch, Germany) applying a mixture of nitric acid, hydrochloric acid, hydrofluoric acid. The surplus HF was eliminated by a final addition of hydroboric acid [21]. Part of the solution was diluted and acidified with HNO_3 to obtain a final HNO_3 concentration of 3 mol L^{-1} prior to Rb/Sr separation. The rest of the solution was further diluted with purified water to obtain approximately 1% (w/w) nitric acid. The latter solution was directly analyzed by ICP-MS without further pre-treatment for Pb isotope ratios and metal concentration.

Sieved, air-dried soil samples were extracted (shaking end-over-end overnight) by 1 mol L^{-1} NH_4NO_3 (pa, Merck) solution at a solution:soil ratio of 2.5 mL solution:1 g soil. The samples were filtered prior to analysis. Element concentrations in this extract represent the mobile and bioavailable fraction bound to the surfaces of soil particles.

All measurements were carried out under clean room conditions with filtered (class 10000), temperature controlled and excess pressured air. Chemical preparations were conducted on special class 100 work benches inside the class 10000 clean laboratory.

3. Results and discussion

3.1. Strontium and lead isotopic composition

The Pb isotopic composition in both the soil extract and the total digest are shown in Fig. 1. The two curves show an almost identical change of the isotopic composition with depth (indicated by the overlap of the uncertainties). We observed an abrupt change in the isotopic composition already at the very topmost surface. The further variation of the isotopic composition along the depth profile shows a gradual change, approaching a stable value of ^{207}Pb/^{206}Pb of about 0.856 in approximately 60 cm depth. The isotopic composition between the surface and layers below 60 cm depth is a clear mixture of Pb from two different sources. The isotopic composition near the surface is mainly of anthropogenic origin, whereas deeper layers are dominated by Pb of geogenic origin. A substantial change of the soil horizon at this depth can be observed for the Sr isotopic composition, the Ti/Zr ratio and the total elemental concentrations, as well, and is discussed later in more detail.

The isotopic composition of Sr along the soil profile is shown in Fig. 2. The first two horizons (1.5 and 10 cm depth) show the same isotopic composition of total Sr, indicating that the main sources of Sr are identical within the top 10 cm. In contrast, we observed an increase of the ratio within these two top layers in the extractable (NH_4NO_3 extract) fraction. Along with increased Sr concentrations in the extractable fraction (Fig. 4) close to the surface, this observation indicates that the mobile Sr in the topmost soil layers is dominated by recent secondary sources deposited at the soil surface. The forest roads in the study region have been paved with large amounts of serpentine gravel during the recent decades. Serpentine is likely to have a ^{87}Sr/^{86}Sr ratio different from the soil parent material consisting of schist and phyllite. Dust derived from the serpentine paving as a consequence of abundant passage of trucks could thus explain the slight increase of the ^{87}Sr/^{86}Sr ratio in the uppermost topsoil. This example shows that isotopic ratios delivered by ICP-MS measurements together with soil chemical investigations can help to trace soil contamination at an early stage where the measurement of total element concentrations would not succeed.

The isotopic composition of total Sr in the deeper layers show an increase of the ratio up to a maximum of about 0.718 at a depth of about 120 cm. The variation between the surface and the depth of about 120 cm clearly reflects the mixture of recently deposited Sr and geogenic Sr. At depths below 120 cm, the ^{87}Sr/^{86}Sr ratio decreases, approaching a stable value of about 0.715 in the lowermost layers of the soil profile. The change at this depth is discussed in more detail later.

3.2. Distribution of metal concentrations in the soil profile

Strontium, Rb, Ba, Ca, Fe, Zn, Mn, Cu, Pb, Cd and Cr were analyzed in both the total digest (total element concentrations) and the NH_4NO_3 extracts (representing the mobile fraction). (Table 3).

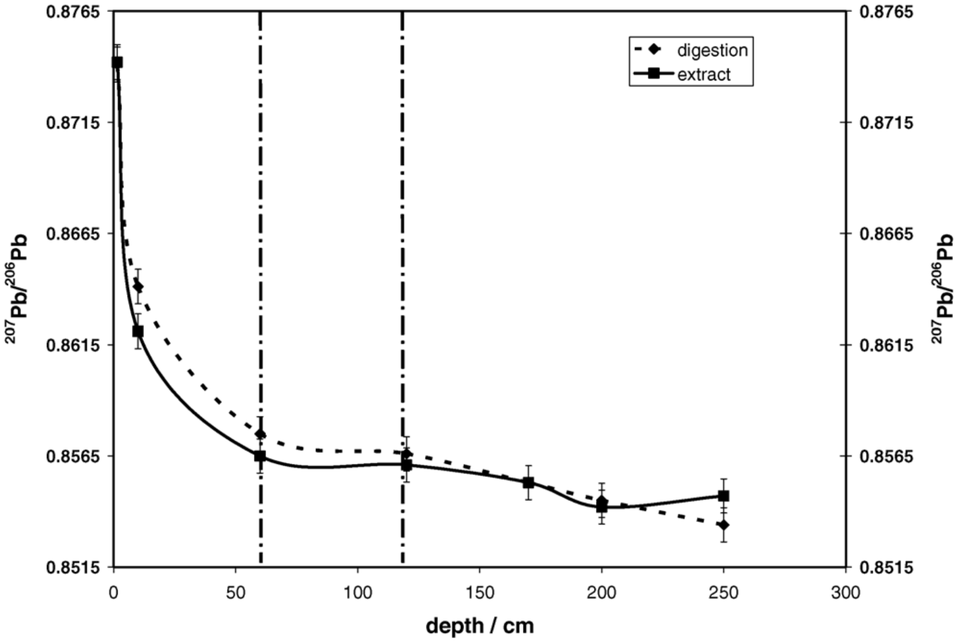

Fig. 1. ^{207}Pb/^{206}Pb ratios of the soil profile in the total digest and the NH_4NO_3 extract (mobile phase).

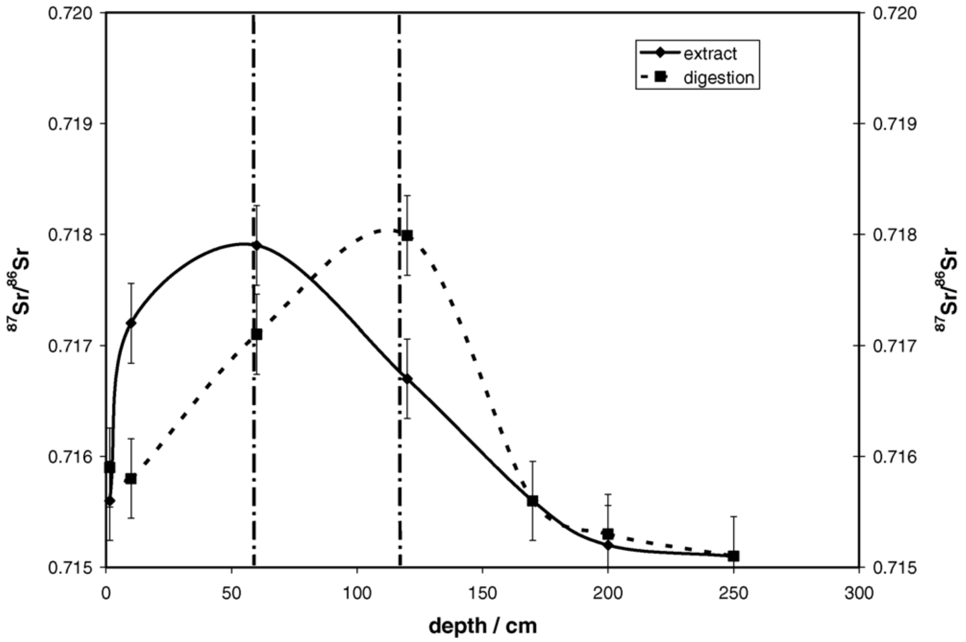

Fig. 2. $^{87}Sr/^{86}Sr$ ratios of the soil profile in the total digest and the NH_4NO_3 extract (mobile phase).

The distributions of the total concentrations of Cr, Cu, Mn and Fe in the soil profile (Fig. 3a) reflect the expected deep leaching due to long-term weathering of the Dystric Cambisol. The region, where the soil was collected, has never been covered by glaciers during the Pleistocene and Holocene and has therefore been subject to strong weathering and associated leaching of elements for long periods. The strong, deep-reaching acidification of the soil is indicated by the low pH values to depths of more than 220 cm and by the distribution of acid NH_4-oxalate extractable Fe, Mn and Al [9]. According to Schwertmann [22], this fraction, often referred to as sesquioxides, represents roughly the amount of Fe, Al and Mn fixed in amorphous hydroxides during soil formation. Together with the low pH, the distribution of the sesquioxides indicates excessive dissolution in the uppermost part of the soil profile and leaching to deep soil layers [23].

Similarly, the increase of the concentration of Sr and Ba indicates leaching of these elements, as well, whereas Ca has accumulated in the topsoil as a consequence of biological cycling between soil and vegetation (Fig. 3b). This accumulation is restricted to the main root zone of the forest stand growing on the investigated soil. Interestingly, the total Ca concentration shows its maximum at about 60 cm depth.

The total concentrations of Zn, Pb and Cd show a different pattern (Fig. 3c). We have discussed the variation of the Pb concentration in a previous paper [9]. Briefly, the

Table 3
Elemental concentration in the NH_4NO_3 extract and the total digestion (calculated for $\mu g\,g^{-1}$ dry soil)

Depth (cm)	Sr ($\mu g\,g^{-1}$)	Rb ($\mu g\,g^{-1}$)	Ba ($\mu g\,g^{-1}$)	Ca ($\mu g\,g^{-1}$)	Fe ($mg\,g^{-1}$)	Zn ($\mu g\,g^{-1}$)	Mn ($\mu g\,g^{-1}$)	Cu ($\mu g\,g^{-1}$)	Pb ($\mu g\,g^{-1}$)	Cd ($\mu g\,g^{-1}$)	Cr ($\mu g\,g^{-1}$)
Extract											
1.5	7.6	1.9	50	144	1.4	18	86	2.9	54	0.33	0.82
10	1.9	2.0	33	74	1.6	9.8	83	3.3	24	0.12	2.2
60	2.0	3.7	44	244	0.81	6.7	131	3.6	12	0.10	3.5
120	1.2	2.6	39	68	0.64	6.1	199	3.3	12	0.08	2.5
200	2.9	5.4	82	89	0.87	3.9	616	8.2	14	0.13	1.2
250	3.0	5.1	135	106	0.76	8.0	361	27	22	0.15	1.1
Digestion											
1.5	57	82	341	1407	28	67	160	45	317	2.3	78
10	68	102	440	861	41	101	260	33	382	1.5	102
60	69	106	477	2122	40	91	336	36	52	0.99	103
120	74	113	505	994	40	98	431	38	284	0.95	106
200	80	148	689	569	57	121	1596	113	325	1.6	128
250	83	144	691	666	111	270	1041	463	411	2.3	148

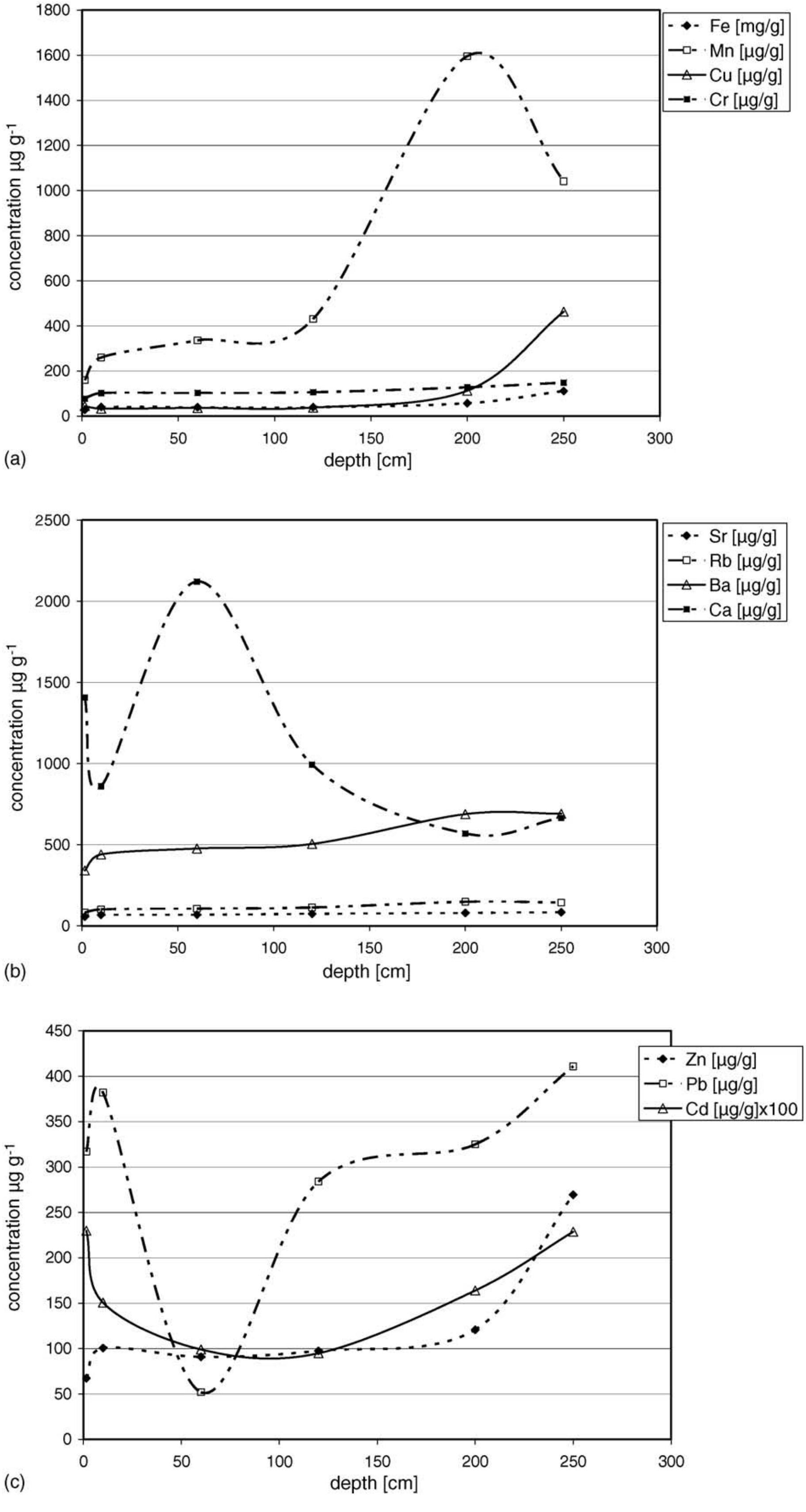

Fig. 3. (a) Variation of the total concentration of Fe, Mn, Cu and Cr vs. depth ($\mu g\,g^{-1}$). (b) Variation of the total concentration of Ca, Sr, Ba and Rb vs. depth ($\mu g\,g^{-1}$). (c) Variation of the total concentration of Zn, Pb and Cd vs. depth ($\mu g\,g^{-1}$).

depth distribution indicates strong leaching due to long-term weathering of the soil, confounding with accumulation of anthropogenic lead in the topsoil. Similarly, Zn and Cd have accumulated in the topsoil. Surface accumulation of Cd can be explained mainly by atmospheric deposition, whereas biological cycling may have also contributed in the case of Zn which is an essential plant nutrient.

We used 1 M NH_4NO_3 extraction to characterize the exchangeable element fractions in the soil. This fraction is considered to be in rapid exchange with the water passing through the soil profile and therefore reflects the mobile or extractable fraction that can be leached to the groundwater. This fraction is also readily available to plants and soil organisms. Lower 1 M NH_4NO_3 extractable metal concentrations in the topsoil are likely to reflect long-term leaching of this element from the soil. On the other hand, larger concentrations in the topsoil compared to deeper layers would typically indicate mobilization, often as a consequence of topsoil acidification. As the investigated soil is strongly acidic throughout to a depth of >220 cm (Table 2), it is more likely that topsoil accumulation of an element in the mobile fraction would be related to atmospheric deposition. This seems to be the case for Pb, Cd, Zn, Ba and Sr (Fig. 4). This is supported by the likewise elevated total concentrations of Pb, Cd and Zn. However, Ba and Sr concentrations in the topsoil are significantly more increased in their exchangeable fractions compared to the total digest. This may indicate a more recent input of Ba and Sr into the soil, a circumstance, which cannot be detected by the measurement of the total concentrations, solely. This observation is underlined by the Sr isotopic composition. The different ratios in the uppermost soil horizon would be consistent with input of Sr to the topsoil as also indicated from the pattern in the exchangeable fraction. Moreover, Sr, Ca, Ba and Rb show a pronounced peak of the concentration at a depth of about 60 cm, confirming the known similarity of the geochemical behaviour of these earth alkali elements.

3.3. Inhomogeneities in the soil layers

As mentioned earlier, the $^{87}Sr/^{86}Sr$ ratio in the acid digests shows a pronounced peak at a depth of about 120 cm. The conventional measurement of total Sr does not show any anomaly, but gradually increases from the topmost surface to a depth of 250 cm. Based on these observations, it is unlikely that the peak of the $^{87}Sr/^{86}Sr$ ratio is related to Sr leaching and corresponding accumulation below the topsoil. We conclude that this anomaly could be related to some change in the parent material at this depth. Such a change was not obvious from the field observations. The only but weak indication for a lithogenic difference could be the occurrence of 18% rock fragments with a diameter >63 cm between 60 and 120 cm depth, whereas the layers above and below do not contain such coarse material. The soil is located on a 25% steep slope. During the transition from the last cold period (the so called Würm glaciation in Central Europe) to the warmer Holocene, the vegetation free, water saturated upper soil layers were subject to alternating thawing–freezing cycles, resulting in substantial mixing and lateral transport of soil material on the frozen subsoil. In many situations, material from the upper slopes was transported to lower locations, creating lithogenically different layers in the parent material for the subsequent soil formation during the Holocene. Often, there is only indirect evidence for the different origin of these layers, for instance indicated by the abundance and morphology of rock fragments. A sound analysis of the homogeneity of the parent material is important if the distribution of element concentrations in the deeper soil profile is used as a baseline for the detection of changes due to soil formation (e.g., due to leaching) or of anthropogenic impacts. A

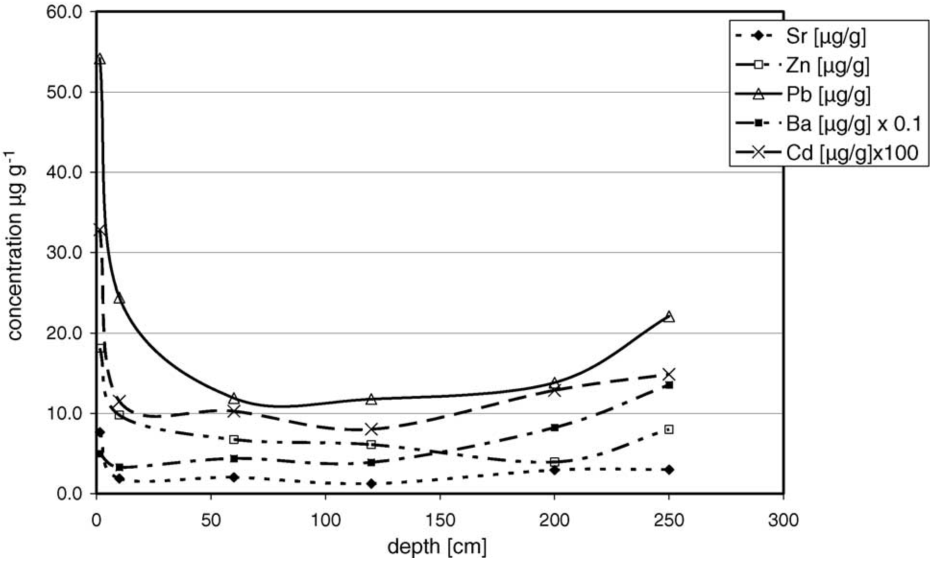

Fig. 4. Variation of the concentration of Sr, Ba, Zn, Pb and Cd vs. depth in the extractable fraction (NH_4NO_3 extract) (µg g^{-1}).

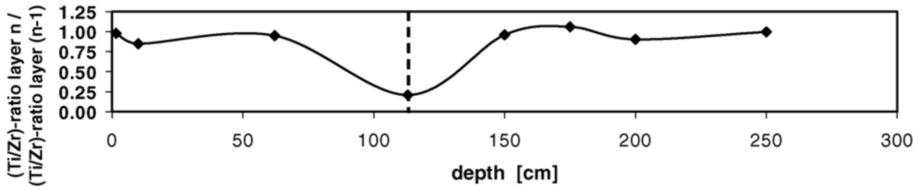

Fig. 5. Relative variation of the Ti/Zr ratio vs. depth.

traditional approach to analyze the lithogenic homogeneity of a soil profile is the use of the Ti/Zr ratio. Both elements are considered to be fairly unaffected by weathering and leaching. A change in the Ti/Zr ratio is therefore likely associated with a change of the lithology of the parent material. However, this method has its limitations and should be used in combination with other approaches. The Ti/Zr ratio in the investigated soil is shown in Fig. 5. We can observe a pronounced minimum in the same layer where we found the peak of the $^{87}Sr/^{86}Sr$ ratio of total Sr (Fig. 2) and a slight decrease of the $^{207}Pb/^{206}Pb$ ratio, as well. The combination of the two approaches provides sound evidence for lithogenic differences in the investigated soil profile.

4. Conclusion

The approach presented here combines ICP-MS-based measurements of isotopic element ratios and of element pattern in a soil profile with classical soil chemical analysis. This combination provides a powerful tool for the discrimination of external (anthropogenic) and geogenic sources of Sr and Pb in soils. Moreover, it is possible to use the isotopic ratio of Sr to trace lithological differences in soils formed on inhomogeneous parent materials. We used this approach together with the classical pedological Zr/Ti ratio. This combination helps to increase the certainty and to overcome limitations of the individual approaches. The comparison of isotopic ratios measured in total digests and soil extracts representing the mobile fraction of an element can further refine the interpretations. Differential isotopic ratios in the mobile fraction compared to those found in the total digest of topsoils can be used as indicators of recent external inputs, especially if the element concentrations in the mobile fraction and/or the total digest support the interpretation.

Acknowledgements

Financial support was granted through the Hochschuljubilaeumsfonds der Stadt Wien and the Austrian Science Fund (FWF P12840-CHE).

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