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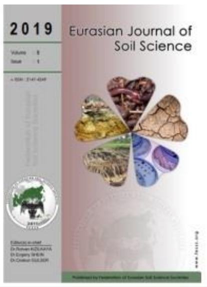

Organic-inorganic interactions in an aridisoil of Oman along vertical and lateral trends of the soluble major, trace and rare-earth elements

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Abstract

Major, trace and rare-earth elements "(REEs)" dissolved by successive water and acetic-acid leaching of soil samples were quantified along a vertical and a lateral trend relative to a reference aridisoil covered by palm trees. The total content of the organic carbon ranges from 0.07 to 2.7% with the highest values in the topsoil closely below vegetation, confirming a higher organic activity. The water-removed elements decrease irregularly with depth and with increasing distance to the vegetated area, the highest concentrations being observed at 20 cm depth and 18 m away from vegetation. The nutrients removed by acetic-acid decrease with depth and until 22 m from vegetation. Maximum leaching was observed in the surface sample and 32 m away from vegetation. In fact, no straight trends were obtained in both the vertical and horizontal samplings; it looks that the elemental contents of each soil layer are only representative for themselves. The metallic trace elements are more abundant in the topsoil than in the subsoil, suggesting some anthropogenic supply. Mainly controlled by solid organic exudates, the REEs are the only ones with general vertical and horizontal trends: they decrease at depth, together with an increase laterally away from vegetation. The Ce and Eu positive anomalies increase deeper below the vegetation and away: an oxidation-reduction change is visible for the former anomaly, probably due to decreasing organic activity. The latter anomaly away from vegetation could reflect a larger contribution of soluble minerals to the leachates.

Keywords: Lateral and vertical distribution records; vegetated aridisoil; major, trace and rare-earth elements; water and acetic-acid leachings; organic matter activity; anthropogenic supply.

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Introduction

Plant roots and their soil interface constitute an intense interactive zone where many biochemical reactions take place. In the light of such reactions, the nutrient dynamics control the activity of the microorganisms, the growth of the plants, as well as a variable dissolution and alteration of minerals from hosting soils (Jobbágy and Jackson, 2001; Shen et al., 2011; Camenzind et al., 2018). Understanding of such vital reactions is fundamental and may be investigated by characterizing the role and distribution of the nutrients, especially in the rhizosphere. Varied studies focused on the distribution of specific elements, such as phosphorus in the host soils (Hedley et al., 1982a; Helal and Dressler, 1989; Gahoonia and Nielsen 1992; Zoyza et al., 1997). Others outlined the vertical distribution of nitrogen and carbon (Nielsen et al., 1988; Knops and Bradley, 2009), or the pH variations in the rhizosphere (Hedley et al., 1982b). Manea et al. (2011) investigated the vertical distribution of Cu, showing that it decreases with depth, the highest content in the topsoil being due to anthropic human activity. Fekiacova et al. (2013) described the vertical distribution of Fe in soils, while other studies (Mathan, 1991; Jayaganesh et al., 2011) investigated the vertical distribution

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of Mg, still in soils, Wood and de Turk (1940) and Hirekurabar et al. (2000) examining that of K. However, only a few investigations established a clear relationship between the vertical distribution in the rhizosphere and the lateral trend of elements, such as of the lanthanides for instance, that can be useful for soil management and plant preservation. In turn, understanding the elemental dynamics in soils by using their spatial distribution is necessary to decrypt the elemental evolution and their impact on their immediate environment.

The objectives of this study carried in a region under arid climate were then in an identification of the vertical partitioning of essential and non-essential elements in a soil with a vegetal cover, and the lateral distribution of the same elements in the same soil at an increasing distance from vegetation to identify best the local interactions of the vegetal and mineral worlds. This experiment was also undertaken to estimate the availability of nutrients to plants and their immediate mobility. Micronutrients of soils may be associated with different phases, such as exchangeable cations, carbonates, Fe and Mn oxides, organic matter, sulphides and silicates, as well as salts in arid countries, because these chemical forms can influence their mobility, toxicity and bioavailability. Furthermore, soil characteristics, such as the pH and Eh, the clay content and cation-exchange capacity, and the occurrence of Mn, Fe oxides and organic matter are also contributing to the distribution of heavy metals and their availability to plants in soils (Martínez and Motto, 2000; Sterckeman et al., 2000; Aydinalp and Marinova, 2003). Water-exchangeable and acid-extractable soluble fractions contain mobile compounds that are easily bioavailable. Since nutrients of the accessible fractions are mostly involved in the growth of plants and in the activity of microorganisms in soils, reflecting potentially both the soil bedrock supply and anthropogenic inputs, the present study was based on the examination of major, trace and rare-earth elements removed by successive water and acetic-acid leaching experiments. As examination of rare earth-elements (REEs) in soils has repetitively shown specific applications (e.g., Tyler, 2004; Semhi et al., 2009; Chang et al., 2016) in the assessment of soil genesis, the increase of soil fertility, the evaluation of anthropogenic impacts, and also the identification of pedogenic processes, we have dedicated a special interest to these elements.

REEs also identified as lanthanides consist of elements that are characterized by a ground state electronic configuration with at least one electron in the 4f electronic orbitals, mostly non-interactive but with a strong ionic bonding character making them as strong acids (Piper and Bau, 2013). REEs occur generally with three electrons removed from their d, s and f orbitals; only Eu has a half-filled f-orbital that allows stability for the Eu^{2+} species, and Ce exhibits an oxidation-reduction state that allows Ce to occur as either Ce^{3+} or Ce^{4+}, especially in soils (Taylor and McLennan, 1985). Wyttenbach et al. (1998) studied REEs of leaves from plants and the associated soils and found that Ce yields a negative anomaly in all plants with respect to the corresponding soil. Miao et al. (2008) reported that the geochemical characteristics of REEs from plants depend on the types of soils, that their concentrations are higher in B and C soil horizons than in the above A horizon, and that they outline an Eu negative anomaly and a Ce positive anomaly. They also described REE fractionations from soil to plant roots, stems and leaves, with heavy REEs (HREEs) relatively less available relative to the light REEs (LREEs). Alternatively, Loell et al. (2011) reported a Ce negative anomaly in German soils, as did Wyttenbach et al. (1998) in plants, together with correlations between REEs and clay, Fe, and Mn oxide contents.

Material and Methods

The selected site is the palm-tree nursery of the Agricultural Experiment Station from the Sultan Qaboos University in Oman. The station covers an area of 70 hectares and among the variety of fruit crops grown at the station, are date palm trees (*Phoenix dactylifera L*) that account for about 500 trees distributed in open fields and along road paths. The area is characterized by an average relative humidity of 46% and an average annual temperature of 29°C, the minimum night and maximum day temperatures ranging from 13 to 48°C, respectively. The evapotranspiration rate was measured at 3-12 mm/day. The samples belong to the groves and vicinity of a date palm cultivar called “Khalas”. This cultivar has an average production of 120 kg/season dates at the station. The date palms are irrigated with a bubbler system with two bubblers in each grove supplying 280 to 320 L/day of low salinity groundwater (< 2 dS/m) to each date palm tree. The soils were collected at different depths and distances from palm trees with determination of the pH values during sampling. For the vertical investigation, the samples were collected 10 cm below the surface, as well as at 20, 50 and 100 cm depths in the subsoil. For the lateral investigation, a second set of samples was collected at a constant depth of 50 cm at 10, 12, 18, 22 to 32 m from the vegetation.

All soil samples were dried for 2 days at room temperature and then were placed in an oven at 60 °C for about 10 h before being hand-crushed in a mortar. One gram of dry soil sieved at <63 µm was first leached with double-distilled water during 15 min at a room temperature of 20 °C. The extracts were separated from residues by centrifugation at 4,000 rpm (SIGMA model 3-15). The residues were washed again afterwards with double-distilled water by shaking and centrifugation. Then, the residue was treated with 40 ml of acetic acid (CH_3COOH at 0.1 mol/L). The extracts were also separated from solid residues by centrifugation for their chemical analysis.

The elemental contents were determined on an inductively coupled plasma atomic emission spectrometer (ICP-AES of the Laboratoire d'Hydrologie et de Géochimie de Strasbourg, France) for the major (Si, Al, Mg, Ca, Na, K and P) and some trace elements (Sr, Fe, Mn and Zn), and on an inductively coupled plasma mass spectrometer (ICP-MS also of the Laboratoire d'Hydrologie et de Géochimie de la Surface de Strasbourg, France) for the other trace elements (V, Cu, Ba, Cr, Co, Ni, Rb, As, Zr, Cd, U and Th) and the rare-earth elements (REEs). Repeated analysis of international standards such as B-EN and GL-O on a weekly basis provided an analytical precision of ±2.5% for the major elements, ±5% for the trace elements and ±10% for the REEs, on the basis of the analytical procedure by Samuel et al. (1985). The total organic carbon (TOC) was measured with a TOC analyzer (Simadzu Model TOC-V) on a precision better than ±5% and a detection limit of 0.05 mg/kg).

Results

The results include pH, TOC (in %) and concentrations (in mg/g, µg/g and ng/g) of the elements analyzed in the collected leachates by either water or dilute acetic-acid action. In the study site, the soils are alkaline with a pH ranging from 7.34 to 8.71 (Table 1), the vertical and lateral variability being very limited.

The TOC ranges from 0.07 to 2.7% with the highest value in the surface horizon close to vegetation, decreasing vertically and horizontally away from vegetation, which confirms the expected organic activity decrease away from vegetation (Table 1). The vertical TOC are higher than the lateral ones, confirming that the organic activity in the vegetation area is higher than in the corresponding de-vegetated one. As organic matter plays a determining role in binding heavy metals in soils and sediments (Akan et al., 2003), it is also considered to immobilize them and reduce their uptake by the plants, which is not what was found here. Alternatively, organic complexation of heavy metals in soils (Weng et al., 2002; Silveira et al., 2003; Tukura et al., 2007; Ashworth and Alloway, 2008) reduces heavy-metal pollution of plants including consumable vegetables.

The elements removed by water leaching

The contents of the major elements

The water extracts contain mainly elements that are easily removable, mainly adsorbed on the mineral particles and organic compounds sensitive to water contact. The most extracted elements here are Na, Ca and Mg with a vertical distribution indicating an important extraction of Ca, Mg, Na, K, Mn and P at 20-cm depth, while the highest extraction of Fe and Al occurred further down in the horizon at a 50-cm depth (Fig. 1), Si being most leached in the uppermost 10-cm deep horizon. To be noticed also is the parallel changes of the Ca and Na contents in both the vertical and the horizontal trend. On the other hand, the P contents are drastically decreasing when sampling is away from vegetation, vertically and horizontally. The K contents appear more complex as they decrease when buried, which could relate to increasing distance to vegetation. However, in the horizontal display, they increase with increasing distance to vegetation (Figure 1).

The lateral distribution indicates that Al and Fe are enriched 10-m away from vegetation with ups and downs beyond: decrease at 12 m, increase again at 18 and 22 m, before another decrease at 32 m. Ca, Si and K yield also waving contents when collected away from vegetation. None outlines a constant change, either increasing or decreasing, which suggests that the interference between organic and inorganic influences is not straight (Figure 1). In summary, the total amounts of major elements leached by water decrease with depth by about half between the uppermost and lowermost samples. On the other hand, it fluctuates by a similar ratio when the distance to vegetation increases, the lower contents being recorded at 10 and 22 m away from vegetation (Figure 2).

The Na/K ratio varies between 1.6 and 29.1, the highest value being observed in the vertical trend at the 100-cm depth, which suggests crystallization of Na salts at depth rather than in the topsoil due to the arid climate. The lateral distribution of this ratio indicates also a decrease of Na soluble phases when the distance from vegetation increases, even at similar depth (Table 1; Figure 3). The highest value for the K/Rb ratio is at a 50-cm depth in the vertical profile. Along the horizontal display, the same ratio decreases first when distance to vegetation increases, then it increases until 22 m away from vegetation. The Ca/Sr ratio increases with depth, while zigzagging horizontally when distance increases (Figure 3). The Mg/Ca ratio ranging from 0.2 to 1.35 tends to decrease with depth and with distance from vegetation due to an increase of the Ca content. Its highest value is observed in the topsoil due to a higher Mg concentration relative to Ca.

Table 1. Major, trace and rare-earth elemental compositions of the water and acetic acid leachates along the vertical and horizontal trends. The contents of the analyzed elements are plotted in the data columns of each. bdl stands for below detection limit and nd for not determined.

Water leachates	Depth (m)	Si (µg/g)	Al (µg/g)	Mg (µg/g)	Ca (µg/g)	Fe (µg/g)	Mn (µg/g)	Na (µg/g)	K (µg/g)	P (µg/g)	Sr (µg/g)	Zn (µg/g)	Na/K	Ca/Sr	K/Rb	TOC (%)	pH values
1 W	0.10	45.5	0.32	193	170	0.59	0.04	650	90.3	44.0	2.69	2.25	7.20	63.0	1859	2.09	8.29
2 W	0.20	30.8	1.85	400	297	1.52	0.25	948	108	43.9	4.60	2.11	8.75	64.6	2062	2.66	8.45
3 W	0.50	23.8	4.84	83.1	127	3.44	0.06	538	103	26.5	1.21	1.17	5.22	105	5886	0.70	8.97
4 W	1.00	40.5	1.73	111	177	1.25	0.20	640	22,0	24.5	1.74	0.79	29.1	102	2200	0.45	8.68
	Distance (m)																
5 W	10.0	82.3	23.0	77.7	312	14.8	0.43	184	62.8	4.45	2.72	0.40	2.93	111	1569	0.08	8.89
6 W	12.0	26.3	0.11	65.2	200	0.08	0.14	313	56.3	5.80	13.4	0.43	5.56	14.9	4500	0.09	8.90
7 W	18.0	31.5	4.94	141	719	2.76	1.02	468	132	4.68	10.1	1.93	3.53	71.1	5878	0.07	9.03
8 W	22.0	40.0	4.37	46.4	154	2.78	0.21	192	117	7.95	9.26	1.08	1.63	16.6	6700	0.07	8.75
9 W	32.0	33.5	0.32	93.2	467	0.20	0.05	370	114	5.68	4.81	0.30	3.24	96.9	4570	0.07	8.95
Acid leachates	Depth (m)	Si (mg/g)	Al (mg/g)	Mg (mg/g)	Ca (mg/g)	Fe (mg/g)	Mn (mg/g)	Na (mg/g)	K (mg/g)	P (mg/g)	Sr (mg/g)	Zn (µg/g)	Na/K	Ca/Sr	K/Rb		
1 AC	0.10	0.22	0.23	2.97	326	0.16	0.15	0.83	0.33	0.14	0.45	14.5	2,49	724	1335		
2 AC	0.20	0.25	0.20	7.60	175	0.06	0.28	1.41	0.24	1.07	0.36	24.5	5,86	491	2008		
3 AC	0.50	0.36	0.36	6.32	172	0.14	0.39	1.12	0.39	1.26	0.26	27.8	2,86	670	4255		
4 AC	1.00	0.29	0.10	9.98	130	0.07	0.51	1.52	0.36	4.70	0.42	66.8	4,21	311	2395		
	Distance (m)																
5 AC	10,0	0.61	0.19	9.87	127	0.12	0.59	1.34	0.36	4.52	0.49	0.116	3.69	259	2851		
6 AC	12,0	0.25	0.35	4.69	174	0.08	0.10	0.86	0.39	0.17	0.36	0.008	2.18	484	3154		
7 AC	18,0	0.22	0.22	2.97	307	0.12	0.13	0.58	0.36	0.073	0.54	0.007	1.62	572	7189		
8 AC	22,0	0.18	0.23	3.37	155	0.08	0.12	0.97	0.33	0.14	0.38	0.007	2.94	410	8835		
9 AC	32,0	0.22	0.17	3.67	390	0.11	0.16	0.83	0.36	0.093	0.69	0.006	2.29	565	6908		

Table 1. (continued)

Water leachates	Depth (m)	V (ng/g)	Ba (ng/g)	Cr (ng/g)	Co (ng/g)	Ni (ng/g)	Cu (ng/g)	As (ng/g)	Rb (ng/g)	Zr (ng/g)	Cd (ng/g)	Zn (ng/g)	Pb (ng/g)	Th (ng/g)	U (ng/g)	Zn/Cu
1 W	0.10	182	123	89.8	4.61	192	379	24.3	48.5	16.8	2.79	2.25	8.25	6.07	2.91	5.94
2 W	0.20	163	168	92.5	7.25	210	373	42 .5	52.5	12.8	2.33	2.11	9.25	1.25	2.25	5.66
3 W	0.50	225	85.0	123	5.75	485	498	27.5	17.5	10.0	2.43	1.17	7.00	1.50	3.00	2.35
4 W	1.00	255	103	85.0	7.00	383	265	37.5	10.0	9.50	1.58	0.79	6.25	0.75	1.00	2.96
	Distance (m)															
5 W	10.0	129	273	188	22.8	655	420	37.5	40.0	18.8	0.60	0.40	20.0	2.00	2.00	0.94
6 W	12.0	131	398	45.0	6.50	60.0	52.5	37.5	12.5	bdl	0.30	0.43	2.75	bdl	0.50	8.14
7 W	18.0	45.5	235	42.5	27.5	218	113	15.0	22.5	bdl	1.63	1.93	14.3	bdl	0.50	17.1
8 W	22.0	96.5	230	62.5	12.8	95.0	0.09	32.5	17.5	2.50	1.48	1.08	5.75	bdl	1.25	12.7
9 W	32.0	30.5	143	57.5	2.75	67.5	0.04	10.0	25.0	bdl	0.03	0.30	nd	bdl	0.75	7.44
Acetic acid leachates	Depth (m)	V (µg/g)	Ba (µg/g)	Cr (µg/g)	Co (µg/g)	Ni (µg/g)	Cu (µg/g)	As (µg/g)	Rb (µg/g)	Zr (µg/g)	Cd (µg/g)	Zn (µg/g)	Pb (µg/g)	Th (µg/g)	U (µg/g)	Zn/Cu
1 AC	0.10	1.10	17.6	9.75	1.65	11.6	7.35	0.62	0.25	0.19	0.20	14.5	0.90	0.49	0.48	8.82
2 AC	0.20	0.54	17.4	7.54	2.58	10.0	1.72	0.32	0.12	0.17	0.12	24.5	0.47	0.11	0.25	9.50
3 AC	0.50	0.70	11.6	11.0	3.38	11.5	1.07	0.46	0.09	0.27	0.15	27.8	0.27	0.08	0.45	8.22
4 AC	1.00	0.32	21.1	6.60	2.46	4.17	1.06	0.28	0.15	0.18	0.19	66.8	0.24	0.04	0.26	27.1
	Distance (m)															
5 AC	10.0	0.93	20.2	14.3	3.99	10.4	0.72	0.72	0.13	0.19	0.23	1.00	0.24	37.2	0.62	29.1
6 AC	12.0	0.14	10.1	6.79	2.32	9.87	1.16	0.27	0.12	0.06	0.06	8.00	0.37	118	0.25	3.45
7 AC	18.0	0.92	17.4	7.04	1.51	8.75	0.84	0.49	0.05	0.04	0.10	6.75	0.48	236	0.41	4.47
8 AC	22.0	0.19	6.84	5.55	2.33	8.21	0.68	0.28	0.04	0.03	0.05	7.25	0.30	130	0.17	3.11
9 AC	32.0	1.47	28.3	7.95	1.91	10.9	0.98	0.40	0.05	0.03	0.13	6.00	0.53	260	0.52	3.15

Table 1. (continued)

Water leachates	Depth (m)	La (ng/g)	Ce (ng/g)	Pr (ng/g)	Nd (ng/g)	Sm (ng/g)	Eu (ng/g)	Gd (ng/g)	Tb (ng/g)	Dy (ng/g)	Ho (ng/g)	Er (ng/g)	Tm (ng/g)	Yb (ng/g)	Lu (ng/g)	Total (ng/g)
1 W	0.10	4.37	9.22	1.07	3.40	0.83	0.46	0.97	0.34	0.66	0.29	0.46	0.22	0.49	0.17	22.9
2 W	0.20	3.00	7.25	0.73	2.25	0.58	0.30	0.72	0.23	0.45	0.18	0.33	0.15	0.25	0.13	16.5
3 W	0.50	4.50	9.25	1.23	4.25	0.95	0.33	1.08	0.25	0.95	0.23	0.45	0.10	0.53	0.10	24.2
4 W	1.00	2.25	6.50	0.55	2.50	0.55	0.18	0.50	bdl	0.53	bdl	0.20	0.05	0.23	0.05	14.1
	Distance (m)															
5 W	10.0	10.3	21.5	2.30	9.75	1.95	0.80	2.10	0.28	1.40	0.40	0.75	0.13	0.65	0.10	52.4
6 W	12.0	bdl	1.00	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	nd
7 W	18.0	1.50	10.8	0.43	1.75	0.38	bdl	0.50	bdl	0.28	bdl	0.15	bdl	0.13	bdl	nd
8 W	22.0	1.00	4.25	bdl	1.00	bdl	bdl	0.18	bdl	bdl	bdl	bdl	bdl	bdl	bdl	nd
9 W	32.0	0.25	0.75	bdl	0.25	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	nd
Acetic acid leachates	Depth (m)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	Total (µg/g)
1 AC	0.10	3.34	4.76	0.95	4.01	1.00	0.24	0.96	0.15	0.85	0.17	0.42	0.057	0.31	0.005	17.3
2 AC	0.20	1.29	1.88	0.32	1.49	0.38	0.11	0.42	0.06	0.37	0.08	0.20	0.027	0.15	0.002	6.81
3 AC	0.50	1.29	1.93	0.31	1.51	0.39	0.12	0.46	0.07	0.44	0.09	0.25	0.034	0.20	0.003	7.12
4 AC	1.00	0.38	0.52	0.08	0.37	0.09	0.03	0.11	0.15	0.09	0.02	0.05	0.001	0.04	0.007	1.80
	Distance (m)															
5 AC	10.0	0.45	0.66	0.10	0.49	0.13	0.04	0.16	0.02	0.13	0.03	0.08	0.01	0.07	0.01	2.38
6 AC	12.0	1.47	1.65	0.40	1.71	0.43	0.10	0.40	0.06	0.35	0.07	0.17	0.02	0.13	0.02	6.98
7 AC	18.0	2.28	3.00	0.63	2.69	0.66	0.16	0.63	0.01	0.58	0.11	0.29	0.04	0.22	0.03	11.4
8 AC	22.0	1.09	1.40	0.29	1.22	0.29	0.07	0.29	0.04	0.25	0.05	0.12	0.02	0.09	0.01	5.22
9 AC	32.0	2.83	3.79	0.79	3.41	0.85	0.21	0.82	0.12	0.76	0.14	0.38	0.05	0.28	0.04	14.5

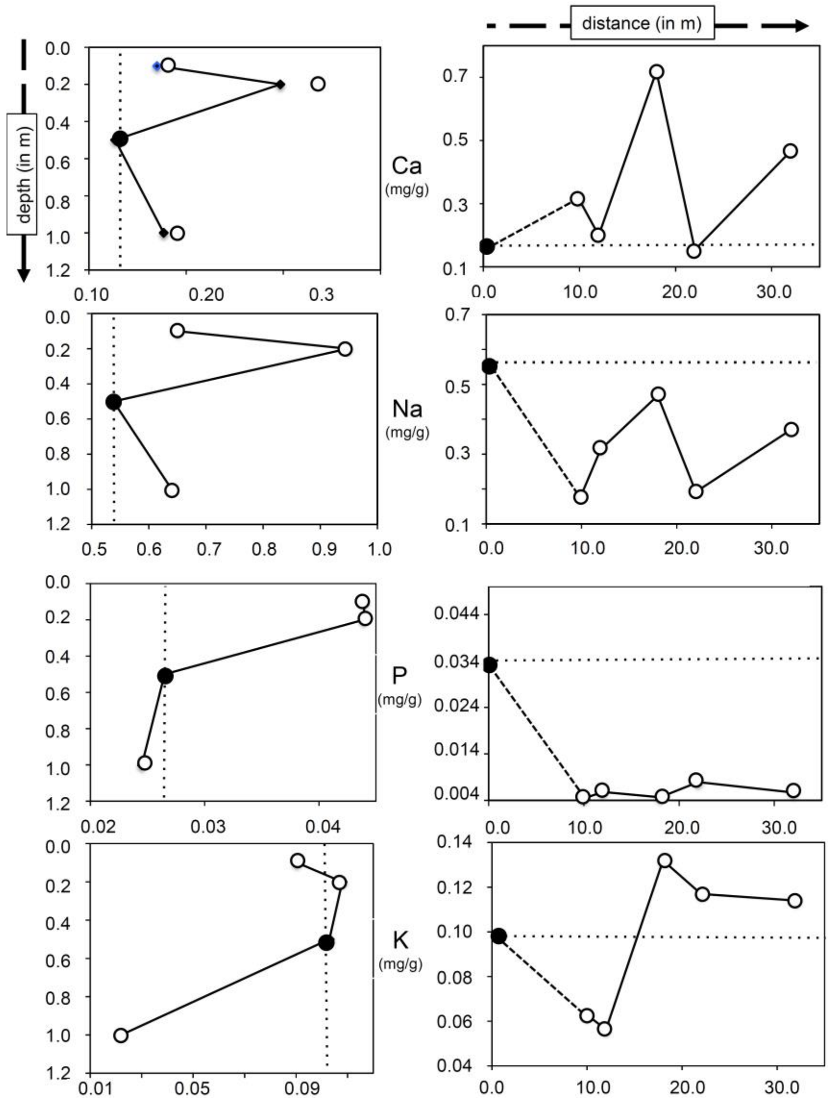

Figure 1. Vertical and lateral variations of some major element in the water leachates relative to depth in the left column and to distance to vegetation in the right column. The black dot in the graphs corresponds to the reference sample in both trends. The finely dotted lines represent the reference contents in the vertical and horizontal samplings.

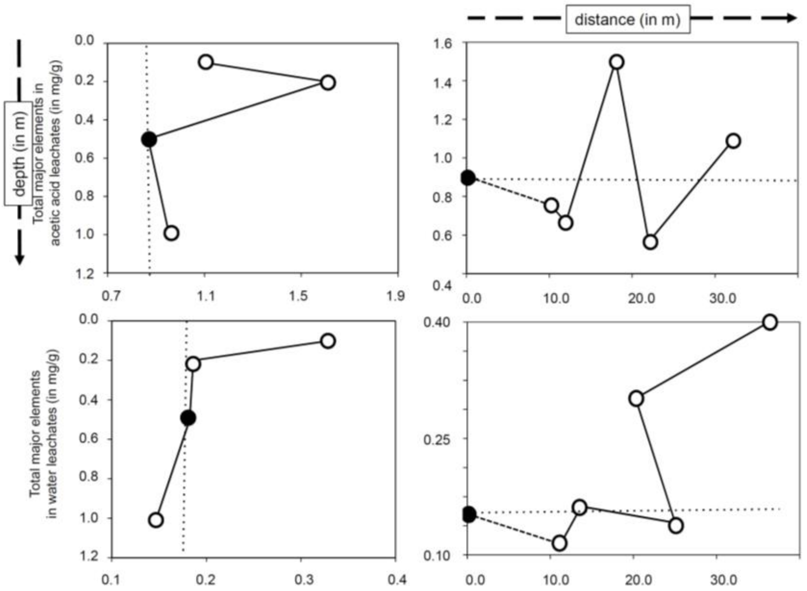

Figure 2. Total major elemental contents of the water leachates in the top row and of the acetic leachates in the bottom row, relative to depth to the left and to distance to the vegetation to the right. The black dot in the graphs corresponds to the reference sample in both trends. The finely dotted lines represent the reference contents in the vertical and horizontal samplings.

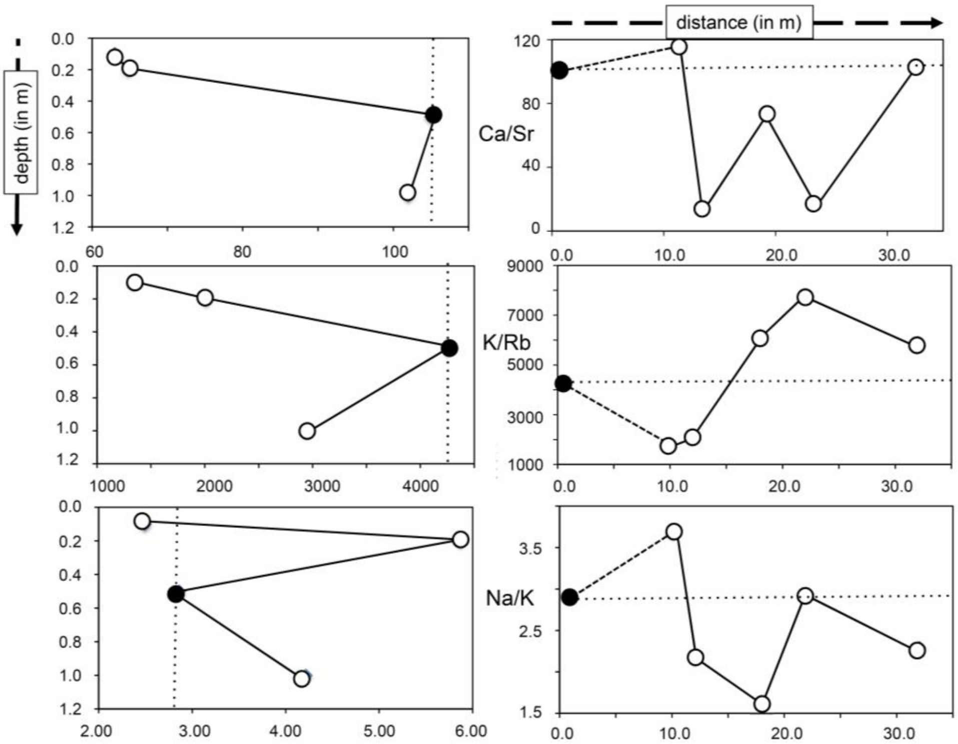

Figure 3. The Ca/Sr, K/Rb and Na/K ratios of the water leachates relative to depth in the left column and to distance to vegetation in the right column. The black dot in the graphs corresponds to the reference sample in both trends. The finely dotted lines represent the reference contents in the vertical and horizontal samplings.

The contents of the trace elements

Vertical distribution of the trace elements shows a progressive decrease with depth for the Rb, Th, Zr, Pb, Cu, Cd and U contents. While Ni increases with depth, the contents of Cr do not show any significant change except at 50 cm depth where it increases. Ba decreases with depth with an increase at 20 cm depth. Co and As increase at 20 cm and at 1 m depth, whereas the V contents decrease at 20 cm depth and increase at the 50 cm and 100 cm. Zn increases progressively, while Sr increases at 20 cm and decreases deeper. The lateral distribution of the trace elements in the water extracts highlights increasing Co, Rb, Cr and Ni contents at 10 m from vegetation that decrease at 12 m away. The concentrations of Cu and V decrease with increasing distance from vegetation. The concentration of As is characterized by a significant reduction 32-m away from vegetation, Cd and U are decreasing with increasing distance from vegetation, Cd having a significant decrease at 12 m and 32 m from vegetation. The concentration of Pb waves away from vegetation with an increase at 10 m, a decrease at 12 m, an increase at 18 m and a decrease again at 22 m. The Sr content of the leachates increases significantly at 12 m, while Zn decreases until 12 m, increasing at 18 m and decreasing at 32 m.

In sum, the trace elements removed by water and expressed as the total dissolved elements decrease generally irregularly with depth and with increasing distance from vegetation. The highest availability is observed in the 20-cm deep horizon and at 18 m away from vegetation (Figure 1).

The contents of the REEs

The total REE contents of the water extracts from vertical trend are about 23 ng/g at 10 cm below the surface, 17 ng/g at 20 cm and 25 ng/g at 50 cm, decreasing to about 14 ng/g at 1-m depth (Table 1). Relative to the surface, transfer of REEs to the deeper horizons occurred without any major fractionation, as their distribution patterns remain flat relative to that of the most surficial sample (Figure 4A). The small ups and downs among the element contents are most probably due, at least partly, to the analytical uncertainty of very small amounts. Only a slight decrease towards the heavy REEs (HREEs) can be observed, which is probably not significant analytically either. However, the slope has the tendency to increase with depth even if only slightly. Also to be noticed are the positive Eu anomaly for the deepest leachate and the negative Eu anomaly in the two deeper leachates. Changing oxidation-reduction conditions for the former and an increasing inorganic impact for the latter could explain these modifications that will be discussed in a further section.

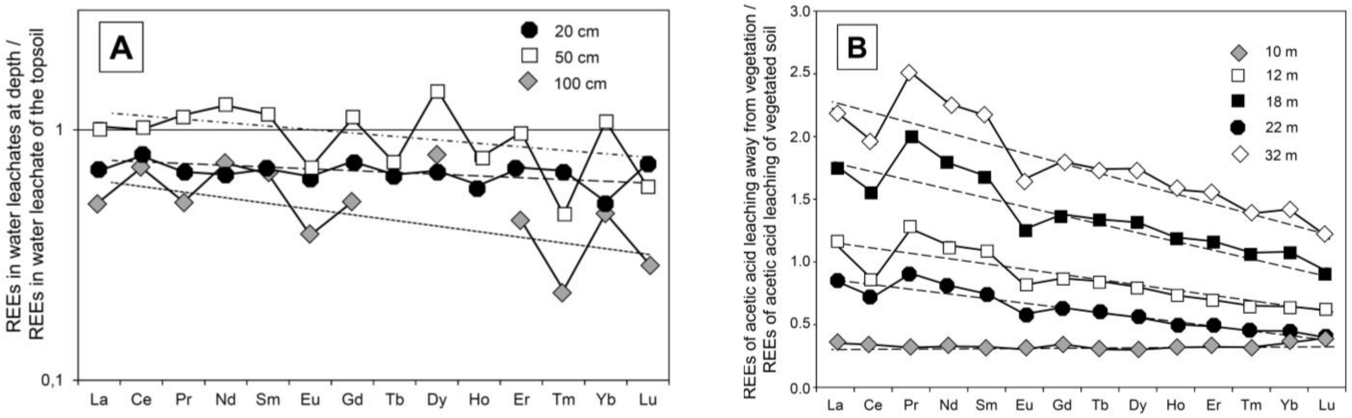

Figure 4. (A) The REE distribution patterns from water leachates of the vertical trend, relative to the topsoil leachate. (B) The REE distribution patterns of the acetic acid leachates along the horizontal trend.

The lateral distribution could only be examined at 10 m away from vegetation as most REE contents of the water leachates were below detection limit of the used equipment. When compared to the water leached of the soil sample at 50 cm below vegetation, that located 10 m away from vegetation shows a pattern with a significant decrease in the heavy REEs' contents (HREEs; Figure 5A). Furthermore, together with a significant negative Tb anomaly that is yet difficult to explain, a small positive Nd anomaly and a more significant positive Eu anomaly are visible.

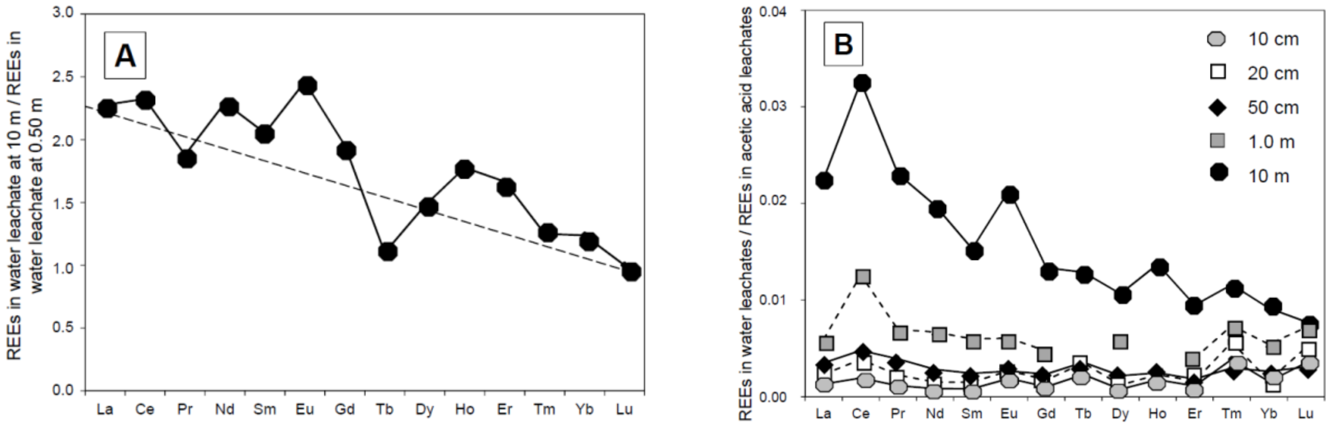

Figure 5. (A) The REE distribution pattern of the water leachate at 10-m distance from vegetation relative to the same pattern of the reference water leachate at 0.50 m depth. (B) The REE distribution patterns of the water leachates relative to the equivalent acetic acid leachates along the vertical trend and in the horizontal sample from 10-m distance.

The elements removed by acetic acid leaching

The contents of the major elements

Acetic acid is often used to leach metallic elements present in exchangeable mineral fractions that are sensitive to changing pH in sediments (Sahuquillo et al., 2003). The acetic-acid extracts from soil samples collected here contain elements that were released subsequently at the initial water-leaching step, meaning that basically the samples did no longer contain such adsorbed elements. In fact, Ca and Fe are the most removed elements near the surface, to the opposite of Mn, Na, P and Mg that accumulate at depth (Figure 6), and of Si, Al and K that accumulate at 50 cm. The vertical elemental trends indicate that Mg, P, Mn and Na increase with depth, Al increases at 50 cm depth and decreases above at 20 cm and below at 100 cm, while Si increases in the upper horizons and decreases at 100 cm depth.

The lateral distribution relative to vegetation indicates a reduction of Mg, P, Si, Fe and Al, an irregular increase of Ca and no change for K with increasing distance (Figure 6). The content of Na increases slightly at 10-m distance and decreases beyond, while Fe decreases significantly at 12 m and 22 m, Mn increases at 10 m before decreasing to the opposite to Al that decreases strongly at 10 m. The availability of nutrients illustrated by the total removed major elements by acetic-acid leaching decreases 22 m away from vegetated area, as it did with increasing depth. Compared to the soil with the vegetal cover at 50 cm depth, the maximum availability of the major elements is obtained 32 m away from vegetation, as it was in the topsoil under vegetation. In summary, the total amounts of major elements leached by water and acetic acid are very different, but unexpectedly they mimic also each other. The patterns relative to the distance to vegetation are especially quite identical, those obtained for the vertical profile being very similar (Figure 2). Even if not leaching the same fractions, water and acetic acid have a similar impact on similar soil compositions.

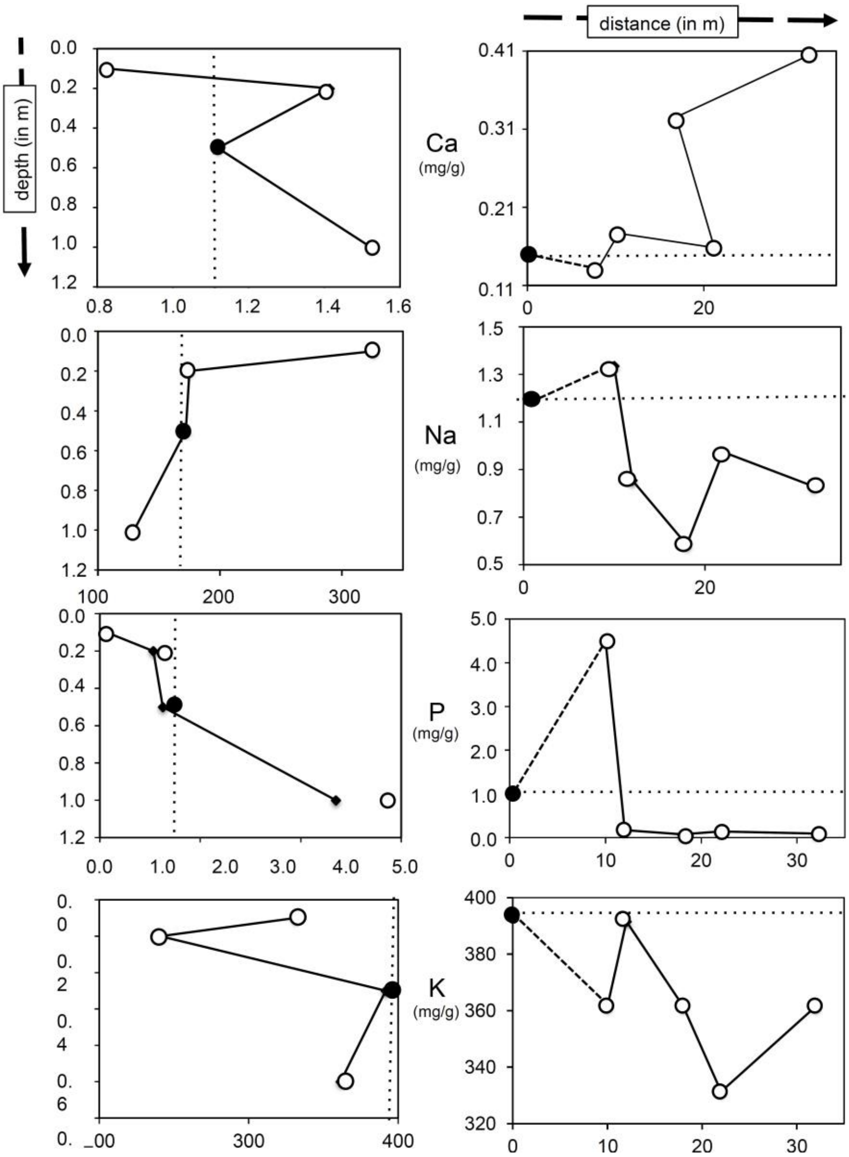

Figure 6. Vertical and lateral variations of major elements in the acetic-acid leachates relative to depth in the left column and to distance to vegetation in the right column. The black dot corresponds to the reference sample in both trends.

The Na/K ratio ranges from 2.5 to 5.9, this latter value being observed in the topsoil at 20 cm depth. The ratio decreases at 50 cm depth and increases in the subsoil along the vertical trend. Relative to the soil around the vegetation, the same Na/K ratio does not outline any lateral variation away from vegetation. After a significant decrease in the 10 initial meters, the Ca/Sr ratio remains quite identical when distance to vegetation increases (Figure 7). Ranging from 0.01 to 0.08, the Mg/Ca ratio tends to increase with depth and to decrease with distance from vegetation as for the leachates by water do, in fact, to an increase of Ca (Table 1).

The contents of the trace elements

The vertical distribution of the trace elements outlines progressive decreases of the As, Rb, Th, Pb, U, Ni, Cu and V contents with depth, those of Cr decreasing at 20 cm, increasing at 50 cm, and those of Co increasing until 50 cm and decreasing at 100 cm. Ba decreases at 50-cm depth, decreasing further at 100 cm, while Zr increases at 50 cm depth and again at 100 cm. The lateral distribution relative to vegetation of the elements leached by acetic acid outlines increases in the Pb and Th contents with increasing distance, while those of Zr decrease. The Ni contents decrease progressively until an increase at 32-m distance. The contents of Cr and Co increase at 10 m and then decrease, while those of V and Cu decrease at 12 m and 22 m. The As contents increase at 10 m and 18 m, while Rb increases at 10 m and 12 m, decreasing further away. Ba is more concentrated at 32 m than near the vegetation. The U and Cd contents increase at 10 m, decrease at 12 m and 22 m, increasing again at 32 m.

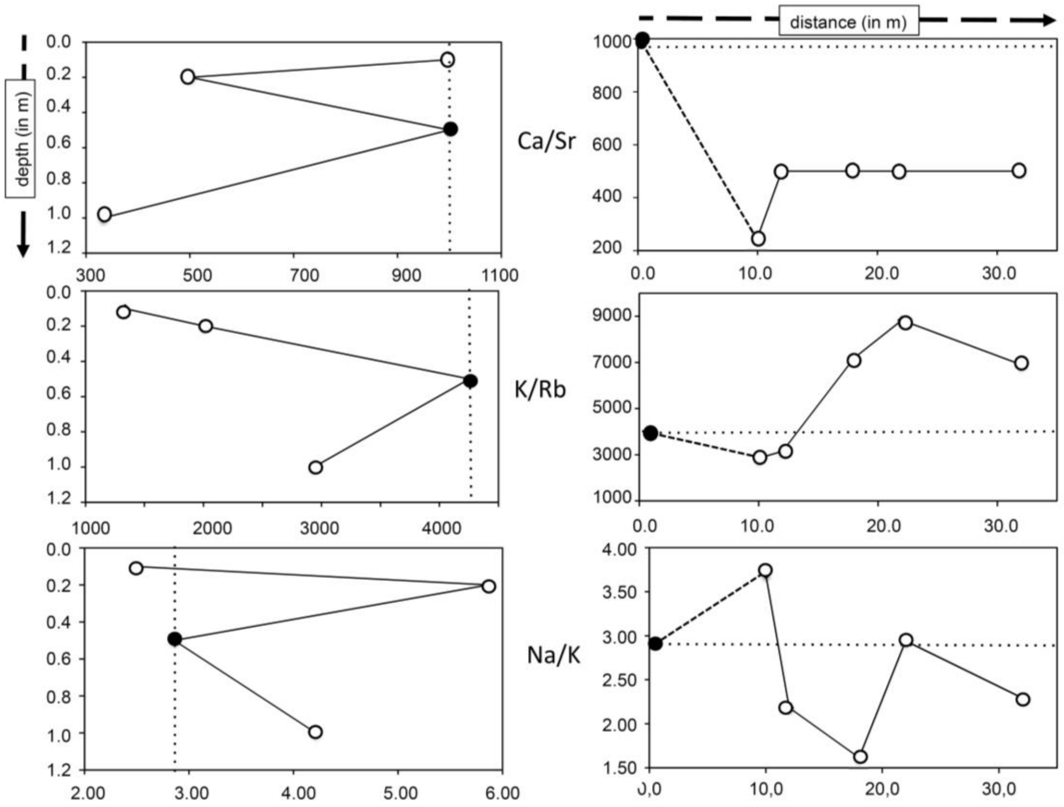

Figure 7. The Ca/Sr, K/Rb and Na/K ratios of the acetic-acid leachates relative to depth in the left column and to distance to vegetation in the right column. The black dot corresponds to the reference sample in both trends.

No correlation was observed between the contents of the elements leached by water and those of the elements leached by the acetic acid except for Na and Si, especially in the lateral distribution. There seems to be a competition between the water and acetic-acid leachates for these two elements, suggesting the leaching of phases that are soluble in either water or acetic acid are of varied sources, unless they were incorporated into mineral phases variably sensitive to the leaching solutions. This outline may also indicate that soil washing with water may have decreased the solubility of Na and Si in the acetic acid. Among the trace elements, only the water-leached Cr is proportional to the acetic-acid leached Cr, suggesting the same source for both phases, while Rb behaves as do Na and Si.

The contents of the REEs

The total contents of REEs in the acetic-acid leachates from vertical trend is much higher than in the water leachates: at about 17.3 μg/g near the surface close to the plants, it decreases to 1.8 μg/g at 100 cm depth. The overall distribution shows a somehow higher accumulation in the topsoil. The lateral REE distribution indicates that the lowest amount occurs at 10 m from vegetation with a progressive increase at 32 m away from vegetation (Table 1). The REE patterns of the acetic-acid leachates from vertical sampling plotted relative to their contents in the reference soil at 50 cm depth outline increasing heavy REEs (HREEs) at 20 and 50 cm depth, while the distribution pattern is flat for the leachate from 1-m deep sample (Figure 8). Also to be noticed are the two positive Ce and Eu anomalies. In sum, this very different pattern relative to those of the water leachates confirms that the REEs extracted by water and acetic acid were located in different components of different origins.

Relative to the REEs contents of the 50-cm deep reference level below vegetation, the distribution patterns at increasing distance from vegetation yield a significant enrichment in light REEs (LREEs) as well as increasing negative anomalies in Ce and Eu (Figure 4B). Earlier studies showed that higher concentrations of LREEs are observed in soils developed on phosphate and carbonate rocks (Chen and Yang, 2010), which is not the case here. The already mentioned negative Ce anomaly also visible in most leachates is often considered to characterize oxidizing environments (McLennan, 1989). The distribution patterns of the REEs trends are very similar, except varied extends of the Ce and Eu anomalies, with only an increasing slope from La on the light side of the REE distribution to Lu at the heavy side correlated with the distance to the vegetation. At the 32-m distance, the pattern has the steepest slope, while completely flat at the 10-m distance.

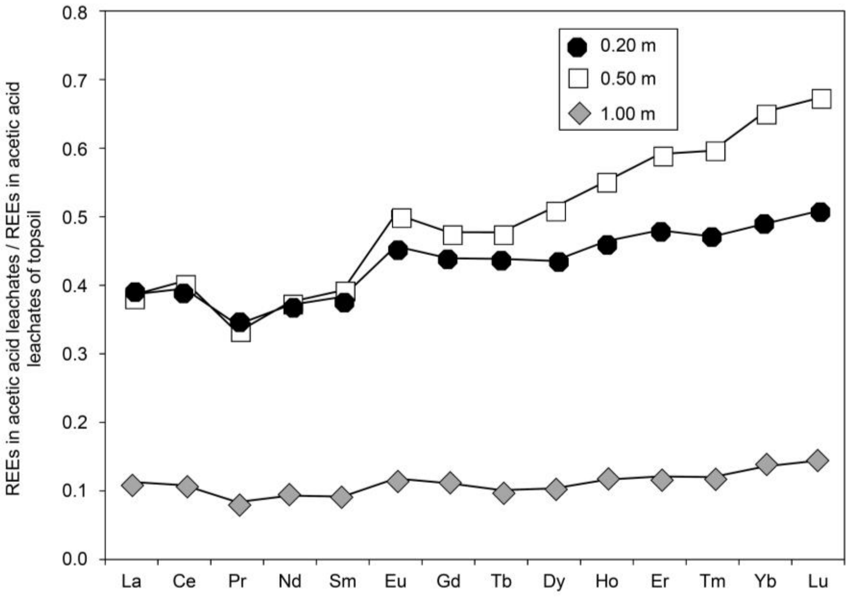

Figure 8. REE distribution patterns of the acetic-acid leachates relative to the acetic-acid leachate of the topsoil sample along the vertical trend at 0.20-m, 0.50-m and 1-m depth.

Of interest is the progressive increase of the Ce negative anomaly from 10 to 32 m distance to vegetation, which suggests a progressive change in the oxidation-reduction conditions in the soil when the distance to vegetation increases. From a somewhat reduced environment imposed by the vegetation, the conditions become more oxidizing away. The negative Eu anomaly that basically is representative for increasing contents of silicate minerals (Weill and Drake, 1973) is also increasing progressively with the distance to the vegetation. This progressive change could record a progressive input of an inorganic REE supply to the leachates relative to the organic supply.

When possible, comparison of the REE patterns of the water and acetic acid leachates from the same samples outlined instructive displays. In fact, the water and acid-acetic solutes of the soil samples close to vegetation at 10, 20 and 50 cm are very similar with flat patterns (Figure 5B). Only two leachates yield different patterns: that from 1-m depth outlines a significant positive Ce anomaly, the rest of the pattern being still flat, and that from 10 m away yields a downwards slope for the HREEs, and very visible positive Ce and Eu anomalies that have been already mentioned.

Discussion

Differences in the vertical and lateral distributions of elements can be assigned to changes in the physicochemical properties of the studied soil including pH, amount and activity of the occurring organic matter, as well as amount and type of minerals, especially clays such as smectite characterized by high cation-exchange capabilities. As a preliminary hypothesis, the vertical downwards increase of elements could indicate either some dissolution of secondary phases or leaching of elements adsorbed on crystal surfaces in the topsoil, while a vertical decrease may indicate either the supply of elements into a plant activity volume in the rhyzosphere near the surface, or an input from anthropogenic sources via the atmosphere at the upper soil level and a decrease downwards. The lateral increase of elements can be due to either dissolution of secondary phases, a decrease of the micro-organic soil components, or even fixation of anthropogenic supplies by the micro-organisms near the vegetation and a lateral decrease focusing on their role in plant growth.

The message of the elements leached by water

Increasing of the Al, Ca, Mg, Fe, Mn, K and Na contents from water leachates at 20 cm depth relative to those of the topsoil above suggests an evapo-transpiration that usually induces such increase of nutrient concentrations (Cramer et al., 2008; Onwuka and Mang, 2018). On the other hand, while elements primarily taken up by plants, such as K and P, decrease with depth, the important increase of Al and Fe at 50 cm depth may indicate a downwards leaching with possible incorporation into secondary phases. Ifansyah (2013) reported that humic acid is able to increase the P availability and to reduce the Al and Fe solubility in soils. High solubility of Al and Fe, together with a P decrease at 50 cm depth, does not correlate here with a change of the pH, which increased only slightly from 8.29 to 8.97 at 50 cm, compared to the topsoil. Ifansyah (2013) reported also that the high Al and Fe solubility is accompanied by hydrolysis that induces a release of hydrogen ions into the soil fluids and consequently an acidification of the soil. The interpretation of the data obtained here is different. As humic substances are strongly complexing Al and $Fe_{(III)}$, the total Al concentration and its speciation in the soil depend mainly on the pH and the chemical environment of the pore waters (Gerke, 1997; Kisnierienė and Lapeikaitė, 2015). On the other hand, Al has no specific biological function (Poschenrieder et al., 2008). Adsorption affinity of phosphate by ferro-hydrite complexes (Wang et al., 2015) could also explain the P decrease at 50 cm depth.

The lateral distribution of the leached elements most probably highlights a progressive decrease of the plant activity; the lower K leaching obtained close to vegetation may then be due to the soil contribution to the plant cycling. This hypothesis is confirmed by the K increase in the samples away from vegetation. It is also supported by the P contents decreasing progressively in the leachates away from vegetation. Elements such as Si, Al and Ca, which contents increase with the distance from vegetation, may also be indicative of a progressively increased contribution of altering minerals from soil. Na decreasing away from vegetation, while Mg and Fe rather fluctuate with the distance to the vegetation, could then relate to either decreasing minerals containing the former or varied amounts of minerals with the latters. Elements such as Cu, Cr and Pb are enriched in the upper horizons and depleted at depth, which suggests some anthropogenic supply. Conversely, As, V and Ni are enriched at depth, which could result from a more active leaching near the surface and a transfer downwards. In general, elements, which contents decrease with distance to vegetation as is the case for V, Cu, Cd and U, suggest also a complexation process with organics of the soil that are also expectedly decreasing when the distance to vegetation increases.

The message of the elements dissolved by acetic acid

Elements such as Mg, Na, P, Si and Mn are increasing at depth that results from a combined leaching and precipitation of secondary phases in the deeper soil. Relative to the topsoil close to vegetation, the Al, Si, Mg, Mn, Na and P contents increase at 10 m, and then decrease with distance, while Fe shows a lateral decrease. The Ca contents decrease at 10 m, while increasing at the other sampling stations. The content of K remains unchanged with distance, which suggests that when involved in plant activities it contributes more to the water leachates as a potential nutrient than to the acetic-acid leachable phases.

The message of the trace elements

The increasing contents of the trace elements relative to depth characterize a leaching from topsoil downwards as the contents may originate from soluble minerals, while any decrease at depth reflects rather a precipitation with increasing pH. Alternatively, leached trace elements characterized by decreasing contents with depth may also indicate surficial supplies of anthropogenic sources. The elements most leached from soil surface are V, Ni, Cu, Th, As and Rb (with an important decrease at 50 cm). Co increases downwards with an important step at 50 cm. The REEs are more accumulated in the topsoil, whereas the decrease of the trace elements relative to depth parallels the increase of pH.

The REE contents of the leachates decrease at depth relative to those from topsoil with, laterally, an increase at 18 m, a decrease at 22 m, and a renewed increase at 32 m. The distribution confirms that there is a higher plant activity and/or amount of organic matter in the topsoil that complexes and fixes REEs. Alternatively, the irregular increases of the REE contents with distance could illustrate local inputs from dissolved minerals. A comparison of the water and acetic acid leachates in the vertical trend shows that the Ce and Eu positive anomalies are significantly larger when sampling is deeper in the vertical trend and further away from vegetation in the unique available pattern. These anomalies point to the fact that the earlier reported negative anomalies in soils (Wyttenbach et al., 1998; Loell et al., 2011) seem not to be general rules. Here, the Ce anomaly indicates apparently that there is a progressive oxidation-reduction change when sampling is more distant from plant activity, surprisingly towards a more reduced environment, which could relate to some lower activity of the microorganisms, or even to a more or less decrease of their occurrence. The increasing Eu anomaly obtained away from vegetation might reflect a larger contribution of mineral compounds in the leachates, confirming in turn a decreasing organic contribution. The higher contents in the HREEs relative to the LREEs in the leachates away from vegetation, vertically and horizontally, seem to be quite systematic (Figure 4A and B; Figure 5A and B).

The K/Rb, Ca/Sr and Na/K ratios

The K/Rb ratio of the water-soluble fractions ranges from about 1,569 to 6,700 in the different soil samples. As reported by Chaudhuri et al. (2007), these high values are more common for organic than mineral materials. The vertical distribution indicates a higher ratio in the subsoil relative to the topsoil, as is the case in the lateral distribution. This trend is somewhat to the opposite to that of the associated total organic carbon.

The Ca/Sr ratio ranges from about 14.9 to 111 with the highest value 10 m away from vegetation and the lowest 12 m away. It is lower in the topsoil than in the subsoil because of Sr decrease with depth. In its lateral fluctuation, the changes of the Ca/Sr ratio parallel the changes in the Ca of the acetic acid leachates (r^2=-0.65), while they parallel the Sr changes (r^2=0.80) in the water extracts. No alternative correlations between Ca/Sr ratio and Ca contents are observed in the water extracts and between Ca/Sr ratio and Sr contents in the acetic acid extracts.

The K/Rb ratio ranges from about 1,335 to 8,835 in the acetic-acid leachates of the analyzed samples. Its fluctuations are better correlated with Rb than with K. The general tendency is an increase with depth and with distance from vegetation, because of a preferential Rb decrease. The Ca/Sr ranges from 259 to 670 with no clear trend in the subsoil, the fluctuations being correlated with the Ca rather than with the Sr changes (Figure 3).

The Na/K ratio ranges from about 1.63 to 29.1 in the water leachates. The vertical fluctuations show a higher ratio in the subsoil because of an increased content in Na. Alternatively, the lateral distribution of the ratio outlines a decrease with the distance from vegetated area except at 12 m where no change relative to samples collected close to vegetation is visible. In the acetic acid leachates, the Na/K ratio ranges less widely from 1.62 to 5.86. For both the water and acetic-acid leachates, a positive correlation is observed between Na/K ratio and the concentration of Na, which suggests a uniform supply of Na along both the vertical and the lateral trend.

Conclusion

The elemental distribution in water and acetic-acid leachates shows that plant cycling is not systematically the dominant control of the nutrient distribution in soils. However, elements such as Mg, Na, P, Si and Mn enriched here at depth in the acetic acid leachates appear to be controlled essentially by the organic cycle. Usually involved in plant cycling, K remains unchanged in the acetic-acid solutes with depth and distance to the plants. For the water leachates, its vertical distribution outlines a decrease with depth because essentially involved in the plant activity. Opposite results characterize the P contents that decrease in the water and acetic acid leachates away from vegetation. A human impact is suspected for the metallic trace elements that are enriched in the acetic-acid leachates at the surface relative to the subsoil. The vertical distribution of the K/Rb ratio ranging from about 1,569 to 6,700 in the water-soluble fractions indicates a higher ratio in the subsoil than the topsoil. It ranges from about 1,335 to 8,835 in the acetic acid leachates, increasing with depth and distance to vegetation. In turn, this experiment raises the basic heterogeneity of soils below and away from vegetation: no constant trend being observed in both directions. It looks like the soluble elements of each soil sample are only representative for themselves.

Not controlled directly by the plants but more probably by solid organic exudates, REEs are more accumulated in the acetic-acid leachates of the topsoil. Their contents in the leachates decrease at depth relative to those in the leachates of the topsoil with an irregular increase laterally away from vegetation. The REEs distribution confirms a higher amount of organic matter in the topsoil that complexes and fixes REEs. Alternatively, the irregular increases of the REE with distance illustrate local irregular inputs from solid phases dissolved by acetic acid. Ce and Eu positive anomalies are significantly larger when sampling is deeper in the soil and away from vegetation. The Ce anomaly apparently indicates that there is a progressive oxidation-reduction change when sampling is distant from plant activity, probably induced by a significantly lower activity of the microorganisms. On the other hand, the increasing Eu anomaly away from vegetation might reflect a larger contribution of the mineral compounds to the leachates. Higher contents in the HREEs relative to the LREEs in the leachates away from vegetation, vertically and horizontally, seem to be quite systematic outlines.

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