Rare earth elements in soil profiles of various ecosystems across Germany

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ABSTRACT

Rare earth elements (REEs) are of emerging interest. In the environment, they occur in minerals, however, they are also used in many key technologies and in agriculture. In consequence, REEs are released into the environment and have thus an impact on it. However, our knowledge regarding REEs in soils is incomplete. We selected eight soil profiles across Germany aiming to determine REE contents (aqua regia) and potential mobilization (hydroxylammonium chloride and hot water extractable) and to explore relations between REEs and soil properties. The composition of the parent material strongly influenced by the ice ages during the Pleistocene (especially in northeastern Germany) is a crucial factor differentiating the content of REEs in our studied soils. The silty, clayey soils in the western part of Germany possessed higher REE contents than the sandy and peaty soils in the northeast (average REE content Cambisols: 825 µmol kg^{-1}, Retisols: 407 µmol kg^{-1}, Arenosol 180 µmol kg^{-1}, Histosols 122 µmol kg^{-1}) because REE can adsorb onto clay minerals. The characteristic soil genetic processes of each soil type were reflected by the vertical distribution of the REE content. The vertical distribution of REEs and the hydroxylammonium chloride-extractable REE contents were mainly controlled by Al, Fe, Mn and their oxides (additional to clay) which provide important sorption sites for REEs. High contents of clay, Al/Fe/and Mn oxides caused high REE contents. The hydroxylammonium chloride-extractable REE contents varied in average from 266 to 8 µmol kg^{-1} in the soils. The hot water extractable REE contents (in average 0.94 µmol kg^{-1}) tended to be higher in horizons which were rich in organic matter. In future, mechanistic experiments concerning the dynamics of REE mobilization should be performed as well as monitoring in plants and wildlife to improve our knowledge about REEs in the environment.

1. Introduction

Rare earth elements (REEs; Sc, Y, and the 15 lanthanoides La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) naturally exist in soils and their contents vary according to the parent material and soil properties such as clay mineralogy, pH, and organic matter. The elements occur in over 200 minerals, for instance in phosphates, silicates, carbonates, and fluorides (Goodenough et al., 2016; Laveuf and Cornu,
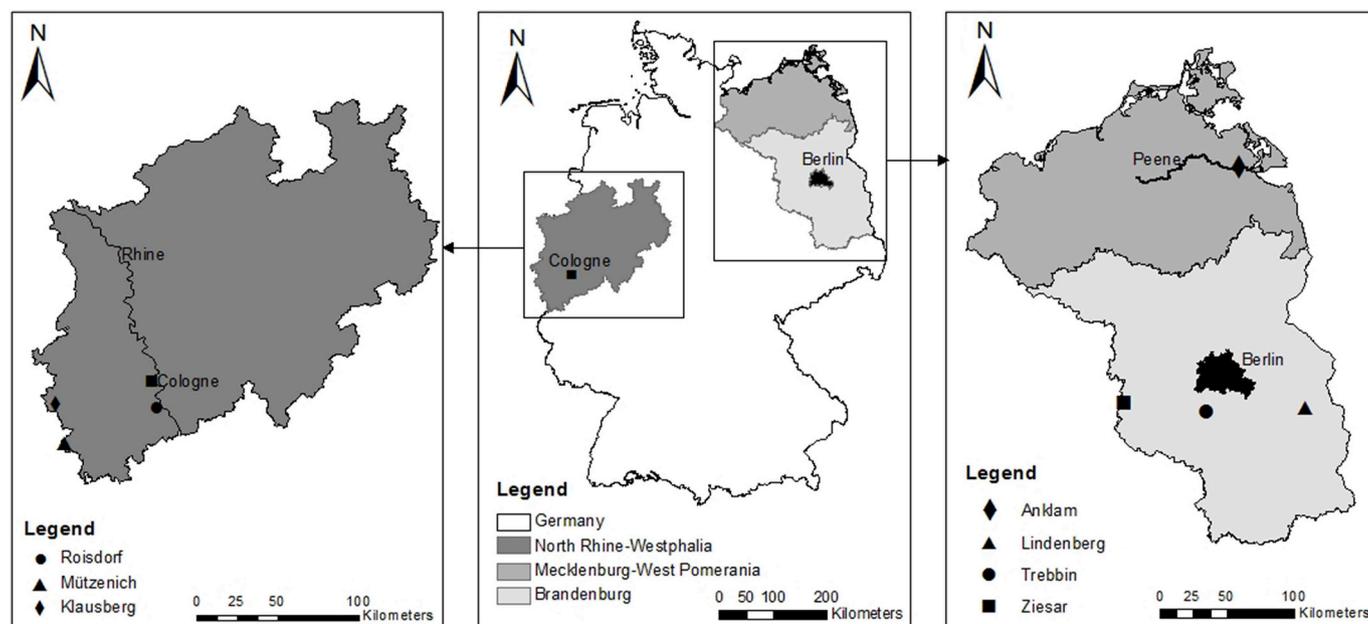

Fig. 1. Locations of the study sites.

2009). Notably, phosphates possess high contents of REEs (Laveuf and Cornu, 2009). Low REE contents are predominantly present in carbonates; and in silicates appears a great variability concerning the REE content (Laveuf and Cornu, 2009). According to Zhu and Liu (1988), the REE content in Chinese soils reduces depending on the parent material as follows: granite > quaternary > basalt > sandstone. Hu et al. (2006) mentioned that the total REE content amounts 174–219 mg kg^{-1} in soils developed from basic/acid igneous soils, sandstone and shale rock, whereas soils originated from loess and calcareous rock have contents from 137 to 174 mg kg^{-1}. Thus, the content of REE also seems to be influenced by different regional origin of the parent material, degree of weathering and type of soil.

Rare earth elements can also accumulate in soils due to their use in technologies (e.g. photovoltaic cells, mobile phones, catalyzer in cars) and as feed additive or fertilizer in agriculture (Yuan et al., 2018). Many rivers (e.g. Rhine) possess anthropogenic La and Gd concentrations (Kulaksız and Bau, 2011). However, various negative reactions of plants, organisms, and humans on REEs have been documented (Tyler, 2004; Kay, 2008; Oral et al., 2010). Up to now, REEs have been categorized neither as essential elements for life nor as toxic elements for the ecosystem (Tyler, 2004). The sustainable use of REE resources, the mobilization and transport of these elements in the environment are of rising interest in face of possible damages on the ecosystem due to REEs production. Regarding the management of environmental resources it is also important to study soils. Substantial gaps of comprehension exist about the REE content and potential mobilization in German soils up to date. Only very few publications about REEs in soils were known (Brioschi et al., 2013; Grawunder et al., 2009, 2015; Loell et al., 2011a,b; Markert and Li, 1991; Mihajlovic et al., 2014a,b, 2015, 2017; Wiche et al., 2017). Therefore, possible risks for the ecosystem cannot be adequately evaluated. The inorganic or metal-organic binding forms of REEs are important for their potential mobilization and toxicity in soils. The existence of important factors for complex forming such as clay minerals, Fe/Mn oxides, sulphur, and organic material largely depends on the soil properties. The soil composition/development, in turn, are connected with the parent material and climatic conditions. All these influencing factors can be found in the diverse soils in the western and northeastern part of Germany. The selected study sites featuring different geological and geomorphological properties provide a basis to analyze contents and potential mobilization of REEs.

Germany is characterized by a large diversity of soil types which is reflected by the different landscapes and the associated geological parent material (Schubert, 2016). The ice ages had a considerable impact on the pedogenic factors such as parent material and relief. The northeastern part of Germany was covered with ice at least three times during the Pleistocene; the glacier and its meltwater deposited huge amounts of material in this region (Umweltbundesamt, 2010). Many sediments were relocated by wind and water, and became poor on fine-grained particles such as clay and silt (Kühn et al., 2015). This had a great influence on their physical and chemical properties because the particle-size distribution is important for soil properties such as pH value, sorption capability, and base saturation. Most of the soils in the northeastern part of Germany are sandy and had its origin in ground moraines, meltwater or eolian sand (Kühn et al., 2015). Fens could develop in meltwater depressions.

In the western part of Germany, permafrost conditions existed during the glacial epochs of the Pleistocene. Periglacial slope deposits developed under these periglacial conditions (Umweltbundesamt, 2010). The discharge of the Rhine was distinct higher during the glacial epochs than today, the River flooded more surrounding land, and transported huge amounts of boulders from the alpine ice sheet (Berendsen, 2003; Boenigk, 1978). During the warm periods of the Pleistocene, the Rhine carried less water, and sediments such as loam were deposited in the adjacent wetlands. Furthermore, the fine-grained clay and silt particles (loess) deposited in the western part of Germany because the intensity of the katabatic wind of the glacier which transported the loess reduced with increasing distance from the glacier front (Kühn et al., 2015; Schubert, 2016). Many current soils in Germany are the result of a post-ice age development which began around 11000 years ago, and the soils reflect the environmental conditions during this period (Umweltbundesamt, 2010).

In the high precipitation western part of Germany, we selected for our research Cambisols which are widely spread in Germany; but they are not present on Holocene material what is presumably due to an absence of cryoclastic pre-weathering or due to the fact that the oxide formation takes distinct more time without a periglacial transforming (Kühn et al., 2015). Two selected Cambisols are characterized by wetness what preferentially occurs in silty to clayey material. In the low precipitation northeastern part of Germany, we choose Retisols which are typically for glacial cover sand (Kühn et al., 2015), an Arenosol

which mainly develops on meltwater sand of former glacial drainage channels (Kühn et al., 2015), and Histosols in former meltwater depressions. Our objectives are: i) to quantify the current contents of REEs and their depth functions in eight soil profiles in Germany to provide a scientific data basis to this topic; ii) to evaluate the potential mobilization of REEs in these soil profiles; iii) to detect relationships between soil properties/different soil genesis and the contents and potential mobilization of REEs; iv) to compare the contents and potential mobilization of REEs in the different soil profiles under different land use and with different parent material.

2. Materials and methods

2.1. Study areas, study sites, and soil description

One study area was located in the western part of Germany, in the federal state North Rhine-Westphalia (Fig. 1). Three study sites were chosen in this area for digging one soil profile at each site. One profile was situated south of Cologne, relatively close to the River Rhine (profile Roisdorf: 50°45′30.49″N, 7°2′5.72″E). Here, a Hypereutric Cambisol (Siltic, Protocalcic) developed from high-flood loam of the Rhine (late Weichselian glaciation until Holocene). This site was used as arable land where hoe crops grew. The two other sites were close to the German-Belgian border (profile Klausberg: 50°43′34.90″N, 6°4′29.43″E; profile Mützenich: 50°33′40.74″N, 6°11′8.84″E) and classified as Hyperdystric Stagnic Cambisol (Siltic) developed from loess (Weichselian glaciation) over periglacial slope deposits (Pleistocene) (profile Klausberg), and Hyperdystric Stagnic Folic Cambisol (Densic, Siltic) developed from periglacial slope deposits consisting of loess and Cambrian period sediments (Weichselian glaciation) over periglacial slope deposits consisting of Cambrian period sediments (Weichselian glaciation) (profile Mützenich), respectively. The sites of the profiles were covered with a deciduous forest consisting of beech *(Fagus sylvatica)* (Hyperdystric Stagnic Cambisol), and a coniferous forest mainly consisting of spruce *(picea)* with inferior deciduous trees (Hyperdystric Stagnic Folic Cambisol), respectively. The mean long-term annual precipitation is approximately 838 mm and the mean long-term annual precipitation is around 10.3 °C in the region around Roisdorf (Deutscher Wetterdienst, 2017). In Mützenich, the average annual air temperature is below 6 °C and the average annual precipitation is above 1100 mm. In Klausberg, the temperature is around 9.7 °C and the precipitation is about 850 mm.

The other study area is located in the northeast of Germany (Fig. 1). We chose five study sites in this area and one soil profile was dug at each study site. The two peatland sites (profile 1: 53°51′54.69″N, 13°40′56.12″E; profile 2: 53°51′59.28″N, 13°40′58.44″E) are situated next to the town Anklam in a nature reserve in the valley of the river Peene, a valley of the Weichselian glaciation epoch, which is considered as one of the largest connected fen area of Central Europe (Landesamt für Umwelt, Naturschutz und Geologie Mecklenburg-Vorpommern, 2017). The sites of the profiles were covered with carices *(Carex)*, yellow flag *(Iris pseudacorus)*, and horsetail *(Equisetum)* (profile 1), and shrubberies of willow *(Salix)*, carices *(Carex)*, and horsetail *(Equisetum)* (profile 2), respectively. Both fen soils are classified as base-rich Rheic Drainic Sapric Histosol. The three other sites are located south of Berlin (profile Lindenberg: 52°13′2.43″N, 14°10′0.67″E; profile Trebbin: 52°15′12.35″N, 13°14′9.27″E; profile Ziesar: 52°17′10.04″N, 12°26′49.51″E). The soils are classified as Albic Dystric Retisol (Abruptic, Arenic, Cutanic) developed from gravel containing cryoturbate loamy sand over periglacial slope sandy loam over loamy, sandy till (profile Lindenberg), and as Albic Eutric Retisol (Abruptic, Arenic, Cutanic) developed from cryoturbate loamy sand over deluvial loamy sand over periglacial slope loam over limy, sandy till (profile Trebbin), and as Chromic Dystric Arenosol developed from cryoturbate loamy sand over deluvial sand (of meltwater sand). The sites of the profiles were covered with a mixed forest consisting of pine *(Pinus silvestris)*,

oak *(Quercus robur)*, and beech *(Fagus silvatica)* (Albic Dystric Retisol; so-called Retisol forest), agricultural grassland (Albic Eutric Retisol; so-called Retisol agricultural grassland), and pine forest *(Pinus silvestris)* (Arenosol). The mean long-term annual precipitation is approximately 592 mm and the mean long-term annual air temperature is around 9.5 °C in this region (Deutscher Wetterdienst, 2017).

"Bodenkundliche Kartieranleitung" (Ad-Hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe, 2005), and "World reference base for soil resources 2014, Update 2015" (IUSS Working Group WRB, 2015) were used to describe and classify the soils. Here, mentioned symbols of horizons are according to FAO (2006). Information about soil sampling, and sample preparation is given in supplemental information A.1.

2.2. Laboratory analyses

2.2.1. Soil properties

It was worked with standard methods to determine soil properties (supplemental information A.1). Concentrations of Al, Fe, Mn, and S in the aqua regia, hydroxylammonium chloride, and hot water extract were measured with inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Jobin Yvon GmbH, Unterhaching, Germany). Single standard and multi element solutions (CertiPur, Merck) were diluted with deionized water for execution of a four-point calibration. Analyses were performed in three replications. The relative standard deviation of replicate analysis was below 3%.

The concentration of the anions Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} in the hot water extract were measured using an ion chromatograph (790 Personal IC, Deutsche Metrohm GmbH & CO, Filderstadt, Germany). The content of total organic carbon (C_{HWE}) in the hot water extract was detected by a TOC-analyzer (TOC-VE, Shimadzu Deutschland GmbH, Duisburg, Germany).

2.2.2. REEs

Aqua regia (37% HCl + 65% HNO_3, 3:1) (DIN ISO 11466; Deutsches Institut für Normung, 1997) was used to digest (pseudo) total concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu as well as Al, Fe, Mn, and S, although it is known that certain parts may persist in the residuum. However, extraction with aqua regia is an established technique which is considered to digest those fractions which are relevant for the ecosystem (e.g. Rao et al., 2010; Rauret et al., 1999). The German Soil Protection Ordinance (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, 1999) suggests this standard for assessing the exposure pathway "soil-human". Hydroxylammonium chloride ($0.5 \, mol \, l^{-1}$) was used to assess the exchangeable and reducible fraction of the REEs as well as Al, Fe, Mn, and S by adding 40 ml of this solution to 1 g soil and 16 h mechanical shaking at a speed of 30 rpm (e.g. Rauret et al., 1999). A hot water extraction according to Verband Deutscher Landwirtschaftlicher Untersuchungs-und Forschungsanstalten (2003) was conducted to evaluate the highly mobile fraction of REEs, Al, Fe, and S as well as Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, and total organic carbon (C_{HWE}). Fifty ml deionized water were added to 10 g soil and this solution was boiled for 1 h. The hot water extraction was only applied to the Cambisols because in these soils we found the highest aqua regia extractable REE contents and beforehand we supposed that measurable concentrations in the hot water extract are most likely present there. Each soil sample was extracted in parallel with good accordance. International certified reference soil material (GBW07407) was employed to ascertain the analytical accuracy of the total concentration. According to Hornburg and Lüer (1999), we assumed that 95% of the total metal concentrations can be extracted with aqua regia. Therefore, we defined the reference level for the recovery as 95% of the total REE concentration. The recovery amounted in average 78–98%; except La with 72%, Yb with 70%, Lu with 67%, and Tm with 64%.

Concentrations of REEs were determined by a quadrupol-based

Table 1
Properties of the three studied Cambisols.

International Soil Classification[a]	German Soil Classification System[b]	Depth	Horizon[c]	Horizon[b]	Particle-size distribution [%][b]			pH [KCl]	C_org	N_t	CO_3	P	K	S	Al	Fe	Mn	CEC_eff
					sand	silt	clay											
					0.063–2	2–63	< 2											
		[cm]			[mm]	[µm]			[%]			[g kg^{-1}]						[mmol$^+$ kg^{-1}]
Hypereutric Cambisol	„Braunerde"	0–40	Ap	Ap	17.0	57.8	25.2	6.1	1.4	0.13	0.0	/	/	0.1	11.7	15.9	0.8	143.4
		40–55	Bw	Bv	9.1	53.0	37.9	6.3	0.6	0.08	0.0	/	/	0.1	11.7	16.0	0.8	184.3
		55–80	CBw	Bv-Cv	7.4	52.5	40.1	6.8	0.4	0.06	0.1	/	/	0.1	11.7	16.0	0.8	207.1
		80–100	CkBw	Bv-Ccv	13.6	60.2	26.2	7.7	0.2	0.04	9.5	/	/	0.1	11.7	16.0	0.6	/
		100–130	Ck	ICc1	26.5	53.3	20.2	5.4	0.2	0.03	8.1	/	/	0.1	11.7	16.0	0.6	/
Hyperdystric Stagnic Cambisol	„Braunerde-Pseudogley"	0–6	Ah	Ah	24.7	62.1	13.2	3.0	8.1	0.46	0.0	/	/	0.2	4.1	4.5	0.0	106.0
		6–30	Bw	Bv	25.2	61.2	13.6	4.1	1.0	0.07	0.0	/	/	0.1	11.6	12.1	0.5	37.0
		30–50	Bg	Sw	23.9	64.1	12.0	4.2	0.2	0.02	0.1	/	/	0.1	11.6	12.2	0.3	32.0
		50–80	Bg	Sw	33.7	47.2	19.1	4.0	0.2	0.02	0.0	/	/	0.1	11.6	12.6	0.2	46.0
		80–150	2Bg	II Sd	44.6	36.2	19.2	3.8	/	/	/	/	/	0.0	11.6	12.6	0.2	71.0
Hyperdystric Stagnic Folic Cambisol	„Pseudogley-Braunerde"	−12 to −7	OeOi	L-Of	/	/	/	2.6	47.3	1.83	0.0	0.87	0.65	1.2	0.6	1.3	0.0	/
		−7 to 0	Oa	Oh	/	/	/	2.7	28.3	1.18	0.0	0.69	0.78	0.0	0.0	0.0	0.0	/
		0–10	Ahg	Sw-Ahe	34.5	41.5	24.0	2.9	4.6	0.20	0.0	/	/	0.2	6.2	5.8	0.0	122.0
		10–30	Bwg1	Sw-Bv	22.3	59.4	18.3	3.7	1.8	0.11	0.0	/	/	0.0	8.7	12.2	0.0	72.0
		30–60	Bwg2	Sd-Bv	14.8	59.8	25.4	3.9	0.6	0.06	0.0	/	/	0.1	13.2	21.5	0.1	83.0
		60–100	2Bwg	II Sd-Bv	9.4	56.5	34.1	3.9	/	/	/	/	/	0.1	12.7	19.8	0.1	53.0
		100–120	2CBg	II ilCv-Sd	15.3	58.6	26.1	3.8	/	/	/	/	/	0.2	12.7	19.8	0.1	41.0

CEC_eff: effective cation exchange capacity.

[a] IUSS Working Group WRB, 2015: World Reference Base for Soil Resources 2014, update 2015.
[b] Soil description and particle-size distribution according to the German Soil Classification System (Ad-Hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe (Ed.), 2005).
[c] FAO, 2006: Guidelines for soil description.

Table 2
Properties of the two studied Retisols, and the Arenosol.

International Soil Classification[a]	German Soil Classification System[b]	Depth [cm]	Horizon[c]	Horizon[b]	Particle-size distribution [%][b]			pH [CaCl2]	Corg [%]	Nt [%]	CO3	P [g kg⁻¹]	K	S	Al	Fe	Mn	CEC_eff [mmol⁺ kg⁻¹]
					sand 0.063–2 [mm]	silt 2–63 [µm]	clay <2 [µm]											
Albic Dystric Retisol (profile forest)	„Fahlerde-Braunerde"	0–3	AhE	Aeh	86.3	11.7	2.0	3.4	1.51	0.07	/	0.10	0.49	0.13	2.48	3.13	0.07	2.6
		3–15	AhBw	Bv-Ah	88.6	10.8	0.6	3.8	0.44	0.03	/	0.10	0.49	0.07	2.94	3.24	0.13	1.7
		15–45	BwE	Ael-Bv	84.5	14.9	0.6	4.0	0.32	0.03	/	0.14	0.62	0.06	4.33	3.86	0.11	1.5
		45–55	E	Ael	82.0	18.0	0.0	4.1	0.10	0.03	/	0.05	0.94	0.05	4.33	4.87	0.07	1.5
		55–90	2Bt	2Bt	72.0	14.8	13.2	4.4	0.09	0.03	/	0.09	2.81	0.06	13.41	13.13	0.15	5.6
		90–245	3C1	3ilCv	59.7	26.3	14.0	5.3	0.10	0.03	/	0.20	4.60	0.14	18.80	18.43	0.27	8.7
		245–300	3C2	3elCv	/	/	/	7.2	/	0.03	5.2	0.21	4.36	0.08	15.40	14.91	0.27	/
Albic Eutric Retisol (profile agricultural grassland)	„Fahlerde-Braunerde"	0–25	Ap1	rAp1	86	6.5	7.5	4.2	0.40	0.04	/	0.52	0.67	0.08	4.20	3.75	0.32	1.53
		25–40	Ap2	rAp2	79.9	11.6	8.5	5.0	0.09	0.02	/	0.42	0.80	0.06	5.30	4.14	0.40	/
		40–60	Bw	Bv	80.5	11.6	7.9	5.1	0.12	0.02	/	0.22	0.81	0.03	4.98	4.15	0.24	/
		60–70	2EBw	2Bv-Ael	77.3	16.6	6.1	4.7	0.09	0.08	/	0.14	0.84	0.03	4.21	4.01	0.16	/
		70–90	2E	2Ael	81.6	12.6	5.8	4.6	0.09	0.02	/	0.09	0.78	0.02	3.24	3.69	0.13	/
		90–120	3Bt/E	3Ael + Bt	67.2	15.5	17.3	5.9	0.09	0.02	/	0.28	2.96	0.05	12.46	12.89	0.22	/
		120–140	3Bt	3Bt	64.4	17.1	18.5	7.5	/	0.02	1.9	0.31	3.60	0.10	14.92	15.26	0.31	/
		140–200	4C	4elCv	73.1	18.7	8.2	7.9	/	0.02	7.2	0.24	2.24	0.32	7.67	8.86	0.21	/
Chromic Dystric Arenosol	„Fuchserde"	1–20	B	By[d]	91.6	1.8	6.6	3.8	0.34	0.02	/	0.34	0.32	0.06	2.87	11.76	0.10	1.5
		20–35	Bl1	rGo-By[d]	87.6	2.8	9.6	4.1	0.38	0.03	/	0.49	0.41	0.10	4.65	19.64	0.31	2.8
		35–79	Bl2	By-rGso[d]	85.6	4.8	9.6	4.2	0.20	0.03	/	0.70	0.49	0.19	6.86	38.63	0.52	3.5
		79–90	2Bl3	2rGso	90.6	3.3	6.1	4.7	0.09	0.02	/	0.24	0.47	0.05	3.72	11.39	0.11	2.1
		90–105	2EBl	2rGo-Ael	95.2	2.6	2.2	4.7	0.09	0.02	/	0.15	0.51	0.04	3.27	7.53	0.09	1.4
		105–125	2BtBl	2rGo-Bbt	85.6	5.8	8.6	4.7	0.09	0.02	/	0.16	0.70	0.05	7.51	9.26	0.05	4.8

CEC_eff: effective cation exchange capacity.

[a] IUSS Working Group WRB, 2015: World Reference Base for Soil Resources 2014, update 2015.

[b] Soil description and particle-size distribution according to the German Soil Classification System (Ad-Hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe (Ed.), 2005).

[c] FAO, 2006: Guidelines for soil description.

[d] The State Authority for Mining, Geology, and Resources Brandenburg (Germany) introduced the nomenclature 'By' to differentiate this red horizon; soil genesis of this horizon is speculative until now.

Table 3
Properties of the two studied Histosols.

International Soil Classification[a]	German Soil Classification System[b]	Depth [cm]	Horizon[c]	Horizon[b]	Pedogenic features and characteristics of substrate[b]	pH [H2O]	C_org [%]	N_t [%]	P_DL [g kg⁻¹]	K_DL	S	Al	Fe	Mn
Rheic Drainic Sapric Histosol (profile 1)	„Basenreiches Erdniedermoor"	0–20	H1	nHv	organogenic amorphous peat; free of carbonate; extremely strongly rooted	6.4	47.1	2.9	0.265	1.36	0.11	0.05	0.05	0.00
		20–40	H2	nHw	organogenic amorphous peat; free of carbonate; clod structure; very strongly rooted	6.7	41.1	3.8	0.018	0.10	6.10	4.76	4.76	0.11
		40–60	Hr1	nHr1	organogenic fen peat; free of carbonate	7.2	45.6	3.5	0.018	0.07	0.09	0.06	0.06	0.00
		60–90	Hr2	nHr2	organogenic fen peat; free of carbonate (c0)	6.7	50.4	2.8	0.023	0.09	13.91	7.01	7.01	0.25
		90–170	Hr3	nHr3	organogenic fen peat; very poor in carbonate	/	/	/	/	/	13.55	7.52	7.52	0.11
		220–300	Hr5	nHr5	organogenic fen peat; very poor in carbonate	6.8	31.4	1.7	/	0.06	33.04	27.87	27.87	0.22
		360–390	Lbr	fFr2	Limnic organo-mineral mud; rich in carbonate	7.3	14.6	1.0	/	0.05	36.03	27.63	27.63	0.88
Rheic Drainic Sapric Histosol (profile 2)	„Basenreiches Erdniedermoor"	0–10	H1	nHv-nHfw1	organogenic amorphous peat; free of carbonate; clod structure; extremely strongly rooted with fine roots and medium rooted with coarse roots	6.4	45.4	2.6	0.148	0.59	3.97	3.07	3.07	0.13
		10–20	H2	nHv-nHfw2	organogenic amorphous peat; free of carbonate; extremely strongly rooted with fine roots and medium rooted with coarse roots	6.6	41.1	3.5	0.008	0.19	7.26	19.18	19.18	0.27
		20–60	Hr	rnHv-nHr	organogenic amorphous peat; very poor in carbonate; very strongly rooted	6.5	26.3	2.3	0.000	0.03	4.41	9.84	9.84	0.19

P_DL: Double lactate-soluble P; K_DL: Double lactate-soluble K.

[a] IUSS Working Group WRB, 2015: World Reference Base for Soil Resources 2014, update 2015.
[b] Soil description according to the German Soil Classification System (Ad-Hoc-Arbeitsgruppe Boden der Staatlichen Geologischen Dienste und der Bundesanstalt für Geowissenschaften und Rohstoffe (Ed.), 2005).
[c] FAO, 2006: Guidelines for soil description.

inductively coupled plasma mass spectrometer with pneumatic nebulisation (ELAN-DRCe, Perkin Elmer). Analytical details can be found in supplemental information A.1. Concentrations are given in relation to dry matter. The aqua regia extractable REE contents were normalized to the upper continental crust (UCC) (Taylor and McLennan, 1985). Cerium and Eu anomalies were computed as follows: $Ce/Ce^* = Ce_N/(La_N*Pr_N)^{0.5}$, and $Eu/Eu^* = Eu_N/(Sm_N*Gd_N)^{0.5}$ (subscript N stands for UCC normalised values). Contents are depleted compared to UCC/the neighboring elements of Ce and Eu (negative anomaly) if the value is below "1" or enriched (positive anomaly) if the value is above "1". Table 4 shows the contents of REEs according to type of soil and parent material. In general, C horizon is regarded as parent material. However, in few soil profiles the C horizon was missing and therefore, B/H horizons were also considered for the calculation.

2.3. Statistical analysis

The figures were created with ORIGIN 8.0. Pearson correlation analysis was carried out by SPSS 22.0. The strength of the correlations was classified according to Brosius (2002) in this study: r = 1 perfect correlation; $1 > r > 0.8$ very strong correlation; $0.8 > r > 0.6$ strong correlation; $0.6 > r > 0.4$ modest correlation; $0.4 > r > 0.2$ weak correlation; $0.2 > r > 0$ very weak correlation; r = 0 represents no correlation. The two-tailed tests had a significance level of 0.05 and 0.01, respectively.

3. Results

3.1. Soil characteristics

All three profiles in the western part of Germany are mainly composed of silt, while the Hyperdystric Stagnic Cambisol possessed a higher sand content compared to the other two profiles (Table 1). The soil texture of the two Retisols and the Arenosol in the northeast of Germany is mainly composed of sand (Table 2). The two fen soils consist of organic material (Table 3). The pH value of the Hypereutric Cambisol and the two Histosols soils was relatively neutral, and (mainly) acidic for the Hyperdystric Stagnic Cambisol, the Hyperdystric Stagnic Folic Cambisol, the two Retisols and the Arenosol. The C_org and N_t content tended to decrease with increasing depth in all profiles. They were highest in the Histosols with around 35% (C_{org})/2.5% (N_t) as well as in the OeOi and Oa horizon of the Hyperdystric Stagnic Folic Cambisol. The contents of S, Al, Fe, and Mn were relatively constant in the Hypereutric Cambisol, and higher in the deeper horizons compared to the upper horizons in the Hyperdystric Stagnic Cambisol, Hyperdystric Stagnic Folic Cambisol, Retisols, and Histosol profile 1 whereas horizons at medium level exhibited the highest content in the Histosol profile 2 and Arenosol.

3.2. Rare earth elements

3.2.1. Aqua regia extractable contents

The single aqua regia extractable REE contents showed a similar vertical distribution in each profile (Figs. 2–4). The REE content increased with increasing depth in the Hyperdystric Stagnic Cambisol, in the Hyperdystric Stagnic Folic Cambisol, and in one Histosol (profile 2), whereas an increase followed by a decrease existed in the Hypereutric Cambisol, and the Retisols. A multiple change from increasing to decreasing REE contents existed in the Arenosol, and the other Histosol (profile 1). However, we determined distinct differences in the content of REEs between the different types of soil developed on different parent material. The REE content tends to lessen in the order: loess > loamy/sandy Pleistocene and Holocene sediments > organic material (Table 4). Hence, the three profiles in the western part of Germany exhibited higher contents than the soils in the northeast of Germany: Hypereutric Cambisol in average 975 µmol kg⁻¹

Table 4
Contents of REEs according to type of soil and parent material.

International Soil Classification[a]	Parent material	Sum REE							
		mg kg⁻¹				mmol kg⁻¹			
		Mean	Median	Minimum	Maximum	Mean	Median	Minimum	Maximum
Hypereutric Cambisol	High-flood loam of the Rhine (late Weichselian glaciation until Holocene)	122.25	121.34	101.04	145.25	0.99	0.98	0.81	1.19
Hyperdystric Stagnic Cambisol	Loess (Weichselian glaciation) over periglacial slope deposits (Pleistocene)	92.28	86.53	80.32	115.74	0.72	0.68	0.60	0.93
Hyperdystric Stagnic Folic Cambisol	Periglacial slope deposits consisting of loess and Cambrian period sediments (Weichselian glaciation) over periglacial slope deposits consisting of Cambrian period sediments (Weichselian glaciation)	147.84	137.37	124.40	192.20	1.14	1.07	0.93	1.49
Albic Dystric Retisol (profile forest)	Gravel containing cryoturbate loamy sand over periglacial slope sandy loam over loamy, sandy till	80.76	90.28	55.39	96.61	0.65	0.72	0.44	0.77
Albic Eutric Retisol (profile agricultural grassland)	Cryoturbate loamy sand over deluvial loamy sand over periglacial slope loam over limy, sandy till	83.28	88.93	60.65	100.27	0.66	0.71	0.48	0.80
Chromic Dystric Arenosol	Cryoturbate loamy sand over deluvial sand (of meltwater sand)	22.94	21.94	17.47	29.77	0.18	0.17	0.14	0.24
Rheic Drainic Sapric Histosol (profile 1)	Organic material	15.92	16.01	2.38	41.30	0.13	0.13	0.02	0.34
Rheic Drainic Sapric Histosol (profile 2)	Organic material	13.32	7.98	6.70	25.29	0.10	0.06	0.05	0.20

[a] IUSS Working Group WRB, 2015: World Reference Base for Soil Resources 2014, update 2015.

(810–1186 µmol kg⁻¹), Hyperdystric Stagnic Cambisol 669 µmol kg⁻¹ (465–930 µmol kg⁻¹), and Hyperdystric Stagnic Folic Cambisol 829 µmol kg⁻¹ (48–1487 mg kg⁻¹) (data not shown). The aqua regia extractable REE content was in average 407 µmol kg⁻¹ in the horizons of the two Retisols (165–801 µmol kg⁻¹) (data not shown). The REE content was slightly higher in the soil under agricultural grassland compared to the soil under forest. The horizons of the Arenosol possessed an average REE content of 180 µmol kg⁻¹ (136–238 µmol kg⁻¹) (data not shown). The lowest aqua regia extractable REE contents were found in the horizons of the two Histosols with in average 122 µmol kg⁻¹ (18–335 µol kg⁻¹) (data not shown). Single contents varied in average between 169 µmol kg⁻¹ for Ce and 0.29 µmol kg⁻¹ for Lu in the profiles. According to Oddo-Harkins rule, the REE contents tended to decrease with rising atomic number, and REEs with even atomic numbers were present in higher contents than their adjacent ones with odd atomic numbers: Ce > La > Nd > Y > Pr/Sc > Sm > Gd > Dy > Er > Eu > Yb > Tb > Ho > Tm > Lu. Cerium had an average proportion of 36% on the total aqua regia extractable REE content, whereas Lu amounted in mean 0.1% of the total aqua regia extractable REE content.

In general, the light REEs (LREEs; i.e. REEs with mean atomic mass lower than ca. 153 u and effective ion radius above 95 p.m., i.e. La, Ce, Pr, Nd, Sm, and Eu (Tyler, 2004)), and Gd were lesser depleted in comparison to UCC than Sc, Y, and most of the heavy REEs (HREEs; i.e. REEs with mean atomic mass above ca. 153 u and effective ion radius below 95 p.m., i.e. Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu (Tyler, 2004)) (supplemental table A.1).

Almost all horizons displayed a deficiency of REEs compared to UCC; except some REEs which were enriched in the CBw horizon of the Hypereutric Cambisol, and in the two deepest horizons of the Hyperdystric Stagnic Folic Cambisol. Especially the two Histosols and the Arenosol were strongly depleted in REEs compared to the UCC. The La$_N$/Yb$_N$-ratio, is considered to reflect the degree of fractionation between LREEs and HREEs (Sholkovitz et al., 1994). This ratio indicated an enrichment of LREEs compared to HREEs in all profiles; except Hr3 horizon of Histosol profile 1, where La$_N$/Yb$_N$-ratio signified with a value of 0.9 a depletion of LREEs compared to HREEs. The average value of 4.3 pointed to a stronger fractionation in the Hyperdystric Stagnic Folic Cambisol compared to the other profiles.

The Hyperdystric Stagnic Cambisol and the Arenosol showed positive Ce anomalies (Ce/Ce*), thus, an enrichment of Ce compared to its adjacent elements La and Pr. Almost all horizons of the Hypereutric Cambisol and the Hyperdystric Stagnic Folic Cambisol exhibited (slightly) negative Ce anomalies (Ce/Ce*). Negative as well as positive Ce anomalies occurred in the other four profiles. Negative Eu anomalies (Eu/Eu*) were found in all profiles (except 2CBg horizon of the Hyperdystric Stagnic Folic Cambisol), signifying a depletion of Eu in comparison to its neighboring elements Sm and Gd.

Correlation coefficients (Pearson) between aqua regia extractable REEs and soil properties are given in Fig. 5. In the Cambisols and in the Retisols, the aqua regia extractable REEs were modestly to very strongly positively correlated with clay, CEC$_{eff}$ (Cambisols solely Y, Ho, Er, Tm, Yb, Lu), and pH (Cambisols solely Y, Eu and HREEs) (Fig. 5 a + e). Aluminum showed a (very) strong correlation with aqua regia extractable REEs in the Retisols, the Cambisols (except Sc), and the Histosols (except Sc) as well as with Tb, Er, and Yb in the Arenosol (Fig. 5 b). We determined (very) strong correlations between Fe and aqua regia extractable REEs in the Retisols, the Cambisols, the Arenosol (except Sc, Ce, Pr, Tb), and the Histosols (solely Nd, Sm, Eu, and HREEs) (Fig. 5 c). We calculated (very) strong positive correlations between Mn and aqua regia extractable REEs (except Sc, Tb) in the Arenosol as well as Y, and HREEs (except Gd, Tb) in the Cambisols (Fig. 5 d). We found a (very) strong positive correlation between S and aqua regia extractable REEs in the Arenosol (except Sc, Ce, Pr, Tb) as well as Y, and HREEs (except Gd, Tb) in the two Histosols (Fig. 5 d). In the Cambisols, S was modestly to strongly negatively correlated with aqua regia extractable REEs (except Sc, Y, Tm, Yb, Lu) (Fig. 5 d). Organic carbon showed a modest to very strong negative correlation with aqua regia extractable REEs in the Cambisols (except Sc) as well as with Sm, Gd,
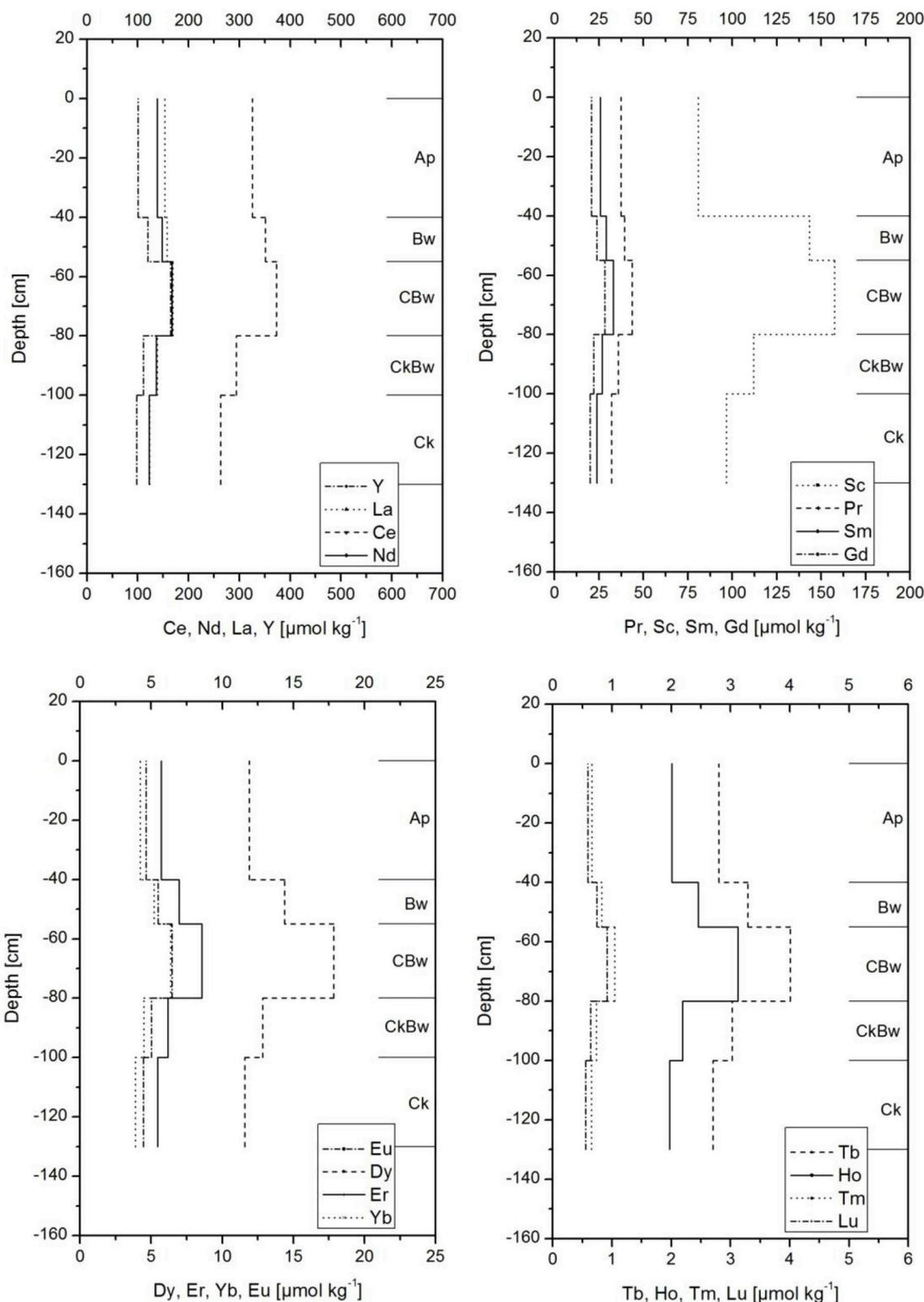
Fig. 2a. Vertical distribution of REEs in the Hypereutric Cambisol.

Tb, Dy, and Yb in the two Histosols (Fig. 5 a).

3.2.2. Hydroxylammonium chloride-extractable contents

The hydroxylammonium chloride-extractable REE contents were highest in the Hypereutric Cambisol with values from 46 to 513 μmol kg^{-1} (average 266 μmol kg^{-1}) (Fig. 6). The lowest contents were found in the

Histosols with contents from 1.4 to 105 μmol kg^{-1} (in average 17 μmol kg^{-1}). The hydroxylammonium chloride-extractable REE contents reached values from 14 to 423 μmol kg^{-1} (average 152 mg kg^{-1}) in the Retisols; the content in the soil under agricultural grassland was slightly higher compared to the soil under forest. We determined hydroxylammonium chloride-extractable REE contents from 31 to
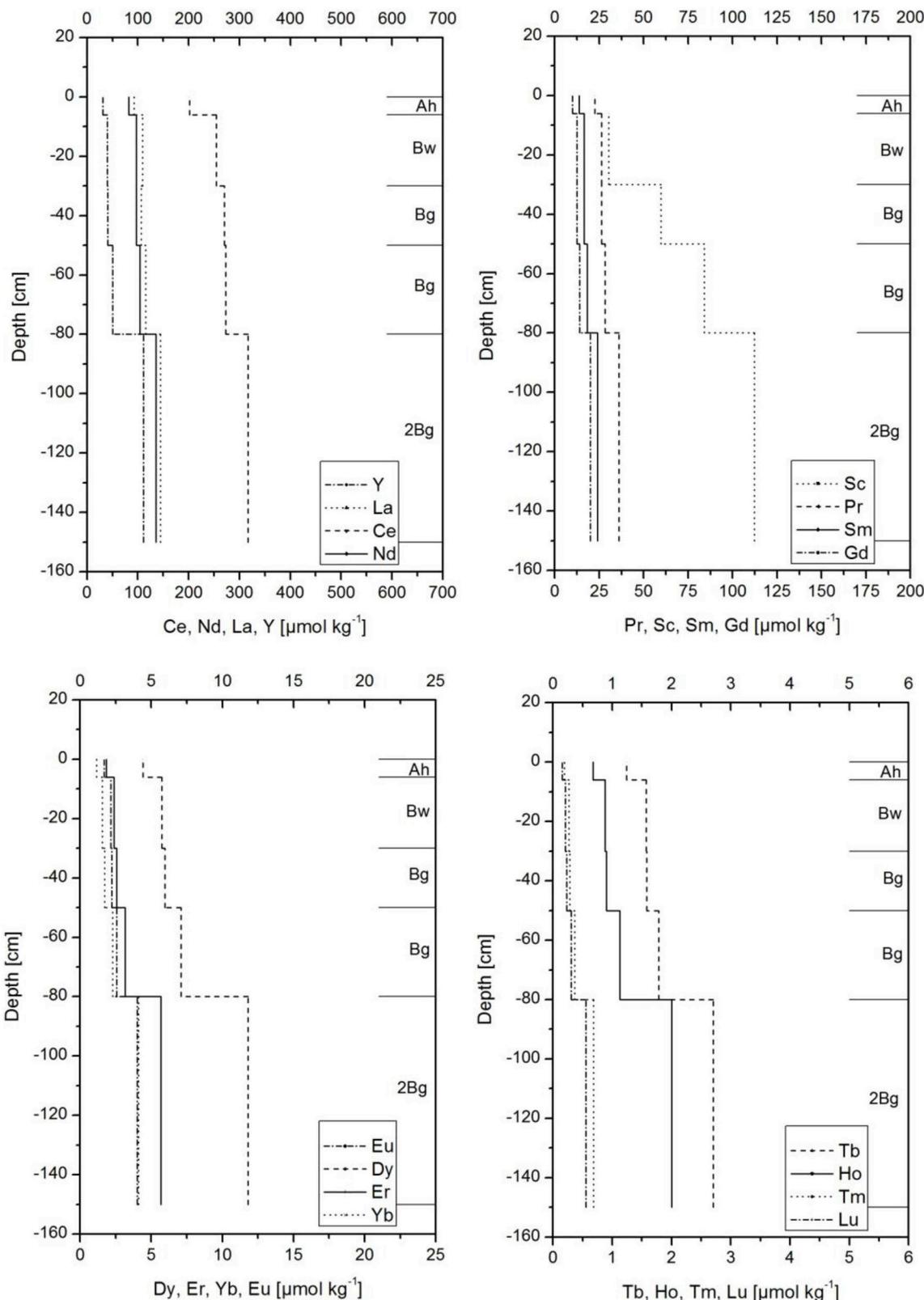
Fig. 2b. Vertical distribution of REEs in the Hyperdystric Stagnic Cambisol.

349 µmol kg^{-1} (average 129 µmol kg^{-1}) in the Hyperdystric Stagnic Cambisol, from 12 to 332 µmol kg^{-1} (average 90 µmol kg^{-1}) in the Hyperdystric Stagnic Folic Cambisol, and from 32 to 113 µmol kg^{-1} (in average 70 mg kg^{-1}) in the Arenosol. 2–55% (average 22.2%) of the aqua regia extractable REE contents was extractable with hydroxylammonium chloride. Single hydroxylammonium chloride-extractable contents were

highest for Ce, Y, Nd, and La (average content: 40 to 24 µmol kg^{-1}) and lowest for Lu (in average 0.13 µmol kg^{-1}) (data not shown). Yttrium and most HREEs (Dy, Ho, Er, Tm, Yb, and Lu) were most extractable with hydroxylammonium chloride (percentage: 32–37% of aqua regia extractable content; data not shown). The lowest percentage of 4% was calculated for Sc (data not shown).
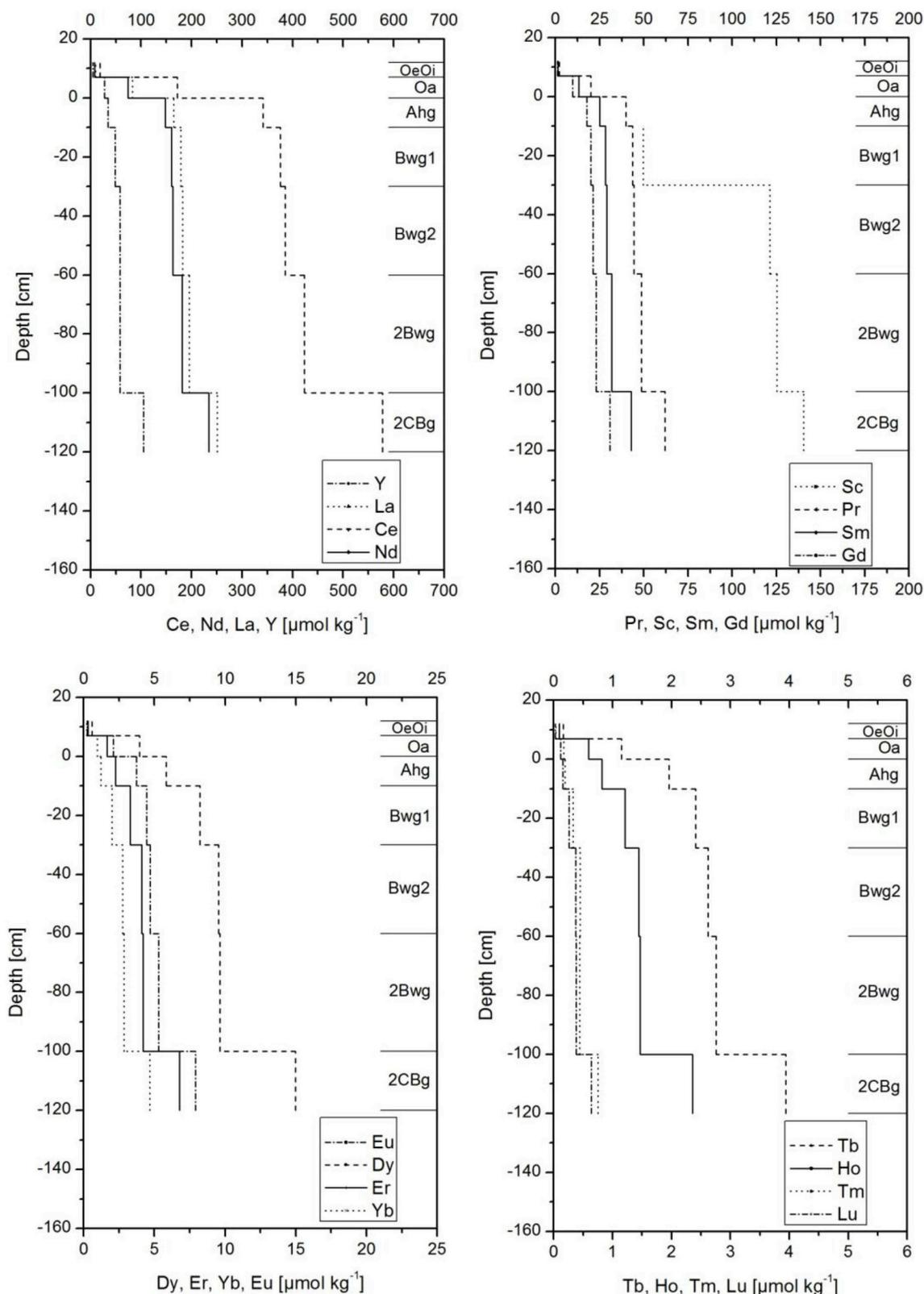
Fig. 2c. Vertical distribution of REEs in Hyperdystric Stagnic Folic Cambisol.

Correlation coefficients (Pearson) between hydroxylammonium chloride-extractable REEs and soil properties as well as Al, Fe, Mn, and S in the hydroxylammonium chloride extract (supplemental table A.2) are given in Fig. 7. In the Cambisols and in the Retisols, hydroxylammonium chloride-extractable REEs were modestly to very strongly positively correlated with clay (except Sc), CEC_eff (except Sc in Retisols), and pH

(except Sc; and additionally Ce, Pr, Tm, Lu in Cambisols) (Fig. 7 a + d). Hydroxylammonium chloride-extractable Eu and nearly all HREEs (except Gd, Lu) showed very strong positive correlations to CEC_eff in the Arenosol (Fig. 7 a). We found very strong positive correlations between hydroxylammonium chloride-extractable REEs (except Sc) and Fe in the Retisols and the two Histosols (Fig. 7 b). Hydroxylammonium chloride-
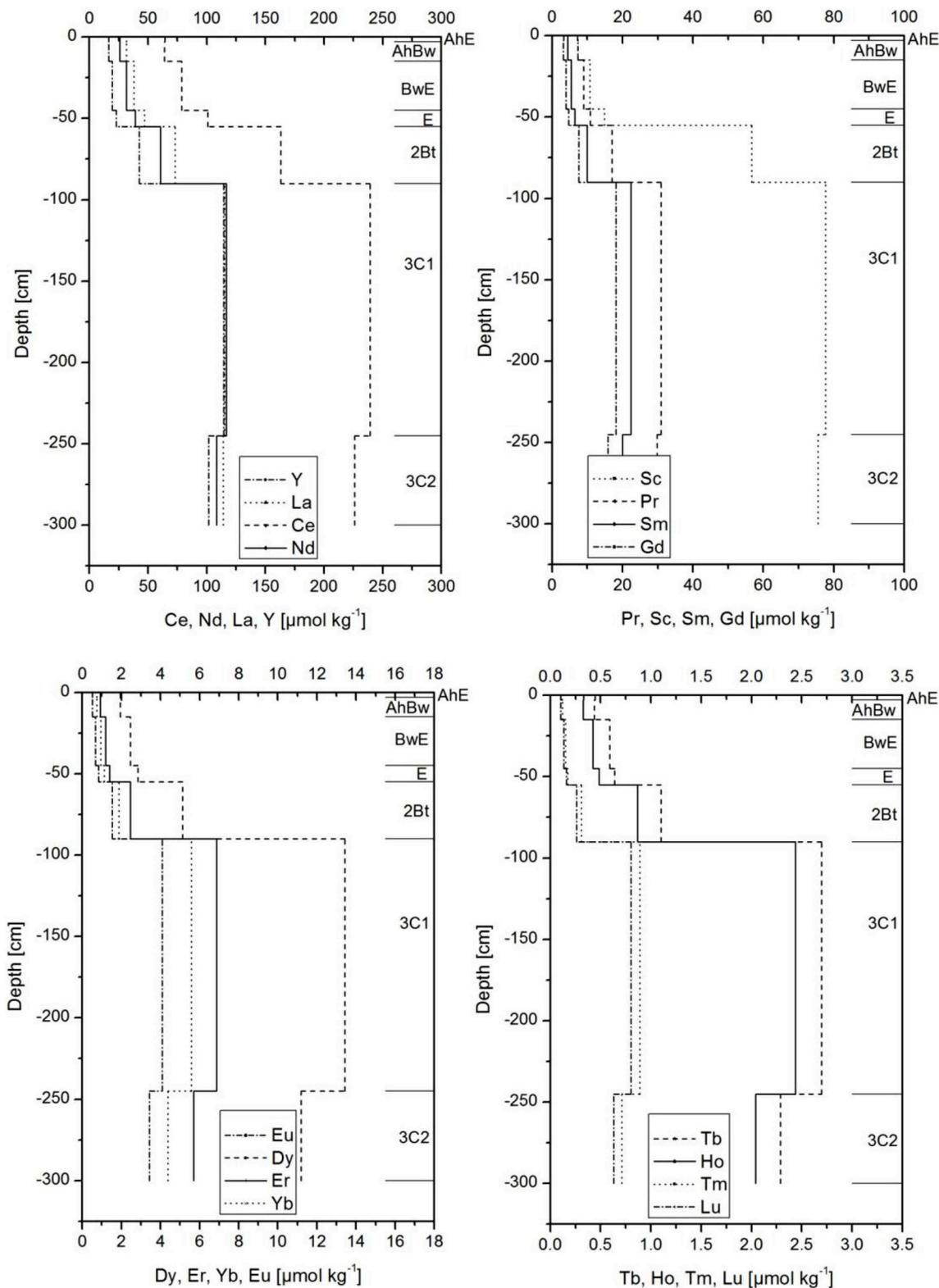
Fig. 3a. Vertical distribution of REEs in the Albic Dystric Retisol (profile forest).

extractable Sc was very strongly positively correlated with Fe in the Cambisols (Fig. 7 b). Hydroxylammonium chloride-extractable REEs were very strongly positively correlated with Al in the Retisols (except Sc) and in the Histosols (except Sc, Eu) (Fig. 7 c). We determined modest to strong positive correlations between hydroxylammonium chloride-extractable REEs (except Sc) and Mn in the Cambisols and in the Retisols (Fig. 7 b). Hydroxylammonium chloride-extractable REEs were modestly

to very strongly positively correlated with S in the Retisols (except Sc, La) and in the Histosols (except Sc) (Fig. 7 c). In the Cambisols, Sc, Tm, and Lu were modestly to very strongly negatively correlated with S (Fig. 7 c).

3.2.3. Hot water extractable contents

The hot water extraction was only conducted at the Cambisols because we supposed that measurable concentrations in the hot water extract are
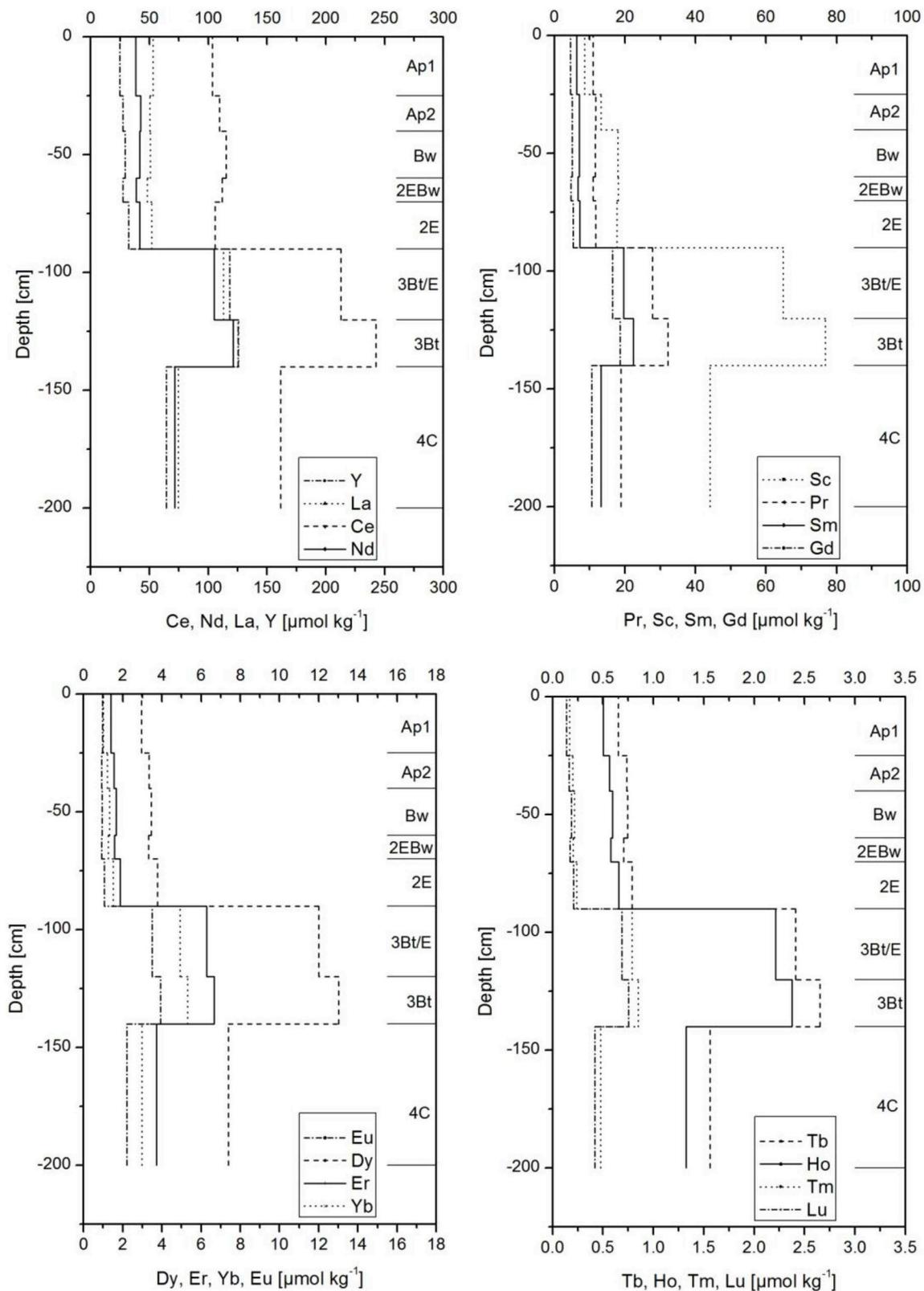
Fig. 3b. Vertical distribution of REEs in the Albic Eutric Retisol (profile agricultural grassland).

most likely present there. The hot water extractable REE content amounted in average 0.75 μmol kg^{-1} (0.19–1.34 μmol kg^{-1}) in the Hypereutric Cambisol, 0.93 μmol kg^{-1} (0.44–1.86 μmol kg^{-1}) in the Hyperdystric Stagnic Cambisol, and 1.09 μmol kg^{-1} (0.35–1.98 μmol kg^{-1}) in the Hyperdystric Stagnic Folic Cambisol (supplemental Fig. A.1). The highest

contents were found in the Ah horizon of the Hyperdystric Stagnic Cambisol, and in the Oa, and Bwg1 horizons of the Hyperdystric Stagnic Folic Cambisol. 0.02–1.07% (average 0.2%) of the aqua regia extractable REE contents was extractable with hot water.

Correlation coefficients (Pearson) between hot water extractable
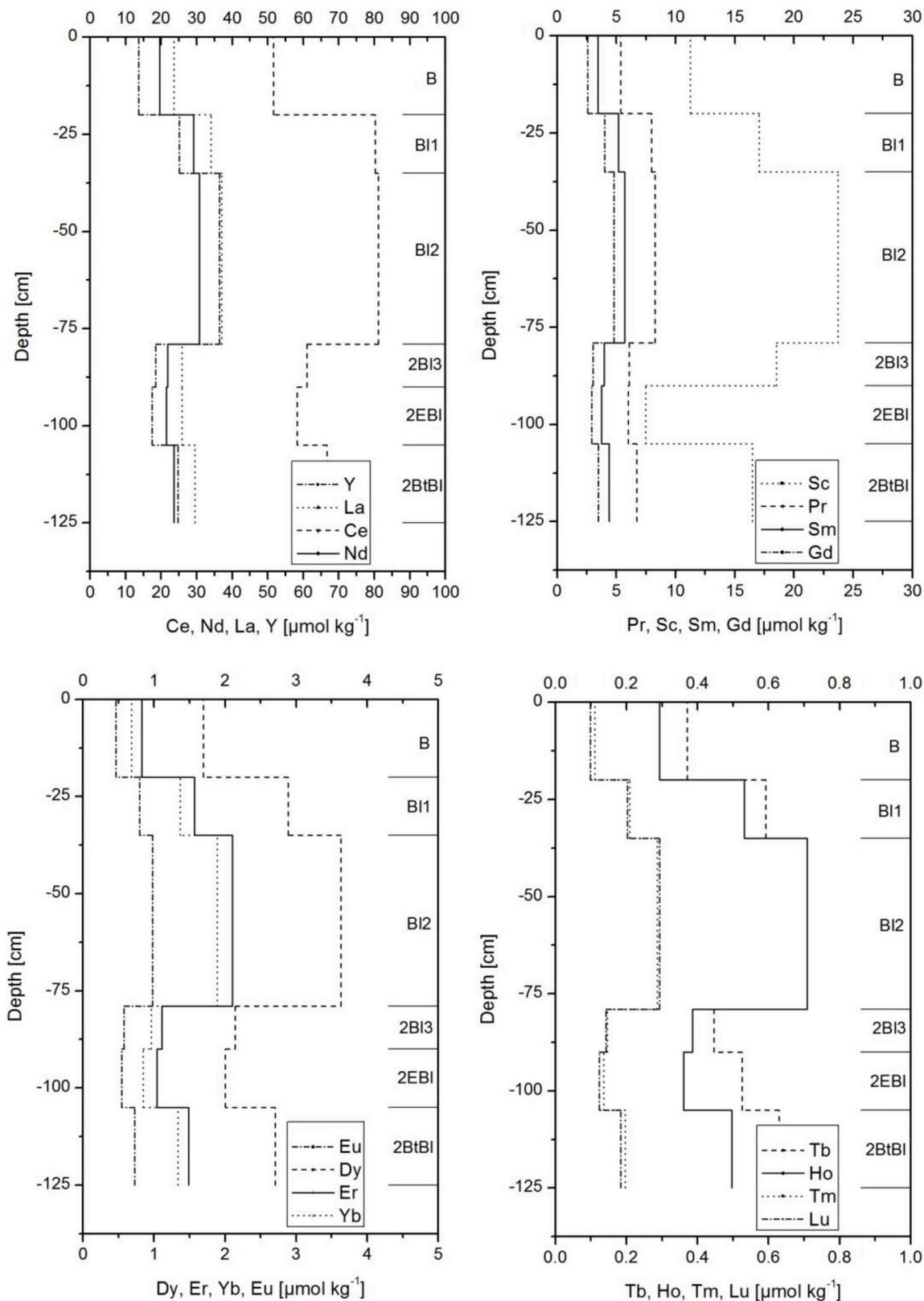
Fig. 3c. Vertical distribution of REEs in the Chromic Dystric Arenosol.

REEs and pH, C_{org} as well as Fe, Al, S, C, the anions Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} in the extract (supplemental table A.3) are given in supplemental Fig. A.2. Supporting information can be found in supplemental information A.2.

4. Discussion

4.1. Aqua regia extractable contents

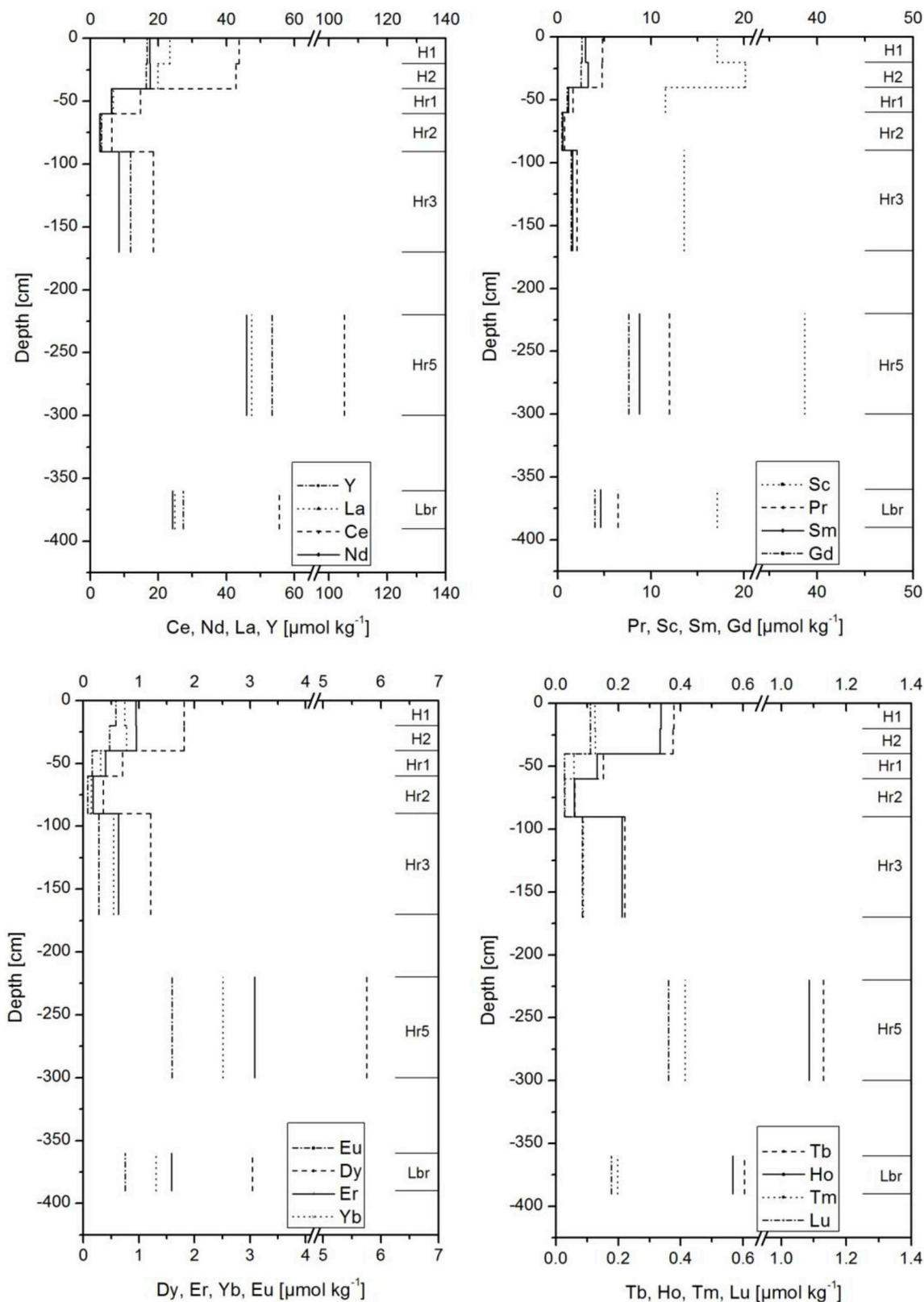The REE content in soils strongly linked with the parent material.

Fig. 4a. Vertical distribution of REEs in Rheic Drainic Sapric Histosol (profile 1).

Soils developed from loess possessed higher REE contents than soils derived from other materials such as (sandy/loamy) Pleistocene and Holocene sediments or organic material. Soils originated from the latter had the lowest REE contents in the studied soil profiles.

The differences in the content of REEs between the horizons and the profiles seem strongly linked with the soil properties, especially the particle-size distribution. Clay minerals can contain REEs and serve as carriers for them (Laveuf and Cornu, 2009), and clayey soils consequently have high REE contents (Tyler and Olsson, 2005). In general, the REE content rises with decreasing particle-size and with growing percentage of the clay-size fraction (Compton et al., 2003; Kimoto et al., 2006). The selected soils in the western part of Germany (especially the
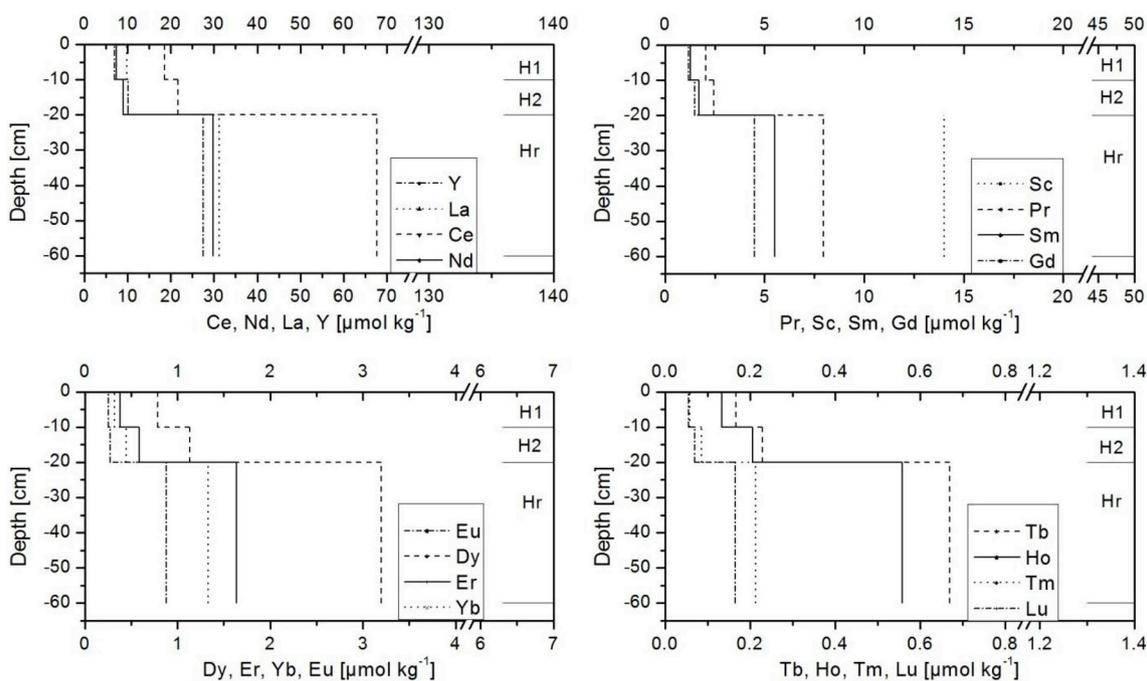
Fig. 4b. Vertical distribution of REEs in Rheic Drainic Sapric Histosol (profile 2).

Hypereutric Cambisol and the Hyperdystric Stagnic Folic Cambisol) possess higher clay contents (Tables 1–3) and accordingly higher REE contents compared to the studied soils in the northeast. Consequently, the soils in the western part of Germany reveal a lower degree of depletion compared to the UCC (supplemental table A.1). Sá Paye et al. (2016) also found that Brazilian soils developed from clayey sediments exhibited higher REE contents than soils derived from silty/sandy sediments. The REE contents in the Histosols were lowest what might be because they consists of decayed vegetation and the REE contents in plants are generally very low (Brioschi et al., 2013; Tyler, 2004; Tyler and Olsson, 2005). The parent material is a crucial factor for different REE contents. Recently, Bau et al. (2018) presented a new dataset of REE aiming for a shale-normalization of natural materials originate in Europe. They determined a total REE content of 246 mg kg^{-1} (without Sc) for the European Shale what is obviously higher than the parent material content of our studied soils UCC (Table 4).

Furthermore, Sá Paye et al. (2016) detected higher REE contents in Cambisols than in Arenosols. We determined the same. Loell et al. (2011b) reported for three loess soil profiles in Hesse (Germany) a REE content from 222 to 423 mg kg^{-1} and Mihajlovic et al. (2015) detected in two Luvisols developed from loess in Bavaria (Germany) a REE content from 166 to 230 mg kg^{-1}. These are partly distinct higher contents than we determined in the Hyperdystric Stagnic Cambisol developed from loess. This shows that soils developed on similar parent material can have distinctly different REE contents if they were subject to different soil genesis.

In the Hypereutric Cambisol, the Retisols, and the Arenosol, we found the highest aqua regia extractable REE contents and lowest depletion in the horizons with the highest clay and lowest sand contents. This indicates that REEs seem to be linked with the soil genesis. One characteristic soil-forming processes of the Cambisol is the clay mineral formation. Thereby clay minerals such as smectite, illite, and vermiculite were formed, and this results in a higher clay content in the Bw horizon compared to the parent material (C horizon). In contrast to the Cambisol, the differences in the clay content of the Retisol are not mainly caused by the process of clay mineral formation, but by migration of clay minerals. The clay is translocated from the E horizon and accumulates in the Bt horizon. Consequently, the CBw horizon of the Hypereutric Cambisol and the 3Bt horizon of the Retisol under

agricultural grassland were enriched in REEs whereas clay-depleted horizons due to soil genesis tended to possess lower REE contents. These observed results are in accordance with the positive correlation between REE content and clay content regarding the Cambisols and Retisols (Fig. 5).

The other soil forming process of the Cambisol is the oxide formation. In this process, Fe^{2+} ions are dissolved from silicates and oxidized to Fe^{3+} ions. This is relevant to REEs because they could connect as REE^{3+} or $REE(OH)^{2+}$ with OH^- on the Fe/Mn oxide surface (Fleet, 1984; Laveuf and Cornu, 2009). These Fe/Mn (hydr)oxides are able to form coatings on clay minerals. The influence of Al, Fe, and Mn on the REEs is supported with the close positive correlation for the Hypereutric Cambisol as well as for the Retisols, and the Arenosol (Fig. 5). There are minor differences in the content of Al/Fe/Mn in the horizons of the Hypereutric Cambisol. Therefore, we assume that these metals not seem to be important factors for the differences in the content of REEs in this profile. However, Al/Fe/Mn seem to be important for the REEs in the Retisols and the Arenosol. Here, we detected the highest REE contents in the horizons which are rich in these metals. In general, the characteristic red B horizon of the Arenosol has a high Fe content with minerals such as goethite and hematite. The soil genesis of this horizon is speculative until now. However, several processes such as weathering, podzolization or influence of groundwater are currently being discussed as possible reasons for the red color and the high iron content. Also, a combination of different soil developing processes might be possible. In this context, it should be also noted that the REE contents detected by Melis (2001) in Red Soils (Terra Rossa) from Sardinia (Italy) and by Mao et al. (2009) in Red Soils from China are around eight times higher than the contents we determined in the Arenosol. This may be explained by different underlying bedrock on which soil formation processes base and by contribution from external eolian/alluvial sources. Mao et al. (2009) mentioned that red soils formed by bedrock weathering had higher REE contents than red soils formed by dust-storms.

The soil development from the Cambisol can lead to Hyperdystric Stagnic Folic and Hyperdystric Stagnic Cambisols. In these soils, the clay-rich horizon dams the rainwater in the overlying clay-depleted horizon. A solution and redistribution of Fe and Mn within the soil profile occurs due to the periodic alternation of wetness and dryness as
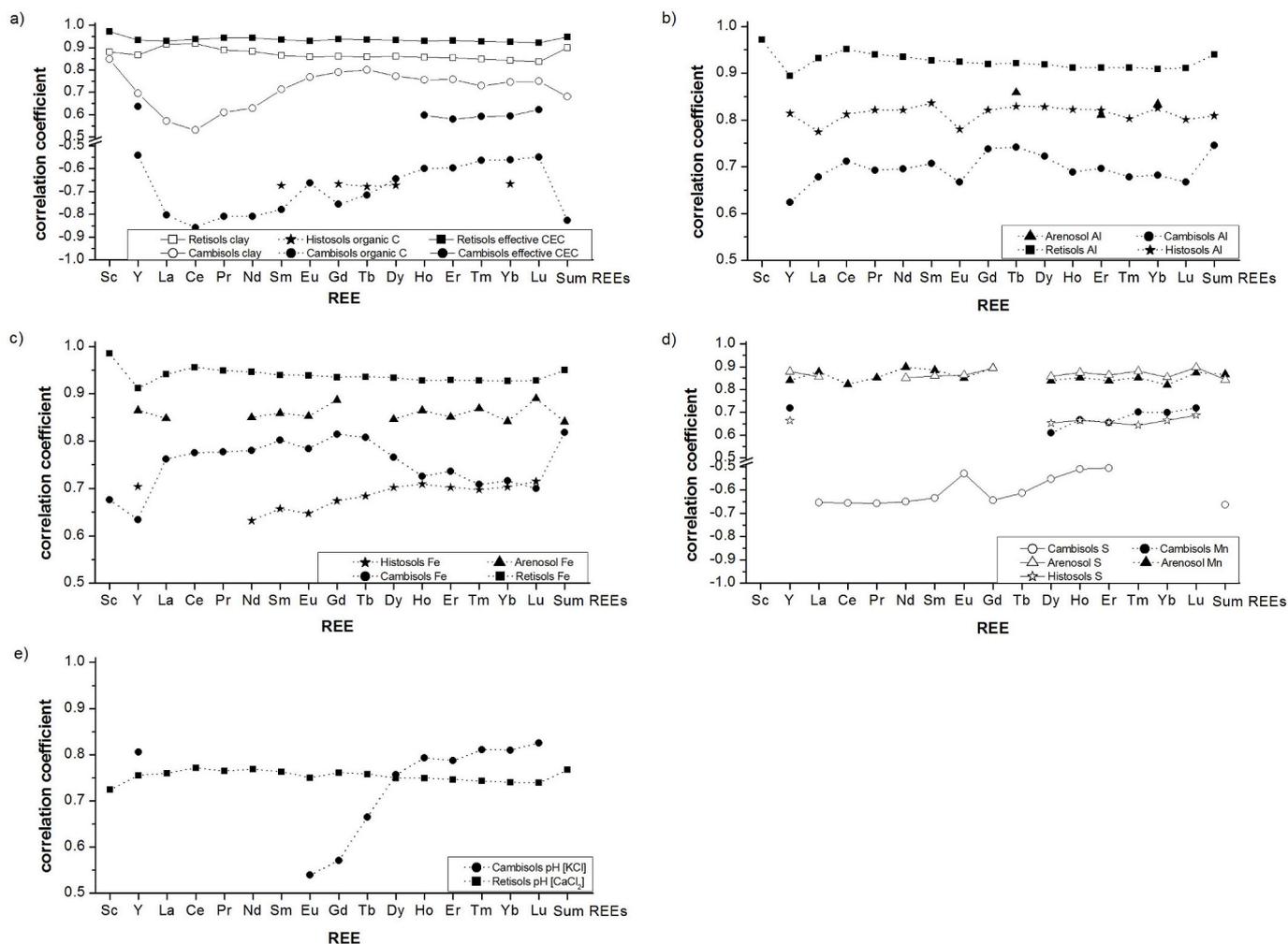
Fig. 5. Correlation coefficients (Pearson) between aqua regia extractable REEs and soil properties.
Correlations with organic C, S, and Mn were not significant regarding the Retisols. Correlations with clay, organic C, effective CEC, and pH were not significant regarding the Arenosol. Correlations with Mn, and pH were not significant regarding the Histosols.

well as temporary lack of oxygen. The redox morphosis leads to rust stain and gray-bleached zones in the clay-rich horizon (Blume et al., 2016). In the Hyperdystric Stagnic Cambisol and in the Hyperdystric Stagnic Folic Cambisol, there seems to be no obvious relation between REE content and clay content regarding the differences between the horizons. The 2Bw horizon of the Hyperdystric Stagnic Cambisol which is rich in REEs has at least the highest clay content but also the highest sand content (Table 1). The Al, Fe, and Mn contents seem to be less important for the high REE contents in the 2Bg horizon of the Hyperdystric Stagnic Cambisol because there are minor differences in the content of Al/Fe/Mn in the horizons (except Ah horizon). Regarding the Hyperdystric Stagnic Folic Cambisol, there exist at least relatively high Al, Fe, and Mn contents in the REE enriched 2CBg horizon. However, we detected a positive correlation between REEs and clay as well as Al, Fe, and Mn for the Cambisols (Fig. 5).

Iron and Mn are obviously relevant for the two Histosols according to the correlation coefficients (Fig. 5). Regarding Histosol profile 1, there exist at least relatively high Fe and Mn contents in the REE enriched Hr5 horizon. The two upper horizons of this profile have slightly higher REE contents compared to the directly subjacent horizons. This might be explained by aerobic conditions caused by drainage which led to an earthification of the peat and maybe also to a formation of oxides which can bind the REEs. Another reason might be atmospheric deposition of REEs onto the topsoil. Wang et al. (2000) reported a REE concentration of 0.22–33.0 ng m^{-3} in atmospheric particulate matter

for the western part of the Netherlands. The highest REE contents in the Histosols were found in the lower horizons. This may be due to dissolution of the underlying bedrock/sediments of the peat. Hattori and Hamilton (2008) showed that the underlying rocks contribute to the metal contents in the peat via vertical transport toward the surface. In general, fens are influenced by groundwater input. Ferrat et al. (2012) determined the highest contents in the mineral-rich layer of a peat bog. The REE contents varied between 19 and 165 mg kg^{-1} in this Chinese peat core what is clearly higher than in our fen soils and seems to be due to atmospheric dust deposition. However, the role of organic material is relevant by analyzing organic soils such as Histosols. Rare earth elements can form chelate with C_{org} and those dissolve under oxidizing conditions and release REEs (Davranche et al., 2015; Lijun et al., 1998). In generally, a low C_{org} content decreases the REE content in the bulk soil because of an increased solubility of REEs. The negative surface charge of organic matter reduces with decreasing pH and elements are released (Du Laing et al., 2009). However, we found a negative correlation between C_{org} and five REEs (Sm, Gd, Tb, Dy, Yb) for the Histosols (Fig. 5). The same applies for the Cambisols, where we found a negative correlation between REEs (except Sc) and C_{org}. Rare earth elements can also form chelate with (organic) sulphides and they were released in this case under oxidizing/acidic conditions (Lijun et al., 1998). The Arenosol has oxidizing and acidic conditions. Maybe, REEs are complexed with (organic) sulphate. We found a positive correlation between S and REEs (except Sc, Ce, Tb) in the Arenosol as well as Y, and
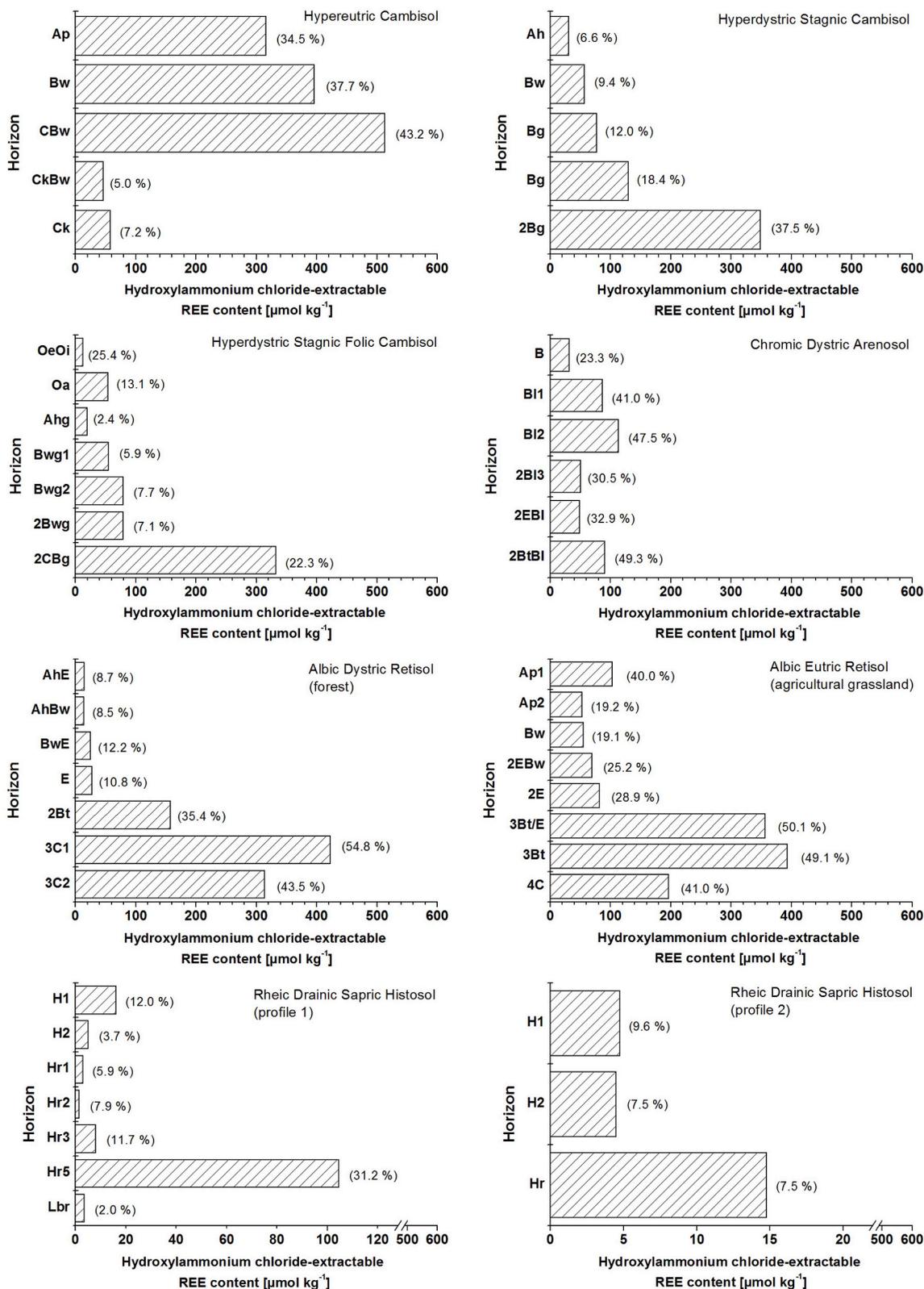
Fig. 6. Hydroxylammonium chloride-extractable REE content.
Percentages on the aqua regia extractable contents are given in brackets

HREEs (except Gd, Tb) in the Histosols; but the correlation was negative regarding the Cambisols (Fig. 5). In general, a low pH promotes the mobilization of REEs. At high pH, the complexation of REE ions and negatively charged groups may more easily because the surface of soil particles and organic matter is more negatively charged (Zhu et al.,

1993). In agreement with this we found a positive correlation between REEs and pH value for the Cambisols and Retisols (Fig. 5). The correlation between REEs and carbonate was not significant although it is known that less carbonates cause less REEs (Laveuf et al., 2008). A low CEC_{eff} also enhances the solubility of REEs and decreases the REE
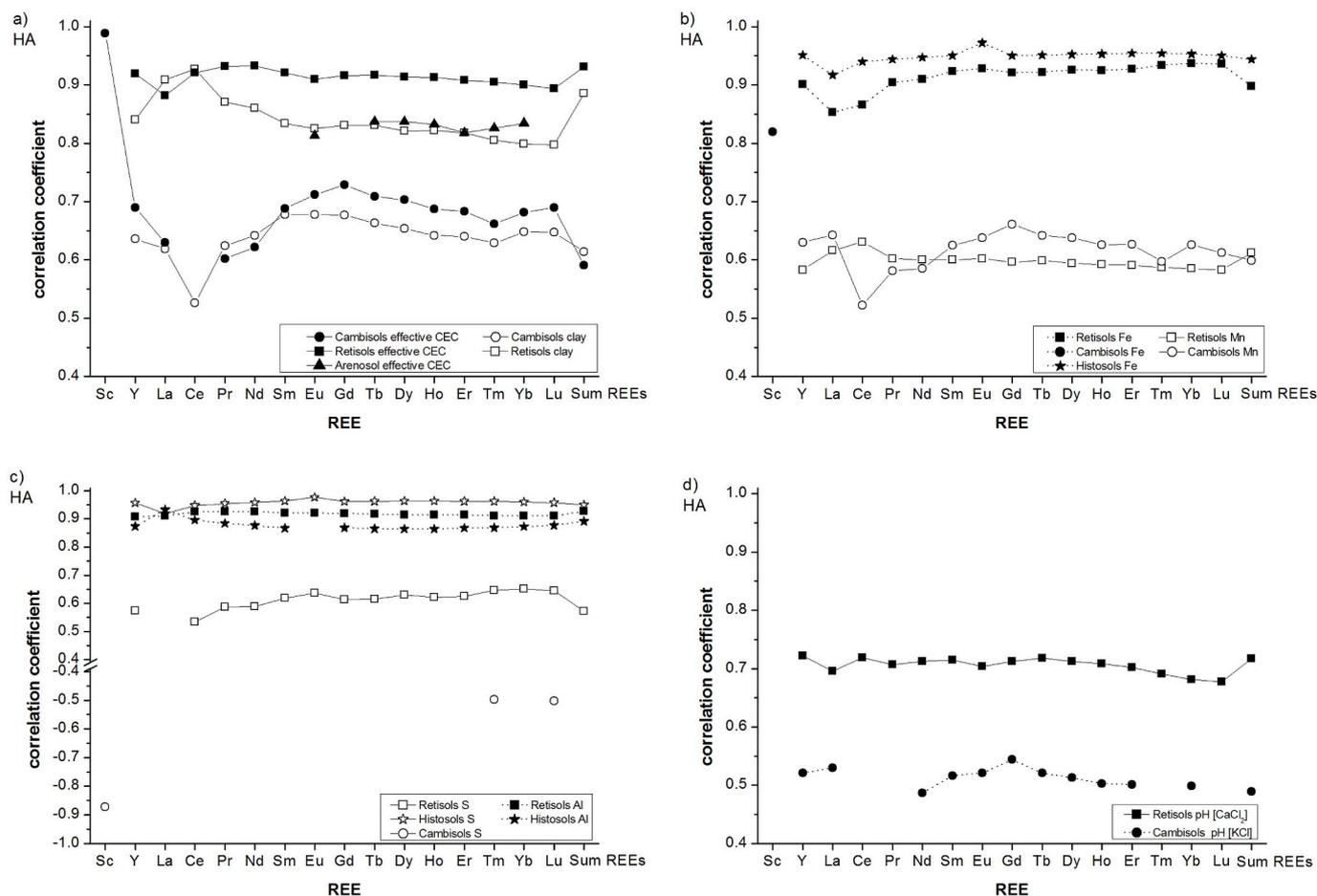
Fig. 7. Correlation coefficients (Pearson) between hydroxylammonium chloride-extractable REEs and soil properties.

content in the bulk soil. Accordingly we found a positive correlation between CEC_{eff} and REEs for the Retisols and six REEs (Y, Ho, Er, Tm, Yb, Lu) for the Cambisols (Fig. 5).

Regarding the Retisols, it is noticeable that the profile under agricultural grassland possessed slightly higher REE contents than the profile under forest (Fig. 3a + b). An explanation for this might be the introduction of P-containing fertilizer on the soil under agricultural grassland. Rare earth elements have a strong affinity to phosphate compounds and for that reason phosphates naturally include significant amounts of REEs (Laveuf and Cornu, 2009; Tyler, 2004). The solubility of REE phosphates is very low which results in low leaching and high accumulation of REEs in soils (Cetiner et al., 2005; Zhang et al., 2006). A continuous intensive P fertilization of $300\,kg\,ha^{-1}\,year^{-1}$ can result in an REE input between 30 and $170\,g\,ha^{-1}\,year^{-1}$ (Todorovsky et al., 1997); the REE content may double in 159 years under regular application (Wang et al., 2004). The P content is especially in the two upper horizons of the Retisol under agricultural grassland higher than in the Retisol under forest (Table 2) which could be an indication for P fertilization.

The depletion compared to the UCC was more distinct for HREE compared to LREE (supplemental table A.1). Heavy REE are more leachable and mobile than LREE because they form more easily soluble complexes with e.g. amorphous Fe/Mn oxides, carbonates, and organic matter (Braun et al., 1990; Laveuf and Cornu, 2009). In contrast, LREEs prefer to occur as free species (Cantrell and Byrne, 1987) and are easier retained by clay (Compton et al., 2003). These dissimilarities can provide the fractionation between LREEs and HREEs, and enrichment of LREEs compared to HREEs (supplemental table A.1). Soil processes (such as oxide formation, dissolution of carbonates, migration of organic complexes) may be responsible for the tendency to decreasing

fractionation degree between LREEs and HREEs from top to bottom of the profile.

The high contents of Ce may have resulted from the occurrence of Ce in the less mobile Ce(IV) valence state so that the element may preferentially accumulate in the soil compared to the other REEs (Cao et al., 2001). The sorption of Ce(IV) onto Fe/Mn (hydr)oxides and humic acids is stronger (Pourret et al., 2008; Janots et al., 2015), and the element can accumulate as insoluble cerianite (CeO_2) (Braun et al., 1990; Koppi et al., 1996; Compton et al., 2003). However, these favored adsorption processes can result in positive Ce anomalies but they can also contribute to a preferential removal of Ce, and might clarify the (slightly) negative Ce anomaly in the soil profiles (supplemental table A.1). Akagi et al. (2002) detected no cerium anomaly in peat moss and peat grass in contrast to soil-grown plants and they assume that this was because of a too low E_H or pH. Redox processes might explain the development or not a development of a Ce anomaly (Nakada et al., 2013).

A depletion of Eu in comparison to its adjacent elements Sm and Gd occurred in all profiles (supplemental table A.1). In general, Eu is more mobile than other REEs because of its +2 valence state. The depletion was partly more pronounced in the upper horizons probably because of preferential plant uptake from the rhizosphere soil and movement of Eu in deeper horizons (e.g. by percolating water). Furthermore, temporary reducing conditions may contribute to the presence of the mobile Eu(II) and its selective loss (cf. Hyperdystric Stagnic Cambisol, Hyperdystric Stagnic Folic Cambisol).

4.2. Hydroxylammonium chloride-extractable contents

The potential mobilization of REEs seems to be strongly controlled by reduction of amorphous Fe/Mn oxides and dissolution of Al

precipitates in the analyzed soils because a high percentage of REEs could be extracted with hydroxylammonium chloride (crystalline oxides could not be digested with it) (Fig. 6). Rare earth elements are released if amorphous oxides dissolve under reducing conditions. High content of Al, Fe, Mn and their oxides led to high hydroxylammonium chloride-extractable REE contents in the horizons. Accordingly, we calculated positive correlations between hydroxylammonium chloride-extractable REEs and Al/Fe/Mn (except for the Arenosol) (Fig. 7). The Arenosol is perhaps an exception due to the deepest horizon, where relatively low Al/Fe/Mn contents are present, but a comparatively high hydroxylammonium chloride-extractable REE content. The latter may be caused by a relatively high clay content/CEC_{eff}. Amorphous Fe/Mn (hydr)oxides can form coatings on clay minerals. This might let increase the sorption of REEs onto clay minerals and may explain the positive correlation between hydroxylammonium chloride-extractable REEs (except Sc) and clay regarding the Cambisols and Retisols (Fig. 7). It might also give a reason for the positive correlation between hydroxylammonium chloride-extractable REEs and CEC_{eff} (Fig. 7). Few REEs can be adsorbed by soil when the CEC is low and REE concentrations are consequently relatively high in soil solution. Our finding is in accord with (Spencer et al., 2007; Spencer et al., 2011) who identified a positive correlation between the CEC of clay minerals and Ho, La, and Sm contents. In general we can state that the clay-rich horizons possessed high hydroxylammonium chloride-extractable REEs contents; except in the Hyperdystric Stagnic Folic Cambisol where we determined the highest hydroxylammonium chloride-extractable content in the 2CBg horizon which is not the clay-richest horizon. A possible explanation for this exception might be that the parent material loess was subject to a very slight chemical alteration what resulted in a weak depletion of mobile REE species, and consequently, in a high hydroxylammonium chloride-extractable content. This hypothesis might be supported by the fact that the average REE content of this horizon is close to the UCC (normalized total $REEs_N = 1.07$; supplemental table A.1) which do not appear in the other horizons of this soil profile. Furthermore, REEs can be bound to (organic) sulphides/sulphates and these in turn can form complexes with Al and Fe. This is indicated by the positive correlation between hydroxylammonium chloride-extractable REEs and S for the Retisols and Histosols (Fig. 7). However, hydroxylammonium chloride-extractable Sc, Tm, and Lu were negatively correlated with S in the Cambisols (Fig. 7). (Cao et al., 2001) mentioned that amorphous Fe/Mn (hydr)oxides dissolve at low pH and release the REEs. In contrast to this we found a positive correlation between hydroxylammonium chloride-extractable REEs and pH for the Cambisols and Retisols (Fig. 7). Yttrium and most of the HREEs (Dy, Ho, Er, Tm, Yb, and Lu) had a higher hydroxylammonium chloride-extractable proportion than the LREEs because HREEs tend to form more easily soluble complexes with amorphous Fe/Mn oxides. However, the potential mobilization of REEs is controlled by various factors (e.g. soil redox potential, pH value as well as content of Fe, Mn, Al, S, organic and inorganic carbon) and the differences between the horizons can only regarded to a certain extent being caused by differences of a single factor. The factors interact with each other and therefore, the relation between hydroxylammonium chloride-extractable REEs and single soil properties is not always clearly identifiable.

The different values of the soil properties in the horizons due to the soil development led to partly distinct different percentages of the hydroxylammonium chloride-extractable content on the aqua regia extractable content (Fig. 6). This is in contrast to marsh and floodplain soils in Germany where the hydroxylammonium chloride-extractable fraction slightly differed between the horizons because of interrupted soil development due to flooding events and linked processes of erosion and sedimentation (Mihajlovic et al., 2014a,b). However, the magnitude of the percentages is comparable to floodplain soils (in average 20%) and marsh soils (in average 36%) (Mihajlovic et al., 2014a,b). The percentage of the hydroxylammonium chloride-extractable content on the aqua regia extractable content is partly higher in the deeper parts of the profiles compared to the upper part (e.g. Retisols) what may indicate that the mobile part of REEs is leached and transported downwards.

4.3. Hot water extractable contents

The hot water extraction offers the possibility to consider easy available REEs in dependence on easy metabolizable carbon and nitrogen. Accordingly, we observed that the hot water extractable REE contents tended to be higher in those horizons where high C_{org} contents/C_{HWE} and NO_3^- concentrations existed (Table 1, supplemental Fig. A.1 & supplemental table A.3). The formation of organic complexes with REEs seems to be an important factor influencing the potential mobilization of easy available REEs. However, we solely found a strongly positive correlation of Sc to C_{org} and C_{HWE}; the correlations with the other REEs were not significant (supplemental Fig. A.2b). This is maybe caused by the fact that Sc is not a lanthanoid; it has a different atom configuration (e.g. smaller effective ion radius, lower mean atomic mass) and this may led to a different geochemical reaction. Water-soluble compounds with NO_3^- are relevant for most REE (except Sc, Nd, Sm, Eu, Tb) regarding the positive correlation coefficients (supplemental Fig. A.2b). Furthermore, we detected high hot water extractable REE contents in the horizons which are rich in hot water extractable Al and Fe (supplemental table A.3). This, and the positive correlations between hot water extractable REEs and Fe (except Sc) as well as Al (except Eu) (supplemental Fig. A.2a) can be maybe explained by following: Al/Fe oxides become water-soluble and release REEs under the prevailing acidic pH-conditions in the Hyperdystric Stagnic Cambisol and in the Hyperdystric Stagnic Folic Cambisol. In this context, we detected a modestly negative correlation between hot water extractable Sc and Tm with pH (supplemental Fig. A.2a) what means that a low pH causes high Sc and Tm contents in the hot water extract. By the reason that Sc seems to form so many easy water soluble connections, this element (as well as Y, and some HREEs) was to a larger extent extractable with hot water than LREE.

5. Conclusions

In our investigated soils, the composition of the parent material is a crucial factor differentiating the content of REEs. The studied soils compared to the UCC are depleted in REEs. For instance, the organically Histosols, and the sandy Arenosol are strongly depleted, whereas the silty, clayey Cambisols are lesser depleted. The different soil genesis consisting of migration and accumulation of clay minerals, Al, Fe, and Mn controls the vertical distribution of REEs, because processes like sorption, complexation, and precipitation modify the REE contents in the soil profiles. High contents of clay, Al/Fe/Mn oxides, S, and organic matter cause high REE contents since they provide important sorption sites for REEs. A similar relation is also observed by extraction with hydroxylammonium chloride and hot water. The potential mobilization of REEs seemed to be relatively low. Scandium, Y, and the HREEs (except Gd, Tb) have a higher hydroxylammonium chloride and hot water extractable proportion than the LREEs because they tend to form more easily soluble complexes. In future, it is suggested to verify the results in further soil profiles in Germany and around the world. Also, mechanistic experiments concerning the dynamics of REE mobilization should be performed to improve our knowledge of the geochemical nature of REEs in soils world-wide. Additionally, a monitoring of REE in plants and wildlife is recommend.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2019.02.002.

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