



Rare earth elements and their release dynamics under pre-definite redox conditions in a floodplain soil



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HIGHLIGHTS

- Redox-conditions influence release of rare earth elements (REEs) via changes of pH.
- REEs release is enhanced under oxic/acidic conditions.
- Dissolved REEs are positively correlated with sesquioxides.
- Dissolved REEs are negatively correlated with dissolved organic carbon.
- REEs dominate in residual fraction followed by reducible, and oxidisable fraction.

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ABSTRACT

For the first time, the impact of pre-definite redox conditions on the release dynamics of rare earth elements (REEs) and the determining factors pH, iron (Fe), manganese (Mn), aluminum (Al), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), and sulfate (SO_4^{2-}) in a floodplain soil was elucidated using an advanced, highly sophisticated automatic biogeochemical microcosm apparatus. The redox potential (E_H) ranged between +82 and +498 mV during the experiment. The systematic increase of E_H caused a decreasing pH from 6.6 to 4.6 which resulted in an enhanced mobilization and release of REEs along with Fe, Al, and Mn under oxic and acidic conditions. Also, organic matter seems to contribute to the mobilization of REEs under changing redox conditions. A factor analysis identified that the REEs form one group with E_H , Fe, Al, and Mn what indicates that REEs and sesquioxides have a similar geochemical behavior. The pH, DOC, and DIC are together in another cluster which demonstrates that their behavior substantially differs from the other group. The sequential extraction procedure revealed that the majority of the REEs were bound in the residual fraction, followed by the reducible, the oxidisable and the water soluble/exchangeable/carbonate bound fraction. Future studies should further elucidate the specific release kinetics of REEs, the controlling factors on the release dynamics and the underlying mobilization processes in highly dynamic wetland soils around the globe.

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1. Introduction

Floodplain soils are highly dynamic ecosystems. They are frequently flooded, and sediments as well as various pollutants accumulate during flooding events with low flow velocity

(Rinklebe, 2016; Rinklebe et al., 2017). The pollutants can originate from industrial, municipal, and agricultural discharges of waste, and can be transported over several (hundreds) kilometers with the river water. For example, the Wupper River as a tributary of the Rhine River in Germany, was highly polluted due to discharges of textile and metal industry during the last few centuries. Nowadays, large floodplain areas along the river are still heavily contaminated with toxic elements (Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westfalen, 2016). Rare earth elements may also enter rivers and the groundwater (cf. e.g. Noack

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et al., 2014) because they are used in many industrial key technologies and as microelement fertilizer or feed additive in agriculture. An example is Gadolinium (Gd) which is used as contrast agent in magnetic resonance imaging in hospitals. Via the hospital sewage it enters surface waters, and therefore, anthropogenic Gd is present in high concentrations in several rivers (Bau and Dulski, 1996; Möller et al., 2002; Kulaksız and Bau, 2011; Hissler et al., 2016). Likewise, the Rhine River transports high Lanthanum (La) concentrations of industrial origin into the North Sea (Kulaksız and Bau, 2011).

Several ecotoxicological effects of REEs have been observed: La can negatively influence the fertility of sea urchins (Oral et al., 2010); Gd can cause kidney failure (Ergün et al., 2006), anaphylactic shock (Hasdenteufel et al., 2008), and finally lead to death (Kay, 2008) by humans. The potential toxicity of REEs in soils depends amongst other factors such as their concentration on the mobility of the elements. The latter is influenced by the changes of the water table level and resulting alterations between oxidizing and reducing conditions. The soil redox potential (E_H), the pH value as well as elements and other carriers such as iron (Fe), manganese (Mn), aluminium (Al), dissolved organic and inorganic carbon (DOC and DIC), and sulfate (SO_4^{2-}) may be important factors controlling the release dynamics of REEs in soils (cf. e.g. Cao et al., 2001; Grybos et al., 2007). In general, it is considered that changing redox conditions can influence the dynamics of REEs directly or indirectly via related changes in pH, Fe (hydr)oxides, Mn (hydr)oxides, Al, S, and DOC (cf. Rinklebe and Du Laing, 2011). Insoluble Fe and Mn oxides were reduced to soluble Fe^{2+} and Mn^{2+} during flooding and resulting decrease of E_H (Reddy and DeLaune, 2008); as a consequence of this, elements which are associated with the oxides are released to soil solution. Conversely, many elements are immobile at high E_H due to adsorption to Fe and Mn oxides or coprecipitation. Metals can be also immobilized under reducing conditions in the case of existence of insoluble sulfides (Du Laing et al., 2008). Cao et al. (2001) observed an increasing release of La, Ce, Gd, and Y as E_H decreased. However, the pH value was kept constant in their experiments and thus, they did not study the release dynamics of REEs under the influence of a free variable pH.

To our best knowledge, the impact of systematic and pre-definite redox conditions on the release dynamics of REEs in floodplain soils has not been mechanistically studied up to date. Thus, our aim was to quantify the impact of pre-definite E_H -conditions on the release dynamics of dissolved REEs, and to elucidate underlying redox-driven processes including the role of pH, Fe, Al, Mn, DOC, DIC and SO_4^{2-} in a floodplain soil. For this purpose, we were able to use an advanced, highly sophisticated automatic biogeochemical microcosm system allowing controlled adjustment of redox conditions.

2. Materials and methods

2.1. Soil characterization and geochemical fractionation

The sampling site is located close to the confluence of the Wupper River into the Rhine River near Cologne in North Rhine-Westphalia, Germany (51°4′0.48″N, 6°4′0.48″E). The site is used as grassland and seasonally flooded by the Wupper River, usually in springtime. The soil is classified as Eutric Fluvisol (FAO, 2014). The soil sample was collected from a genetic horizon (24–46 cm depth). About 400 kg soil material (in eight replicates of about 50 kg) was picked up from an area of 4 m². The soil material of the replicates was pooled to one composite sample, carefully homogenized, air-dried, and handily crushed. All results presented here have been carried out on exactly the same soil sample. Basic properties and element concentrations of the studied soil are given in Table 1. The

Table 1

Basic properties and element concentrations of the studied soil.

	parameter	unit	value
	silt	[%]	92
	clay	[%]	2
	pH [H ₂ O]		6.4
	Total carbon	[%]	7.103
	Total organic carbon	[%]	7.100
	Total inorganic carbon	[%]	0.003
	Total nitrogen	[%]	0.354
	CEC _{eff}	[cmol ⁺ kg ⁻¹]	15.1
	Al	[g kg ⁻¹]	18.5
	Fe	[g kg ⁻¹]	43.8
	Mn	[g kg ⁻¹]	0.87
	S	[g kg ⁻¹]	0.99
	Sc	[mg kg ⁻¹]	2.67
	Y	[mg kg ⁻¹]	8.99
LREE	La	[mg kg ⁻¹]	18.66
	Ce	[mg kg ⁻¹]	40.98
	Pr	[mg kg ⁻¹]	5.00
	Nd	[mg kg ⁻¹]	18.99
	Sm	[mg kg ⁻¹]	3.77
	Eu	[mg kg ⁻¹]	0.63
HREE	Gd	[mg kg ⁻¹]	3.27
	Tb	[mg kg ⁻¹]	0.44
	Dy	[mg kg ⁻¹]	2.00
	Ho	[mg kg ⁻¹]	0.35
	Er	[mg kg ⁻¹]	1.00
	Tm	[mg kg ⁻¹]	0.12
	Yb	[mg kg ⁻¹]	0.77
	Lu	[mg kg ⁻¹]	0.11
	Sum REEs	[mg kg ⁻¹]	107.75

CEC_{eff}: effective CEC.

LREE: REEs having a mean atomic mass lower than ca. 153 u and an effective ion radius above 95 p.m.; HREE: REEs having a mean atomic mass above ca. 153 u and an effective ion radius below 95 p.m. (Tyler, 2004).

soil texture was dominated by silt (determined according to Deutsches Institut für Normung, 2002). The soil was weakly acidic and contained high organic carbon. Soil pH was determined according to Deutsches Institut für Normung (2012). Total C (Ct) and N (Nt) were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Analytik Jena, Germany). Inorganic C was quantified by dry combustion and IR-Detection (Blume et al., 2011) with a C-MAT 550 (Ströhlein). Soil organic C was calculated as the difference between Ct and inorganic C. Effective cation exchange capacity (CEC_{eff}) was determined using BaCl₂ according to Deutsches Institut für Normung (2011). Concentrations of Al, Fe, Mn, and S were quantified by digestion in a microwave system (Milestone MLS 1200 Mega, Germany) according to U.S. Environmental Protection Agency (2007) and measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Scientific, Unterhaching, Germany).

Separate subsamples were digested with aqua regia (Deutsches Institut für Normung, 1997) to determine the (pseudo)total concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu ignoring that certain parts may remain in the residuum. Nevertheless, aqua regia extraction is established as the best available technique for determination of the ecologically relevant fractions (e.g. Rao et al., 2010; Rauret et al., 1999) and the German Soil Protection Ordinance (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, 1999) recommends this procedure for estimating the exposure pathway “soil-human”. A sequential extraction developed by the Commission of the European Communities Bureau of Reference, improved by Rauret et al. (1999) was conducted to determine the geochemical fractions of the REEs. The first step was performed with acetic acid and releases the water soluble/exchangeable/carbonate bound fraction (F 1). In the second step, hydroxylammonium chloride was used to digest the

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