



Geochemical fractions of rare earth elements in two floodplain soil profiles at the Wupper River, Germany



Julia Mihajlovic^a, Hans-Joachim Stärk^b, Jörg Rinklebe^{a,*}

^a University of Wuppertal, Department D, Soil- and Groundwater-Management, Pauluskirchstraße 7, D-42285 Wuppertal, Germany

^b UFZ – Helmholtz Centre for Environmental Research, Department of Analytical Chemistry, Permoserstraße 15, 04318 Leipzig, Germany

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ABSTRACT

We aimed to determine the concentrations and geochemical fractions of rare earth elements (REEs) according to the genetic soil horizons of two soil profiles (Eutric Fluvisols) at the Wupper River, Germany. The concentrations were determined using aqua regia extraction and the geochemical fractions were assessed using a sequential extraction procedure developed by the Commission of the European Communities Bureau of Reference. Single REE concentrations varied from 0.09 mg kg⁻¹ (Lu) to 40 mg kg⁻¹ (Ce). We have detected small differences of the REE concentrations between the horizons that seem to be due to flooding and the linked homogenisation processes. Rare earth elements dominate in the residual fraction (73.5%), followed by reducible (19.6%), oxidisable (6.6%), and water soluble, exchangeable (0.4%) fraction (calculated from the sum of the fractions and mean of both soil profiles). The proportion of the residual fraction tends to decrease with increasing atomic number, whereas the proportions of the other three fractions increase. Rare earth elements with higher atomic number seem to take earlier the bonding-places in the first three fractions than REEs with lower atomic number and therefore, rather the latter are bound to residual fraction or occur as free species. Important factors that affect the geochemical fractions and mobility of REEs are the adsorption of REEs onto clay and amorphous Fe–Mn oxides as well as formation of phosphate or organic complexes with REEs. A low pH favours the releases of REEs from the soil. In future, the impact of flooding regime and physico-chemical soil properties on the concentrations, geochemical fractions, and release kinetics of REEs should be determined in frequently flooded soils around the globe to improve our understanding of the geochemical behaviour of REEs.

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1. Introduction

Rare earth elements (REEs; Sc, Y, and the 15 lanthanoides) are used in many industrial key technologies as well as microelement fertiliser or feed additive in agriculture. Through exploitation of REEs and disposal of used products containing REEs, the metals can enter into the soil and may be transferred into the food chain. Many rivers, estuaries, and paddy soils were contaminated from industrial, municipal, communal, and agricultural discharges of waste as well as geogenic sources (e.g., Du Laing et al., 2009a; Rinklebe et al., 2007). The anthropogenic microcontaminants La and Gd have already been detected in rivers, lakes, estuaries, coastal waters, groundwater, and tap water (Bau and Dulski, 1996; Hennebrüder et al., 2004; Kulaksiz and Bau, 2011). Gadolinium is used in contrast agents for magnetic resonance imaging and therefore, elevated Gd concentrations were especially determined near hospitals (Kulaksiz and Bau, 2011). Likewise, high La concentrations attain via the Rhine River into the

North Sea (Kulaksiz and Bau, 2011). Several negative effects of REEs on organisms have been reported, for example Waring and Watling (1990) and Pairon et al. (1995) have documented that some inhaled REEs tend to accumulate in human lung and lymph nodes. Gadolinium complexes can be incorporated into bones of patients (Darrach et al., 2009) which finally lead to death (Kay, 2008). However, the mobility of REEs and their possible impacts on ecosystems are still relatively unknown; thus, potential risks for human health and environment can currently be inadequately estimated.

The Wupper River (Germany), a tributary of the Rhine River, was highly polluted from discharges of textile and metal industry during the last centuries. Generally, pollutants have been transported with the river water and accumulate in floodplain soils during flooding events with low flow velocity (Rinklebe et al., 2007). Thus, certain areas of the floodplain soils along the Wupper River possess nowadays considerable amounts of metals (Frohne et al., 2011, 2012). Sedimentation as well as changes of water table level and resulting alterations between anaerobic (flooding) and aerobic conditions (aeration due to desiccation) have an impact on the content, geochemical fractions, and mobility of metals. The geochemical phase the metals occur is important for the mobility and potential toxicity of metals in soils, and factors such as sorption–desorption, redox processes, content of metal, organic material, clay minerals, carbonates, sulphur, iron

* Corresponding author at: Soil- and Groundwater-Management, Department D, University of Wuppertal, Pauluskirchstraße 7, D-42285 Wuppertal, Germany. Tel.: +49 202 439 4057; fax: +49 202 439 4196.

E-mail addresses: j.mihajlovic@uni-wuppertal.de (J. Mihajlovic), ha-jo.staerk@ufz.de (H.-J. Stärk), rinklebe@uni-wuppertal.de (J. Rinklebe).

(hydro-)oxides, and pH which control the mobility and bioavailability (Du Laing et al., 2009b). Generally, REEs from anthropogenic sources seem to be bound in biologically available forms (Rao et al., 2010), however, very little data concerning the concentrations and geochemical fractions of REEs in soils are available up to date. Therefore, it is currently difficult to determine the mobility of REEs in soils and to assess potential risks. Thus, our objectives are: i) to quantify the current concentrations of REEs in two Eutric Fluvisol soil profiles at the Wupper River, Germany; ii) to determine the geochemical fractions of REEs (exchangeable, reducible, oxidisable, residual fraction) as a function of depth; iii) to quantify relations between soil properties, and the concentrations and distribution of REEs within the different geochemical fractions.

2. Materials and methods

2.1. Study area and study sites

The study area is located close to the confluence of the Wupper River into the Rhine River near Cologne in North Rhine-Westphalia, Germany (Fig. 1). The mean long-term annual precipitation is approximately 850 mm and the mean long-term annual air temperature is 10.8 °C (Deutscher Wetterdienst (Eds.), 2012). The Wupper River is approximately 115 km in longitude with an average gradient of 0.4‰ (Wupperversand (Eds.), 2012). The discharge averages 15.4 m³ s⁻¹ and the catchment area of the Wupper River comprises 815 km² (Wupperversand (Eds.), 2012). The Wupper River is in large parts a stream of the average mountain until the inflow into the Rhine Valley. Furthermore, the Wupper River is rich in tributary streams and a gravel dominated river of the basement rock from the middle course to the water mouth. The geological parent material consists of sediments of the Rhine River (“Niederrheinische Bucht”), which is predominantly shale of Devonian origin (“Rheinisches Schiefergebirge”) (Wupperversand (Eds.), 2012).

We selected two study sites in the study area and one soil profile was dug at each study site (profile 1: 51°5′4.1″N, 7°0′12.61″E; profile 2: 51°7′49.86″N, 7°1′35.10″E). The study sites are used as grassland and are flooded seasonally by the Wupper River, usually in springtime. Both soils are classified as Eutric Fluvisol (IUSS Working Group WRB (Eds.), 2006).

2.2. Soil description, sampling, and sample preparation

The soils were described in detail and classified according to “Bodenkundliche Kartieranleitung” (Ad-hoc-Arbeitsgruppe Boden,

2005), and “World reference base for soil resources 2006” (IUSS Working Group WRB, 2006). Here, symbols of horizons are discussed according to IUSS Working Group WRB (2006). Soil samples have been collected in accordance to genetic horizons. Sampling was performed in four replicates of about 1 kg each, which were pooled to one sample. For chemical analysis, all visible roots, macro fauna, and fresh litter were removed from the samples and furthermore, soil material was homogenized, air dried for several days, and sieved to <2 mm. Subsamples were ground using a metal free mortar.

2.3. Laboratory analyses

2.3.1. Soil properties

Particle-size distribution was determined by wet sieving and sedimentation using the pipette sampling technique according to DIN ISO 11277 (2002). The pH was determined according to Blume et al. (2011). Total C (C_t) and N (N_t) 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 C_t and inorganic C. Double lactate-soluble P (P_{DL}) was determined as described by Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (Eds.) (1991). Concentrations of Al, Fe, and Mn in aqua regia were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Scientific, Unterhaching, Germany). A four-point calibration was performed by diluting single standard and multi element solutions (CertiPur, Merck) with deionized water. Analyses were conducted in three replications. The relative standard deviation of replicate analysis was below 2%. Oxalate-extractable iron and manganese were measured according to Schwertmann (1964). Dithionite-extractable iron and manganese were determined as described by Mehra and Jackson (1960). Effective cation exchange capacity (CEC_{eff}) was calculated by using BaCl₂ according to DIN ISO 11260 (2011).

2.3.2. REEs

The samples were digested with aqua regia (DIN ISO 11466, 1997) to determine the concentrations of Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu as well as concentrations of Al, Fe, Mn, and S. These concentrations will be considered as ‘total concentrations’ in this study, ignoring that certain parts may remain in the residuum. However, it is well established that the aqua regia extraction is the best available technique to determine the ecologically relevant fractions (e.g. Löll et al., 2011; Rao et al., 2010; Rauret et al., 1999), although its

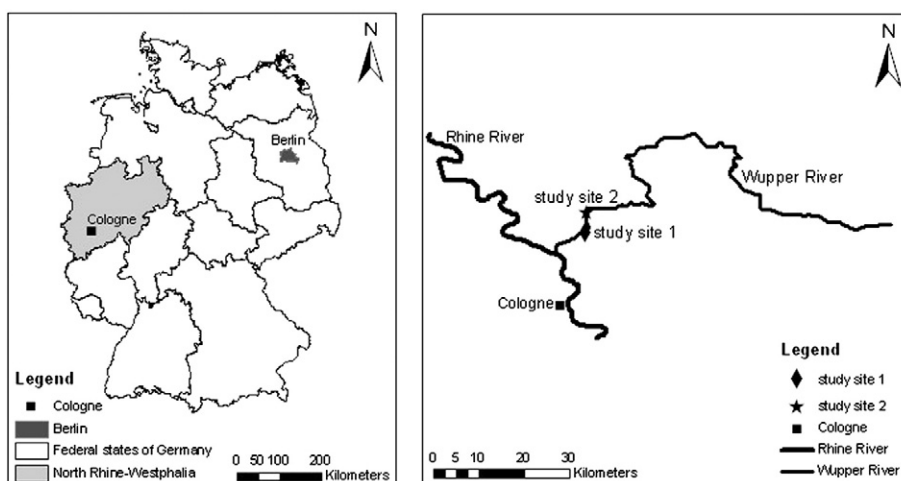


Fig. 1. Location of the study site in North Rhine-Westphalia, Germany.

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