Statistical evidence of REE distribution and effective factors in groundwater of former uranium mining site, eastern Thuringia, Germany

Anahita Pourjabbar[1], Anja Grawunder[1], Martin Lonschinski[1], Dirk Merten[1], Jürgen W. Einax[2], Georg Büchel[1]

Address: Friedrich-Schiller-University, Institute of Geoscience, Burgweg 11, 07749 Jena, Germany
Tel: +49 3641 948 618
E-mail address: anahita.pourjabbar@uni-jena.de
1: Friedrich-Schiller-University, Institute of Geoscience, Jena, Germany
2: Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University, Jena, Germany

Abstract
Acid Mine Drainage (AMD) caused by mining activities is a serious problem influencing the environment. Often the existence of numerous datasets from a study site makes statistical analysis a helpful and necessary tool for evaluation. In this study, multivariate analyses including multivariate outlier detection and image analysis have been used for 174 groundwater samples taken at the test site Gessenwiese in the former uranium mining area of Ronneburg to define the metal distribution and their effective factors. The gained results will be helpful to interpret the geochemical processes.
Even 20 years after stopping the leaching operations, the groundwater is still in acidic range (pH 3.2 5.4) and highly mineralized. The highest metal concentrations were measured for Al, Co, Mn, and Ni. A special focus of this work is laid on rare earth element (REE) distribution in the contaminated groundwater, reaching concentrations of up to 8.15 mg/l. Their distribution in the groundwater is mainly controlled by pH value and geology. Decreasing in pH generally causes higher metals mobility. The relation between Al, Fe and REE is more indirectly coupled with pH. Especially HREE show similar behavior to Al. Furthermore, the result got by multivariate outlier detection shows the different data structure based on geology and emphasizes the geology effect. Samples in the sandy, southern part have lower concentration of metals than the samples in the silty central and northern part of the test site.

Key words: *Multivariate statistics, groundwater, heavy metals, REE*

1. Introduction
The former uranium mine district in Eastern Thuringia and Saxony, Germany with more than 220,000 tons of uranium mining, was the third-largest uranium producer in the world (Jakubick et al., 2002; Lange, 1995). Mining activities started in 1949 and closed in 1990. The remnants of the mining included a large open pit mine, an underground mining system, and waste rock piles in which acid mine drainage (AMD) occurred (Wismut, 1994). Due to this process, surface water, seepage water and groundwater are highly mineralized with an acidic pH and have been contaminated by heavy metals including uranium and rare earth elements (REE) (Merten et al 2005). Hence, in 2004 the test field “Gessenwiese” was created in this region with the aim of improving remediation strategies for heavy metals contaminated area (Carlsson, Büchel, 2005; Büchel, G. et al, 2005)
This paper studies about the heavy metals distribution in groundwater and the effective factors in the test field with special emphasis on REE. The unique attraction of using REE to solve the geochemical problems is that they form the coherent group of trace metals whose

properties change systematically across the series. REE comprise the coherent group of La to Lu that is often grouped into the light REE (LREE: La to Nd), middle REE (MREE: Sm to Dy) and heavy REE (HREE: Ho to Lu). In general, REE concentrations in AMD influenced areas are significantly higher (Bozau et al., 2004; Merten et al., 2005) than in areas not influenced by AMD. Thus, acidic environments as the test site Gessenwiese are suitable for studying the behavior of REE in the system soil-water. In general, effective factors on REE concentration are e.g. the composition of the host rocks in the source region, pH and hydrochemical composition of the water, especially possible interactions with metals as Al, Mn and Fe that can occur as important (hydr)oxides in AMD influenced areas.

Most of the problems in REE studies involve complex and interacting factors, which are impossible to isolate and study individually. In such situation, multivariate analyses are helpful tools, since they place the objects into more or less homogeneous groups revealing the relation between the groups. Multivariate outlier detection and image analyses have been used to define the relation between REE and other elements such as Al, Cu, Fe, Th, U and Y, but also pH. Since samples were taken in different seasons, also the seasonal effect on metal concentrations was studied.

2. Geology Setting

The test site was installed in Quaternary sediments with at least 10 m thickness, comprising four units: (1) a graded bedding of silty and gravelly sand at the base and sand at the top, (2) silt, (3) clayey silt/ warved clay and finally an allochthonic soil material added to the area during remediation. The southern test site is dominated by unit (1); the middle test site by unit (2) and to a certain extent (3) since the clayey material occurs embedded in the silt. The north again is sandy, but this sand has a higher proportion of silt (Fig. 1) (Grawunder et al., 2009). The sand in the north and the silty material in the middle test site are connected within a facial interlocking, while the sand in the south appears more as an overlying unit. The distributive province was expected to be limno-fluvial. Below the Quaternary sediments, Paleozoic rocks of Ordovician to Devonian age can be found.

3. Sampling and Data Set

In total, 174 groundwater samples were taken from 33 groundwater measuring points (Fig.2) between December 2004 and September 2008. The parameters pH, Eh, temperature and electrical conductivity (EC) were determined in situ, using portable instruments pH320, LF320 and an external thermocouple (WTW). Samples for anions (except for HCO_3^-) and elements (cations) were filtered to 0.45 µm using glass fiber profilers and cellulose acetate filters (both Sartorius). Then, water samples for cation analysis were acidified with HNO3 (65%, subboiled) to pH < 2. All samples were stored at 6°C until analysis. HCO_3^- was analyzed at day of sampling by titration (Titrino 716 DM, Metrohm). Cl^-, $F^-$and SO_4^{2-} concentration were determined by ion chromatography (DX-120, Dionex). The elements Al, Ca, Fe, Mg, Mn and Na were measured using inductively coupled plasma – optical emission spectrometry (ICP-OES; Spectroflame, Spectro), whereas Cu, Mn, , Th, U, Y, Zn and REE were analyzed by inductively coupled plasma – mass spectrometry (ICP-MS ; PQ3-S, Thermo Elemental until 2007, then X-Series II, ThermoFisher Scientific).

To compare the seasonal effect on REE behavior and distribution, samples were separated into four data sets as April, May, September and December. In this way, statistical analyses have been done in all data sets to identify the probable role of seasonal factors.

4. Material and Methods

4.1. Outlier Data

An outlier is an observation that lies an abnormal distance from other values in a population. Outlier data in a data set are usually related to contamination or elements anomalies, and contain important information.

In this study function “symbol.plot” from “mvoutlier” library by Filzmoser (2005) in R environment has been used. This function is a multivariate technique which defines the observations which have different structures. This function is based on robust Mahalanobis distance (MD), minimum covariance determinant (MCD) estimator and adjusted quintile (Filzmoser , 2005; Bernholt, 2004). The outcome is a numerical matrix that reports the MD of the observations and the MD value which is the criteria to recognize the outliers. The samples that have a MD higher than the criteria are defined as outliers. In this case the outliers are not only the data which are very high or low in relation with the other data, but their shape and structure are different (Filzmoser, 2005).

4.2. Image Analysis

Image analysis is a visual display of cluster analysis. The outcome of cluster analysis which is shown by a dendrogram in many publications reveals data structures, but it allows no interpretation of the observed patterns in the term of the original variables. Image analysis is a 2- dimensional color scale image which shows the clustered samples and variables. The horizontal axis in the sorted samples and vertical axis is sorted variables. Data sorting has been done based on the Q mode (samples) clustering and R mode (variables) clustering. Hence, the resulting image has a smooth appearance, since the neighbor cells are ordered according to their similarity (Smolinski et al 2002).

5. Results and discussion

For groundwater of the test site Gessenwiese an Mg-(Ca)-SO_4^{2-} -water type in acidic range (pH 3.2-5.4) with high mineralization was found. The Eh was in oxic range. Highest metal concentrations were measured for Al (0.2-308 mg/l), Co (0.1-20.1 mg/l), Mn (51.2-705 mg/l), Ni (1-56 mg/l) and REE (8.15 mg/l). Fe was below the detection limit for most measuring points and reached hotspot like highest concentration in GTF 25 with 180 mg/l. The U concentrations are in the range of 0.2-3411 μg/l. REE spatial distribution is heterogeneous. The highest concentration of REE occurred in sample GTF16 (8150 μg/l), and the lowest concentration was measured in GTF7 (11 μg/l). Generally, the sampling points GTF11, 16, and 25, have the maximum REE concentrations in the sampling period. These samples are located in the middle to northern part of the test field. The minimum REE concentrations are found in the southern part in GTF7, 9, and 22. The spatial distributions are similar in different data sets which are based on sampling date.

Applied multistatistical methods were helpful to find the data structure and similarities between the samples and the elements to interpret the effective factors controlling REE distribution.

Generally, multivariate outliers showing two data structures: group 1: GTF 7, 8, 9, 19, 20 and 21; and group 2: GTF 2, 5, 12 and 13. The main factors that split these data into two groups are the element concentration and the sediments distribution in the studied area. The minimum of REE Al, Cu, Fe, Th, U and Y are mostly found in the samples of group 1. These samples are mainly covered by sand. However, samples in group 2 contain the average concentration of the elements. Group 2 comprises measuring points in the central to northern test site which are dominated by facial interlocking. Probably, geology (and with it hydrogeological factors) play an important role in element concentration.

Based on the image analysis, there are meaningful similarities between REE and other metals as Al, Cu, U and Y (Fig. 3). HREE and MREE have great similarities with Al and Y, while the LREE are more similar with Cu. Already Marmolejo-Rodríguez et al. (2007) described a relation between HREE and Al for a river-estruary system. Furthermore, they found a higher affinity of LREE with Fe. Unfortunately, Fe was below detection limit in 17% of groundwater samples of the test site Gessenwiese and shows weakly similarity with HREE. Al as well as Fe can form various (hydr)oxides known to be good scavangers for REE or metals in general due to sorption or (co)precipitation (e.g. Bau, 1999). Also pH-dependant (de)sorption to clay minerals that enrich especially HREE (e.g. Coppin et al., 2002) might play a role especially in the central test site.

The element distribution in all data sets is similar and more relate to the sampling location. However, the role of pH is obvious. The pH value decreasing below 4.5 causes increase in REE concentration. Since the metals Al, Cu, Fe, Th, U and Y behave similar to REE, they also show inverse relation with pH.

6. Conclusion

Applied multistatistical methods are a helpful tool for identification of data structure and similarities between samples or elements allowing interpretation of effective factors controlling metal distribution. In case of the investigation area, the range of element concentrations does not show any emphasis on seasonal influence. The groundwater is even 20 years after leaching in acidic range and enriched especially in Al, Co, Mn, and Ni. REE concentrations reached maximal concentration of 8.15 mg/l. Generally, their concentration increases more strongly below pH 4.5, whereas HREE mobility depends slightly stronger on pH. Furthermore, HREE behave similar to Al, U and Y. Outlier analysis indicated that especially the measuring points in the sand-dominated south differ resulting from different geological properties.

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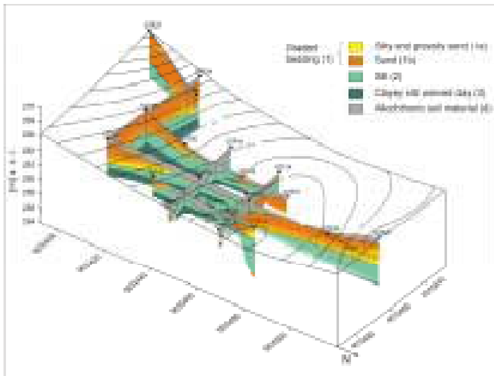

Fig. 1: Sediment distribution in the test field (Grawunder et al., 2009)

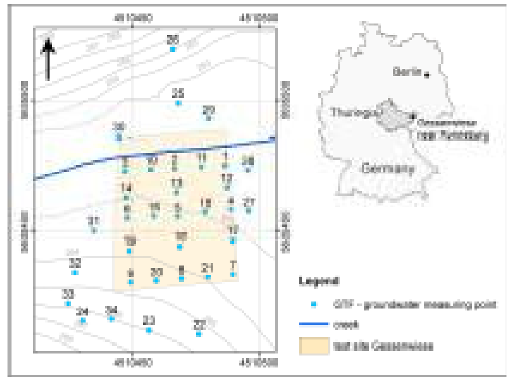

Fig. 2: Sampling location in studied area

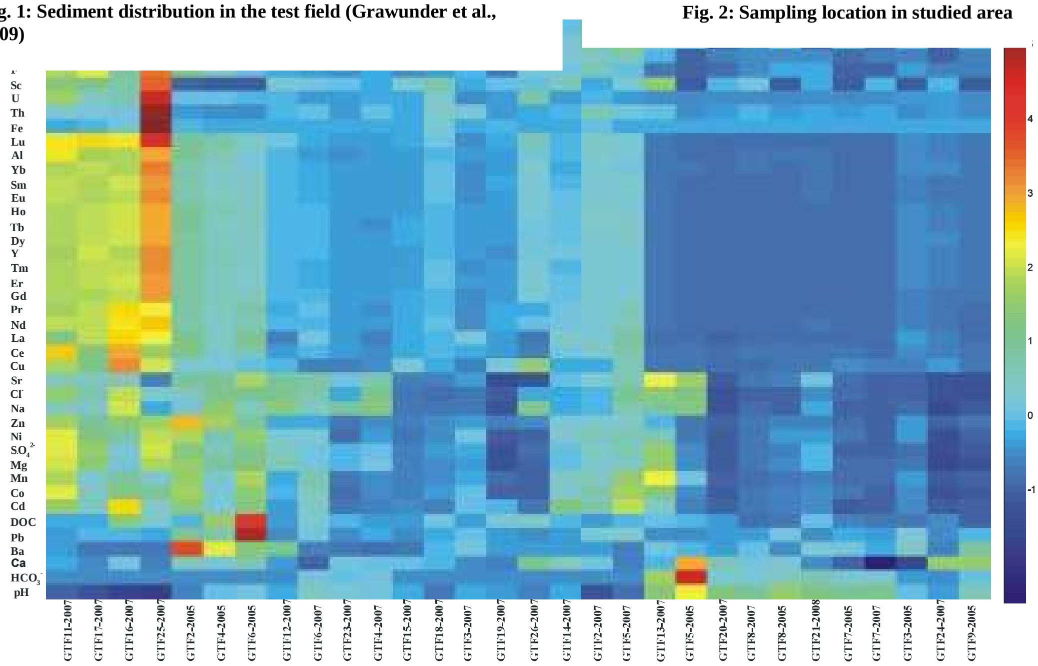

Fig. 3: Image Analysis, the x axis sorted by Q mode clustering and Y axis sorted by R mode clustering