

Short Communication

Lanthanides in Soils of Historical Mining Sites in Poland

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Received: 20 November 2017

Accepted: 22 February 2018

Abstract

Lanthanides are attracting increasing interest due to their technological importance and potential ecotoxicity. Knowledge of lanthanides in Polish soils is very poor, and a question arises whether the soils of former metal ore mining sites are enriched by these elements. Therefore, concentrations of six crucial lanthanides – La, Ce, Pr, Nd, Sm, and Gd – were determined in 92 soil samples collected from 6 historical mining sites in the Sudetes mountain range in southwestern Poland. They correlated strongly with each other, but no significant correlations were found with other metals, either in all samples or within the sites, except for Srebrna Góra, where lanthanides correlated strongly with Ba and Mn. No cases of considerable enrichment in lanthanides were identified in the sites examined, despite very high concentrations of other metals. Median concentrations of La, Ce, Pr, Nd, Sm, and Gd were 25.1, 52.4, 5.8, 21.9, 4.3, and 4.0 mg·kg⁻¹, and did not differ much from the median values for European soils. Maximum concentrations reported from Srebrna Góra were 2,9-6,8-fold higher than global background determined for Earth crust. However, these concentrations should still be considered as low, posing no environmental risk.

Keywords: soil, polymetallic ores, enrichment, lanthanum, rare earth elements

Introduction

Lanthanides are a series of elements with atomic numbers ranging from 51 to 71 that comprise lanthanum and 14 elements of the 4f-block. They have similar chemical properties, and together with yttrium and scandium constitute the group of rare earth elements

(REE). Their increasing use in modern technologies, including the high-tech industry, electronics, and medicine, has stimulated the growing interest of geochemists on their environmental behaviour and potential toxicity [1, 2]. Physiological functions of REE have been relatively poorly recognized, but they all are considered potentially toxic at high concentrations [1, 3-7]. Their environmental reactivity and related bioavailability is usually low [8], but they are prone to complexation with several organic compounds and in a form of complexes they show much higher solubility

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and ecotoxicity [9-11]. Some lanthanides (La, Ce, Nd) occur in soils in concentrations of tens $\text{mg}\cdot\text{kg}^{-1}$, while others are not that abundant and their usual soil concentrations are much lower [1, 4, 5, 12, 13]. Only a few published papers have shown the occurrence of REE in Polish soils [14, 15]. Rough examination was done as part of research aimed at preparing a geochemical atlas of Europe [16] and indicated that the concentrations of lanthanides in Polish soils remain generally much below the European means. Slightly richer are soils in the southern part of the country [14, 16]. A closer look at their geochemical associations indicates that they usually form associations with phosphates and clay minerals [1, 2, 17], but in certain conditions they may co-occur with other heavy metals in mineralized zones [1, 13, 17-19]. The largest deposits are primarily linked to carbonatites and peralkaline silicate rocks of hydrothermal origin, or are affected by hydrothermal processes [20, 21]. Until now, any primary deposits of lanthanides that might have economic importance have not been recognized in Poland, but elevated concentrations of these elements have been reported from several mineral deposits and from various wastes, including mine wastes [22].

This study aimed to recognize the occurrence of six lanthanides – La, Ce, Pr, Nd, Sm, and Gd – in soils in selected areas of historical metal ore mining in the Sudetes. It has already been proven that those soils contain high (or in certain cases even extremely high) concentrations of several metals and metalloids, such as As, Cu, Zn, Pb, and Cd [23, 24]. The concentrations of lanthanides in those soils were not examined. New information on their possible elevated levels in soils would be important for assessing related environmental risk [25] as well as for general knowledge about the geochemistry of those areas.



Fig. 1. Locations of former mining sites examined in this study (for description see Table 1)

Materials and Methods

Sampling Sites

Soil sampling sites were situated in 7 locations that represent six areas of former metal ore mining [26-33] in various parts of the Sudetes (Fig. 1). Elevated concentrations of As and heavy metals were previously reported from some of those locations [23, 24, 34, 35]. Representative soil samples were collected mainly from mine dumps (MD) as well as from surrounding soils – both from their mineral top horizon 0-25 cm (TS), and in some sites from subsoil 25-40 cm (SS). The mine dumps examined were either barren or poorly covered with vegetation. Dump material was collected as mixed samples, formed of 8-10 subsamples taken from the surface layers (0-25 cm) of dumps, both on their tops and on the slopes. The stones and coarse gravel particles (>20 mm) were sieved out on site. Ninety-two soil samples were collected altogether in this number: 60 MD, 24 TS, and 8 SS (Table 1).

Soil Analysis

Coarse soil particles (stone and gravel fractions) were sieved out in the field, and only fine soil (<2 mm) was analyzed in the laboratory. Soil material was dried and homogenized prior to analysis. Basic soil properties, including grain size composition and pH (H_2O , 1:2.5), were determined. Soil concentrations of six lanthanides that usually occur in the environment in relatively high amounts (i.e., La, Ce, Pr, Nd, Sm, and Gd) were determined. Soil samples were digested in aqua regia in a microwave system. The concentrations of lanthanides in digests, as well as related concentrations of nine metals and metalloids (Zn, Pb, Cd, Cu, Cr, Sb, Ba, Mn, and As) were determined by ICP-MS (8800 QQQ, Agilent Tech.). Validation of the analytical method involved the analysis of a certified reference material CNS 392 (Sigma Aldrich) that was used to check determination accuracy for As, Sb, and metals, except for REE, as no reference material for soil REE was available. Therefore, validation of analysis was checked for selected samples by the method of standard addition, and the accuracy of determination for lanthanides was assessed as satisfactory.

Calculations and Statistics

Basic statistics, including the values of minimum, maximum, arithmetic mean, and median values, were provided for each element, particularly for six lanthanides analyzed in the study. The results were related to the data obtained from literature, in particular to geochemical background according to Rudnick and Gao [36], and to the median values for European soils [16]. Pearson correlation coefficients R were calculated after normalization of analytical data to determine the

Table 1. Origin of soil samples and brief description of examined mine sites.

Site	No of samples	The main metal(loid)s in the ore	Geological characteristics of deposits	Bibliography
Złoty Stok	18 MD: 11 TS: 5 SS: 2	Au, As	Serpentinized dolomitic marbles and calc-silicate skarn-type rocks formed in the Variscan orogenesis in dislocation zone of the Łądek-Śnieżnik metamorphic structure	[26]
Dębowa	14 MD: 9 TS: 3 SS: 2	Sb	Vein-type sulphide mineralization of medium to low temperature zone related to hydrothermal processes within greywackes of the Bardo-Młynów Unit at their contact with the Kłodzko-Złoty Stok granitoid intrusion.	[27, 28]
Srebrna Góra	12 MD: 9 TS: 2 SS: 1	Polymetallic	Low temperature hydrothermal veins, mainly of barite and quartz-barite types, following dislocations in Early Permian porphyries.	[29, 30]
Dzieńmorowice and Bystrzyca Górna	18 MD: 13 TS: 4 SS: 1	Polymetallic	Low temperature quartz-barite and barite-calcite veins related to Early Permian porphyries, that follow Sudetic dislocations in gneisses and migmatites of the Sowie Mts block.	[31]
Radzimowice	16 MD: 9 TS: 6 SS: 1	Polymetallic	Moderate and low temperature associations developed in post-magmatic hydrothermal processes around a rhyolite subvolcanic intrusion of the hill Żeleźniak	[32]
Czarnów	14 MD: 9 TS: 4 SS: 1	Polymetallic, mainly As	Veins and lenses between silicate and carbonate rocks, resulted from Variscan hydrothermal activity of granite intrusion and early Paleozoic magmatic and volcanic activity in Rudawy Janowickie.	[33]

patterns of co-occurrence between the lanthanides and between La and other elements.

Results and Discussion

Soil properties differed strongly among the areas and within them (Table 2). The differences of median pH values reflected various mineralogy of metal-bearing rocks and the zones that host mineralization. Large differences were also found in concentrations of REE (Table 3) and other elements (Table 4). Mean concentrations of lanthanides in all soils, expressed as the median values (Table 3), were quite close do the medians determined for European soils by Salminen

et al. [16], though they were much higher than the means assessed for Polish soils [14, 16]. Medians of La, Ce, Pr, Nd, Sm, and Gd concentrations obtained for all samples were, respectively: 25.1; 52.4; 5.8; 21.9; 4.3, and 4.0 mg·kg⁻¹. Soil concentrations of lanthanides correlated strongly with each other, and related correlation coefficients were in the range R: 0.922-0.997 (Table 5). Such a strong dependence between the concentrations of lanthanides and their co-occurrence in the environment is a typical phenomenon that is well documented in the literature [1, 2, 5, 6, 13, 16]. Analysis of the relationships between lanthanides and other metals (Table 4) did not prove their co-occurrence in soils, which can be explained by different mineralogical compositions of ores mined in various areas, and their

Table 2. Basic properties of soil samples and concentrations of La in various mining areas.

Site	Soil pH		Clay in fine earth, %		La, mg·kg ⁻¹	
	Range	Median	Range	Median	Range	Median
Złoty Stok	5.7-8.0	6.8	1-10	6	7.5-44.2	23.7
Dębowa	3.2-5.3	4.1	5-11	9	5.7-25.8	21.5
Srebrna Góra	6.5-8.0	7.6	1-38	10	23.7-108	51.1
Dzieńmorowice, Bystrzyca G.	5.8-7.5	7.0	2-10	4	18.8-31.6	26.5
Radzimowice	4.4-6.9	6.1	3-26	9	19.9-54.6	32.5
Czarnów	5.2-7.0	6.3	1-21	7	9.6-36.4	24.7

Table 3. Concentrations of six lanthanides (La, Ce, Pr, Nd, Sm, and Gd) in soils of all mine sites as related to geochemical background; statistical parameters calculated for all samples.

Values	La	Ce	Pr	Nd	Sm	Gd
	mg·kg ⁻¹					
Min	5.7	11.5	1.30	4.7	0.89	0.85
Mean	26.6	55.7	6.4	23.8	4.8	4.6
Median	25.1	52.4	5.8	21.9	4.3	4.0
Max	108.4	184.6	26.8	110.0	25.8	27.2
Variability (100%*SD/Mean)	54	47	57	61	69	73
Earth crust background [31]	31	63	7.1	27	4.7	4.0
European topsoils [13]	23.5	48.2	5.6	20.8	4.0	3.8
European subsoils [13]	25.6	53.7	6.0	22.4	4.4	4.2
Maximum enrichment as related to Earth crust background	3.5	2.9	3.8	4.1	5.5	6.8

different geochemical features (Table 1). In fact, there were no significant correlations of REE concentrations with heavy metals and metalloids, except for poorly significant relationships with Ba and Mn (R: 0.53-0.64). A closer analysis of the latter indicated that relatively high R values were generated and conditioned by the highest concentrations of lanthanides, Ba and Mn, in soils of the mining site Srebrna Góra. Maximum concentrations of La, Ce, Pr, Nd, Sm, and Gd there were: 108, 185, 26.8, 110, 25.8, and 27.2 mg·kg⁻¹, respectively (i.e., 2.9-6.8-fold higher than those assessed as geochemical background for terrestrial Earth crust) [36]. For comparison, the maximum concentrations of Cu, Zn, and Cd in soil material examined in this study (Table 5) were by two orders of values (100-fold) higher, the maximum concentrations of Pb and Sb 3-fold higher, and those of As by more than 5 orders higher than related values of geochemical background.

As mentioned above, the group of soil samples collected from the Srebrna Góra mine site contained the highest concentrations of lanthanides. In 11 of 12 samples, La concentrations were in the range 40.8-108 mg·kg⁻¹, and only one of all MD samples was considerably poorer in La, with its concentration

of 23.7 mg·kg⁻¹ (Table 2). Lanthanides in the Srebrna Góra soils correlated strongly with Ba, which indicates that they probably were present in local alkaline rocks in association with this element. This finding stays in agreement with the fact that REE typically occur in associations with alkaline igneous complexes, carbonatite intrusives, or hydrothermal deposits [1, 13, 17]. Migaszewski and Gałuszka [1] stressed that the concentrations of lanthanides are usually much higher in mined mineralized areas than in relatively pristine unmineralized areas. Considerable enrichment, particularly in light REEs (La-Sm), is typical for soils developed from carbonate rocks [37]. Strong positive correlation with Mn, confirmed for soils of the Srebrna Góra site, may likely result first of all from the secondary enrichment. A significant role played by Mn oxides and hydroxides in adsorption of REE in soils and natural waters was confirmed by various studies [1, 4, 6, 38].

The second site, where relatively high concentrations of lanthanides occurred in MD samples, was the mining site of polymetallic ores in Radzimowice, where total concentrations of La ranged 19.9-54.6 mg·kg⁻¹ with a median value of 32.5 mg·kg⁻¹. Soils that developed on

Table 4. Concentrations of heavy metals and metal(oids) Zn, Pb, Cd, Cu, Cr, Ni, Ba, Mn, and As in soils of mine sites examined, as related to geochemical background.

Values	Zn	Pb	Cd	Cu	Cr	Sb	Ba	Mn	As
	mg·kg ⁻¹								
Median	164	144	0.6	74	48	0.8	170	610	423
Max	10660	57300	11.9	4245	265	437	45800	7940	49900
Variability (100%*SD/Mean)	251	347	149	246	66	395	382	111	251
Earth crust background [31]	67	17	0.09	28	92	0.4	628	1000	4.8
Maximum enrichment as related to Earth crust background	159	3372	132	152	2.9	1092	72.9	7.9	159

Table 5. Correlations between concentrations of lanthanum and other elements in soils.

Lanthanum (La) vs. other lanthanides										
Element considered	Ce	Pr	Nd	Sm	Gd					
R / all samples	0.972***	0.977***	0.971***	0.942***	0.922***					
Lanthanum vs. other metals and semi-metals										
Element considered	Zn	Pb	Cd	Cu	Cr	Sb	Ba	Mn	Fe	As
R / all samples	-0.072	-0.006	-0.057	0.074	-0.090	-0.120	0.526	0.636*	-0.119	-0.307
R / Srebrna Góra	0.198	0.894**	0.039	0.690*	-0.436	0.746*	0.909***	0.930***	0.014	0.622*

Explanation: Significance of correlation coefficients: *** $P < 0.001$, ** $P < 0.01$, * $P < 0.05$. The data without asterisks stand for insignificant ($P < 0.05$) correlations.

mine dumps in that area were richer in all the lanthanides examined in comparison with surrounding soils, which indicates that their origin is associated mainly with the rocks affected by hydrothermal processes [1, 20, 21], and the geochemistry of initial soils reflects that of associated rocks [1, 3, 37].

To sum up, it should be stressed that none of the mining sites examined, and none of collected soil samples indicated considerable enrichment in lanthanides that might contribute to increased environmental risk – either the risk for human health or ecological risk. However, the risk caused by other elements, in particular As, Cd, and Pb, should raise concern [39] and should be additionally examined. The analysis of environmental risk related to the presence of REE in soils, and their potential or measured bioavailability, performed by Loell et al. [11] and Li et al. [40], indicates that those concentrations of lanthanides that were found in the present study cannot cause any considerable risk either to humans or to biota.

Conclusions

The soils examined in this study were not considerably enriched in lanthanides despite their strong enrichment in several other metals and metalloids. The concentrations of all six lanthanides (La, Ce, Pr, Nd, Sm, and Gd) were strongly correlated with each other, but did not correlate with other metals except for proven relationships between lanthanides and Ba and Mn in the site Srebrna Góra, where they probably co-occur in barite-type hydrothermal veins.

Acknowledgements

This research was supported by the National Science Centre of Poland, project No. 2014/13/B/ST10/02978.

Conflict of Interest

The authors declare no conflict of interest.

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