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RARE-EARTH elements in the topsoils of a Russian industrial city: Sources and human health risk assessment

Tatyana Krupnova  , Olga Rakova, Valeria Simakhina[Show more](#)  Share  Cite<https://doi.org/10.1016/j.chemosphere.2024.142059> [Get rights and content](#) 

Highlights

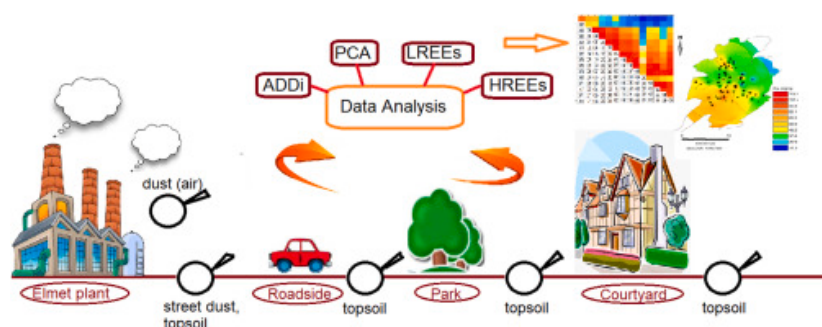
- REE accumulation in Chelyabinsk soils are disturbed by human activities.
- Fractionation between LREEs and HREEs was observed.
- The main industrial source of REEs is zinc production plant.
- Natural sources of REEs are granites and sedimentary rocks.
- Low health risks of REEs for local residents were shown.

Abstract

Research on rare-earth elements (REEs) in urban soils of Russian industrial cities is extremely limited. This study investigates the potential sources and human health risks of REEs contained in the topsoils of the industrial Russian city of Chelyabinsk. The study also takes into account natural sources of REE as the city is located on the border of granites (Urals) and sedimentary rocks (Western Siberia). We analyzed the concentration and distribution of REEs in the soils of four types of locations: residential courtyards, city parks, roadsides, and industrial locations. The total REE concentrations ranged from 44 to 255 mg/kg, with average concentrations of 140, 124, 113 and 89 mg/kg in the courtyards, roadsides, industrial location and city parks, respectively. The REE content in courtyard soils could be

influenced by poor cleaning of fallen leaves. The ratios of light REE (LREE) to heavy REE (HREE) ranged from 9.5 to 10.1, revealing an obvious fractionation between them. The fractionation of LREE and HREE, and the REE/ES (European Shale) pattern showed that REE accumulation in Chelyabinsk soils has been disturbed by human activities. It was shown that the dust from industrial emissions was the main anthropogenic source of REE accumulation in urban soil. The largest amounts of REEs are emitted from an electrometallurgical plant and zinc production plant. Fortunately, the estimated daily intakes of REE from soils for children and adults were well below the safety thresholds. At the same time, in order to prevent social tension and reduce the anthropogenic load on the urban area, it is recommended to use phytoremediation technologies, smart landscaping of industrial and residential areas, more thorough cleaning of fallen leaves and road dust. It is also recommended to move the most dangerous production processes outside the urban area.

Graphical abstract



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Introduction

The rare-earth elements (REEs) include the lanthanide elements (La–Lu), scandium (Sc) and yttrium (Y). Yttrium (Y) is always classified in the group of heavy REEs due to its chemical similarity, but scandium (Sc) is often excluded due to its different chemical properties. In addition to scandium, REEs have coherent chemical properties (Xi et al., 2023) due to a similar electronic configuration in the entire series (partially filling the 4f electron shell), unique properties, including electromagnetic ones. Based on their atomic numbers and masses, REEs are usually classified as light REE (LREE, including La and Eu) and heavy REE (HREE, including Gd and Lu) (Liu et al., 2022). Despite the term “rare-earth”, their average content in the lithosphere is 0.015 %. For example, Ce surpasses Cu and Pb in abundance (Baranovskaya et al., 2020).

The increased attention to the study of REE in recent decades is associated with their numerous applications in advanced materials and new technologies. REEs are important components of many modern electronic devices. These elements are called “vitamins of the industry” because even a small amount of them in alloys and other compounds improves their properties (Kumar et al., 2023). REEs are used to create components for modern electronics, batteries, permanent magnets, and high-temperature superconductors (Leal Filho et al., 2023). In metallurgy, alloying additives of REE (La, Ce and Pr) make it possible to extend the life of metal structures in the automotive industry (Sims et al., 2022). REEs are also used in the acid and heat-resistant glass. More than 90 % of REE in Russia are imported, but the

authorities intend to change the situation (Pimenova et al., 2022; Bortnikov et al., 2022; Cherepovitsyn and Solovyova, 2022). In 2022, REEs were listed as strategic mineral raw materials. It is planned that by 2025 import dependence will decrease to 50 % (Shevchenko, 2022). Therefore, it is important to study the content of REE in the urban environment of industrial cities.

The effects of REE on humans can be a result of anthropogenic activities. REEs have caused widespread concern because of their persistence in the environment (Liang et al., 2005; Panichev, 2015) and bioaccumulation in biota (Li et al., 2013). REEs are regularly associated with highly fractionated granites and pegmatites (García et al., 2020). The significant amounts of REEs extracted and subsequent industrial production have increased the release of REEs into the environment. Some REEs enter the human body through the food chain as they are used as feed additives to improve animal health (Abdelnour et al., 2019), as well as in pesticides and fertilizers to increase crop yields (Pang et al., 2002). These are concerns about human health due to exposure to REE (Brouziotis et al., 2022). High exposure to REE causes organ-specific toxicity, growth retardation, pneumoconiosis, and nervous diseases (Liu et al., 2022). REEs can enter the human body in several ways and have cytotoxicity. They can cause DNA damage and cell death (Brouziotis et al., 2022). An increase in REE in the urban environment is therefore a threat, since it can lead to negative consequences and increase environmental (Hoshyari et al., 2023) and human health risks (Liu et al., 2022; Sun et al., 2017). Recent studies have shown that REE negatively affects the mental abilities, cognitive and behavioral functions of children. Children with higher blood REEs level had relatively lower intelligence quotient (Yongwei et al., 2019). REEs were found accumulating in human brain (McDonald et al., 2017). Significant correlation in REEs concentrations was observed between the resident blood and corresponding soil samples from a mining area in Southeast China (Li et al., 2013). On the other hand, lead exposure has been proved to have impact on intellectual development in children, with both toxicological and epidemiological findings widely reported (Yu, 1995; Banner and Kahn, 2014). Yongwei et al. (2018) studied the impact of co-exposure to both rare earth elements and lead on children's cognitive functions, as well as potential interactive effect of the two exposures.

Urban soil is a complex and heterogeneous natural-anthropogenic biogeochemical system. Usually, the urban environment has artificial technogenic soil-like bodies and natural anthropogenically modified soils. Industrial pollutants accumulate in topsoils, change their chemical composition, and enter natural and technogenic migration cycles (Abd El Ghaffar, 2018). Soil is part of the migration of chemical elements and soil composition reflects the cumulative effect of the long-term technogenic impact. Urban soils are an informative indicator of REE accumulation. Studies of the REE content in Russian soils are limited. Several recent papers have been published on REE in various natural geological landscapes (Antonova and Ladonin, 2022; Samonova et al., 2020; Panichev et al., 2023).

REEs are not, as their name suggests, rare but abundant in the earth's crust. REEs are found in more than 250 minerals as phosphates, silicates, carbonates, oxides and halides (Dushyantha et al., 2020). Russia ranks fourth in terms of REE reserves in the world (Cherepovitsyn and Solovyova, 2022). The word 'rare' essentially implies that REEs are not commonly concentrated as economic ore deposits, though viable deposits are distributed across the world in relatively low concentrations. Mining operations, vehicle exhaust emissions, and industrial dust emissions are the principal anthropogenic sources of REE entering the urban environments and enhancing the risk of urban soil contamination. Russian industrial cities with a large number of metallurgical enterprises including those with sinter plants designed for processing ores and concentrates can be significantly contaminated with REE, but there are no studies on REE in Russian industrial urban landscapes. Here, we present the first REE assessment of the urban soil of Chelyabinsk, which is a typical industrial Russian city. The aim of this paper was to study the concentration, sources, and human health risks of REEs in the urban soils of Chelyabinsk. Our main hypothesis was that there are both natural sources (granites)

of REE and numerous anthropogenic sources such as the largest zinc plant in Russia, a steel plant, and electrochemical production. The world's largest enterprises producing steel of various grades, zinc and ferroalloys (ferrochrome, ferromanganese, ferrosilicon) are concentrated in the Chelyabinsk urban area. Enterprises use ores or alloying additives containing REE. At the same time, the city is located on two types of granite, which contain different amounts of REE. Our research presents an innovative and original approach. We determined the REE content in industrial and road dusts from industrial sources in addition to urban soil analysis. Using Ce and Eu anomalies and fractionation REE in dust as original labels, we identified the sources of REE in soils (Pimenova et al., 2022).

Section snippets

Description of sites and pollution sources

This study was conducted in four land-use types in Chelyabinsk (residential courtyards, industrial zones, roadside locations, and parks) positioned at a latitude of 55.154 N and longitude of 61.4291 E with an area of 530 km² (Fig. 1). Metallurgical enterprises can be sources of REE in urban soils (Lahd Geagea et al., 2007). Fig. 1 shows the locations of 77 selected sites and sources of REE. We chose three main sources: a steel plant (source 1, S1), a zinc production plant (source 2, S2) and an...

Distribution of rare earth elements in soils of Chelyabinsk

Concentrations of REEs in the topsoils of Chelyabinsk are given in Table 1. The average concentrations of REEs in the topsoils followed a generalized order: Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu which followed the Oddo-Harkins rule (Fig. 2a). The Oddo-Harkins rule holds that an element with an even atomic number is more abundant than the elements with immediately adjacent atomic numbers (Rétif et al., 2023).

The concentrations of REEs in the soils were in the...

Conclusion

This study investigated the pollution characteristics and the potential pollution sources of REEs in Chelyabinsk soils and demonstrated the probable exposure risk in children and adults. The high concentrations of REEs were mainly distributed in the south of Chelyabinsk. Geochemical characteristics indicated an obvious fractionation of LREE and HREE, and the REE/ES pattern showed that REE accumulation in Chelyabinsk soils has been disturbed by human activities. It was shown that the dust from...

CRedit authorship contribution statement

Tatyana Krupnova: Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **Olga Rakova:** Writing – original draft, Visualization, Methodology, Data curation. **Valeria Simakhina:** Visualization....

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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