



Thallium isotopes in metallurgical wastes/contaminated soils: A novel tool to trace metal source and behavior



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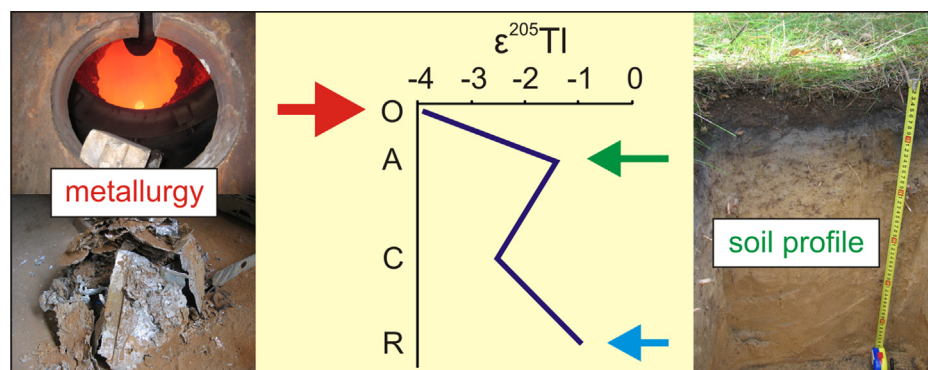
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HIGHLIGHTS

- Thallium isotopes in industrial wastes from zinc metallurgy.
- Thallium contamination in soils can be traced using isotopes.
- Thallium isotope fractionation may occur in soil.
- Sorption and/or precipitation processes are responsible for isotope redistribution.

GRAPHICAL ABSTRACT



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ABSTRACT

Thallium (Tl) concentration and isotope data have been recorded for contaminated soils and a set of industrial wastes that were produced within different stages of Zn ore mining and metallurgical processing of Zn-rich materials. Despite large differences in Tl levels of the waste materials (1–500 mg kg⁻¹), generally small changes in $\epsilon^{205}\text{Tl}$ values have been observed. However, isotopically lighter Tl was recorded in fly ash ($\epsilon^{205}\text{Tl} \sim -4.1$) than in slag ($\epsilon^{205}\text{Tl} \sim -3.3$), implying partial isotope fractionation during material processing. Thallium isotope compositions in the studied soils reflected the Tl contamination ($\epsilon^{205}\text{Tl} \sim -3.8$), despite the fact that the major pollution period ended more than 30 years ago. Therefore, we assume that former industrial Tl inputs into soils, if significant, can potentially be traced using the isotope tracing method. We also suggest that the isotope redistributions occurred in some soil (subsurface) horizons, with Tl being isotopically heavier than the pollution source, due to specific sorption and/or precipitation processes, which complicates the discrimination of

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primary Tl. Thallium isotope analysis proved to be a promising tool to aid our understanding of Tl behavior within the smelting process, as well as its post-depositional dynamics in the environmental systems (soils).

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1. Introduction

Anthropogenic sources of thallium (Tl) include emissions and solid wastes from ferrous/non-ferrous mining and metallurgy, coal combustion, or possibly cement production. Complex processing of Tl-bearing ores/sulfides (FeS₂, ZnS etc.) probably dominates in areas where extreme pollution levels of this element have been recorded [1–7]. Since most Tl compounds are volatile at high temperatures, its removal from the metallurgical emissions using bag and/or electrostatic filters may be difficult. Hence, a large Tl portion could potentially enter the atmosphere and affect surrounding environmental compartments [2,4]. It should be highlighted that apart from the chalcophile nature of Tl(I), monovalent Tl(I) can also substitute K in K-silicates (feldspars, micas, etc.) [8,9]. Efficient sorbents for Tl in soils and sediments include Mn(III,IV) oxides (mainly birnessite, δ-MnO₂) and illite [10–14], which may bind Tl through specific adsorption resulting from Tl(I)–K replacement reactions within the mineral (inter)layers. Manganese oxides may also bind Tl via Tl(I) oxidation to Tl(III) and complexation of the Tl(III) [14].

Despite the achievements in Tl isotope geochemistry during the last decade, little is still known about the processes that influence the isotope fractionation of Tl of anthropogenic origin. The pioneering works of Kersten et al. [15] and Vaněk et al. [16] demonstrate differences in the stable isotope signature between Tl of geogenic and industrial origin. However, to date there are no data available on the isotope signatures of Tl in waste materials and emissions from non-ferrous metal smelters and in surrounding contaminated soils. For example, we do not know to what extent Tl may isotopically fractionate from the primary material to different waste materials during this kind of high-temperature industrial process. Moreover, it is unknown to what extent chemical processes in soils contaminated by smelter emissions affect the Tl isotope composition. Here, we report for the first time, the Tl isotope record in soils heavily contaminated by Zn metallurgy and we attempt to describe the isotope shift from the start to the end of the Tl “life cycle”. The presented Tl isotope results can contribute to a better understanding of anthropogenic Tl inputs into soils and the processes that affect all Tl mobility, enrichment and cycling in the environment.

2. Experimental

2.1. Study area, sampling and characterization process

The Olkusz district, situated in the Silesia-Krakow region of southern Poland, is known for extensive mining and processing of Zn ores/sulfides since the early 1950s. The ores are enriched in Tl, and particulate and gaseous emissions from the local primary/secondary Zn smelter (Boleslaw Zn smelter) are considered the predominant source of Tl contamination in the area (Supplementary material, Fig. S1). The smelter has been operational for more than 60 years (opened 1952) and the deposition of pollutants has led to significant inputs of Zn, Pb, Cd and Tl. Average concentrations reported for the forest floor humus or the upper soil layers near the smelter typically exceed 5000 mg kg⁻¹ for Zn and 50 mg kg⁻¹ for Tl or Cd [17]. Despite the fact that detailed data on Tl emissions/deposition are not available, a comparable trend with historical dust/metal emissions (mainly Zn and Cd) is sug-

gested [18]. Regarding the smelter technology, pyrolytic processes followed by electrolytic Zn extraction are combined throughout the whole history of the plant. All Zn ores, Zn-Fe residues and other Zn-rich materials have been used as raw/feed materials here. After enhancement of the electrolytic section in 1962, the importance of roasted sulfide concentrates originating from local ores was continuously growing in the feed. Apart from the secondary materials, Zn ores from up to six European localities (including the local one) have been used for calcine (ZnO) production since 2012.

For tracing Tl sources in soils, both natural and industrial (including waste) samples from the recycling division of the Zn smelter (Boleslaw Recycling, Ltd.) were investigated:

- (i) Local Zn ore (sphalerite, ZnS; Pomorzany mine, mineralogical collection of the University of Silesia).
- (ii) Post-flotation Zn-Fe residue.
- (iii) Fly ash, collected from the de-dusting system placed on a technological line within the Waelz furnaces (Supplementary material, Fig. S2). In these furnaces, different Zn-bearing waste materials are processed, including Zn-Fe residues from steelmaking, Zn-C batteries, residual slimes from Zn hydrometallurgy, etc.
- (iv) Slag from the Waelz furnaces, which occurs as solid agglomerates, containing ash from coke combustion, Fe oxides, etc. (Supplementary material, Fig. S2).
- (v) Granulated waste resulting from different stages of hydrometallurgical processing of Zn, containing unwanted components in the electrolytic process, but still incorporating Zn and accompanying metals/metalloids. This material is combined with Zn-Fe residues, granulated and introduced into the smelting furnace as a secondary batch feed.
- (vi) Final refinement waste, coming from the wet filtration of ZnSO₄ electrolyte in the hydrometallurgical process. This material was collected from Larox filter which is used for the solution purification prior to Zn electrolysis (Supplementary material, Fig. S2). The material typically contains a variety of sulphates (Zn, Pb, Fe, As, etc.) and similarly to granulated waste (sample v), it is recycled within the pyrometallurgical stage.

Historical wastes from the Zn smelter were not available; therefore, we were not able to test these materials for their Tl isotope composition. Similarly, we do not know the exact Tl isotope signature for the initial feed material, which is processed in the recycling plant using the Waelz technology. The problem is that its composition depends on the type of furnace charge, which is heterogeneous and variable, consisting of a variety of Zn- and Zn-Fe-rich materials with different starting Tl concentrations and probably different isotope signatures.

To investigate the fate of Tl in the environment, three profiles of forest and meadow soils (1—forest, 2—meadow and 3—forest) were sampled approximately 1 km S and N of the Zn smelter (Supplementary material, Fig. S1; GPS coordinates in Table 1). Soil samples were collected from 1 × 1 m wide pits according to the natural development of soil horizons, down to the bottom horizon C. Soils were classified as a Haplic Regosol Arenic, a Rendzic Leptosol and an Eutric Arenosol [19]. Soil samples were air-dried, homogenized and sieved through a 2-mm stainless-steel sieve prior to further

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