



The mobility of thallium from bottom soil of the Silesian-Cracowian zinc-lead ore deposit region (Poland)



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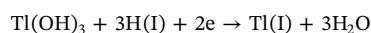
ABSTRACT

Thallium is a nonessential toxic element that may pose an environmental hazard. A crucial factor for the toxic effect of Tl is the mobility of the element. The aim of this work was to investigate Tl mobility in typical soil samples formed over six different lithological backgrounds (glaciofluvial sands and gravel, slope-wash sands and loams, siltstones and conglomerates, loesses, dolomites and ore-bearing dolomites) from the south-eastern part of the Silesian-Cracowian zinc-lead ore deposit region in Poland. Five geochemical fractions (water soluble, ion-exchangeable/carbonates, reducible, oxidizable, and residual) were obtained by using a sequential extraction scheme coupled with flow-injection anodic stripping voltammetry. The results showed that the Tl in most of the soils investigated is mainly entrapped in the parent matter, which is immovable and inert in terms of environmental effects. However, a significant part of the Tl was found in the reducible and oxidizable fractions of the soil formed over ore-bearing dolomites. It highlights that the environmental hazard caused by Tl should be measured by the content of mobile Tl rather than by its total content.

1. Introduction

Thallium is a nonessential toxic element that causes an environmental hazard (Rodríguez-Mercado and Altamirano-Lozano, 2013). Tl is present in two speciation forms, Tl(I) and Tl(III), which strongly differ in terms of environmental mobility and toxicity. Compounds of Tl(I) are generally water soluble, apart from the sulfide ($K_{sp} = 1 \times 10^{-20}$ (Charlot, 1969)), while the solubility of Tl(III) compounds is generally low and dependent on pH. The solubility product of Tl(OH)₃ is very low ($pK_{sp} = 45.2$) (Ciszewski and Baraniak, 2006; Lin and Nriagu, 1998). Therefore soluble Tl(III) ions can exist only in an extremely acidic medium. Additionally, Tl(III) is a strong oxidant. The transition between the two forms of Tl has the standard potential $E = +1.252$ V.

Due to the low solubility of Tl(OH)₃, the transition



strongly depends on pH:

$$E = 1.252 - (0.0585/2) \lg [\text{Tl(I)}] - (3/2)0.0585\text{pH}$$

It is also dependent on Tl(I) concentration.

Two environmentally significant conclusions can be drawn:

- Tl(III) becomes less oxidative in neutral and alkaline pH;
- Oxidation of soluble Tl(I) causes the formation of insoluble Tl(OH)₃,

and vice versa.

This general picture can be modified due to the formation of strong complexes of Tl(III).

Tl(I) substitutes for potassium(I) or rubidium(I) in such aluminosilicates as feldspar or mica in geochemical systems. The content of the element in igneous rocks ranges from 0.05 to 1.7 $\mu\text{g g}^{-1}$ (Nriagu, 1998). Volcanic ash contains approximately 0.5 $\mu\text{g g}^{-1}$ of Tl (Karbowska and Zembrzusi, 2016). Enrichment of Tl occurs in hydrothermal systems where the element is bound to sulfides (pyrite, sphalerite, marcasite). Weathering of primary sources of Tl leads to the element's dispersion in sedimentary rocks, as well as in iron and manganese hydroxides and organic matter, including coals (Lis et al., 2003). The global median of Tl soil concentration is 0.5 $\mu\text{g g}^{-1}$, while the European median is 0.66 $\mu\text{g g}^{-1}$ (Salminen, 2005). According to the same source, Tl soil concentration in Europe ranges from 0.1 to 24 $\mu\text{g g}^{-1}$ depending on the geochemical background. Even higher Tl concentrations, up to 55 $\mu\text{g g}^{-1}$, caused by natural pedogeochemical processes were reported by Tremel et al. (1997). Much higher Tl soil concentrations, up to several thousand $\mu\text{g g}^{-1}$, have been determined in places where Tl-rich sulfide-containing formations are partly exposed on the surface or in the vicinity of arsenic-antimony ore, zinc-lead ore or pyrite mining, processing and smelting (Lis et al., 2003; Xiao et al., 2012; Stafilov et al., 2013; Vaněk et al., 2013; Bacheva et al., 2014; Gomez-Gonzalez

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et al., 2015; Voegelin et al., 2015; Liu et al., 2016a, 2016b). Elevated Tl concentration has also been determined in soil in the vicinity of a steel plant in South China (Liu et al., 2017a, 2017b).

Tl(III) is more toxic to aquatic organisms than Tl(I). In the case of *Daphnia magna*, the EC₅₀ for Tl(III) is 24 µg l⁻¹ (Lan and Lin, 2005), while the EC₅₀ for Tl(I) is 500–1000 µg l⁻¹ (Tatsi et al., 2015). In the case of the unicellular alga *Chlorella*, Tl(III) is 50,000 times more toxic than Tl(I) (Ralph and Twiss, 2002). However, Tl(I) is the predominant form of Tl in the aquatic environment. Regarding Tl(I), the alga *Pseudokirchneriella subcapitata* (EC₅₀ 30–87 µg l⁻¹) is more vulnerable than *D. magna* and similar crustacean organisms (Tatsi et al., 2015). The no-effect concentration for *P. subcapitata* was found to be as low as 10 µg l⁻¹, compared with 60 µg l⁻¹ for *D. magna* (Tatsi et al., 2015).

Apart from total concentration, a crucial factor for the toxic effect of Tl in the environment is the element's mobility. A significant part of the Tl in soil is strongly entrapped in the aluminosilicate parent matter, and is immovable even under very aggressive treatment, such as with aqua regia (Lukaszewski and Zembrzusi, 1992; Jakubowska et al., 2006). Only the total destruction of soil with HF-containing mixtures mobilizes this part of the Tl. This immovable Tl is passive in terms of toxic effect. The mobile part of Tl can be determined by sequential extraction. In accordance with the BCR protocol (Ure et al., 1993), the acid soluble and exchangeable fraction, reducible fraction and oxidizable fraction can be distinguished by the use of suitable extractants. The respective extractants used are 0.11 mol l⁻¹ acetic acid, 0.1 mol l⁻¹ hydroxylamine hydrochloride (pH 2) and 30% hydrogen peroxide. The first two fractions are extracted at ambient temperature, and the third at 85 °C. The last extraction is followed by additional extraction with 1 mol l⁻¹ ammonium acetate (pH 2) at ambient temperature, performed to mobilize the Tl entrapped on the surface of the sample residue. The first fraction contains ion-exchangeable Tl or Tl entrapped in carbonates dissolved during the procedure. This Tl should be the most easily available to plant roots (Vaněk et al., 2012). The reducible fraction contains Tl entrapped in iron(III) and manganese(III and IV) oxides and hydroxides. These compounds, together with the entrapped Tl, are dissolved under reducible conditions. Birnessite (K₄Mn₁₄O₂₇ · 9H₂O), which is representative for this fraction, is able to extract more labile Tl from soil (Vaněk et al., 2011). The oxidizable fraction contains Tl entrapped in sulfides or organic matter. The gradual oxidation of insoluble sulfides to soluble sulfates makes the entrapped Tl more accessible. The BCR procedure is frequently supplemented by dissolving a residue with HF to check the Tl balance (e.g. Vaněk et al., 2010). The BCR scheme is also supplemented with a water soluble fraction (Jakubowska et al., 2006). This is due to the fact that any redistribution of Tl between fractions should occur by dissolution in water. Thus, sequential extraction containing five fraction steps provides relatively complete information concerning the mobility of Tl from analyzed soil. These fractions are: water soluble, ion-exchangeable/carbonates, reducible, oxidizable, and residual. The fraction sequence corresponds to the increasing leaching ability of the extractants used at the successive stages. The BCR procedure (also called the IRRM protocol) is frequently used in the investigation of Tl in soil and sediments (Vaněk et al., 2011, Gomez-Gonzalez et al., 2015, Liu et al., 2017a, 2017b, Liu et al., 2016a, 2016b, Karbowska et al., 2014, Jakubowska et al., 2007).

It may be noted that the ratio of ²⁰⁵Tl and ²⁰³Tl is a promising new tool in environmental Tl investigation (Kersten et al., 2014; Vanek et al., 2016).

The aim of this work was to investigate Tl mobility as determined by sequential extraction in samples of soil formed over different lithological backgrounds. The selected area (see Fig. 1) includes soil formed over slope-wash sands and loams (Quaternary, Holocene), glaciofluvial sands and gravel (Quaternary, Pleistocene), loesses (Quaternary, Pleistocene), dolomites (Triassic), ore-bearing dolomites (Triassic) and siltstones and conglomerates (Permian). The top soil in this area is 1.3–3 times richer in Tl than the bottom soil, due to Zn-Pb ore

processing (Lis et al., 2003). Therefore only the bottom soil (0.8–1.0 m) was investigated.

2. Experimental

2.1. Site description and samples

Six sampling points were selected, located in the south-eastern part of the Silesian-Cracowian zinc-lead ore deposit region in Poland (see Fig. 1), and samples representing soil formed over various geological backgrounds were taken. The geological structure of the studied area is variable in terms of age and lithology. The Triassic dolomites and ore-bearing dolomites and the Permian siltstones and conglomerates are partly exposed on the surface and partly covered by Pleistocene (loesses, glaciofluvial sands and gravel) and Holocene (slope-wash sands and loams) sediments.

50 mm² cores were sampled with an Eijkelkamp Co. Sampler from a level of 0.8–1.0 m, dried, sieved with a 2 mm nylon sieve, and then pulverized in an agate mortar to a fraction below 0.063 mm.

2.2. Apparatus and reagents

A MICROAUTOLAB electrochemical analyzer (Ecochemie, Utrecht, Netherlands) was used for differential-pulse voltammetric measurements. A previously described (Lukaszewski and Zembrzusi, 1992) home-made flow-through cell of wall-jet type was used. The cell enables medium exchange and medium circulation. A three-electrode measuring cell, consisting of a mercury film working electrode based on glassy carbon, a saturated calomel reference electrode and a platinum wire auxiliary electrode, was used. The mercury film was electrolytically deposited and was used for a whole day of measurements.

As a certified reference material the soil GBW 07401, of Chinese origin, containing $1 \pm 0.2 \mu\text{g g}^{-1}$ of Tl, was used.

Hydrofluoric acid (pract. 73%, Fluka), nitric acid (65%), acetic acid (99.8%), ammonia solution (25%), hydroxylamine chloride, hydrogen peroxide (30%), EDTA, ascorbic acid (all puriss. p.a., Fluka) and ammonium acetate (puriss. p.a., Aldrich) were used.

All solutions were prepared in water by reverse osmosis followed by triple distillation from a quartz apparatus. Only freshly distilled water was used.

2.3. Procedures

2.3.1. Total decomposition of soil samples

The sample (c. 1 g) was placed in a PTFE beaker, moistened with water, 2 ml of 73% hydrofluoric acid was added, and the sample was put aside for 2 h. An additional 0.6 ml of hydrofluoric acid was added at the end of this period. The obtained solution was heated until evaporation. For mineralization of the residual organic substances, 1 ml of 67% nitric acid was added, and 2.5 ml of 30% hydrogen peroxide was introduced in 0.5 ml portions. After the addition of each portion, the sample was evaporated. Next, 1 ml of nitric acid was added and the beaker covered with a watch glass. The sample was heated for 3 h. Finally, 2.5 ml of 1 M ascorbic acid and 6.25 ml of 0.2 EDTA were added, and the pH was adjusted to 4.5 with ammonia. The sample was then transferred into a 25 ml volumetric flask and topped up with water.

The correctness of this stage was controlled using the certified reference material (soil GBW 07401) with certified value $1.0 \pm 0.2 \mu\text{g g}^{-1}$. Nine determinations of Tl in GBW 07401 made alternately with tested samples gave a mean of $0.92 \mu\text{g g}^{-1}$ with SD $0.092 \mu\text{g g}^{-1}$.

2.3.2. Sequential extraction of soil samples

This procedure was performed in accordance with the modified BCR procedure (see Karbowska et al., 2014). Briefly, an additional water



Fig. 1. Sampling points. Lithological background: (after Kurek et al., 1994) 1. flood plain sands, gravel and silts, 2. slope-wash sands and loams, 3. loesses, 4. glaciofluvial sands and gravel, 5. Triassic clays-tones and limestones, 6. Middle Triassic dolomites, limestones and marls, 7. ore-bearing dolomites, 8. Lower Triassic dolomites and marls, 9. Permian claystones, siltstones and conglomerates, 10. dumps, 11. abandoned Zn-Pb ore mines.

soluble fraction was obtained by shaking a 1 g sample of soil in 40 ml of triple distilled water at 25 °C for 16 h. The extract was centrifuged, and 0.2 mol l⁻¹ EDTA and water were added in the volumes necessary for the preparation of a 0.05 mol l⁻¹ solution (pH 4.4). The acid soluble/exchangeable fraction was obtained by shaking the residue from the previous stage with 40 ml of 0.11 mol l⁻¹ acetic acid, as recommended under the BCR procedure (Ure et al., 1993). The further treatment of the sample was the same as for the previous fraction, with suitable pH adjustment. Subsequently, the reducible fraction was obtained from the residue of the previous stage by treatment with 40 ml of 0.1 mol l⁻¹ hydroxylamine hydrochloride adjusted to pH 2 with 2 mol l⁻¹ nitric acid. Again the further treatment of the sample was the same as for the previous fraction, with suitable pH adjustment at the final stage. The oxidizable fraction was obtained in two stages. First, the residue of the previous stage was treated with 10 ml 30% hydrogen peroxide and shaken at ambient temperature for 1 h and then at 85 °C for 16 h. Another 10 ml of 30% hydrogen peroxide was added and shaken at 85 °C for 1 h and then evaporated. At the second stage, the sample was treated with 50 ml 1 mol l⁻¹ ammonium acetate adjusted to pH 2.0 with 2 mol l⁻¹ nitric acid and shaken at ambient temperature for 16 h. The mixture was centrifuged. The residue was treated with 10 ml water, shaken for 10 min and centrifuged. Then 10 ml of 1 mol l⁻¹ ascorbic acid was added to the extracts, the pH was adjusted to 4.4, 25 ml of 2 mol l⁻¹ EDTA was added, and the sample was topped up with water to 100 ml.

The residue after the previous stages was the fraction of the element

entrapped in parent matter. This fraction was processed as described in the section [Total decomposition of soil samples](#).

2.3.3. Determination of Tl by flow-injection anodic stripping voltammetry

Determination was performed in accordance with the procedure broadly described previously (Jakubowska et al., 2008). Tl was pre-concentrated on the mercury film electrode at a potential of (–900) mV vs. SCE over 60–1200 s, depending on the Tl concentration. Pre-concentration was followed by exchange of the base electrolyte with pure 0.05 mol l⁻¹ EDTA and the recording of voltammograms. Several standard additions (typically three additions) were used for evaluation of the results. The detection limit of the method (calculated on the basis of 3SD) was 50 pg l⁻¹ (0.25 picomol l⁻¹). The method tolerates a 1000-fold excess of lead, due to the application of EDTA base electrolyte.

3. Results and discussion

The average values of the total Tl content in soil samples formed over six different lithological backgrounds (glaciofluvial sands and gravel, slope-wash sands and loams, siltstones and conglomerates, loesses, dolomites and ore-bearing dolomites) are shown in Fig. 2. Soil samples formed over dolomites and ore-bearing dolomites exhibit a relatively high Tl content. It should be pointed out that the elevated Tl concentration in soil formed over dolomites is not the rule. The Tl concentration in soil formed over dolomites in another location was

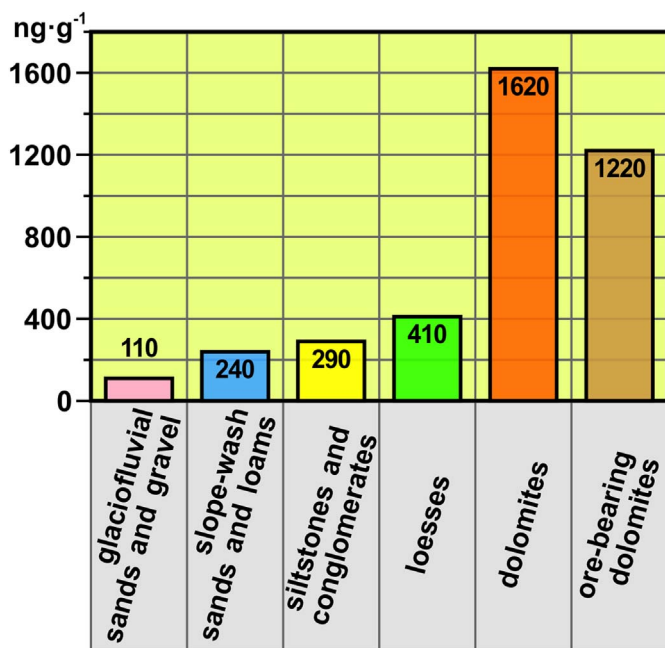


Fig. 2. Average total Tl concentration in investigated soils formed over different geological backgrounds. Precision of determination expressed as RSD (%): 4.8, 5.5, 1.6, 11.1, 8.7 and 8.5 respectively (from left).

reported to be only 0.33 μg g⁻¹ (Karbowska et al., 2014).

Six soils formed over the different geological backgrounds listed above were sequentially extracted as described in Sections 2.3.2 and 2.3.3. Five subsamples of each soil were processed, and each extract was analyzed three times for Tl concentration. Average Tl concentrations in the water soluble fractions are shown in Fig. 3A. The results represent the loss of Tl caused by the extraction. This loss of Tl was equal to 5.7% in the case of soil formed over glaciofluvial sands and gravel, 1.1% for slope-wash sands and loams, 0.1% for siltstones and conglomerates, 0.2% for loesses, 0.14% for dolomites, and 0.74% for

ore-bearing dolomites. Although the loss of Tl caused by extraction with water is very small, it is necessary to take into account that any re-distribution of Tl between the other fractions should take place by an initial dissolution. The lowest water extractability is exhibited by soil formed over loams, siltstones and conglomerates, and loesses, and the highest by soil formed over ore-bearing dolomites. Surprisingly, relatively high extractability was recorded for soil formed over glaciofluvial sands and gravel.

Average Tl concentrations in the ion-exchangeable/carbonates fractions of the investigated soils are shown in Fig. 3B. The lowest extractability is exhibited by soil formed over siltstones and conglomerates and over loesses: respectively 0.3% and 0.6% of total Tl. The highest loss of Tl was recorded for the soil formed over ore-bearing dolomites, and was equal to 4.5% of the total Tl concentration. However, in terms of percentage loss, the highest values are those for soils formed over slope-wash sands and loams and glaciofluvial sands and gravel (9% and 8.5% respectively). The Tl loss in the case of soil formed over dolomites (1.2%) is surprisingly low considering the chemical nature of this geological background.

Average Tl concentrations in the reducible fractions of the investigated soils are shown in Fig. 3C. The highest extractability is exhibited by soil formed over ore-bearing dolomites. Reducible Tl accounts for 32% of the total Tl in this soil. The lowest Tl extractability is that of soil formed over siltstones and conglomerates (1.5% of the total Tl). The other soils have approximately 10% reducible Tl (11.5%, 9% and 8.9% respectively for glaciofluvial sands and gravel, slope-wash sands and loams, and loesses).

Average Tl concentrations in the oxidizable fractions of the investigated soils are shown in Fig. 3D. Generally, these fractions contain the highest concentration of extractable Tl in all of the investigated soils. The highest extractability is exhibited by soil formed over ore-bearing dolomites: 26.6% of the total Tl is located in this fraction. The lowest Tl extractability is that of soil formed over siltstones and conglomerates (4.8% of the total Tl). The relative concentrations of Tl in the other investigated soils are 13.4%, 12.4%, 13.4 and 9.8% respectively for glaciofluvial sands and gravel, slope-wash sands and loams, dolomites, and loesses.

A significant part of the Tl is not extracted with the four extractants

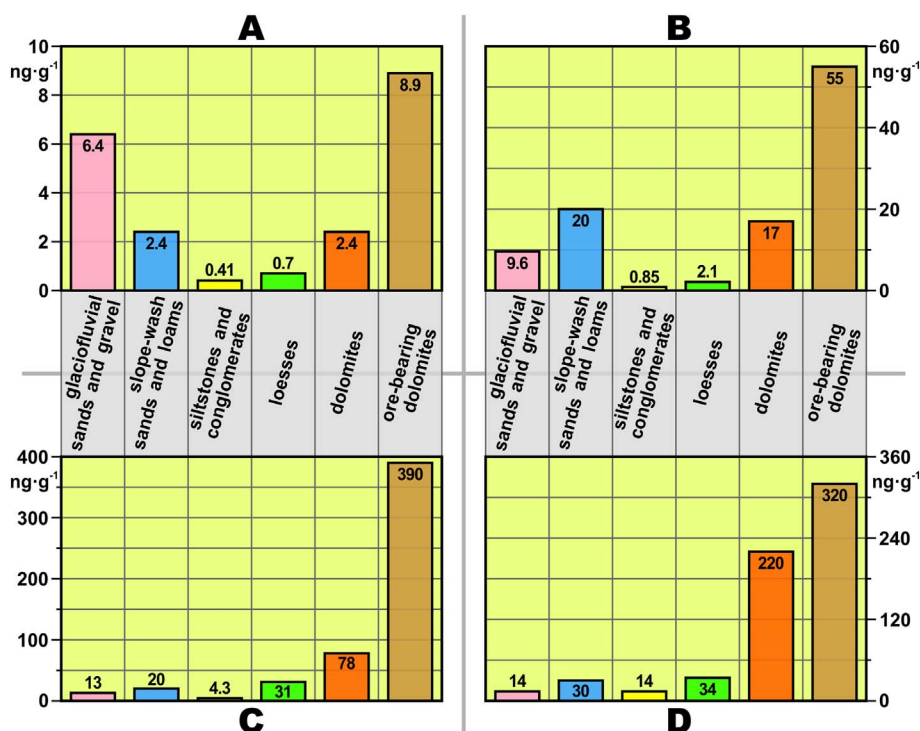


Fig. 3. Average Tl concentrations in particular fractions obtained by the sequential extraction of soils formed over different geological backgrounds. A. water soluble fraction, B. ion-exchangeable/carbonates fraction, C. reducible fraction, D. oxidizable fraction.

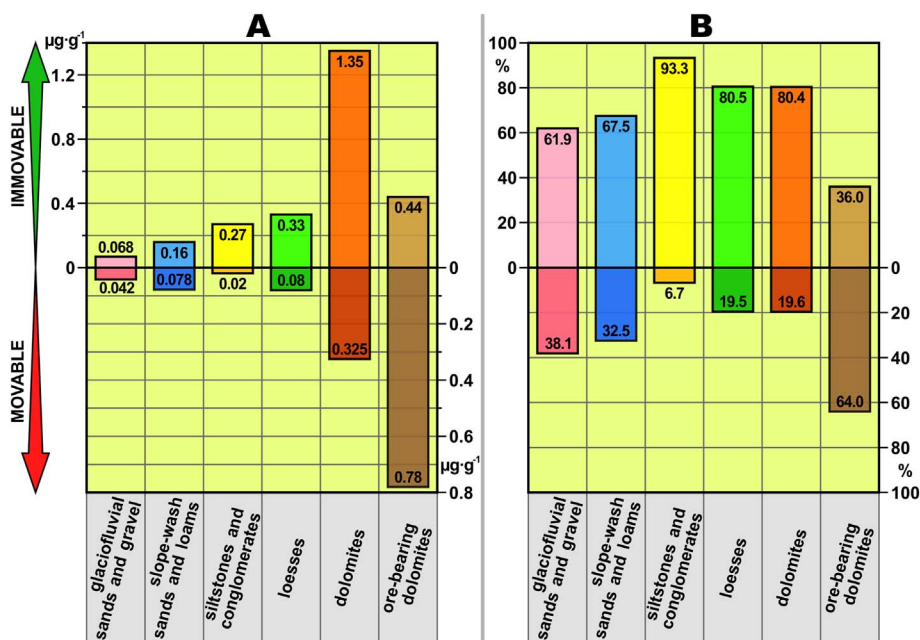


Fig. 4. Movable TI (total of four fractions) vs. immovable (residual fraction) in soils formed over different geological backgrounds: A. $\mu\text{g g}^{-1}$, B. % of total TI.

Table 1
Literature data concerning immobile TI.

Object	Residual fraction [%]	Source
Bottom soil (China)	> 90	Yang et al. (2005)
Soil, reference material GBW 07401	94	Jakubowska et al. (2006)
Soil, flood plain (Poland):		
Soil a	45	Jakubowska et al. (2007)
Soil b	81	
Soil, grassland and forest soil (Czech Republic)	95	Vaněk et al. (2009)
Soil, reference material GBW 07311	75	Liu et al. (2016a) and (2016b)
Volcano ash (Iceland)	63	Karbowska and Zembrzuski (2016)
Soil formed over dolomites	86	Karbowska et al. (2014)
Sediments and soil (Spain)	92	Gomez-Gonzalez et al. (2015)
Reference material, NIST SRM 2711 (Montana soil)	71	Gomez-Gonzalez et al. (2015)
Tsunami sediments Phuket Island (Thailand)	94	Lukaszewski et al. (2012)
Tsunami sediments Nam Khem (Thailand)	88	Lukaszewski et al. (2012)
Tsunami sediments Bang Mor (Thailand)	91	Lukaszewski et al. (2012)
Soil formed over glaciofluvial sands and gravel	62	This paper
Soil formed over slope-wash sands and loams	68	This paper
Soil formed over siltstones and conglomerates	93	This paper
Soil formed over loesses	81	This paper
Soil formed over dolomites	80	This paper
Soil formed over ore-bearing dolomites	36	This paper
Median	84	

used, which have increasing leaching ability. This part of the TI entrapped in the parent matter is referred to here as ‘immovable’. Average immovable TI concentration in the six investigated soils is shown in Fig. 4A, compared with the total TI concentration contained in the four fractions (called ‘movable’ TI). Fig. 4B shows the percentages of movable and immovable TI in the investigated soils. It is clear that the major part of the TI in all investigated soils is immovable, with the exception of ore-bearing dolomites. This is a significant finding from the experiments.

The precision of measurement of TI concentration was very divergent. In the case of the water soluble fraction S_r varied over the range 3–55% with median 23%. The ranges were 6–22% (median 17%), 4.4–37% (median 11%), 4.6–59% (median 14%) and 1.6–11% (median 8.7%) for the ion-exchangeable/carbonates fraction, reducible fraction, oxidizable fraction and residual fraction respectively. In the cases of poorer precision, large differences were observed between the results for the five subsamples. This indicates the inhomogeneity of the

investigated samples, with micro-inclusions of TI-rich minerals. Poor precision is also typical for measurements of the very low TI concentrations observed in the case of the water soluble and exchangeable/carbonates fractions.

The question arises whether the finding that the major part of the TI in all investigated soils is immovable has more general significance or is valid only within the limited area of investigation. Although available data concerning the sequential extraction of TI are limited, they support the main conclusion of this work. This is shown in Table 1, which presents available data from China, Poland, Spain, Thailand and the Czech Republic. The majority of the data show that the immovable residual fraction of TI accounts for 60–90% of the total content of the element. This fact has great environmental significance; only a small part of the TI present in soil presents an environmental hazard. The case of soil formed over dolomites well illustrates this conclusion. The total TI concentration in this soil is $1.62 \mu\text{g g}^{-1}$, which is a high value, even higher than the total TI concentration in the investigated soil formed

over ore-bearing dolomites ($1.22 \mu\text{g g}^{-1}$). However, the mobile Tl concentration in this soil is only $0.325 \mu\text{g g}^{-1}$, while for the soil formed over ore-bearing dolomites the movable Tl concentration is almost 2.5 times higher ($0.78 \mu\text{g g}^{-1}$). Thus, a real environmental hazard is created only by soil with high Tl mobility, e.g. containing dispersed sulfide ores (Zn-Pb ores, pyrites, As-Sb ores).

Apart from Tl mobility, the sequential extraction provides information about the nature of Tl entrapment in particular components of the soil. The leaching solutions and procedures used are characterized by increasing leaching ability. Water soluble Tl, as well as Tl which is ion-exchangeable or bound to carbonates, is monovalent ($K_{sp} = 2.4$ for Tl_2CO_3). The ion-exchangeable Tl can be mobilized much more easily than the reducible Tl entrapped in iron and manganese oxides and hydroxides, which requires reducible conditions. The formation of iron and manganese oxides and hydroxides is subject to mechanisms similar to those of $\text{Tl}(\text{OH})_3$ formation. Therefore the Tl contained in the reducible fraction of soil may be present in the trivalent form. However, during leaching it is converted to monovalent Tl. On the other hand, birnessite, which is representative for this fraction, is able to extract Tl (I) from the other soil components (Vaněk et al., 2011). It is supposed that oxidizable Tl is contained in sulfides, and only slow oxidation of sulfides to sulfates mobilizes this Tl. Residual Tl appears to be entrapped in aluminosilicate parent matter, where it substitutes for K(I).

4. Conclusion

The final conclusion of this work is that the majority of the Tl in bottom soil formed over different lithological backgrounds is entrapped in the parent matter and is immovable, i.e. totally inert in terms of environmental effects. This conclusion is supported by available literature data. Therefore it is the mobile Tl that should be used as the measure of the environmental hazard caused by this element, rather than the total Tl concentration. An exception is soil formed over ore-bearing dolomites, where a significant part of the Tl is located in the reducible and oxidizable fractions.

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