Title: Thallium and lead variations in a contaminated peatland : a combined isotopic study from a mining/smelting area

Author: Aleš Vaněk, Kateřina Vejvodová, Martin Mihaljevič, Jakub Trubač, Lesław Teper, Katarzyna Sutkowska [i in.]

Citation style: Vaněk Aleš, Vejvodová Kateřina, Mihaljevič Martin, Trubač Jakub, Teper Lesław, Sutkowka Katarzyna [i in.]. (2021). Thallium and lead variations in a contaminated peatland : a combined isotopic study from a mining/smelting area. "Environmental Pollution" (2021), Vol. 290, art. no. 117973, s. 1-9. DOI: 10.1016/j.envpol.2021.117973

UNIWERSYTET ŚLĄSKI W KATOWICACH   Biblioteka Uniwersytetu Śląskiego   Ministerstwo Nauki i Szkolnictwa Wyższego

Thallium and lead variations in a contaminated peatland: A combined isotopic study from a mining/smelting area☆

Aleš Vaněk [a,*], Kateřina Vejvodová [a], Martin Mihaljevič [b], Vojtěch Ettler [b], Jakub Trubač [b], Maria Vaňková [b], Viktor Goliáš [b], Leslaw Teper [c], Katarzyna Sutkowska [c], Petra Vokurková [a], Vít Penížek [a], Tereza Zádorová [a], Ondřej Drábek [a]

[a] Department of Soil Science and Soil Protection, Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 00, Praha 6, Czech Republic
[b] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 00, Praha 2, Czech Republic
[c] Institute of Earth Sciences, Faculty of Natural Sciences, University of Silesia, Bedzinska 60, 41-200, Sosnowiec, Poland

A R T I C L E   I N F O

A B S T R A C T

Vertical profiles of Tl, Pb and Zn concentrations and Tl and Pb isotopic ratios in a contaminated peatland/fen (Wolbrom, Poland) were studied to address questions regarding (i) potential long-term immobility of Tl in a peat profile, and (ii) a possible link in Tl isotopic signatures between a Tl source and a peat sample. Both prerequisites are required for using peatlands as archives of atmospheric Tl deposition and Tl isotopic ratios as a source proxy. We demonstrate that Tl is an immobile element in peat with a conservative pattern synonymous to that of Pb, and in contrast to Zn. However, the peat Tl record was more affected by geogenic source(s), as inferred from the calculated element enrichments. The finding further implies that Tl was largely absent from the pre-industrial emissions ($> \sim 250$ years BP). The measured variations in Tl isotopic ratios in respective peat samples suggest a consistency with anthropogenic Tl (ε^{205}Tl between $\sim$ -3 and -4), as well as with background Tl isotopic values in the study area (ε^{205}Tl between $\sim$0 and -1), in line with detected ^{206}Pb/^{207}Pb ratios (1.16–1.19). Therefore, we propose that peatlands can be used for monitoring trends in Tl deposition and that Tl isotopic ratios can serve to distinguish source origin(s). However, given that the studied fen has a particularly complicated geochemistry (attributed to significant environmental changes in its history), it seems that ombrotrophic peatland(s) could be better suited for this type of Tl research.

1. Introduction

Due to their organic nature, peatlands behave as efficient scavengers of trace elements from the atmosphere (e.g., Cabala et al., 2013; De Vleeschouwer et al., 2009, 2020; Farmer et al., 2006; Fiałkiewicz-Kozieł et al., 2018, 2020; Kylander et al., 2005; Shotyk et al., 1992, 1996, 1998, 2001, 2016a, 2017; Shotyk and Krachler, 2004; Smieja-Król and Bauerek, 2015; Smieja-Król et al., 2015, 2019; Weiss et al., 1999, 2002, 2007). Regarding pollutant capture in peatlands, both physical and chemical mechanisms of binding have to be considered. This is a result of the gradual degradation of dust microparticles accompanied by element leaching and retention onto the organic matter (OM) or even coprecipitation (Cabala et al., 2013; Smieja-Król et al., 2010, 2015). There are a number of studies on trace element variations in peat profiles which demonstrate that peatlands (both bogs and fens), due to their sedimentary character, can be used to trace changes in atmospheric deposition, albeit with some limitations for specific elements and environmental conditions (Mihaljevič et al., 2006; Novak et al., 2008; Novak and Pacherova, 2008; Shotyk et al., 2000; Zuna et al., 2011, 2012). In general, peatlands cannot serve as efficient archives for elements which are mobile and tend to migrate through the peat layers (Smieja-Król and Bauerek, 2015; Weiss et al., 2007).

To our knowledge, there is only limited information about the geochemistry of thallium (Tl) in peatlands (Shotyk and Krachler, 2004; Shotyk et al., 2017; Smieja-Król et al., 2015), in fact, nothing is known about the behavior of its isotopes in this geosystem. In Upper Silesia in southern Poland there are several smaller peatlands. One of them is situated at Wolbrom, a town that has been subjected to long-term

---

☆ This paper has been recommended for acceptance by Yong Sik Ok.
* Corresponding author.
E-mail address: vaneka@af.czu.cz (A. Vaněk).

deposition of trace elements, including Tl, caused by sulfide ore mining/processing. This type of activity is among the most significant local/global sources of anthropogenic Tl in the environment (e.g., Aguilar-Carrillo et al., 2018; Garrido et al., 2020; Gomez-Gonzalez et al., 2015; Lis et al., 2003; Liu et al., 2016, 2019, 2020a, 2020b; Lukaszewski et al., 2018; Wang et al., 2018, 2021; Xiao et al., 2004a, 2004b, 2012).

In this study, we report combined Tl, Pb and Zn concentrations and the Tl and Pb isotopic data from two contaminated peat profiles so that the following fundamental questions can be addressed. (i) Is Tl immobile in peat in the long term? (ii) Do Tl isotopes fractionate over post-depositional dust alteration and/or Tl adsorption? (iii) Do peatlands behave as efficient archives of atmospheric Tl pollution – can Tl isotopic signatures serve as proxies for Tl sources in peat, i.e., similar to Pb?

2. Experimental

2.1. Study site characterization and peat sampling

The studied peatland is situated at Wolbrom, a town in Upper Silesia (Silesian–Kraków region), southern Poland (GPS coordinates: N 50.376220, E 19.780626) (Fig. 1). The area is relatively small (~1000 × 500 m), it is characterized by a mean annual temperature of ~7 °C and ~700 mm/year precipitation. The botanical analysis revealed numerous remains of *Carex* and *Phragmites* species (e.g., *Carex rostrata* and *Phragmites australis*), proving that the peatland is a fen (Pawełczyk et al., 2017). However, due to recent urbanization in Wolbrom (Fig. 1), the original fen vegetation suffers from degradation in several habitats; alder and birch in combination with *Molinietalia* communities or *Nardo-Callunetea* swards represent the prevailing secondary plant species (Latałowa and Nalepka, 1987). The total peat thickness is up to 260 cm and the peat is generally assigned a good stability (Pawełczyk et al., 2017). Tudyka and Pazdur (2012) report that the oldest peat sections at Wolbrom date back to ~9900 BC.

The Wolbrom peatland has been contaminated by atmospheric fallout rich in trace elements including Zn, Pb and Tl, due to nearby mining/processing of Tl-rich Zn–Pb sulfide ores (ZnS and PbS; MVT deposit type) at Olkusz, situated ~20 km SW (Fig. 1). Being operational since 1952, the local Boleslaw Zn plant (primary/secondary Zn smelter) is considered the prevailing modern source of Tl/trace element contamination in the area (Cabala and Teper, 2007; Vaněk et al., 2011, 2013). Nevertheless, mining-related activities and even metal-containing dust loads derived from local flotation tailing dams both have to be considered as a decades-long source of Tl remobilization/deposition (Jakubowska et al., 2007; Karbowska et al., 2014; Lis et al., 2003; Lukaszewski et al., 2018). Furthermore, it should be noted that first metal extractions in the region, mainly silver and lead, are documented by archeologists and date back to both Roman and medieval periods (Bodnar and Rozmus, 2004; Cabala et al., 2013; Rozmus, 2014).

In this study, we sampled one complete peat profile (0–110 cm, à 2 cm, 55 samples) and one shallow profile (0–40 cm, à 2 cm, 20 samples) from ~0.5 × 1 m-wide pits in November 2019 (Fig. 1). The latter (incomplete) profile was sampled for comparison, so that the concentration trends of trace elements for the contaminated section could have been verified. The samples were stored in PE bags, then dried to a constant weight and properly homogenized in the laboratory. The underlying mineral layers (rocks) bordering the peat column, represented by Quaternary clayed sand (120–150 cm) and Cretaceous (Turonian) chalk rock (≥150 cm), were sampled by drilling. It should be emphasized that we revealed a marked compaction of peat during core sampling and that was the reason why we decided to collect peat samples manually.

For the isotopic tracing of Tl and Pb, we used the isotopic records from respective industrial and natural samples (Table 1). These materials involve: (i) massive Pb ore (PbS) (adopted from Vaněk et al., 2011); (ii) Zn ore concentrate (ZnS) from the Olkusz mine, produced by flotation; (iii) Reflot – Zn/Pb ore concentrate (ZnS + PbS), produced by mine waste recycling (flotation); (iv) modern fly ash and slag – waste materials derived from Zn roasting/Waelz technology (Boleslaw Zn plant), i.e., by roasting different recyclable Zn-rich materials (adopted from Vaněk et al., 2018); (v) modern granulated waste – a complex mixture of materials from pyro- and hydrometallurgy (adopted from Vaněk et al., 2018); (vi) Larox sludge – waste from the wet filtration of $ZnSO_4$ electrolyte within the hydrometallurgical process. This material is a waste product from the initial feed, which consists of ~50% of local ZnS (Olkusz mine). At this point it should be noted that old processing wastes are not available, therefore we could study only the available modern materials. As far as the geogenic Tl is concerned, the isotopic data relating to the underlying rocks were used as a background reference (Table 1).

2.2. Peat properties

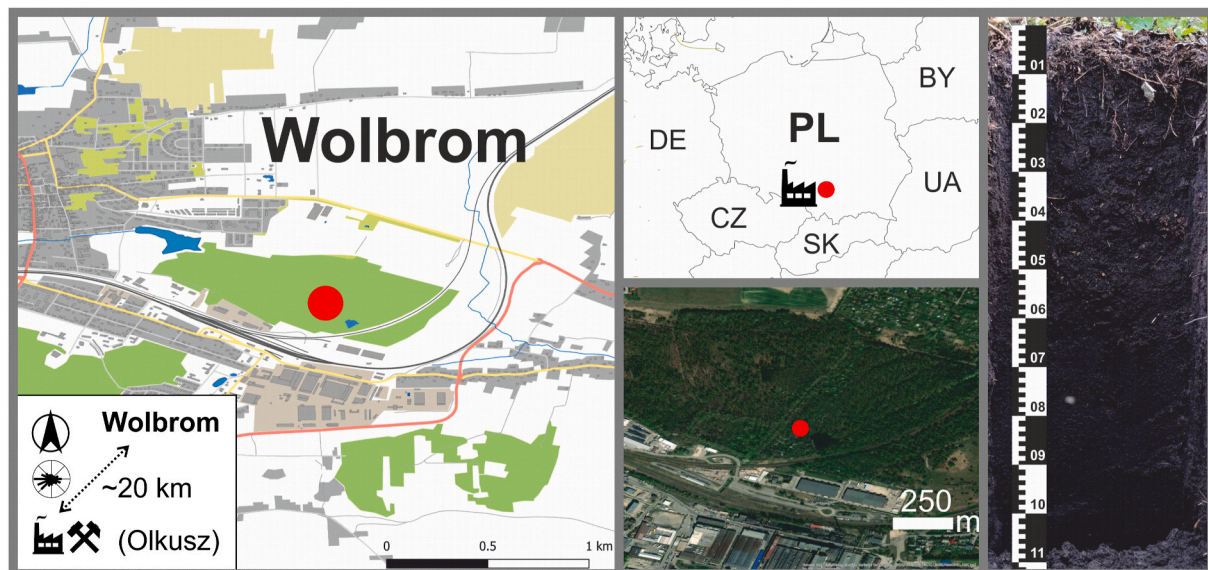The soil pH (active and potential) was measured in H_2O/KCl

Fig. 1. The peat sampling site (GPS coordinates: N 50.376220, E 19.780626); the studied peat profile.

Table 1

The physicochemical properties, total and exchangeable Tl concentrations (Tl$_{TOT}$, Tl$_{EXCH}$) and the Tl and Pb isotopic signatures (in ε^{205}Tl, ^{206}Pb/^{207}Pb) in peat samples (≤40 cm) from the main/complete peat profile (0–110 cm), the underlying mineral layers/rocks (≥120 cm) and the reference ore/waste materials.

Sample/ Layer	Depth (cm)	Age Date	pH H$_2$O	KCl	Density (g/cm^3)	LOI (%)	TC* (%)	TS* (%)	CEC (cmol+/ kg)	Tl$_{TOT}$ (mg/kg)	Tl$_{EXCH}$* (mg/ kg)	ε^{205}Tl ±0.7	^{206}Pb/^{207}Pb
1	0–2	2016 ± 4 AD	4.3	4.2	–	74.3	40.7	0.5	99	0.71*	0.11	–	1.1792
2	2–4	2009 ± 5 AD	4.2	3.9	0.21	76.9	38.7	0.5	96	0.72	0.12	–	1.1759
3	4–6	2004 ± 5 AD	3.8	3.8	0.21	75.2	38.2	0.5	96	0.76	0.13	−3.09	1.1742
4	6–8	1998 ± 6 AD	3.9	3.8	0.25	72.7	36.9	0.5	96	0.84	0.11	−2.30	1.1641
5	8–10	1991 ± 7 AD	4.2	3.8	0.25	74.0	37.3	0.5	93	0.80*	0.12	−2.78	1.1712
6	10–12	1981 ± 8 AD	4.1	3.8	0.29	–	36.9	0.5	95	0.82	–	−3.57	1.1658
7	12–14	1971 ± 10 AD	4.3	3.9	0.29	–	38.6	0.5	103	0.72	–	−3.16	1.1707
8	14–16	1962 ± 12 AD	4.5	4.1	0.29	–	38.5	0.5	98	0.51	–	–	1.1651
9	16–18	1954 ± 13 AD	4.8	4.3	0.29	–	40.3	0.5	98	0.41	–	–	1.1706
10	18–20	1946 ± 14 AD	4.8	4.3	0.29	–	40.3	0.6	102	0.48	–	–	1.1773
11	20–22	–	4.9	4.3	0.28	–	39.2	0.6	96	0.48	–	–	1.1750
12	22–24	–	4.9	4.4	0.28	–	42.5	0.6	103	0.36	–	–	1.1750
13	24–26	–	4.9	4.4	0.28	–	42.3	0.6	107	0.30	–	–	1.1768
14	26–28	–	4.9	4.4	0.28	–	44.0	0.7	112	0.29	–	–	1.1741
15	28–30	–	5.0	4.5	0.28	–	45.5	0.7	111	0.25	–	–	1.1699
16	30–32	–	5.0	4.5	0.26	–	40.7	0.6	110	0.45	0.04	–	1.1761
17	32–34	–	5.0	4.5	0.26	–	42.8	0.7	111	0.39	0.03	–	1.1749
18	34–36	–	4.9	4.4	0.26	–	42.0	0.7	100	0.41	0.02	−1.06	1.1760
19	36–38	–	4.9	4.5	0.26	–	43.4	0.7	91	0.35	0.02	−1.25	1.1751
20	38–40	300 ± 90 BC	5.1	4.5	0.26	–	41.1	0.7	109	0.42*	0.02	−1.59	1.1693
Clayey sand	120–150	Quaternary	–	–	–	–	–	–	–	0.12 ± 0.06#	–	−1.47	1.1893
Chalk rock (bedrock)	150-	Turonian	–	–	–	–	–	–	–	0.21 ± 0.10#	–	+0.47	1.1856
Massive Pb ore (PbS)	–	–	–	–	–	–	–	–	–	–	–	–	1.173
Zn ore concentrate (ZnS)	–	–	–	–	–	–	–	–	–	70.1 ± 12.8#	–	−4.40	–
Reflot (ZnS + PbS)	–	–	–	–	–	–	–	–	–	94.8 ± 3.6#	–	−4.20	–
Fly ash (Zn metallurgy, roasting)	–	–	–	–	–	–	–	–	–	15.0 ± 1.0#	–	−4.09	1.174
Slag (Zn metallurgy, roasting)	–	–	–	–	–	–	–	–	–	1.19 ± 0.60#	–	−3.31	–
Granulated waste (Zn metallurgy)	–	–	–	–	–	–	–	–	–	322 ± 110#	–	−3.60	–
Larox sludge (Zn metallurgy)	–	–	–	–	–	–	–	–	–	122 ± 0	–	−3.63	–

The ε^{205}Tl data assign an estimated error (±0.7, 2 SD) which is based on our long-term external reproducibility for the SRM AGV-2 (Andesite, USGS, USA). *The data depict means (n = 3; RSD ≤10%). #The Tl concentrations depict means (n = 3; ±2 SD). LOI: loss on ignition. –: not determined. Reflot – a concentrate produced by mine waste recycling (flotation). The isotopic data in Pb ore, fly ash, slag and granulated waste were adopted from Vaněk et al. (2011, 2018). See the SM section for details.

solutions (v/v ratio, 1/5). The ash content (loss of ignition) was determined by combusting 1 g of peat at 550 °C (expressed as % of the dry weight sample). The total carbon and sulfur concentrations (TC, TS) were determined using a CNS analyzer (Flash, 2000; Thermo Scientific, Germany). The soil cation exchange capacity (CEC) was determined on the basis of sodium acetate method (Bower et al., 1954). For the determination of exchangeable Tl fraction in peat, representing the potentially labile Tl pool, a 1 M NH$_4$NO$_3$ extraction solution was used (S/L ratio, 1/10, 2 h).

Total Zn, Pb, Tl, Fe, Mn and Sc concentrations in peat samples, rocks and ore/waste materials were determined using Q-ICP-MS Xseries II (Thermo Scientific, Germany); a total mass of ≤0.5 g of a finely-ground sample was digested in a mixture of HNO$_3$, HCl and HF (3/1/1 ratio, ≤20 mL, ~200 °C, 3 h, ±5 mL H$_2$O$_2$) (Merck, Germany) using a microwave system (Multiwave 5000, Anton Paar, Austria). The obtained solutions were evaporated and redissolved in 2% HNO$_3$ (25 mL) before further use or analysis. An analogous dilution was used for the exchangeable Tl determination. Scandium concentrations were determined by Q-ICP-MS using a single Sc calibration prior to the measurement. All mineral and selected peat samples (no. 1, 5 and 20) were 3-

times replicated. This data, in combination with data obtained for the SRM 2711 (Montana Soil, NIST, USA) (Table S1, Supplementary Material, SM) were used for the quality control (QC) of concentration measurements (Tl, Zn, Pb).

^{210}Pb γ spectrometry was used for age dating of the uppermost peat layers (≤20 cm). A Canberra DSA 2000 multichannel analyzer controlled by GENIE 2000 software was used to determine the specific activities of ^{210}Pb, ^{226}Ra and ^{137}Cs isotopes. Selected peat samples from the deeper layers (≥40 cm) were dated by the ^{14}C technique using an EnvironMICADAS compact tandem accelerator. Detailed information about both ^{210}Pb/^{14}C-dating methods is available in the SM section.

2.3. Thallium and Pb isotopic analyses

The determination of Tl isotopic ratios preceded Tl isolation. For this purpose, a two-stage chromatographic separation employing the Bio-Rad AG1-X8 (an anion exchange resin, 200–400 mesh, Cl$^−$ cycle) was conducted, i.e., without utilizing HBr. For detailed information about the Tl isolation from sample solutions refer to Grösslová et al., 2018; Vaněk et al. (2016), 2018, 2020. Detailed information about the

measurement of Tl isotopic ratios using MC-ICP-MS Neptune Plus (Thermo Scientific, Germany), including the analytical conditions similar to those described in e.g. Prytulak et al. (2013, 2017), and the respective QC (Table S2, SM), are shown in the SM section. The Tl isotopic composition was calculated using the following equation with ε notation relative to NIST SRM 997 (Eq. (1)):

$$\varepsilon^{205}Tl = \frac{^{205}Tl\big/^{203}Tl_{sample} - {}^{205}Tl\big/^{203}Tl_{NIST997}}{^{205}Tl\big/^{203}Tl_{NIST997}} \times 10^4 \quad (1)$$

The Pb isotopic ratios ($^{206}Pb/^{207}Pb$) were determined using Q-ICP-MS. Solutions were diluted to ~20 µg Pb/L prior to analysis. The mass bias correction was performed using standard-sample bracketing with the SRM 981 (Common lead, NIST, USA). The accuracy of the measurements was controlled using the SRM AGV-2 (Andesite, USGS, USA) with $^{206}Pb/^{207}Pb = 1.2085 \pm 0.0006$ and $^{208}Pb/^{206}Pb = 2.0415 \pm 0.0013$. More information about the analytical conditions for the determination of Pb isotopes is available in Vaněk et al. (2011) and Zuna et al. (2011).

3. Results and discussion

3.1. Trace element concentrations in peat

The concentration trends of Zn, Pb and Tl in the studied peat profiles are shown in Fig. 2 and listed in Tables 1, S3 and S4 (SM). Both deep and shallow profiles identically exhibit significant accumulation of all trace elements in the interval of ~0–40 cm, with the highest concentrations within the uppermost peat (0–16 cm), corresponding to layers formed earlier than 1962 (±12), as dated by the ^{210}Pb method. The question that arises here is to which degree the contribution of recent biomass (e. g., decayed roots/leaves) could have affected our ^{210}Pb data. However, in view of temporal emission data for Boleslaw Zn plant and the data on local Zn–Pb ore production (at Olkusz), in combination with the absence of peat disturbance according to the ^{210}Pb, there is a match in trace element stratigraphy in the studied peat columns, with a peak between the 1960s and the mid 1980s (Liszka and Świć, 2004) (Fig. 2, Table S3, S4, SM). The finding is also consistent with trace element records in the surface layers of different ombrotrophic bogs in southern Poland, mostly attributed to ore mining/processing activities, or extensive coal mining/industrial burning, or due to the general development of local industry (Fiałkiewicz-Kozieł et al., 2018; Smieja-Król and Bauerek, 2015; Smieja-Król et al., 2010, 2015, 2019). Despite the fact that we do not have exact data on historical mining-/smelting-derived Tl emissions in the Wolbrom area, a similar trend as for Zn and Pb is inferred (Lis et al., 2003; Vaněk et al., 2011, 2013). Given the high concentrations of Tl/trace elements in the 0-10-cm peat section (≥1991) (Tables 1, S3, SM), continuing ore mining or more likely dust/trace element remobilization from the adjacent flotation tailing dams are assumed to be the primary cause (Cabala and Teper, 2007; Jakubowska et al., 2007; Karbowska et al., 2014; Lis et al., 2003).

The peat interval of 0–50 cm covers the peat age of more than the last 5000 years. Due to their position in the age-depth model, samples 20 (38–40 cm) and 26 (50–52 cm), ^{14}C-dated 300 BC and 3720 BC respectively, do reflect an ancient hiatus (Fig. S1, SM). The event, which was first revealed by Pawełczyk et al. (2017) in the Wolbrom fen, could be related to specific environmental changes such as a low water table in that time (Pawełczyk et al., 2017). In addition, we assume that increased concentrations of trace elements in the respective peat zone (38–52 cm) (Fig. 2, Tables 1, S3, S4, SM) result from the hiatus as well, reflecting the
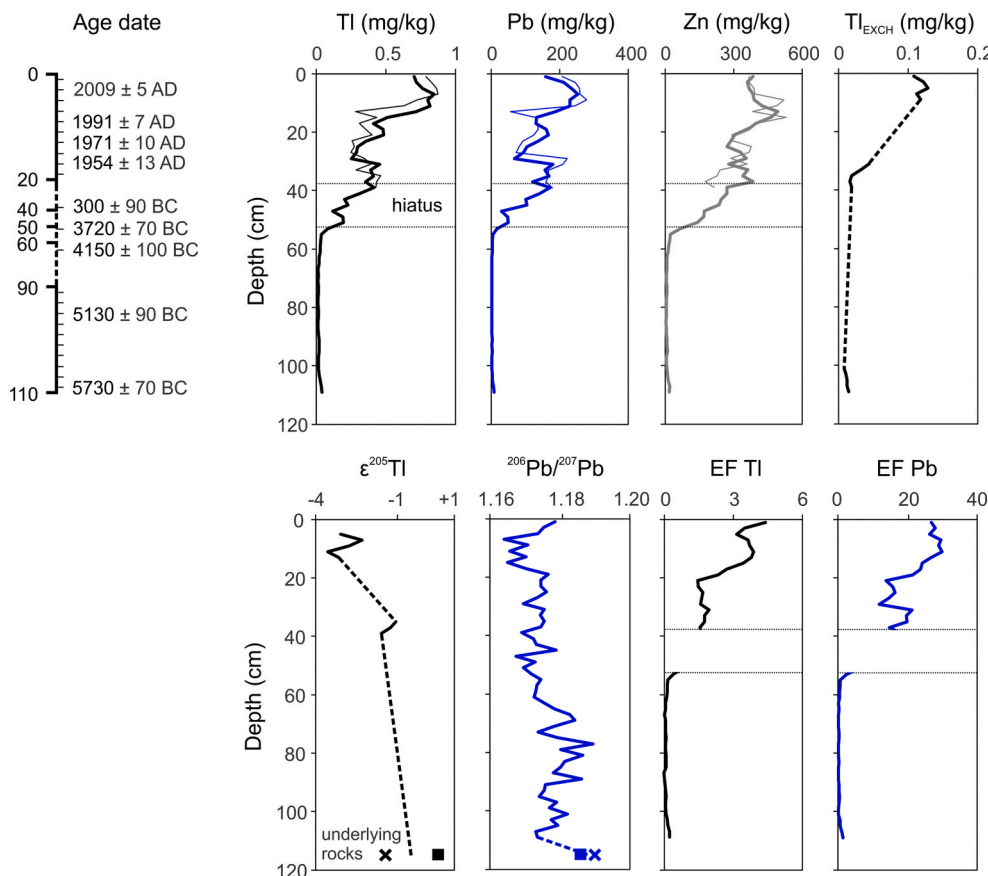

Fig. 2. The depth-dependent evolution of Tl, Pb and Zn concentrations, the exchangeable Tl fraction, the Tl and Pb isotopic signatures (in $\varepsilon^{205}Tl$, $^{206}Pb/^{207}Pb$) and corresponding enrichment factors of Tl and Pb in the studied peat profiles. Dashed lines indicate approximations between the measured samples. Narrow lines for Tl, Pb and Zn concentrations depict trends obtained within the shallow/incomplete peat profile (0–40 cm). See the SM section for details.

decline in OM accumulation, caused by a limited plant growth in that time. Due to the minimum rate of sediment formation (Fig. S1, SM) we were not able to distinguish/quantify the potential effect of pre-Roman mining/processing of local ores (Bodnar and Rozmus, 2004; Rozmus, 2014).

The relatively high concentrations of trace elements in peat samples above the hiatus (≤38 cm) were attributed to a combined effect of historical ore mining/processing at Olkusz. Archeologists document that the area acts as a mining/smelting center (mainly for Pb and Ag ores) within both the Roman and medieval periods (Bodnar and Rozmus, 2004; Cabala et al., 2013; Rozmus, 2014). It is probable that the deposition of trace elements in the area further accelerated with the start of industrial revolution (~250 years BP), which, however, we were not able to link with the peat concentration data, due to the absence of peat dating for this time interval.

To estimate the anthropogenic enrichment of trace elements, we used the Sc concentration for element normalization and local bedrock ratio M/Sc as a geogenic (background) reference (Table S3, SM). The enrichment factor (EF) was calculated as (Eq. (2)):

$$EF = [M/Sc]_{sample} \big/ [M/Sc]_{bedrock} \qquad (2)$$

This approach was chosen with regard to generally increased background concentrations of trace elements in the study area, and thus a less informative value of Sc for the average Earth crust (if used).

Similar to their concentrations, the maximum EFs for both Pb (≤30) and Tl (≤4) (Fig. 2, Table S3, SM), were found in the uppermost peat (0–16 cm), indicative of extensive mining and processing of local ores and even post-mining effects over the course of the second half of 20th century until the present time. In line with Pb concentrations, significant Pb enrichments, starting with EF = 15, were found above the hiatus (≤38 cm), again in line with historical mining/processing of local ores. In contrast, systematically low EF values of Tl (≤4) in combination with Tl concentrations of 0.3–0.8 mg/kg recorded for the same peat section, imply the importance of the introduction of natural (geogenic) Tl into the peatland (Table S3, SM). In other words, the EF values from the range of ≤0.5–1.0 suggest that the vast majority of Tl entered peat naturally (soil erosion, rock weathering, etc.). However, this can be promoted by agricultural tillage (Shotyk et al., 2001), i.e., due to soil/rock dust mobilization and deposition. Such a prediction is possibly supported by matching Tl concentrations in the underlying rock samples (0.1–0.2 mg/kg) or the low amount of exchangeable Tl fraction in the middle profile zone (≤0.04 mg/kg), as well as the isotopic proxies (Fig. 2, Tables 1, S5, SM).

3.2. Trace element mobility in peat

When viewing the highest concentrations of trace elements, a vertical shift of Zn (~4 cm) relative to Pb/Tl can be observed in the uppermost peat (0–16 cm) (Tables S3, S4, SM). Similarly, in the deeper peat (~30 cm) an increased Zn concentration was observed alongside declining Pb/Tl concentrations. As such, this supports the anticipated vertical migration of Zn in the peat profile (Weiss et al., 2007) in line with low peat pH values (~4) (Table 1) and generally "less active behaviors" of Pb and Tl (e.g., Shotyk et al., 1996; Shotyk and Krachler, 2004; Zuna et al., 2011). Although we did not investigate the peat pore waters at the sampling site, the formation of strong Zn complexes with mobile fulvic acids associated with small-size colloidal particles could promote its migration (Novak and Pacherova, 2008). Lead, by contrast, tends to occur in large colloids and it readily forms stable complexes with humic acids (Gao et al., 1999), likely promoting its immobility in peat. Although, Shotyk et al. (2016b) report that some part of the total Pb can be mobilized in peat and enter the peat pore water, on an example of different bogs the authors highlight that less than 0.01% of total Pb is labile (soluble), making the potential for Pb migration very small.

As far as Tl is concerned, there is no evidence on the formation of stable/strong complexes with any simple organic compounds, fulvic or humic acids (Jacobson et al., 2005; Nriagu, 1998). This implies that Tl (if previously mobilized) is possibly adsorbed more simply, following the non-specific/specific reactions onto the OM. The association of Tl with the –SH functional groups can further promote its fixation (Nriagu, 1998). Shotyk and Krachler (2004) report that Tl in bogs exhibits a comparable pattern to Pb (and Ag), supporting the theory that Tl is immobile in peat. Our evidence for the proposed Pb/Tl analogy, as well as a general stability of Tl in the studied peatland is provided by a significant positive relationship (R^2 = 0.95) between their concentrations (Fig. S2, SM). The question that arises here is, what could be the role of K^+ and/or NH_4^+ in exchangeable Tl sorption, reflecting comparable ion chemistry and allowing their competition or potentially specific (stronger) Tl fixation (Vaněk et al., 2012).

In general, we do not expect significant mobilization of trace elements in the underlying mineral formations and their migration upward in the fen. This behavior seems to be negligible for Pb and Tl and only limited for Zn, as inferred by the concentration comparison at the rock-peat interface (Table S3, SM).

3.3. Thallium isotopic variability in peat

The Tl isotopic data found in the peat profile, the underlying rocks and the industrial samples are shown in Fig. 2 and listed in Tables 1 and S5 (SM).

Given the overall variability in the studied industrial samples (~1 ε^{205}Tl) involving local Zn/Pb ores and different waste materials from both roasting/Waelz (fly ash, slag) and hydrometallurgical technologies (granulated waste, Larox sludge) derived from primary and recyclable Zn-rich materials (Table 1), generally small Tl isotopic fractionation is assumed for a complex industrial process (Vaněk et al. (2018). Such an isotopic homogeneity is quite surprising, at least in view of a wide range of Tl concentrations (1–300 mg/kg) (Table 1) or a large variability in Tl isotopic ratios in different solid wastes from pyrite roasting, yielding ~17 ε^{205}Tl units (from −1 to +16), as reported by Liu et al. (2020a). Therefore, our results are similar to data by Kersten et al. (2014), who indicate even the absence of Tl isotopic fractionation for a high-temperature process, albeit in relation cement production. The authors revealed an analogy in the isotopic signature in Tl-rich FeS_2, co-combusted FeS_2 roasting waste (as an additive) and emitted cement kiln dust (CKD), all featuring ε^{205}Tl ~0.

Our peat profile exhibits an apparent isotopic variability with ε^{205}Tl yielding the range of −3.6 and −1.1. Importantly, we identified only negative ε^{205}Tl values (≥-3.6) in the uppermost peat (0–14 cm, ≥1971). Therefore, these values are quite similar to the isotopic signatures found in local ore and/or metallurgical samples (ε^{205}Tl from −3.3 to −4.4), which correspond to the potential source(s) of historical Tl contamination in the area (Table 1). Regarding these findings, there is evidence to suggest that detectable Tl contamination is entering the peat via the isotopically light Tl (enriched in ^{203}Tl) (Fig. 2).

By contrast, in the 34–40 cm peat-profile section we identified a clear shift toward the isotopically-heavy Tl (enriched in ^{205}Tl) (ε^{205}Tl ≥ -1.6) (Fig. 2). By combining this data with generally low EFs for Tl and a missing isotopic link with the reference ores and metallurgical wastes (Table 1), we assume that the peat signatures reflect the introduction of geogenic Tl. Besides the isotopic similarity with the underlying rocks (ε^{205}Tl −1.5 and + 0.5, respectively) (Table 1), the proposed geogenic origin of Tl in the deeper peat is further supported by a model isotopic segregation according to source reservoirs (Fig. S3, SM). Since we did not detect either vertical Tl shift(s) in the studied profiles, suggesting its immobility in peat, or any indication for specific Tl(I) complexation onto the OM, the Tl isotopic fractionation in peat is not very probable. Although in relation to Cu, Bigalke et al. (2010) attributed specific fixation of Cu onto humic compounds to the accumulation of the isotopically heavy fraction of Cu, accompanied by the isotopically light Cu

mobilization/migration.

At this point, it should be highlighted that the introduction and/or recycling of Tl via its uptake by peat vegetation, i.e., due to the K-channel and/or –SH containing compounds in plants (e.g., Kersten et al., 2014; Rader et al., 2019; Vaněk et al., 2019) cannot explain variations in Tl distribution in the studied peatland. The deep peat layers (≥ 60 cm), absent of contamination, are very low in Tl (~ 0.01 mg/kg); this is much less in comparison with the underlying rocks (≥ 0.12 mg/kg) (Table S3, SM). This finding allows us to neglect the biological Tl uptake as a potential source of Tl isotopic fractionation toward the isotopically light Tl in the surface/subsurface peat (Vaněk et al., 2019).

3.4. Lead isotopic variability in peat

The Pb isotopic ratios ($^{206}Pb/^{207}Pb$) determined in the studied peat profile, underlying rocks and selected materials referring to anthropogenic and geogenic Pb are shown in Fig. 2 and listed in Tables 1 and S5 (SM).

The vertical $^{206}Pb/^{207}Pb$ profile shows apparently less radiogenic Pb in the 0-40-cm peat section, yielding 1.1641–1.1792, relative to the deeper peat samples (1.1722–1.1906) (Table S5, SM). Given the overall isotopic variations within the profile, the data strongly suggest that extensive mining and processing of local Zn/Pb ores, including post-mining effects in the second half of 20th century, are the primary cause for a $^{206}Pb/^{207}Pb$ decline in the uppermost peat (<16 cm) (Fig. 2). Such a prediction is favored by similar signatures for local galena and fly ash samples (1.173 and 1.174, respectively), mimicking the model (modern) sources of anthropogenic Pb in the area (Vaněk et al., 2011). This data in combination with $^{206}Pb/^{207}Pb$ values measured in the underlying rocks (1.1856 and 1.1893, respectively), points further to an introduction of only geogenic Pb in peat pre-dating ~ 4000 BC ($\sim \geq 60$ cm). The trend where Pb is less radiogenic for all modern, industrial and pre-industrial periods (De Vleeschouwer et al., 2009; Fiałkiewicz-Kozieł et al., 2018, 2020; Mihaljevič et al., 2006; Novak et al., 2008; Shotyk et al., 2000; Weiss et al., 2002) and becomes progressively more radiogenic downwards in the peat (higher in $^{206}Pb/^{207}Pb$) is best distinguishable for a complete peat profile (Fig. 2, Table S5, SM). Overall, the obtained Pb isotopic data (indicative of Pb mixing between two reservoirs but with a predominance of the anthropogenic pool), are in good agreement with both element and EF systematics of Pb in the studied peat profile (Table S3, SM), as well as with $^{206}Pb/^{207}Pb$ ratios observed in various peatlands in southern Poland (Fiałkiewicz-Kozieł et al., 2018, 2020).

3.5. Limitations of the use of stable Tl isotopes for source tracing in peatlands

If we use the Fe and Mn concentration data or the depth-dependent evolution of Mn/Fe ratio in the studied peat profile (Fig. S4, SM) as proxies for the redox-driven effects, variations reflecting environmental changes in the studied peatland are apparent. For example, the increased Fe and Mn concentrations and a high Mn/Fe ratio in the depth of ~ 10 cm can be related to modern oxidation of the OM just below the peat surface. Similarly, small peaks in Mn concentration and Mn/Fe ratio observed at ~ 50 cm can imply an old oxidation event in the peatland (Fig. S4, SM), which could be linked with the identified hiatus. Cabala et al. (2013), who studied the origin of metallic phases in peat, show that both Fe/Mn-oxides can readily form, following for example the breakdown of metal-organic complexes. Furthermore, the oxidation process can be caused by a low water-table level, an interaction of oxygenated meteoric waters within the surface/subsurface peat section, or even an interaction of peat with oxidizing groundwater (Cabala et al., 2013). On examples of laterite profiles, Howarth et al. (2018) report peaks in Fe-oxide concentrations accompanied by positive $\varepsilon^{205}Tl$ values, which trace the paleowater tables. For Tl, numerous studies suggest that the precipitation of secondary Tl-containing phases in sedimentary

systems, mainly of specific Mn-oxides (e.g., hexagonal birnessite) and associated oxidative Tl uptake (Peacock and Moon, 2012; Voegelin et al., 2015; Wick et al., 2019, 2020), is a major control mechanism for isotopically-heavy Tl enrichments (Fe/Mn-oxide containing sedimentary crusts, precipitates, soil nodules, etc.) (Nielsen et al., 2013, 2017; Ostrander et al., 2019; Owens et al., 2017; Rehkämper et al., 2002, 2004; Schauble, 2007).

Although we did not observe any indications for vertical Tl migration and Tl isotopic fractionation in the studied peatland, cyclic changes in pH and/or redox could result in partial Tl leaching and subsequent preferential Tl enrichment in specific peat layers, accompanied by oxidative Tl sorption. For instance, this Tl behavior has recently been observed in the redoximporhic soils (Vaněk et al., 2020; Vejvodová et al., 2020). Therefore, if these processes take place in a peatland, they could limit the use of Tl isotopic ratios as proxies for anthropogenic/geogenic Tl sources. To gain further insights into this issue, and to verify the conservative feature of Tl, combined Tl isotopic and mineralogical micro-scale studies are required in peatlands with marked oxide accumulations and/or in peat samples enriched in Fe/Mn-oxides (e.g., Smieja-Król et al., 2010, 2015).

4. Conclusions

This study presents vertical patterns of Tl, Pb and Zn concentrations and stable Tl and Pb isotopic ratios from a historically contaminated peatland/fen (Wolbrom, Poland). The following major conclusions were made:

(i) Thallium is characterized as an immobile element in peat which mirrors the conservative pattern of Pb, in contrast to Zn which has a tendency to migrate. Both Tl and Pb reflect the history of atmospheric deposition. However, the peat Tl record is more affected by local geogenic sources, relative to Pb, as inferred from calculated (anthropogenic) element enrichments. Overall, this finding indicates that pre-industrial anthropogenic emissions ($> \sim 250$ years BP) were generally low in Tl, confirming the observation of e.g. Shotyk and Krachler (2004).

(ii) The measured variations in Tl isotopic ratios (in $\varepsilon^{205}Tl$) in peat samples suggest a link with the local source(s) of anthropogenic Tl and the background Tl isotopic values in the study area. Furthermore, we did not detect Tl isotopic fractionation in peat samples, which if present, could be ascribed to Tl-rich dust alteration and/or Tl sorption onto the peat OM during the post-depositional residence time in peat, or even to biological processes. The finding is indicative of the absence of redox Tl(I)–Tl (III) shift(s), being previously proposed as a key control for Tl isotopic fractionation in sediments/soils, etc.

(iii) The obtained stable Tl isotopic data show a consistency with the $^{206}Pb/^{207}Pb$ ratios, which further support the potential use of Tl isotopic ratios as proxies for Tl sources in peatlands. However, given the complicated geochemistry of the studied fen, we propose to focus further research on well-preserved Tl-contaminated ombrotrophic peatlands.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117973.

Author contributions

References

Aguilar-Carrillo, J., Herrera, L., Gutiérrez, E.J., Reyes-Domínguez, I.A., 2018. Solid-phase distribution and mobility of thallium in mining-metallurgical residues: environmental hazard implications. Environ. Pollut. 243, 1833–1845. https://doi.org/10.1016/j.envpol.2018.10.014.

Bigalke, M., Weyer, S., Wilcke, W., 2010. Copper isotope fractionation during complexation with insolubilized humic acid. Environ. Sci. Technol. 44 (14), 5496–5502. https://doi.org/10.1021/es1017653.

Bodnar, R., Rozmus, D., 2004. Wczesnośredniowieczne ślady hutnictwa w Dąbrowie Górniczej-Łośniu oraz na obszarach pogranicznych. In: Rozmus, D. (Ed.), Archeologiczne I Historyczne Ślady Górnictwa I Hutnictwa Na Terenie Dąbrowy Górniczej I Okolic. Księgarnia Akademicka Kraków, pp. 9–60, 2004 (in Polish).

Bower, C.A., Reitemeier, R.F., Fireman, M., 1954. Exchangeable cation analysis of saline and alkali soils. Soil Sci. 73 (4), 251–262. https://doi.org/10.1097/00010694-195204000-00001.

Cabala, J., Teper, L., 2007. Metalliferous constituents of rhizosphere soils contaminated by Zn-Pb mining in southern Poland. *Water*. Air and Soil Pollution 178, 351–362. https://doi.org/10.1007/s11270-006-9203-1.

Cabala, J., Smieja-Król, B., Jablonska, M., Chróst, L., 2013. Mineral components in a peat deposit: looking for signs of early mining and smelting activities in Silesia-Cracow region (Southern Poland). Environ. Earth Sci. 69, 2559–2568. https://doi.org/10.1007/s12665-012-2080-6.

De Vleeschouwer, F., Fagel, N., Cheburkin, A., Pazdur, A., Sikorski, J., Matielli, N., Renson, V., Fialkiewicz, B., Piotrowska, N., Le Roux, G., 2009. Anthropogenic impacts in North Poland over the last 1300 years - a record of Pb, Zn, Cu, Ni and S in an ombrotrophic peat bog. Sci. Total Environ. 407, 5674–5684. https://doi.org/10.1016/j.scitotenv.2009.07.020.

De Vleeschower, F., Baron, S., Cloy, J.M., Enrico, M., Ettler, V., Fagel, N., Kempter, H., Kylander, M., Li, C., Longman, J., Martinez-Cortizas, A., Marx, S., Mattielli, N., Mighall, T., Nieminen, T.M., Piotrowska, N., Pontevedra-Pombal, X., Pratte, S., Renson, V., Shotyk, W., Shuttleworth, E., Sikorski, J., Stromsoe, N., Talbot, J., von Scheffer, C., Weiss, D., Zaccone, C., Le Roux, G., 2020. Comment on: "A novel approach to peatlands as archives of total cumulative spatial pollution loads fromatmospheric deposition of airborne elements complementary to EMEP data: priority pollutants (Pb, Cd, Hg)" by Ewa Miszczak, Sebastian Stefaniak, Adam Michczyński, Eiliv Steinnes and Irena Twardowska. Sci. Total Environ. 737, 138699. https://doi.org/10.1016/j.scitotenv.2020.138699.

Farmer, J.G., Graham, M.C., Yafa, C., Cloy, J.M., Freeman, A.J., MacKenzie, A.B., 2006. Use of 206Pb/207Pb ratios to investigate the surface integrity of peat cores used to study the recent depositional history and geochemical behaviour of inorganic elements in peat bogs. Global Planet. Change 53, 240–248. https://doi.org/10.1016/j.gloplacha.2006.03.006.

Fiałkiewicz-Kozieł, B., Łokas, E., Gałka, M., Kołaczek, P., De Vleeschouwer, F., Le Roux, G., Smieja-Król, B., 2020. Influence of transboundary transport of trace elements on mountain peat geochemistry (Sudetes, Central Europe). Quat. Sci. Rev. 230, 106162. https://doi.org/10.1016/j.quascirev.2020.106162.

Fiałkiewicz-Kozieł, B., De Vleeschouwer, F., Mattielli, N., Fagel, N., Palowski, B., Pazdur, A., Smieja-Król, B., 2018. Record of Anthropocene pollution sources of lead in disturbed peatlands from Southern Poland. Atmos. Environ. 179, 61–68. https://doi.org/10.1016/j.atmosenv.2018.02.002.

Gao, K.Z., Pearce, J., Jones, J., Taylor, C., 1999. Interaction between peat, humic acid and aqueous metal ions. Environ. Geochem. Health 21, 13–26. https://doi.org/10.1023/A:1006592627852.

Garrido, F., Garcia-Guinea, J., Lopez-Arce, P., Voegelin, A., Göttlicher, J., Mangold, S., Almendros, G., 2020. Thallium and co-genetic trace elements in hydrothermal Fe-Mn deposits of Central Spain. Sci. Total Environ. 717, 137162. https://doi.org/10.1016/j.scitotenv.2020.137162.

Gomez-Gonzalez, M.A., Garcia-Guinea, J., Laborda, F., Garrido, F., 2015. Thallium occurrence and partitioning in soils and sediments affected by mining activities in Madrid province (Spain). Sci. Total Environ. 536, 268–278. https://doi.org/10.1016/j.scitotenv.2015.07.033.

Grösslová, Z., Vanek, A., Oborná, V., Mihaljevič, M., Ettler, V., Trubač, J., Drahota, P., Penizek, V., Pavlů, L., Sracek, O., Kribek, B., Voegelin, A., Göttlicher, J., Ondrej, D., Tejnecký, V., Houska, J., Mapani, B., Zádorová, T., 2018. Thallium contamination of desert soil in Namibia: chemical, mineralogical and isotopic insights. Environ. Pollut. 239, 272–280. https://doi.org/10.1016/j.envpol.2018.04.006.

Howarth, S., Prytulak, J., Little, S.H., Hammond, S.J., Widdowson, M., 2018. Thallium concentration and thallium isotope composition of lateritic terrains. Geochem. Cosmochim. Acta 239, 446–462. https://doi.org/10.1016/j.gca.2018.04.017.

Jacobson, A.R., McBride, M.B., Baveye, P., Steenhuis, T.S., 2005. Environmental factors determining the trace-level sorption of silver and thallium to soils. Sci. Total Environ. 345, 191–205. https://doi.org/10.1016/j.scitotenv.2004.10.027.

Jakubowska, M., Pasieczna, A., Zembrzuski, W., Swit, Z., Lukaszewski, Z., 2007. Thallium in fractions of soil formed on floodplain terraces. Chemosphere 66, 611–618. https://doi.org/10.1016/j.chemosphere.2006.07.098.

Karbowska, B., Zembrzuski, W., Jakubowska, M., Wojtkowiak, T., Pasieczna, A., Lukaszewski, Z., 2014. Translocation and mobility of thallium from zinc–lead ores. J. Geochem. Explor. 143, 127–135. https://doi.org/10.1016/j.gexplo.2014.03.026.

Kersten, M., Xiao, T., Kreissig, K., Brett, A., Coles, B.J., Rehkämper, M., 2014. Tracing anthropogenic thallium in soil using stable isotope compositions. Environ. Sci. Technol. 48 (16), 9030–9036. https://doi.org/10.1021/es501968d.

Kylander, M.E., Weiss, D.J., Martínez Cortízas, A., Spiro, B., Garcia-Sanchez, R., Coles, B. J., 2005. Refining the pre-industrial atmospheric Pb isotope evolution curve in Europe using an 8000 year old peat core from NW Spain. Earth Planet Sci. Lett. 240, 467–485. https://doi.org/10.1016/j.epsl.2005.09.024.

Latałowa, M., Nalepka, D., 1987. A study of the late-glacial and holocene vegetational history of the Wolbrom area (Silesian-Cracovian upland). Acta Palaeobot. 27, 75–115.

Lis, J., Pasieczna, A., Karbowska, B., Zembrzuski, W., Lukaszewski, Z., 2003. Thallium in soils and stream sediments of a Zn-Pb mining and smelting area. Environ. Sci. Technol. 37, 4569–4572. https://doi.org/10.1021/es0346936.

Liszka, M., Świć, E., 2004. Dzieje Wydarzenia Ludzie. Zakłady Górniczo-Hutnicze „Bolesław". S. A., Bukowno, Poland (in Polish).

Liu, J., Wang, J., Chen, Y., Xie, X., Qi, J., Lippold, H., Luo, D., Wang, C., Su, L., He, L., Wu, Q., 2016. Thallium transformation and partitioning during Pb − Zn smelting and environmental implications. Environ. Pollut. 212, 77–89. https://doi.org/10.1016/j.envpol.2016.01.046.

Liu, J., Yin, M., Luo, X., Xiao, T., Wu, Z., Li, N., Wang, J., Zhang, W., Lippold, H., Belshaw, N.S., Feng, Y., Chen, Y., 2019. The mobility of thallium in sediments and source apportionment by lead isotopes. Chemosphere 219, 864–874. https://doi.org/10.1016/j.chemosphere.2018.12.041.

Liu, J., Yin, M., Xiao, T., Zhang, C., Tsang, D.C.W., Bao, Z., Zhou, Y., Chen, Y., Luo, X., Yuan, W., Wang, J., 2020a. Thallium isotopic fractionation in industrial process of pyrite smelting and environmental implications. J. Hazard Mater. 384, 121378. https://doi.org/10.1016/j.jhazmat.2019.121378.

Liu, J., Wei, X., Zhou, Y., Tsang, D.C.W., Bao, Z., Yin, M., Lippold, H., Yuan, W., Wang, J., Feng, Y., Chen, D., 2020b. Thallium contamination, health risk assessment and source apportionment in common vegetables. Sci. Total Environ. 703, 135547. https://doi.org/10.1016/j.scitotenv.2019.135547.

Lukaszewski, Z., Jakubowska, M., Zembrzuski, W., 2018. The mobility of thallium from bottom soil of the Silesian-Cracowian zinc-lead ore deposit region (Poland). J. Geochem. Explor. 184, 11–16. https://doi.org/10.1016/j.gexplo.2017.10.009.

Mihaljevič, M., Zuna, M., Ettler, V., Šebek, O., Strnad, L., Goliáš, V., 2006. Lead fluxes, isotopic and concentration profiles in a peat deposit near a lead smelter (Příbram, Czech Republic). Sci. Total Environ. 372, 334–344. https://doi.org/10.1016/j.scitotenv.2006.09.019.

Nielsen, S.G., Wasylenki, L.E., Rehkämper, M., Peacock, C.L., Xue, Z., Moon, E.M., 2013. Towards an understanding of thallium isotope fractionation during adsorption to manganese oxides. Geochem. Cosmochim. Acta 117, 252–265. https://doi.org/10.1016/j.gca.2013.05.004.

Nielsen, S.G., Rehkämper, M., Prytulak, J., 2017. Investigation and application of thallium isotope fractionation. Rev. Mineral. Geochem. 82, 759–798. https://doi.org/10.2138/rmg.2017.82.18.

Novak, M., Pacherova, P., 2008. Mobility of trace metals in pore waters of two Central European peat bogs. Sci. Total Environ. 394, 331–337. https://doi.org/10.1016/j.scitotenv.2008.01.036.

Novak, M., Erel, Y., Zemanova, L., Bottrell, S.H., Adamova, M., 2008. A comparison of lead pollution record in Sphagnum peat with known historical Pb emission rates in the British Isles and the Czech Republic. Atmos. Environ. 42, 8997–9006. https://doi.org/10.1016/j.atmosenv.2008.09.031.

Nriagu, J.O., 1998. Thallium in the Environment. John Wiley & Sons, Inc., New York, USA.

Ostrander, C.M., Nielsen, S.G., Owens, J.D., Kendall, B., Gordon, G.W., Romaniello, S.J., Anbar, A.D., 2019. Fully oxygenated water columns over continental shelves before the Great Oxidation Event. Nat. Geosci. 12 (3), 186–191. https://doi.org/10.1038/s41561-019-0309-7.

Owens, J.D., Nielsen, S.G., Horner, T.J., Ostrander, C.M., Peterson, L.C., 2017. Thallium-isotopic compositions of euxinic sediments as a proxy for global manganese-oxide

burial. Geochem. Cosmochim. Acta 213, 291–307. https://doi.org/10.1016/j.gca.2017.06.041.

Pawełczyk, F., Chróst, L., Magiera, T., Michczyński, A., Sikorski, J., Tudyka, K., Zajac, E., 2017. Radiocarbon and lead-210 age-depth model and trace elements concentration in the Wolbrom fen (S Poland). Geochronometria 44, 40–48. https://doi.org/10.1515/geochr-2015-0046.

Peacock, C.L., Moon, E.M., 2012. Oxidative scavenging of thallium by birnessite: explanation for thallium enrichment and stable isotope fractionation in marine ferromanganese precipitates. Geochem. Cosmochim. Acta 84, 297–313. https://doi.org/10.1016/j.gca.2012.01.036.

Prytulak, J., Nielsen, S.G., Plank, T., Barker, M., Elliot, T., 2013. Assessing the utility of thallium and thallium isotopes for tracing subduction zone inputs to the Mariana arc. Chem. Geol. 345, 139–149. https://doi.org/10.1016/j.chemgeo.2013.03.003.

Prytulak, J., Brett, A., Webb, M., Plank, T., Rehkämper, M., Savage, P.S., Woodhead, J., 2017. Thallium elemental behavior and stable isotope fractionation during magmatic processes. Chem. Geol. 448, 71–83. https://doi.org/10.1016/j.chemgeo.2016.11.007.

Rader, S.T., Maier, R.M., Barton, M.D., Mazdab, F.K., 2019. Uptake and fractionation of thallium by *Brassica juncea* in a geogenic thallium-amended substrate. Environ. Sci. Technol. 53 (5), 2441–2449. https://doi.org/10.1021/acs.est.8b06222.

Rehkämper, M., Frank, M., Hein, J.R., Porcelli, D., Halliday, A., Ingri, J., Liebetrau, V., 2002. Thallium isotope variations in seawater and hydrogenetic, diagenetic, and hydrothermal ferromanganese deposits. Earth Planet Sci. Lett. 197, 65–81. https://doi.org/10.1016/S0012-821X(02)00462-4.

Rehkämper, M., Frank, M., Hein, J.R., Halliday, A., 2004. Cenozoic marine geochemistry of thallium deduced from isotopic studies of ferromanganese crusts and pelagic sediments. Earth Planet Sci. Lett. 219, 77–91. https://doi.org/10.1016/S0012-821X(03)00703-9.

Rozmus, D., 2014. Wczesnośredniowieczne Zagłębie Hutnictwa Srebra I Ołowiu Na Obszarach Obecnego Pogranicza Śląska I Małopolski (Druga Połowa XI–XII/XIII Wiek). Early Medieval District of Silver and Lead Metallurgy in the Frontier Areas of Upper Silesia and Little Poland (Second Half of the 11th-12th/13th Centuries). Księgarnia Akademicka Kraków, p. 321pp (in Polish).

Schauble, E.A., 2007. Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. Geochem. Cosmochim. Acta 71, 2170–2189. https://doi.org/10.1016/j.gca.2007.02.004.

Shotyk, W., Nesbitt, H.W., Fyfe, W.S., 1992. Natural and anthropogenic enrichments of trace metals in peat profiles. Int. J. Coal Geol. 20, 49–84. https://doi.org/10.1016/0166-5162(92)90004-G.

Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D., 1996. Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. Earth Planet Sci. Lett. 145, E1–E7. https://doi.org/10.1016/S0012-821X(96)00197-5.

Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., Van Der Knaap, W.O., 1998. History of atmospheric lead deposition since 12,370 14C yr BP from a peat bog, Jura Mountains, Switzerland. Science 281, 1635–1640. https://doi.org/10.1126/science.281.5383.1635.

Shotyk, W., Blaser, P., Grünig, A., Cheburkin, A., 2000. A new approach for quantifying cumulative, anthropogenic, atmospheric lead deposition using peat cores from bogs: Pb in eight Swiss peat bog profiles. Sci. Total Environ. 249, 281–295. https://doi.org/10.1016/S0048-9697(99)00523-9.

Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Gloor, M., Reese, S., 2001. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 14C yr BP. Geochem. Cosmochim. Acta 65, 2337–2360. https://doi.org/10.1016/S0016-7037(01)00586-5.

Shotyk, W., Krachler, M., 2004. Atmospheric deposition of silver and thallium since 12 370 14C years BP recorded by a Swiss peat bog profile, and comparison with lead and cadmium. J. Environ. Monit. 6, 427–433. https://doi.org/10.1039/b315084b.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L., Froese, D., Grant-Weaver, I., Krachler, M., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Shannon, B., van Bellen, S., Zaccone, C., 2016a. Peat bogs in northern Alberta, Canada reveal decades of declining atmospheric Pb contamination. Geophys. Res. Lett. 43, 9964–9974. https://doi.org/10.1002/2016GL070952.

Shotyk, W., Rausch, N., Nieminen, T.M., Ukonmaanaho, L., Krachler, M., 2016b. Isotopic Composition of Pb in peat and porewaters from three contrasting ombrotrophic bogs in Finland: evidence of chemical diagenesis in response to acidification. Environ. Sci. Technol. 50, 9943–9951. https://doi.org/10.1021/acs.est.6b01076.

Shotyk, W., Appleby, P.G., Bicalho, B., Davies, L.J., Froese, D., Grant-Weaver, I., Magnan, G., Mullan-Boudreau, G., Noernberg, T., Pelletier, R., Shannon, B., van Bellen, S., Zaccone, C., 2017. Peat bogs document decades of declining atmospheric contamination by trace metals in the Athabasca bituminous sands region. Environ. Sci. Technol. 51, 6237–6249. https://doi.org/10.1021/acs.est.6b04909.

Smieja-Król, B., Fiałkiewicz-Kozieł, B., Palowski, B., 2010. Heavy metal behaviour in peat – a mineralogical perspective. Sci. Total Environ. 408, 5924–5931. https://doi.org/10.1016/j.scitotenv.2010.08.032.

Smieja-Król, B., Bauerek, A., 2015. Controls on trace-element concentrations in the pore waters of two *Sphagnum*-dominated mires in southern Poland that are heavily polluted by atmospheric deposition. J. Geochem. Explor. 151, 57–65. https://doi.org/10.1016/j.gexplo.2015.01.010.

Smieja-Król, B., Janeczek, J., Bauerek, A., Thorseth, I.H., 2015. The role of authigenic sulfides in immobilization of potentially toxic metals in the Bagno Bory wetland, southern Poland. Environ. Sci. Pollut. Res. 22, 15495–15505. https://doi.org/10.1007/s11356-015-4728-8.

Smieja-Król, B., Fiałkiewicz-Kozieł, B., Michalska, A., Krzykawski, T., Smołka-Danielowska, D., 2019. Deposition of mullite in peatlands of southern Poland:

implications for recording large-scale industrial processes. Environ. Pollut. 250, 717–727. https://doi.org/10.1016/j.envpol.2019.04.077.

Tudyka, K., Pazdur, A., 2012. 14C Dating with the ICELS liquid scintillation counting system using fixed-energy balance counting window method. Radiocarbon 54, 267–273. https://doi.org/10.2458/azu_js_rc.v54i2.15832.

Vaněk, A., Chrastný, V., Teper, L., Cabala, J., Penížek, V., Komárek, M., 2011. Distribution of thallium and accompanying metals in tree rings of Scots pine (*Pinus sylvestris* L.) from a smelter-affected area. J. Geochem. Explor. 108, 73–80. https://doi.org/10.1016/j.gexplo.2010.10.006.

Vaněk, A., Komárek, M., Chrastný, V., Galušková, I., Mihaljevič, M., Šebek, O., Drahota, P., Tejnecký, V., Vokurková, P., 2012. Effect of low-molecular-weight organic acids on the leaching of thallium and accompanying cations from soil – a model rhizosphere solution approach. J. Geochem. Explor. 112, 212–217. https://doi.org/10.1016/j.gexplo.2011.08.010.

Vaněk, A., Chrastný, V., Komárek, M., Penížek, V., Teper, L., Cabala, J., Drábek, O., 2013. Geochemical position of thallium in soils from a smelter-impacted area. J. Geochem. Explor. 124, 176–182. https://doi.org/10.1016/j.gexplo.2012.09.002.

Vaněk, A., Grösslová, Z., Mihaljevič, M., Trubač, J., Ettler, V., Teper, L., Cabala, J., Rohovec, J., Zádorová, T., Penížek, V., Pavlů, L., Holubík, O., Němeček, K., Houška, J., Drábek, O., Ash, C., 2016. Isotopic tracing of thallium contamination in soils affected by emissions from coal-fired power plants. Environ. Sci. Technol. 50 (18), 9864–9871. https://doi.org/10.1021/acs.est.6b01751.

Vaněk, A., Grösslová, Z., Mihaljevič, M., Ettler, V., Trubač, J., Chrastný, V., Penížek, V., Teper, L., Cabala, J., Voegelin, A., Zádorová, T., Oborná, V., Drábek, O., Holubík, O., Houška, J., Pavlů, L., Ash, C., 2018. Thallium isotopes in metallurgical wastes/contaminated soils: a novel tool to trace metal source and behavior. J. Hazard Mater. 343, 78–85. https://doi.org/10.1016/j.jhazmat.2017.09.020.

Vaněk, A., Holubík, O., Oborná, V., Mihaljevič, M., Trubač, J., Ettler, V., Pavlů, L., Vokurková, P., Penížek, V., Zádorová, T., Voegelin, A., 2019. Thallium stable isotope fractionation in white mustard: implications for metal transfers and incorporation in plants. J. Hazard Mater. 369, 521–527. https://doi.org/10.1016/j.jhazmat.2019.02.060.

Vaněk, A., Voegelin, A., Mihaljevič, M., Ettler, V., Trubač, J., Drahota, P., Vaňková, M., Oborná, V., Vejvodová, K., Penížek, V., Pavlů, L., Drábek, O., Vokurková, P., Zádorová, T., Holubík, O., 2020. Thallium stable isotope ratios in naturally Tl-rich soils. Geoderma 364, 114183. https://doi.org/10.1016/j.geoderma.2020.114183.

Vejvodová, K., Vaněk, A., Mihaljevič, M., Ettler, V., Trubač, J., Vaňková, M., Drahota, P., Vokurková, P., Penížek, V., Zádorová, T., Tejnecký, V., Pavlů, L., Drábek, O., 2020. Thallium isotopic fractionation in soil: the key controls. Environ. Pollut. 265, 114822. https://doi.org/10.1016/j.envpol.2020.114822.

Voegelin, A., Pfenninger, N., Petrikis, J., Majzlan, J., Plötze, M., Senn, A.C., Mangold, S., Steininger, R., Göttlicher, J., 2015. Thallium speciation and extractability in a thallium- and arsenic-rich soil developed from mineralized carbonate rock. Environ. Sci. Technol. 49 (9), 5390–5398. https://doi.org/10.1021/acs.est.5b00629.

Wang, Z., Zhang, B., Jiang, Y., Li, Y., He, C., 2018. Spontaneous thallium (I) oxidation with electricity generation in single-chamber microbial fuel cells. Appl. Energy 209, 33–42. https://doi.org/10.1016/j.apenergy.2017.10.075.

Wang, J., Wang, L., Wang, Y., Tsang, D.C.W., Yang, X., Beiyuan, J., Yin, M., Xiao, T., Jiang, Y., Lin, W., Zhou, Y., Liu, J., Wang, L., Zhao, M., 2021. Emerging risks of toxic metal(loid)s in soil-vegetables influenced by steel-making activities and isotopic source apportionment. Environ. Int. 146, 106207. https://doi.org/10.1016/j.envint.2020.106207.

Weiss, D., Shotyk, W., Appleby, P.G., Kramers, J.D., Cheburkin, A.K., 1999. Atmospheric Pb deposition since the Industrial Revolution recorded by five Swiss peat profiles; enrichment factors, fluxes, isotopic composition, and sources. Environ. Sci. Technol. 33, 1340–1352. https://doi.org/10.1021/es980882q.

Weiss, D., Shotyk, W., Boyle, E.A., Kramers, J.D., Appleby, P.G., Cheburkin, A.K., 2002. Comparative study of the temporal evolution of atmospheric lead deposition in Scotland and eastern Canada using blanket peat bogs. Sci. Total Environ. 292, 7–18. https://doi.org/10.1016/s0048-9697(02)00025-6.

Weiss, D.J., Rausch, N., Mason, T.F.D., Coles, B.J., Wilkinson, J.J., Ukonmaanaho, L., Arnold, T., Nieminen, T.M., 2007. Atmospheric deposition and isotope biogeochemistry of zinc in ombrotrophic peat. Geochem. Cosmochim. Acta 71, 3498–3517. https://doi.org/10.1016/j.gca.2007.04.026.

Wick, S., Peña, J., Voegelin, A., 2019. Thallium sorption onto manganese oxides. Environ. Sci. Technol. 53 (22), 13168–13178. https://doi.org/10.1021/acs.est.9b04454.

Wick, S., Baeyens, B., Fernandes, M.M., Göttlicher, J., Fischer, M., Pfenninger, N., Plötze, M., Voegelin, A., 2020. Thallium sorption and speciation in soils: role of micaceous clay minerals and manganese oxides. Geochem. Cosmochim. Acta 288, 83–100. https://doi.org/10.1016/j.gca.2020.07.037.

Xiao, T., Guha, J., Boyle, D., Liu, C.Q., Chen, J., 2004a. Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China. Sci. Total Environ. 318, 223–244. https://doi.org/10.1016/S0048-9697(03)00448-0.

Xiao, T., Guha, J., Boyle, D., Liu, C.Q., Zheng, B., Wilson, G.C., Rouleau, A., Chen, J., 2004b. Naturally occurring thallium: a hidden geoenvironmental health hazard? Environ. Int. 30, 501–507. https://doi.org/10.1016/j.envint.2003.10.004.

Xiao, T., Yang, F., Li, S., Zheng, B., Ning, Z., 2012. Thallium pollution in China: a geo-environmental perspective. Sci. Total Environ. 421–422, 51–58. https://doi.org/10.1016/j.scitotenv.2011.04.008.

Zuna, M., Mihaljevič, M., Šebek, O., Ettler, V., Handley, M., Navrátil, T., Goliáš, V., 2011. Recent lead deposition trends in the Czech Republic as recorded by peat bogs and tree rings. Atmos. Environ. 45, 4950–4958. https://doi.org/10.1016/j.atmosenv.2011.06.007.

Zuna, M., Ettler, V., Šebek, O., Mihaljevič, M., 2012. Mercury accumulation in peatbogs at Czech sites with contrasting pollution histories. Sci. Total Environ. 424, 322–330. https://doi.org/10.1016/j.scitotenv.2012.02.049.