



Miocene colored waters: A new significant source of thallium in the environment



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ABSTRACT

Thallium is a toxic non-essential element which is subject to some dispersion in the environment due to industrial activity and natural processes. There is a need for this dispersion to be monitored. Colored Miocene water seems to be a newly discovered significant source of such dispersion.

The presence of colored water within the brown coal Miocene formation is related to the formation of organic sediments in that period which changed into layers of brown coal.

The aim of this study was to investigate the concentration of Tl in colored waters, both in soluble form and entrapped in suspended solid matter (SS). Tl was determined by flow-injection differential-pulse anodic stripping voltammetry (FI-DP-ASV).

It was found that Miocene colored waters from the Wielkopolska region contain very high Tl concentrations, and are thus a newly discovered significant source of Tl pollution in the environment. The concentrations are higher than the results for surface water by 2–3 orders of magnitude, and are a serious cause for concern. The majority of the total Tl in the colored waters is entrapped in suspended solids (more than 95% in the majority of samples). Even a low percentage of soluble Tl, however, creates a high concentration of the element in water (median $0.11 \mu\text{g L}^{-1}$), which is approximately 10 times higher than in surface water from the River Warta. Tl concentration in SS is very high (median $15 \mu\text{g g}^{-1}$) and exceeds by one order of magnitude the concentration of the element in crude Zn–Pb ores.

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1. Introduction

Thallium is a toxic, non-essential element having very limited application due to the

toxicity of its compounds to humans, animals, plants and microorganisms (Nriagu, 1998; Kazantzis, 2000; John Peter and Viraraghavan, 2005). Data have been published indicating a relationship between thallium concentration in the environment and the occurrence of cardiovascular disease (Wappelhorst et al., 2000). Tl(I) mostly occurs in geochemical systems, where it substitutes for potassium(I) in such silicates as feldspar or mica. The thallium content in igneous rocks ranges from 0.05 to 1.7 ppm (Nriagu, 1998). In hydrothermal systems, thallium is bound to sulfides such as pyrite, sphalerite or marcasite. Weathering of sulfides leads to Tl dispersion in sedimentary rocks, iron and manganese hydroxides and organic matter, including coals.

Dispersion of Tl in the environment occurs due to industrial activity and natural processes. Tl concentration in non-polluted soils ranges between 0.08 and 1.5 ppm (Wenqi et al., 1992; Lukaszewski and Zembruski, 1992; Ivanova et al., 1996; Asami et al., 1996; Tremel et al.,

1997). Higher thallium concentrations have been exhibited by soils in the vicinity of former ore mines (73 ppm) (Sager, 1998), from thallium-rich sulfide ores of mercury, arsenic and gold (40–124 ppm) (Xiao et al., 2004a, 2004b), from pyrite processing areas (5–15 ppm) (Yang et al., 2005), and from a lead-zinc mining zone (8.8–27.8 ppm) (Lis et al., 2003). Recent papers of Vaněk et al. (2011, 2012, 2015) reported a process of Tl release together with sphalerite weathering in the rhizosphere, as well as the role of illite and birnessite in Tl bioavailability in soil.

Investigation of Tl dispersion in the environment is mostly focused on mining areas as a source of Tl pollution. Colored Miocene water is an entirely new significant source of such dispersion.

The presence of colored water within the brown coal Miocene formation is related to the formation of organic sediments in that period, mainly vast peat bogs, which changed into layers of brown coal. The color is not determined by the layers of coal, however, but by organic matter dispersed within sand sediments. In such an environment, groundwater is enriched with humic acids, which give it its color (Górski et al., 2014).

The area of occurrence of colored water in the Wielkopolska region stretches mainly along the meridian length of the Warta valley, starting at Kościan and Śrem in the south and running to Oborniki Wielkopolskie and Obrzycko in the north. In this area, zones of colored water occur in the north-western part, within the area of Lower Jurassic formations, and form two stretches. One stretch lines the tectonic structures of the

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Poznań fault and the Szamotuły structure, while the other runs along the line Obrzycko–Szamotuły–Więckowice–Joanka (near Trzcielín) (Górski et al., 2014).

The Miocene aquifer is supplied by the process of infiltration of water from the aquifers covered by layers of Quaternary moraine clays and silts from the Poznań series of the upper Miocene. The process occurs most frequently in places with decreased thickness of isolation layers, and also where the Poznań silt layers were glaciotectionally disturbed, and locally in places of hydraulic contact through hydrogeological windows, which were formed as a result of erosive cuts in the Poznań silts in buried valley areas (Przybyłek, 1986; Dąbrowski et al., 2007; Siepak et al., 2010). The ascending inflow of water from the lower basement occurs in the deepest parts of the Miocene formations, in the layers where deposits of high permeability occur and along some hydraulically active tectonic faults.

The natural regional transit zone for the discussed groundwater aquifer consists of the Warsaw–Berlin Old Valley, the Barycza Old Valley and the Warta Valley. Based on isotopic studies by Dąbrowski et al. (1999) and Górski et al. (2014), the age of infiltration water for the supply areas of the Miocene aquifer was determined as 2000–2600 years, while in the regional transit layers the age of the water in the aquifer was determined as 27,000–43,800 years.

The aim of this study was to investigate the concentration of Tl in this water, both in soluble form and entrapped in suspended solid matter (SS). Tl was determined by flow-injection differential-pulse anodic stripping voltammetry (FI-DP-ASV). This analytical technique enables the determination of Tl at concentrations below 1 picomole per liter (of the order of 100 picograms per liter; LOD equal to 0.25 pM) (Jakubowska et al., 2008) and corresponds well with Tl determination in environmental samples (Jakubowska et al., 2007; Łukaszewski et al., 2012).

2. Experimental

2.1. Sample collection

The study covered a part of the Central Wielkopolska region within which the colored water of the Miocene layer is marked by a color of above 80 mg Pt/L, and its vicinity (Fig. 1). The investigated water was neutral (median pH 7.1) and contained Ca(II), Mg(II), Na(I), K(I) in average concentrations of 65, 16, 67 and 4.3 mg/L respectively, as well as 40 mg/L of chlorides (Siek et al., 2010). The samples of groundwater from the Miocene aquifer were collected from 16 wells, 3 hydrogeological boreholes and 11 artesian flows. Water samples were collected from active wells equipped with deep-water pumps which had been working for a minimum of 24 h prior to sampling. The study holes were cleaned by means of a triple exchange of the water profile (Witczak and Adamczyk, 1994; Witczak et al., 2013) using a deep-water pump with a capacity of 3–15 m³/h. The depth of water filtration ranged from 73 to 268 m below the surface. The color was determined on the research site. The water samples were collected in Nalgene® (Rochester, USA) polyethylene bottles (LDPE). Depending on the determined water quality indicators, the samples were fixed with 60% HNO₃ Ultrapur® (Merck, Darmstadt, Germany). After collection, the samples were transported to the chemical laboratory in a car refrigerator at a temperature of 4 ± 2.5 °C.

2.2. Apparatus and reagents

A MicroAutolab electrochemical analyzer from Ecochemie (Utrecht, Netherlands) was used, together with a previously described (Jakubowska et al., 2008) flow-through cell of wall-jet type, which facilitates medium exchange and medium circulation. The differential-pulse amplitude was 50 mV. A mercury film electrode based on glassy carbon was used as a working electrode. A saturated calomel electrode was the reference electrode, and a platinum wire

was the auxiliary electrode. The mercury film was deposited over a period of 10 min from a solution consisting of 0.05 mM mercury(II) nitrate and 0.1 M potassium nitrate. Only one mercury film was required for a whole day's measurements.

A certified reference material – GBW 07401 soil of Chinese origin, containing $1 \pm 0.2 \mu\text{g g}^{-1}$ of Tl – was used. Hydroxylamine chloride, ammonia solution (25%), nitric acid (65%), hydrogen peroxide (30%), acetic acid (99.8%), EDTA and ascorbic acid (all puriss.p.a., supplied by Fluka), hydrofluoric acid (pract. 73%, Fluka), and ammonium acetate (puriss.p.a., Aldrich) were used.

All solutions were prepared in water by reverse osmosis in a Watek-Demiwa 5 Rosa system (Czech Republic), followed by triple distillation from a quartz apparatus. Only freshly distilled water was used.

2.3. Procedures

2.3.1. Preparation of samples for soluble Tl determination

50 mL of a water sample was filtered through a 0.45 μm filter, and 0.908 g EDTA was added. The pH of the solution was adjusted to 4.5 using 25% aqueous ammonia solution or 2 M nitric acid. 10 mL of the prepared solution was used for voltammetric determination of Tl, as described in Section 2.3.4.

2.3.2. Preparation of samples for total Tl determination

10 mL of the tested water was placed in a tall teflon beaker and was gently heated on a graphite heater until evaporation. The residue of the sample was moistened with water, treated with 2 mL of 73% hydrofluoric acid and set aside for 2 h. At the end of this period, an additional 0.6 mL of hydrofluoric acid was added. The obtained solution was heated on a graphite heater until evaporation. Then 1 mL of 67% nitric acid was added, as well as 2.5 mL of 30% hydrogen peroxide in 0.5 mL portions for the mineralization of residual organic substances. The sample was evaporated after the addition of each hydrogen peroxide portion. Finally 1 mL of nitric acid was added, and the beaker was covered with a watch glass and heated for 3 h. Next 2.5 mL of 1 M ascorbic acid and 6.25 mL of 0.2 EDTA were added, and the pH adjusted to 4.5 using ammonia. The solution was then transferred into a 25 mL volumetric flask, which was filled up with water. 10 mL of the prepared solution was used for voltammetric measurement of Tl concentration (as described in Section 2.3.4).

2.3.3. Determination of suspended solids concentration

10 mL of the tested water was placed in a previously weighed beaker and was gently heated on a graphite heater until complete evaporation. The beaker with the residue was kept in a laboratory dryer at 105 °C until a constant weight was attained. The result was corrected by the weight of 10 mL filtered water in order to take account of dissolved salts. The concentration of SS-entrapped Tl was calculated by dividing the total Tl concentration ($\mu\text{g L}^{-1}$) by the SS concentration (g L^{-1}).

2.3.4. Determination of Tl by FI-DP-ASV

Determination was performed in accordance with the procedure described previously (Jakubowska et al., 2008). Tl preconcentration was carried out at a potential of –900 mV vs. SCE over 60–1200 s, depending on the Tl concentration. Voltammograms were recorded after medium exchange on pure 0.05 M EDTA. The results were evaluated on the basis of several standard additions (typically 3 additions). The detection limit of the method (calculated on a 3SD basis) was 50 pg L^{-1} (0.25 pM). Due to the use of EDTA base electrolyte, the method tolerates a 1000-fold excess of lead.

2.3.5. Quality control measurements

Control measurements were performed together with each series of experiments. The average of 15 control measurements of the total Tl concentration in the reference material (soil GBW07401) was $0.90 \pm$

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