



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 Zembrzusi, 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 Trzcielina) (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; Lukaszewski 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 (Siekpak 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 ± 0.2 µg 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 (µg 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 ±

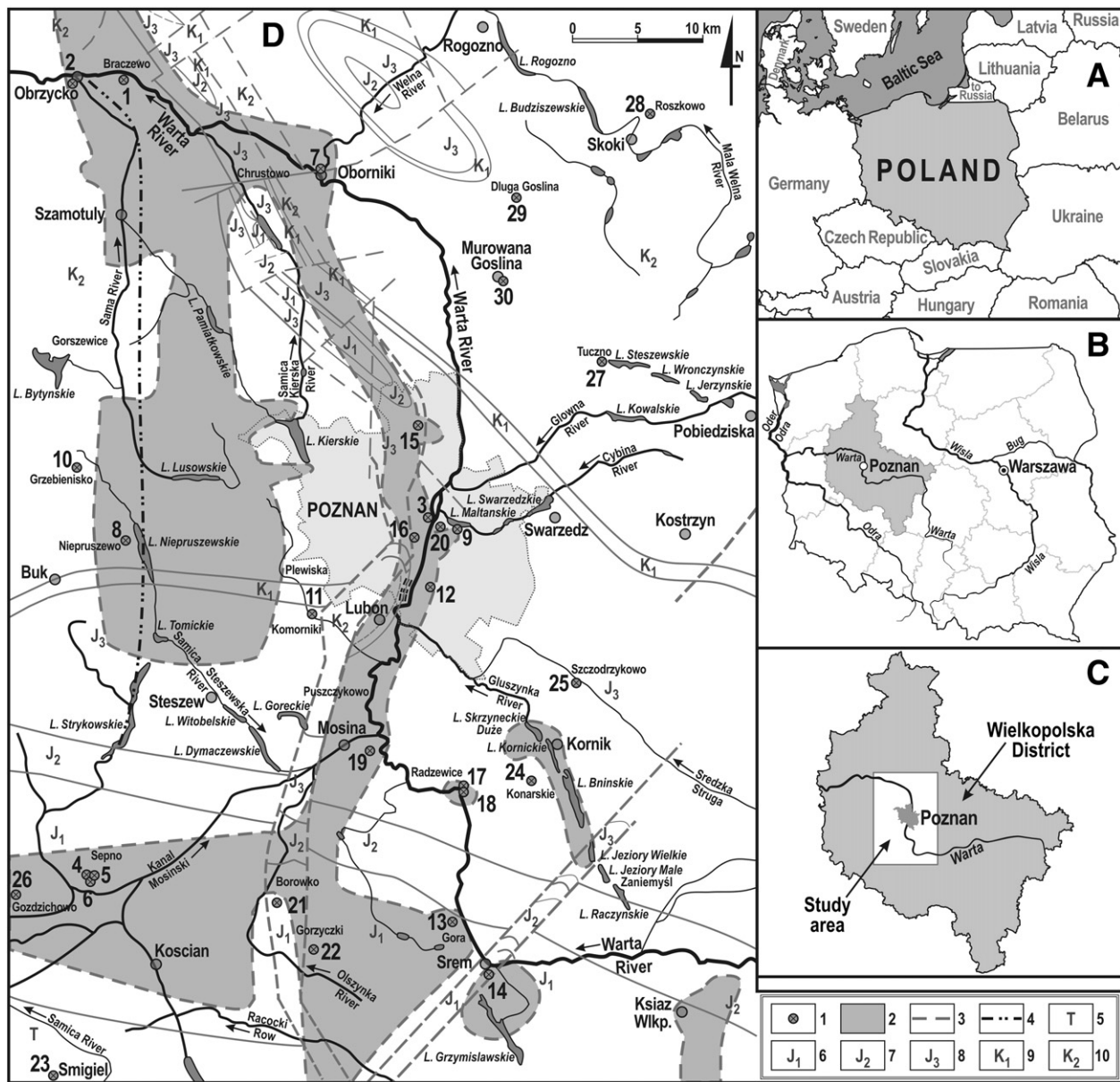


Fig. 1. Sampling points and geological background of the study area. 1 – sample collection points; 2 – zone with water color >80 mg Pt/L; 3 – tectonic faults; 4 – estimated line of tectonic fault based on hydrochemical data (Górski, 1989); 5 – Triassic; 6 – Lower Jurassic; 7 – Middle Jurassic; 8 – Upper Jurassic; 9 – Lower Cretaceous; 10 – Upper Cretaceous.

$0.06 \mu\text{g g}^{-1}$, and the S.D. was $0.13 \mu\text{g g}^{-1}$. The results obtained were within the range $0.76\text{--}1.13 \mu\text{g g}^{-1}$. The certified value was $1.0 \pm 0.2 \mu\text{g g}^{-1}$.

3. Results and discussion

3.1. Total Tl concentration in colored waters and in reference samples

20 samples of colored waters and 10 samples of water from the reference area located outside the colored water area were analyzed for total Tl concentration as described above. The results are shown in Fig. 2A, and the results distribution in Fig. 2B. The results for Tl concentration in the colored waters are distributed between 0.44 and $26 \mu\text{g L}^{-1}$ with a median of $4.05 \mu\text{g L}^{-1}$, while those for water samples from the reference area range between 0.46 and $11 \mu\text{g L}^{-1}$ with a median of $1.4 \mu\text{g L}^{-1}$. It is clear that the colored waters contain, on average, higher Tl concentrations than the reference water from the areas in the vicinity of the colored water area. The highest total Tl concentrations were

determined in samples from locations near the River Warta between the towns of Śrem and Mosina, upstream of the city of Poznań.

Surprisingly, several high total Tl concentrations were also determined in samples from outside the colored water area. These results are higher than the Tl concentration in acidic mine water ($1.5 \mu\text{g L}^{-1}$) (Law and Turner, 2011). Higher Tl concentrations were determined in Chinese deep mine groundwater sampled near the town of Lanmuchang (mean value $62 \mu\text{g L}^{-1}$) by Xiao et al. (2003, 2004a, 2004b). It should be noted that the results concerning colored water are higher than the results for surface water by 2–3 orders of magnitude (Geochemical Atlas of Europe, 2005) and are a serious cause for concern. These results should be taken into account when considering colored water as a source of drinking water, as well as the environmental impact caused by artesian flow.

3.2. Soluble thallium concentration

The same samples were analyzed for soluble Tl concentration. The results are shown in Fig. 3A, and the results distribution in Fig. 3B. The

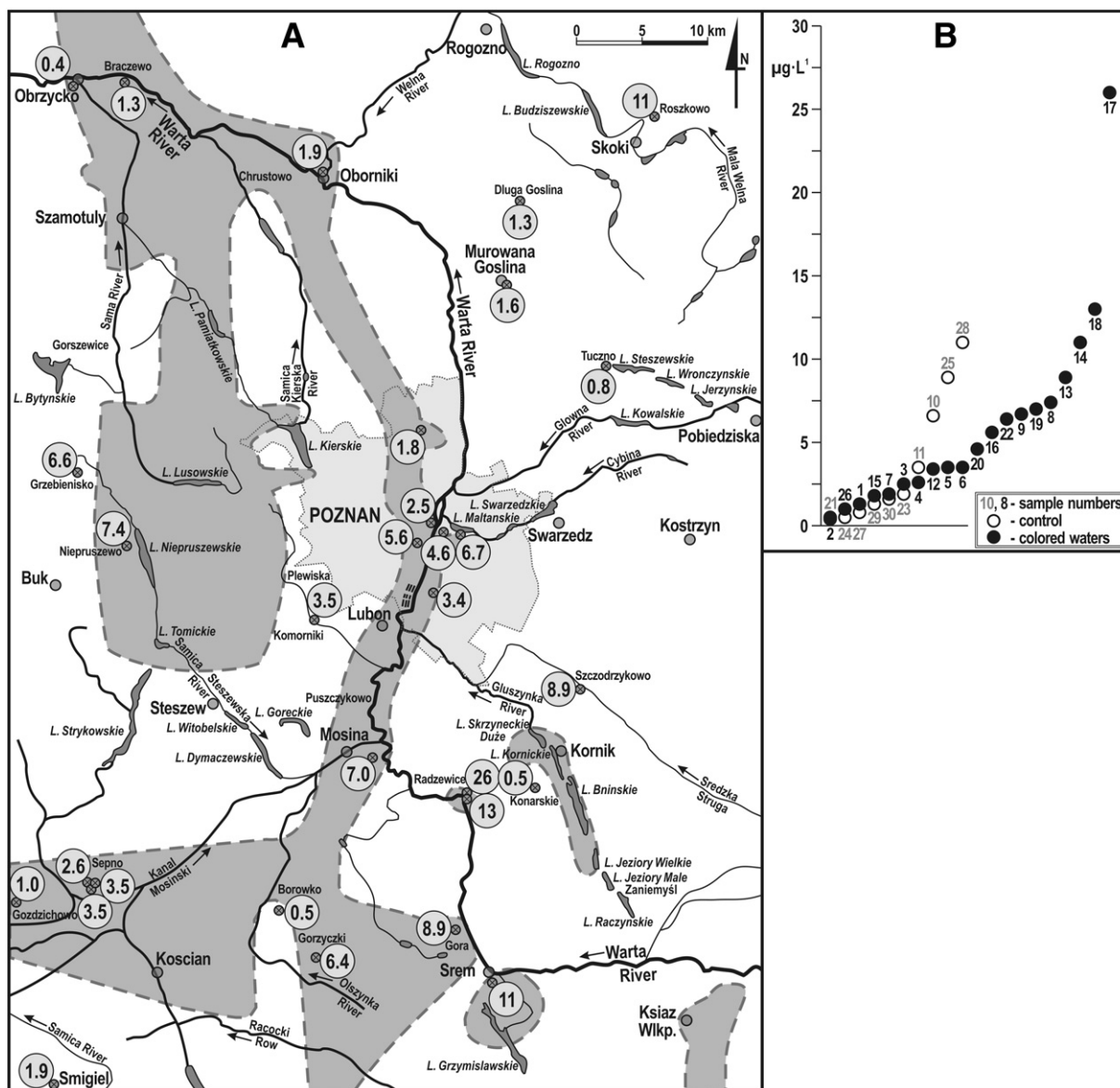


Fig. 2. Total concentration of thallium in the investigated water samples ($\mu\text{g L}^{-1}$) (A) and distribution of results ($\mu\text{g L}^{-1}$) (B). Dark circles: colored water; open circles: reference samples.

percentage contribution of soluble Tl to the total concentration is given in Fig. 3C. The results for soluble Tl concentration in the colored waters are distributed between 0.004 and 0.47 $\mu\text{g L}^{-1}$ with a median of 0.11 $\mu\text{g L}^{-1}$, while those for water samples from the reference area range between 0.01 and 0.11 $\mu\text{g L}^{-1}$ with a median of 0.041 $\mu\text{g L}^{-1}$. It is clear that the colored waters contain, on average, higher Tl concentrations than the reference water from the area adjacent to the colored water area. However, a very significant observation is the generally low percentage of soluble Tl, as indicated in Fig. 3C. Apart from a few samples, the percentage of soluble Tl in the colored waters lies between 0.16% and 3.7%. As regards the reference water samples, the soluble Tl percentage is also small, but higher than in the case of the colored waters. The conclusion drawn from this difference between total and soluble Tl is that the majority of the element is accumulated in suspended solids (SS).

In order to analyze the reasons for differences in the percentage of thallium solubility, three samples from the closest neighborhood were considered (samples 4, 5 and 6). These samples exhibit similar total concentrations of thallium (2.6, 3.5 and 3.5 $\mu\text{g L}^{-1}$ respectively), but very different percentages of soluble thallium (11.5%, 3.7% and 0.8% respectively). The samples represent different depths of water

sampling: 275, 180 and 117 m respectively. Hence the depth of water sampling seems to be the significant factor behind the thallium solubility. The chemical explanation of this effect is probably that the samples from deeper wells contain more thallium(I) than the samples from shallower wells.

Another factor to be taken into account is the concentration of chlorides. Apart from sample 16, the other samples containing high soluble thallium concentration also exhibit a high concentration of chlorides. There is no evidence that chlorides are responsible for the greater solubility of thallium. Numerous samples having high chloride concentration have low concentrations of soluble thallium. The presence of chlorides is rather evidence of water movement from deeper layers, because deeper water contains high chloride concentration. This movement may also be caused by water withdrawing or moving by artesian flow from the investigated wells.

3.3. Thallium concentration in suspended solid

20 samples of colored waters and 10 samples of water from the reference area located outside the colored water area were analyzed for concentration of thallium entrapped in SS, as described above. The

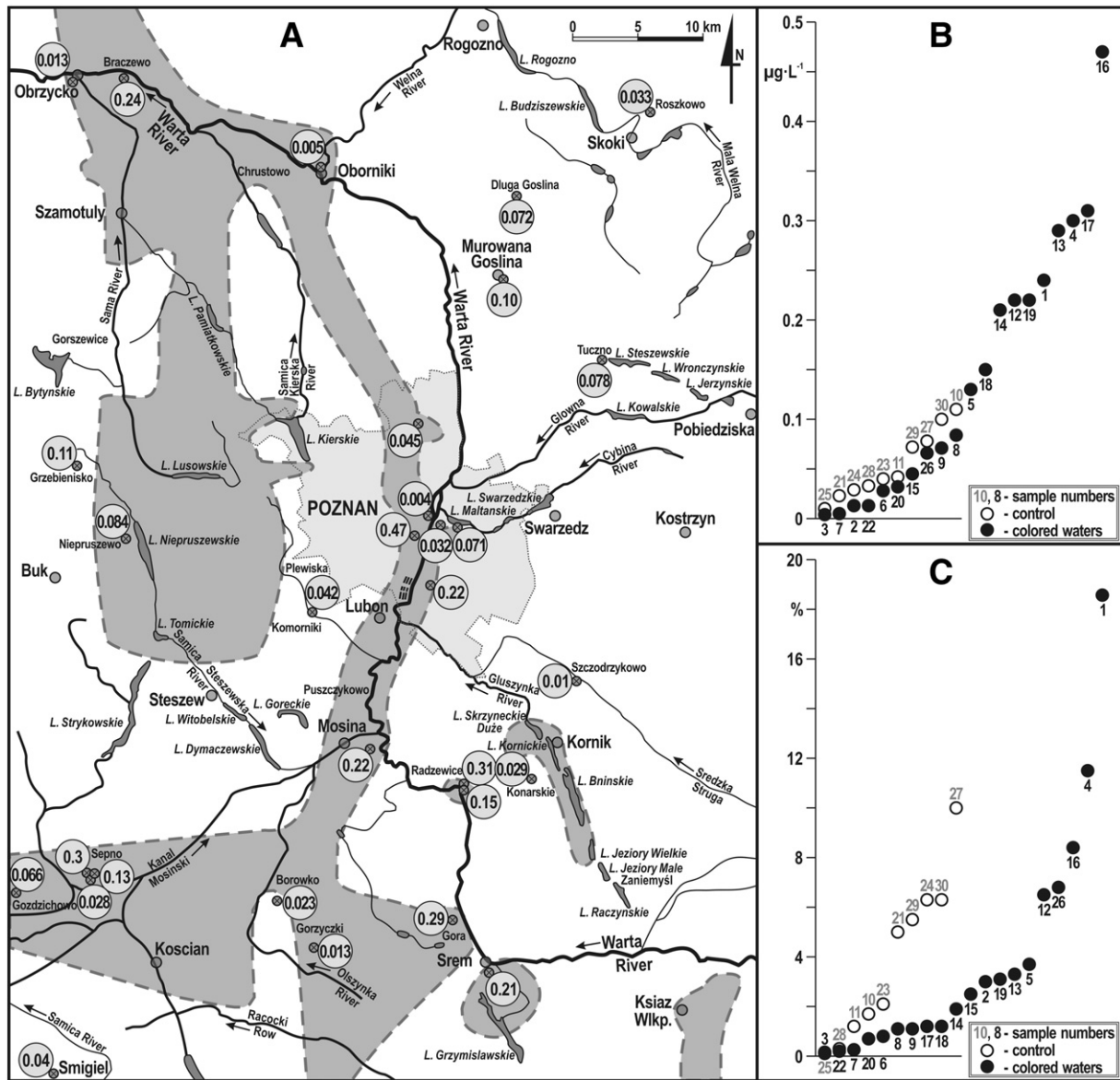


Fig. 3. Concentration of soluble thallium in the investigated water samples ($\mu\text{g L}^{-1}$) (A), distribution of results ($\mu\text{g L}^{-1}$) (B) and percentage of soluble thallium in the total thallium (C). Dark circles: colored water; open circles: reference samples.

results are shown in Fig. 4A, and the results distribution in Fig. 4B. The SS concentration in these samples was also determined. The results are shown in Fig. 4C. Generally, SS concentration in colored waters ranges between 0.033 and 2.7 g L^{-1} with a median of 0.5 g L^{-1} , and with the majority of samples containing between 0.37 and 0.73 g L^{-1} SS. Surprisingly, this concentration is generally lower than those in samples of the control waters, which contain between 0.29 and 1.6 g L^{-1} SS with a median of 0.9 g L^{-1} .

The concentration of thallium entrapped in SS in colored waters is very high, ranging between 0.16 and $58 \mu\text{g g}^{-1}$ with median $15 \mu\text{g g}^{-1}$ and with the majority of samples having concentrations above $10 \mu\text{g g}^{-1}$. It is worth comparing these values with the thallium concentration in zinc–lead ores, which have hitherto been considered to be the most concentrated source of thallium dispersion in the environment. Crude ores contain $1.95 \mu\text{g g}^{-1}$ of thallium, while the ‘blende’ concentrate obtained in flotation contains $8.23 \mu\text{g g}^{-1}$ (Karbowska et al., 2014). Thus the thallium concentrations in the investigated colored waters are alarmingly high and deserve more attention. The highest thallium concentrations in SS were found in samples from locations along the River Warta, similarly as in the case of total thallium

concentration. It should be noted that several samples from the control area also contain thallium concentrations in SS at a level of $10 \mu\text{g g}^{-1}$. Generally, thallium in the Miocene water from the vicinity of Poznań deserves more attention.

Cases with the highest and lowest concentrations of thallium entrapped in SS are not frequent (see Fig. 4B). Samples 7, 20 and 17 represent the highest value of thallium entrapped in SS; however, samples 7 and 20 have very low concentrations of SS, which makes it clear that thallium will be highly concentrated in suspended solids. The case of sample 17 is different: this sample represents the highest total concentration of thallium in the colored waters, as well as the second highest concentration of soluble thallium. On the other hand, the lowest concentration of thallium entrapped in SS (sample 2) corresponds to the highest SS concentration.

The occurrence of the highest concentrations of total, soluble and SS-entrapped thallium along the River Warta is probably connected with the Poznań–Gostyń fault graben region, which is developed longitudinally in the Mesozoic basement of the Miocene aquifer. The fault graben region is marked by the occurrence of active tectonic faults, with deep circulating water ascending from the Mesozoic basement. The zones of

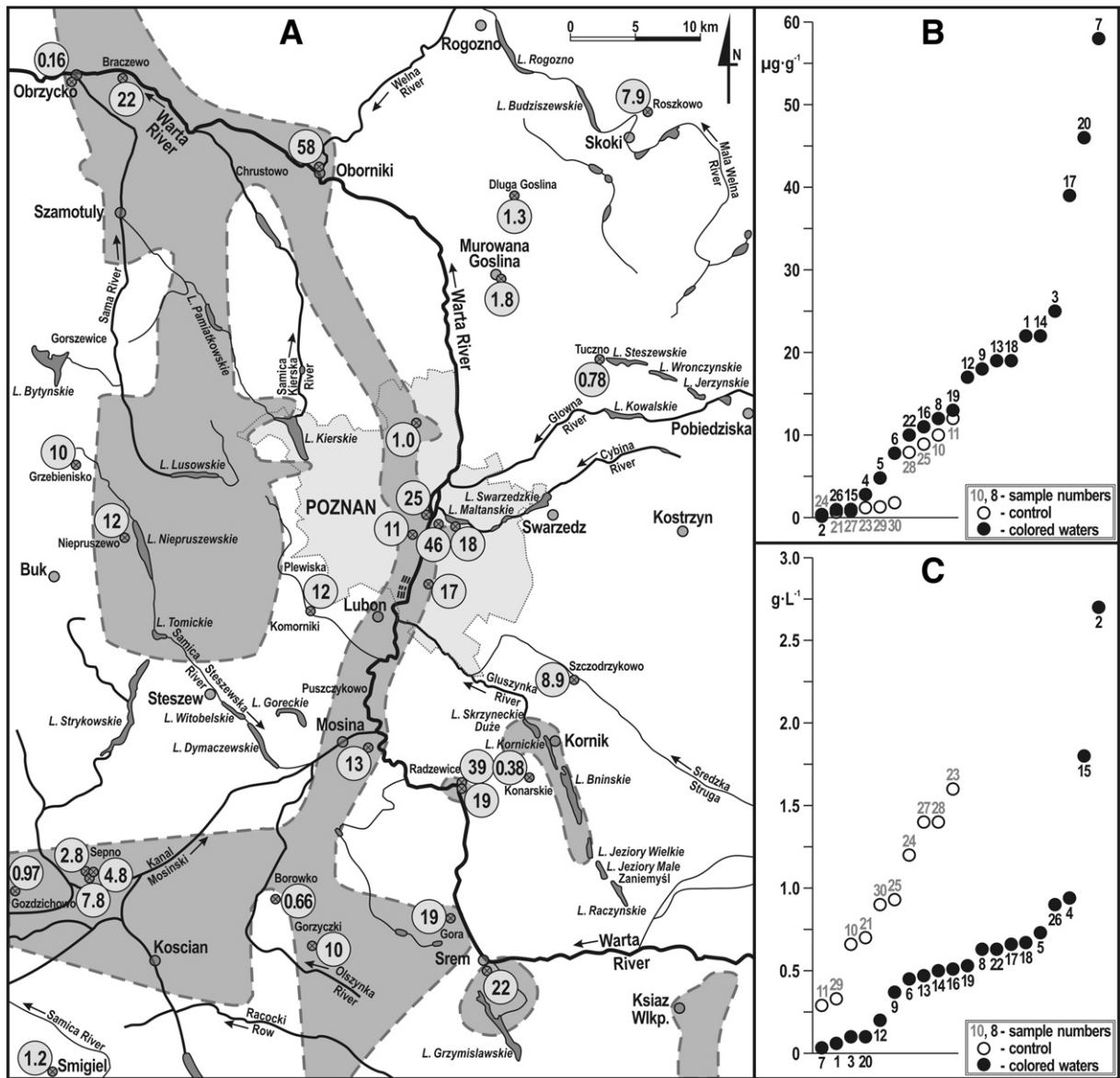


Fig. 4. Thallium concentration in suspended solids ($\mu\text{g g}^{-1}$) (A), distribution of results ($\mu\text{g g}^{-1}$) (B), and concentration of suspended solids (g L^{-1}) (C) in the investigated samples.

anomalous color are probably connected with discharge from the Mesozoic basement (Siepak et al., 2010) or with a layer of silts and brown coals covering fine-grained and dusty sand deposits of the Upper Miocene.

The brown color of SS suggested that it may originate from manganese oxides. To investigate the nature of thallium entrapment in SS, the sediment was treated with a reducible medium (0.1 M hydroxylamine hydrochloride adjusted to pH 2 with 2 M nitric acid) and shaken at 25 °C for 16 h. An insignificant rise in thallium concentration was observed, showing that the element had not bonded to the manganese-containing fraction. Certainly, such a conclusion is superficial, because only easy reducible compounds are dissolved by this reagent. It seems that Tl in SS is most likely entrapped in organic matter of humic acid structure. The mobility of Tl from SS deserves further investigation.

4. Conclusions

Miocene colored waters from the Wielkopolska region contain very high thallium concentrations and constitute a newly discovered

significant source of thallium in the environment. These concentrations are higher than the results for surface water by 2–3 orders of magnitude, and are a cause for serious concern. The majority of the thallium from the colored waters is entrapped in suspended solids (more than 95% in the majority of samples). Even this low percentage of soluble thallium creates a high concentration of the element in water (median $0.11 \mu\text{g L}^{-1}$). This is approximately 10 times greater than in surface water from the River Warta (Lukaszewski et al., 1996). Thallium 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. It should be noted that many of the control water samples also exhibit high thallium concentrations.

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