Mobile forms vs the total content of thallium in activated sludge

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Abstract: Sewage sludge from municipal wastewater treatment plants is currently a serious environmental problem, given its diversity due to the variability of time and heavy metal content. Current research on the monitoring of heavy metals is based on the determination of Pb, Cd, Hg, Ni, Zn, Cu and Cr. This makes any thallium content data difficult to access. The study estimated the degree of contamination of sewage sludge with thallium. The sludge samples came from a sewage treatment plant located in Poland. The results are presented for the total concentration of thallium and its mobile forms. These samples were analyzed by differential pulse voltammetry. The results showed that the average thallium content was 0.203 μg/g and its mobile form was 0.025 μg/g. The conducted research shows that almost 13% of thallium from sewage sludge can be gradually released into the environment.

Abbreviations: BCR Community Bureau of Reference; MFE Mercury film electrode; SCE Saturated Calomel Electrode

Introduction

According to the present regulations in Poland all sewage sludge created in the process of waste treatment in communal and industrial sewage treatment plants is considered as a waste (Resolution of the Council of Ministers of Polish Government 2006). Until recently the problem of sludge management received little attention and was underestimated. However, during the last years in Poland as well as in other countries of the European Union the volume of sewage sludge created is increasing (Fytiri and Zabaniotou, 2008). One of the reasons of this is the tightening of the quality requirements for wastewater discharges to surface waters (Council Directive 1991). It is worth to notice that the main disposal method for municipal sewage sludge in Poland is landfill (Woźniak et al. 2004). Chemistry of sewage sludge is highly varied. Organic substances and micronutrients making the sludge a valuable soil component and fertilizer suggest a natural use of sludge (Smith et al. 2009, Merrington et al. 2003). However, in the sewage sludge there are not only substances that are necessary for the growth of plants and microorganism, there are also toxic substances, among them heavy metals (Szarek, 2020). Their presence is the result of industrial wastewater (metallurgical, tan, dye) in municipal sewage but they also come from household waste and surface runoff. The present regulations limiting the concentration of heavy metals in municipal sewage sludge refer to the total amount of lead, cadmium, mercury, nickel zinc, copper and chromium (Regulation of the Minister of the Environment 2002). This makes any data referring to the contents of another toxic metal, thallium, hardly available. It is necessary to stress that there are big amounts of thallium coming from zinc smelters, lead smelters, cement plants and the highest levels of this element can be found near heat and power plants (De La Rochebrochardet al. 2013, Pathak et al. 2009). Similar to mercury, cadmium and lead, the toxicity of thallium is especially high for humans, animals, plants and microorganisms. This is due to the similarity between K(I) and Tl(I) ions which allows the latter to enter the same metabolic pathways. When thallium substitutes potassium in many biochemical reactions it changes physiological processes. It inhibits the functioning of important enzymes. Moreover, thallium forms bonds with sulphydryl groups that cause an increased permeability of mitochondrial membrane and irreversible damage to ribosomes (Łukaszewski et al. 2010).

The thallium content in the lithosphere ranges from 0.1 to 1.0 μg/g (Zitko, 1975). Unpolluted soils usually contain from 0.08 to 1.5 μg/g (Xiao et al. 2004, Vanek et al. 2013). Higher thallium concentrations – up to 120 μg/g – are found in soils in the areas of zinc and lead mining and metallurgy (Alvarez-Ayuso et al. 2013, Viraraghavan and Srinivasan, 2011). Rapid technological and industrial development has increased the risk of thallium pollution in the environment. It is estimated that approx. 3,000–5,000 t of thallium is released into the environment every year as a result of industrial activities (Dmowski et al 2002), of which approx. 1,000 t from coal combustion (Galván-Arzate and Santamaria, 1998).
A significant amount of thallium is bound to the sulphides (approx. 70%) and the remainder is related to aluminosilicates and organic compounds (Querol et al. 1995). The products of coal combustion – slag and ash – contain higher concentrations of thallium. During combustion of coal and the production of cement, thallium oxidizes at higher temperatures and then condenses on the surface of the ash particles in low temperature regions. The prolonged contact time of ash with coal combustion – slag and ash – contain higher concentrations and organic compounds (Querol et al. 1995). The products of (approx. 70%) and the remainder is related to aluminosilicates

A significant amount of thallium is bound to the sulphides (Finkelman, 1999). Sewage sludges formed in sewage treatment plants have high soil-forming and fertilizing values. They can be used in agriculture as a valuable organic fertilizer, provided that they are hygienized and the content of organic and inorganic micropollutants (heavy metals) will not have negative effects on the soil environment (Kowalik et al. 2020).

The enrichment of certain niches with thallium-based compounds is a direct result of the specific transport pattern of thallium from sewage sludge that can be used, e.g., for brownfield rehabilitation, as shown in Scheme 1.

Thallium from sewage sludge dissipates into the environment and contaminates soil and water, air, and thus, can enter the food chain and accumulate in living organisms, causing serious disturbances and ultimately leading to death.

The data on the total content of thallium in environmental samples do not help estimating possible thallium pollution of soils and waters, because bioavailability and toxicity of an element depends on its chemical forms (Vanek et al. 2011). In the literature, there are many sequential extraction methods for heavy metal fractionation in environmental samples. Single stage extraction is successfully used in examination of sewage sludge, solid waste and soils for determination of the bioavailable fraction. It is used to estimate mobility of the metals (Frankowski et al. 2010, Quevauviller, 2002).

The single extraction is a simple and fast method which provides information concerning a potential environmental hazard. It involves the use of so called ‘soft extractants’, which include non-buffered salt solutions (e.g. KCl, CaCl₂, NaNO₃), acid of different concentrations (e.g. 0.1 M or 1 M HCl) and solutions of complexant agents (e.g. EDTA, DTPA) (Quevauviller, 2002).

Majority of researchers use the inversion voltammetry techniques (stripping methods) for analysis of thallium content (Svancara et al. 1997). These techniques offer the best combination of sensitivity and selectivity compared to other instrumental methods, for example ICP-MS. Voltammetric stripping methods are among the most efficient electrochemical techniques used for trace and speciation analysis.

The aim of the present research was to estimate thallium pollution of the sludge from a municipal wastewater treatment plant. An additional task was to verify whether the 0.1 M HCl extractant, highly effective in the case of Cd, Zn, Cr, Ni extraction, would be equally effective in the case of Tl extraction, and whether and to what extent thallium migrates to the environment.

Materials and methods

Site description and samples

Samples of sludge from municipal wastewater treatment plant were taken according to PN-EN ISO 5667-13:2011 from the top layer (0–10 cm). Sewage sludge samples from the municipal sewage treatment plant located near Poznań, Poland, were collected in polyethylene containers The samples were dried at 110°C until constant weight. A representative sample was obtained by carefully milling the joined sludge samples using an agate mortar. The samples were then sieved through a nylon fiber sieve, particle size <70 μm, and stored in polyethylene bottles in a desiccator at room temperature.

Apparatus and reagents

An Ecochemie (Utrecht, Netherlands) MICROAUTOLAB electrochemical analyzer was used together with the wall-
-jet flow cell described earlier (Łukaszewski et al. 2012). The differential pulse amplitude was 50 mV. A mercury film electrode based on glassy carbon was used as the working electrode. The reference electrode was a saturated calomel electrode, the auxiliary electrode was a platinum wire. The mercury film was deposited over 600 s from a solution consisting of 0.05 mM mercury (II) nitrate and 0.1 M potassium nitrate. Ammonia solution (25 percent), nitric acid (65 percent), hydrogen peroxide (30 percent), EDTA and ascorbic acid (all puriss.pa, supplied by Fluka), hydrochloric acid, hydrofluoric acid (73 percent work), and Fluka were used. To verify the correctness of the analytical process, the certified reference material was used – soil GBW 07401 of Chinese origin, containing 1.0 ± 0.2 μg/g of thallium.

**Procedures**

**Total decomposition of sewage sludge**

A complete decomposition in an open system was applied. A weighed sample of the sludge (0.25 g) was placed in a 200 mL tall form teflon beaker and 2 mL of hydrofluoric acid (73%) was added. Next, 1 mL of 65% HNO₃ and 0.5 mL – 2.5 mL portions of 30% H₂O₂ were added. The sample was carefully evaporated after each stage. The dry residue obtained was dissolved in 1 mL of hot concentrated (65%) HNO₃ for 2 h. During this stage each teflon beaker was covered with a watch glass. This last stage is crucial for thallium recovery in decomposition of sludge samples. 2.5 mL of 1 M ascorbic acid and 6.25 mL of 0.2 EDTA were then added and pH adjusted to 4.5 with ammonia. The solution was then transferred into a 25 mL volumetric flask and supplemented with water.

Determination of the total thallium content in sewage sludge requires total sample decomposition. Silicates are the main inorganic component of many matrices, e.g., soils, sediments, and other similar samples. In the case of silicates present in the sample, it is necessary to apply hydrofluoric acid to decompose the sample completely (Łukaszewski et al. 2012, Łukaszewski et al. 2010).

**Single extraction of sewage sludge**

The scope of this research was to determine the total thallium concentration as well as its mobile fraction in the sewage sludge. The single extraction was performed using the following reagent and extraction conditions (Quevauviller, 2002) 0.1 M HCl (1:10 soil/solution, shaking in over shaker for 1 h). Determinations of the total content and available forms of thallium was conducted using the technique of flow injection differential pulse anodic stripping voltammetry.

Heavy metal concentration was determined using differential pulse voltammetry by means of mercury film electrode and flow-through analytical cell that allows to exchange the base electrolyte. Low detection limit below 0.25 pM (50 pg/L) makes this method one of the best analytical methods for trace analysis of thallium (Łukaszewski et al. 2010).

Mercury film electrode (MFE) was the working electrode. When the mercury film was formed an electrode potential of 0.0V (vs. SCE) was maintained. Leaving the circuit open would lead to the oxidation of the mercury film. Saturated calomel electrode was the reference electrode. It was separated using an electrolytic bridge with 0.1 M potassium chloride. Platinum electrode put directly into the analytical cell was the auxiliary electrode (Fig. 1).

In order to isolate the bioavailable forms of the metal, a single-stage extraction with 0.1 M HCl was used. The accuracy of the analysis was verified using a certified reference material – soil GBW 07401 containing 1.0 ± 0.2 μg/g of thallium.

**Results and discussion**

**Determination of the total thallium concentration in samples of sewage sludge**

After sample decomposition the thallium concentration was determined using standard addition method. Fig. 2 shows series of voltammometric curves without and with three different standard additions. Fig. 3 shows the method of determining the thallium content using the standard addition method. Results of determination of total thallium concentration in sewage sludge are presented in Table 1.

According to the literature data (Zitko 1975, Vanek et al. 2013, Xiao et al. 2004), the total thallium concentration does not exceed normal levels. These values are in the range 0.164 to 0.244 μg/g with an average value 0.203 μg/g.

However, the thallium content data given above do not tell us what amount of thallium is available for plants and can enter
biological cycles. Only the data on the mobile fraction allow to estimate the amount of thallium that can pollute the soils and waters. Therefore, the aim of the further investigation was to examine the sewage sludge taking into account the biologically available fraction of thallium that presents a potential risk of further pollution due to its mobility and easy migration. **Determination of the mobile fraction of thallium in samples of sewage sludge**

Some studies have been published about the comparison of HCl single and BCR sequential extraction procedures. Madrid et al. (2007) estimated the extractability of potentially toxic metals (Cu, Pb and Zn) in urban soils by both methods. Ahumada et

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**Table 1. Statistical data for total thallium and mobile forms concentration in dry sludge**

<table>
<thead>
<tr>
<th></th>
<th>Thallium concentration in sewage sludge [μg/g dry mass]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
</tr>
<tr>
<td>mobile forms</td>
<td>0.0254</td>
</tr>
<tr>
<td>total</td>
<td>0.203</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Voltammograms of the sample (d) with sequential standard additions: 0.5 μg/L, 1 μg/L, 1.5 μg/L (respectively a,b,c) as well as the calibration graph. The base electrolyte 0.05 M EDTA (pH 4.5). Preconcentration potential -900mV vs. SCE; preconcentration time 600s, pulse amplitude 50 mV, step potential 2 mV.

**Fig. 3.** Standard addition curve for determination of thallium concentration with 3 additions.
al. (2004) obtained significant positive correlations between the results from HCl single and BCR sequential extraction procedures for copper and lead in the soils from mining and agricultural zone. Larner et al. (2006) compared BCR SEP with single HCl extraction for fractionation of 12 metals (Cd, Sb, Pb, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) in CRM NIST 2711. In order to isolate the biologically available forms of thallium a single-stage extraction with 0.1 M HCl was used by Ibragimow et al. (2010).

This method allows us to estimate the actual ecotoxicity and phytotoxicity of a metal when it is not necessary to examine all its forms. Results obtained after this type of extraction allow us to estimate biological availability of a metal for plants, microorganisms and to estimate its potential lixiviation.

The results in Table 1 show that average concentration of the mobile form of Tl was 0.0254 μg/g (median value was 0.025 μg/g and standard deviation was 0.0064 μg/g). The results also show that in the near future about 13% of toxic thallium can migrate to the environment.

In Figure 4, all total thallium content results are shown against mobile form of this element.

The results are in ascending order and the averages for total and mobile fraction content are shown. The accuracy of the analysis was verified using a certified reference material – Chinese soil GBW 07401 containing 0.90 ± 0.12 μg/g of thallium. Results of the determination of thallium in reference material are shown in Table 2. The obtained values of thallium concentration for the certified material are in the range 1.00 ± 0.2 μg/g. Taking into account that this is an ultratrace analysis, the precision of determination is satisfactory for thallium determination in environmental samples.

The presence of thallium in sewage sludge is often the result of its excessive concentration in industrial sewage and

![Fig. 4. Total thallium concentration and its mobile forms concentration in sewage sludge (μg/g) Results in ascending order](image)

<table>
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<tr>
<th>No</th>
<th>Sample weight [g]</th>
<th>Thallium concentration [μg/g]</th>
<th>Median [μg/g]</th>
<th>Average±SD [μg/g]</th>
<th>RSD [%]</th>
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surface runoff. In sewage sludge, thallium occurs in dissolved, precipitated, co-precipitated, adsorbed or associated forms on the particles of biological residues. Currently, the methods for determining the bioavailability of metals in agricultural sewage sludge have not been standardized. Techniques developed for soils are most often adopted for this purpose.

The applicable law (Regulation of the Minister of the Environment 2015) concerns the total content of only metals such as lead, cadmium, mercury, nickel, zinc, copper and chromium. This generalization is not used to obtain information about the potential threat to the soil and water environment by thallium immission, moreover, its bioavailability and toxicity depend on the form of occurrence.

Forecasting threats resulting from the presence of thallium in elements of the environment plays an important role in environmental research. Thallium from sewage sludge dissipates into the environment and contaminates soil and water, air, and as a result, can enter the food chain and accumulate in living organisms, causing serious disturbances and ultimately leading to death. Research carried out using the single-stage extraction method broadens the knowledge of the environment and constitutes a reference point in determining the dynamics of changes taking place in ecosystems. A disturbing fact is that the bioavailability of thallium (extracted 0.1 M HCl) in terms of the total percentage is up to 13%. The process of soil fertilization with sewage sludge while introducing, inter alia, thallium into the soil should draw one’s attention to respecting the principles of environmental protection, including soil and water protection. Conducting tests determining the quality of the sediment in terms of the content of heavy metals in this thallium is extremely important for human health.

The main purpose of wastewater treatment is to change the composition and properties of wastewater in such a way that its discharge into a water or ground receiver does not endanger the health and life of people and animals.

Discharging wastewater without prior treatment causes undesirable changes in receivers, which may lead to partial or even complete environmental degradation, if the pollutant load exceeds the receiver’s self-cleaning capacity.

Conclusions

Determination of thallium content in sewage sludge allowed us to determine the concentration of the mobile form of thallium and the total concentration of thallium.

The total thallium concentration in sewage sludge was in the range 0.164 μg/g to 0.244 μg/g while the concentration of its mobile form was in the range 0.017–0.037 μg/g.

The obtained results allow us to estimate that almost 13% of toxic thallium will be released to the environment.

More than 87% of thallium was in immobile forms that have little toxicological significance.

Results of sewage sludge examination were used to evaluate thallium pollution, a very important point in estimating the whole range of potentially bioavailable elements.

Acknowledgments

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Mobile forms vs the total content of thallium in activated sludge

Formy mobilne a całkowita zawartość talu w osadzie czynnym

Streszczenie: Osady ściekowe z komunalnych oczyszczalni ścieków stanowią poważny problem dla środowiska, biorąc pod uwagę ich różnorodność spowodowaną zmiennością czasu i zawartością metali ciężkich. Aktualne badania nad monitoringiem metali ciężkich opierają się na oznaczaniu Pb, Cd, Hg, Ni, Zn i Cr. To sprawia, że jakiekolwiek dane dotyczące zawartości talu są trudno dostępne. Próbki osadów analizowano za pomocą woltampereometrii impulsowej różnicowej. Wyniki wykazały, że średnia zawartość talu wynosiła 0,203 μg/g, a jego form mobilnych 0,025 μg/g. Z przeprowadzonych badań wynika, że prawie 13% Tl z osadów ściekowych może być stopniowo uwalniane do środowiska.

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