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THALLIUM IN ENVIRONMENT

TAL W ŚRODOWISKU

Słowa kluczowe: tal, środowisko, zanieczyszczenie środowiska.
Key words: thallium, environment, environmental pollution.

Tal w środowiskach geochemicznych występuje na trzech stopniach utlenienia choć najczęściej jako Tl^+. Jest on silnie sorbowany przez minerały ilaste, wodorotlenki Fe i Mn, oraz substancję organiczną, co wskazuje na potencjalną zdolność tego pierwiastka do przechodzenia ze środowiska glebowego do łańcucha troficznego.

Tal uznawany jest jako pierwiastek toksyczny, którego oddziaływanie na organizmy kręgowców może być zdaniem specjalistów bardziej niebezpieczne niż rtęci, kadmu czy ołowiu. Jest szczególnie łatwo pobierany jest przez rośliny, a jego szkodliwy wpływ objawia się zahamowaniem rozwoju systemu korzeniowego, karłowaceniem roślin oraz chlorozą. Szkodliwość talu objawia się także zahamowaniem zawiązywania nasion, oraz zmniejszeniem zdolności kiełkowania. Tal jest pierwiastkiem toksycznym także dla organizmów zwierząt i ludzi. Jest on równie toksyczny przy pobieraniu drogą pokarmową, jak i wskutek wdychania pyłów lub par oraz wchłaniania przez skórę. Charakterystycznym objawem zatruć talem jest łysienie. W organizmach zatrutych występują zmiany psychiczne oraz uszkodzenia układu naczyniowo-sercowego.

1. INTRODUCTION

Thallium atomic number 81, was discovered spectroscopically in 1861 by Crookes. The element was named after the green spectral line, which identified the element (Greek „thallos”, green twig). The metal was isolated both by Crookes and Lamy in 1862. They had been

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expecting to isolate tellurium after removing selenium from the byproducts from a commercial sulphuric acid factory but instead found the new element thallium [Winter 2007].

Thallium occurs mainly in association with potassium minerals, such as sylvite and pollucite, in clays, soils and granites. Thallium minerals are well known too; they are rare, but a few are known, such as crookesite, lorandite, christite, avicennite, ellisite or sicherite. They contain 16–60% of thallium, namely as sulphides or selenides in complexes with antimony, arsenic, copper, lead and silver [Anderson et al. 1999; Kazantzis 2000; Xiao et al. 2004a].

Thallium is also produced as a byproduct from zinc and lead refining plants, as well as from particular sulphuric acid factories [Winter 2007].

The natural release of thallium to environment occurs primarily as a result of weathering of rocks and soil erosion. During weathering, Tl is readily mobilized and transported together with alkaline metals. However, Tl is most often sorbed by clays, Fe/Mn oxides and organic matter. The largest anthropogenic source of Tl is coal combustion, but some amount of this element may be released by heavy metal smelting, cement industry and refining processes [Kabata-Pendias, Pendias 2001].

Thallium chemical behaviour resembles the heavy metals (Pb, Au and Ag) on the one hand and the alkali metals (K, Rb, Cs) on the other [Rao et al. 2008].

2. THALLIUM IN THE AIR

Some anthropogenic activities, such as cement factories using iron oxides with high Tl contents, coal combusition and ferrous and non-ferrous metallugry, can release Tl into the biosfere and may increase its availability [Tremel et al.1997b, Hršak et al. 2003].

Determnation of thallium in Zagreb air was performed by Hršak et al. [2003]. The contrentration of thallium in 1998 ranged between 0 to 18.78 $ng \cdot m^{-3}$ in city centre while in residential area it was lower (0–5.04 $ng \cdot m^{-3}$). In the year 2000 same researchers found lower Tl concentration in city centre (0–2.17 $ng \cdot m^{-3}$) than in residential area (0–8.90 $ng \cdot m^{-3}$).

3. THALLIUM IN SOILS

Thallium is found in alloys, minerals, biological samples, and geological materials. Its content of soils depends largely on the geological origin of the parent material. In general, thallium concentrations in surface soils range from 0.1 to 2 $\mu g \cdot g^{-1}$, with most reported concentrations being <1 $\mu g \cdot g^{-1}$. Its concentration in arable soils is between 0.29 and 1.54 $\mu g \cdot g^{-1}$. High concentrations of the metal (up to 55 $\mu g \cdot g^{-1}$) are common in soils derived from limestone, marble, or granite, because these minerals contain appreciable amounts of sulfur, which in turn has high affinity for Tl. Thallium salts are highly water soluble, but can be immobilized by vermikulite once incorporated into soil [Martin, Kaplan 1998, Tremel et al. 1997b, Qi et al. 1992, Jacobson et al. 2005].

Concentration of thallium in soils of the EuroRegion Neisse was analysed by Heim et al. [2002]. The median concentration in this area was 0.5 mg·kg^{-1}. This compares to a median 0.3 mg·kg^{-1} Tl in French topsoils reported by Tremel et al. [1997a] and to 0.44 µg·g^{-1} in soils from the south-eastern part of the Silesian-Cracovian zinc-lead ore deposit region [Jakubowska et al. 2007]. Soil samples collected form grasslands in Czech Republik by Vaněk et al. [2009] contained about 1.1 mg·kg^{-1} of thallium. Thallium concentration in soils from region of Kosovska Mitrovica varied between 0.10 and 5.06 µg·g^{-1} [Borgna et al. 2009]. In Scania, the most southern province of Sweden, concentration of thallium in soils was about 0.32 µg·g^{-1} average [Tyler 2004b]. The results of Qi et al. [1992] research show that soils from 34 provinces of China contains 0.292–1.172 µg·g^{-1}. They reported that soils developed on limestones have the maximum concentration of thallium. They also observed negative correlation between Tl content and pH of the soils and posstive one between Tl content and organic matter of soils.

Yang et al. [2005] also analysed the concentration of the thallium in the Chinese soils. The concentration of Tl in the background soil ranging from 1.63 to 2.02 µg·g^{-1}, while in the upper layer of soils which are spatially closed to the slag pile high concentration of thallium (up to 15.4 µg·g^{-1}) was observed.

4. THALLIUM IN WATERS

The solubility of thallous compounds is relatively high so that monovalent thallium is readily transported through aqueous routes into the environment. Thallium is included in the USEPA list of priority toxic pollutants and fixed 2 µg·L^{-1} [EPA] as maximum contaminant level in drinking water.

Peter and Viraraghavan [2005] present that drinking water sometimes may contain 7.2 µg Tl·L^{-1}, while concentration of thallium in groundwater ranged from 20 to 24 µg·L^{-1}.

Results of Xiao et al. [2004b] research indicates that Tl concentration in deep groundwater is higer (13–1100 µg·L^{-1}) and its decreasing with distance away from mineralized area to background levels (<0.005 µg·L^{-1}).

Jakubowska et al. [2007] reported that water samples collected from Biała Przemsza River flowing through the zinc-lead ore exploration area contained 2.07 µg·L^{-1} Tl. Water samples collected by Krasnodębska-Ostręga et al. [2005] from another Polish zinc-lead ore exploration and smelting area (near Bukowno) contained lower amounts of thallium (0.02–0.15 µg·L^{-1}).

5. THALLIUM IN PLANTS

Thallium is easily available to plants, and when concentrated in roots up to 2 mg·kg^{-1}, can inhibit the germination, plant growth, and chlorophyll content. Plants especially sensitive to increased levels of thallium are the Leguminosae species, cereals, tobacco, and buckwheat. Microorganisms are reported to be relatively sensitive to thallium, and therefore the inhibition of nitrate formation in Tl-polluted soils may have an agronomic impact [Rao et al. 2008].

As far as relatively high content of Tl is appearing in soils, a potential risk for humans can arise at levels around 1 $mg \cdot kg^{-1}$. Especially growing of certain crops e.g. *Brassicaceae* can pose a risk for the food chains because of elevated accumulation of Tl in plant tissues [Pavlickova et al. 2005].

Uptake by plants can lead to substantial accumulation of this heavy metal. Tremel et al. [1997b] determined the content of the thallium in plants. Both grains wheat and maize contained less than 4 $\mu g \cdot g^{-1}$ of thallium. Maize stalk had quite a high Tl concentration (343 $\mu g \cdot g^{-1}$) and elevated Tl concentrations (20 $mg \cdot kg^{-1}$) they found in shoots of rape.

Thallium exhibits the surprising ability to be preconcentrated by green cabbage which significantly increases the daily uptake of thallium by inhabitants of the polluted area [Xiao et al. 2004a]. Roots of some plants also exhibit a high preconcentration of thallium. Tyler [2004a] reports that in Scania (Sweden) roots of *Fagus sylvatica* contain 0.29 $\mu g \cdot g^{-1}$ of this element, while its concetration in soil was 0.06 $\mu g \cdot g^{-1}$. Similar relation was observed by Wierzbicka et al. [2004]. They found that on the waste heap in Bolesław (Poland), on three stands *Plantago lanceolelata* accumulated the largest amount of thallium in its roots, on average 154 (±112) $\mu g \cdot g^{-1}$ (maximum 321 $\mu g \cdot g^{-1}$). The shoots of these plants also contained high thallium levels, on average 54 (±53) $\mu g \cdot g^{-1}$ (maximum 180 $\mu g \cdot g^{-1}$) Thallium concentrations in soils in all of the tested sites were relatively high and averaged 43 (±12) $\mu g \cdot g^{-1}$.

During the research in the EuroRegion Neisse, Heim et al. [2002] found 0.04–0.13 $\mu g \cdot g^{-1}$ of thallium in *Pleurozium schreberi*. Similar content was found by Rühling and Tyler [2004] in *Pleurozium schreberi* sampled in 1975 (0.15 $\mu g \cdot g^{-1}$) and 2000 (0.066 $\mu g \cdot g^{-1}$) in southern Sweden. They tried to find possible causes of this change, and they conclude that „reductions in anthropogenic dust emissions during recent decades have decreased the atmospheric deposition over northern Europe of this element".

Anderson et al. [1999] dicovered unusually high hyperaccumulation of Tl by the brassicaceae *Iberis intermedia* and *Biscutella laevigata* L. growing over lead=zinc mine tailings at Les Malines near Montpellier in southern France. Both *Biscutella laevigata* and *Iberis intermedia* from Les Malines contained very high levels of Tl of up to 1.4% dry weight in *Biscutella* and 0.4% in *Iberis* in the dry matter, therefore they suggested to use these two species of plants for removing (phytomining) the thallium from the environment.

6. THALLIUM IN ORGANISMS OF ANIMALS AND PEOPLE

Thallium is being readily transferred to the human body, from contaminated soils, through food chain, and poses significant threat to the inhabitants of the polluted area [Xiao et al. 2004a].

Most thallium salts are rapidly absorbed through the respiratory and gastrointestinal tracts and through the skin. In humans and animals, thallium circulates in intra- and extra-cellular fluids as a monovalent cation. Its toxicity results from thallium ion mimicking potassium ions in many metabolic processes. Ionic radius of Tl^+ (1.49 Å) is similar to that of the hard cation, potassium K^+ (1.33 Å), so that nondiscriminatory uptake of Tl+ over K+ has been suggested as a mechanism of its toxicity to biota. Thallium may also bind with sulfhydryl groups of proteins to inactivate many enzymatic reactions. Thallium causes gastrointestinal irritation and nerve damage when people are exposed to it for relatively short period of time. For long term, thallium has the potential to cause effects such as change in blood chemistry, damage to liver, kidney, intestinal and testicular tissue. In humans, one of the main symptoms of thallium poisoning is rapid (2–3 weeks) and often complete hair loss. Acute poisioning can lead to paralysis, coma, and death. Thallium also has mutagenic, carcinogenic and teratogenic effects [Galván-Arzate and Santamaría 1998, Leonard and Gerber 1997, Moore et al. 1993, Tremel et al. 1997b, Wang et al. 2007].

Acording to Rusyniak et al. [2002] „thallium has qualities of a perfect criminal poison. Its salts are tasteless, odorless, dissolve completely in liquids, are rapidly absorbed, and defy detection on routine toxicologic screens". Authors sugesting „although thallium poisoning is an uncommon method of criminal poisoning, it should be considered in any patient with rapidly progresive, unexplained peripheralneuropathy with or without alopecia".

In order to establish reference values of thallium in tissues of healthy inhabtants living in Central Italy, Sabbioni et al. [1994] determined this element in blood and urine. Mean measured values of thallium in blood and urine were 0.063 $\mu g \cdot L^{-1}$ and 0.066 $\mu g \cdot L^{-1}$ respectively.

Acording to Moore et al. [1993] the normal total blood thallium concentration is under 2 $\mu g \cdot L^{-1}$ and concentration greater than 100 $\mu g \cdot L^{-1}$ are toxic. Urine thallium concentration greater than 200 $\mu g \cdot L^{-1}$ are also toxic.

Results reported by several researchers suggesting appearing of the trend in the concentration of thallium in the human body. Concentration of thallium is in rising order: brain (0.42–1.5 $ng \cdot g^{-1}$) < liver (1.5 $ng \cdot g^{-1}$) < kidney (6.1 $ng \cdot g^{-1}$) < hair (7–650 $ng \cdot g^{-1}$) ≈ bone (<0.6 $\mu g \cdot g^{-1}$) < nail (1.2 $\mu g \cdot g^{-1}$). This indicates that Tl accumulates preferentially in peripheral organs, for example nails [Engström et al. 2004, Das et al. 2006].

Typical concentrations in animal muscle tissue are: fish (0.74–110.5 $ng \cdot g^{-1}$), rabbit (0.84 $ng \cdot g^{-1}$), pig (1.7 $ng \cdot g^{-1}$), cattle (0.74 $ng \cdot g^{-1}$) [Engström et al. 2004, Das et al. 2006].

There is little information about Tl contamination in wildlife. Mochizuki et al. [2005] were examined thallium content in wild ducks kidneys and liviers. The Tl content ranged from 0.42 to 119.61 and 0.10 to 33.94 $\mu g \cdot g^{-1}$ dry weight, respectively. Dmowski et al. [1998] measured high thallium levels in kidneys and livers of small mammals inhabitng the zinc smelter Boleslaw (Southern Poland). The maximum Tl content in kidneys was 44.06 $\mu g \cdot g^{-1}$ dry weight, while in livers maximum was 15.21 $\mu g \cdot g^{-1}$ dry weight.

7. CONCLUSIONS

Thallium is extremely toxic to humans, plants, and animals, and plays no role in their metabolisms. With respect to degree of toxicity thallium ranks alongside Pb, Hg, Cd. The high toxicity of thallium and its compounds made their accurate determination is demanded.

Much further research is required to investigate the possible adverse health effects of thallium following population exposure.

Thallium accumulation demonstrated in plants, fruits and vegetables, that can make big problem because of absence of threshold limits for thallium in soils, agricultural products, feedstuffs and foodstuffs in most countries.

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