
**IMPACT OF DIFFERENT REDOX CONDITIONS ON THALLIUM
(IM)MOBILIZATION IN SOIL (SERBIA)**

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Abstract

Thallium (Tl) is a highly toxic element, even in small concentrations, to a range of organisms and in different environments. Therefore, our aim was to study (i) Tl geochemical fractionation by the means of the modified BCR sequential extraction procedure and (ii) the impact of redox potential (E_H) alteration and principal factors such as iron (Fe), manganese (Mn), dissolved organic carbon (DOC), chlorides (Cl^-) and sulfates (SO_4^{2-}) on Tl (im)mobilization in periodically flooded arable soil (Serbia). Flooding was simulated using an automated biogeochemical microcosm system that allows systematical control of pre-defined redox-windows. Afterwards, E_H was increased stepwise for approximately 100 mV from reducing (-205 mV) to oxidizing (530 mV) conditions. E_H was automatically monitored at 10 minutes intervals. Total duration of the experiment was 914 hours. The sequential extraction revealed majority of pseudo-total soil Tl (0.15 mg kg^{-1}) in the residual fraction (85.5 %), following by reducible (10.2 %), oxidable (3.8 %) and acid soluble (exchangeable) (0.5 %) fraction. The soluble Tl concentrations ($0.024\text{--}0.116 \text{ } \mu\text{g l}^{-1}$) were significantly affected by E_H , having an increase with E_H increase ($r=0.75$, $p<0.01$, $n=30$). Concentrations of soluble Fe, Mn, and DOC showed significant negative correlations with soluble Tl ($r=-0.78$, $r=-0.73$ and $r=-0.91$, respectively, $p<0.01$, $n=30$), whereas Tl correlated significant positive with SO_4^{2-} and Cl^- ($r=0.89$, $r=0.81$, respectively, $p<0.01$, $n=30$). Thallium mobilization was attributed to several simultaneous processes, involving the reductive dissolution of Fe-Mn

oxides and gradual oxidation of Tl-bearing metallic sulfides. Our results imply that soluble Tl concentrations might increase when soil redox status evolves from reducing to oxidizing conditions. Due to high Tl toxicity at low doses, and increasing flooding events, our findings suggest that Tl should be included in future monitoring of plants and groundwater on the site or on similar sites.

Key words: thallium, sequential extraction, mobilization, redox potential, sulfides, environmental risk

INTRODUCTION

Thallium (Tl) is a highly toxic trace element to a range of organisms and in different environments (Rodriguez-Mercado and Altamirano-Lozano, 2013). Although widely distributed, the average Tl content in soil all over the world is usually low ($< 1 \text{ mg kg}^{-1}$) (Kabata-Pendias and Mukherjee, 2007). However, high Tl contents of geogenic origin may be found in soils developed from K-rich rocks or rocks hosting metal sulfides (e.g. Vaněk et al., 2009, Karbowska et al., 2014, Voegelin et al., 2015). Soils in such areas may contain up to several $1000 \text{ mg Tl kg}^{-1}$ (Xiao et al., 2004). Anthropogenic Tl in soil mainly derives from nonferrous and ferrous metal mining, coal combustion, and cement production (e.g. Álvarez-Ayuso et al., 2013, Kersten et al., 2014).

Thallium usually occurs in two oxidation states, the thallos cation (Tl(I)) and the thallic cation (Tl(III)) (Nriagu, 1998). Tl (I) exhibits both chalcophilic character, such as an affinity for sulfides (Hettmann et al., 2014) and lithophilic character, such as replacing K(I) in K-feldspars or micas due to its similar ionic radius (Voegelin et al., 2015; Vaněk et al., 2015). Tl (III) is reported to be by far more toxic than Tl(I), however, its available contents are much lower than that of Tl(I) (Ralph and Twiss, 2002), since Tl(III) is insoluble, as opposite to Tl(I) (Lin and Nriagu, 1998). In contrast, Tl is more stable in the oxidation state I than oxidation state III (Rodriguez-Mercado and Altamirano-Lozano, 2013) due to very high reduction potential of Tl(III)/Tl(I) couple (1.28 V, Lin and Nriagu, 1998).

Beside sulfides and silicates, Tl retention in soils has been attributed to strong affinity of δ -MnO₂ toward Tl sequestration (Jacobson et al., 2005; Vaněk et al., 2011; Grösslová et al., 2015). Therefore, redox-sensitive processes that affect sulfur and manganese chemistry in soil simultaneously may affect Tl (im)mobilization and its potential toxic effects. Impact of those processes on dynamics of Tl and other trace elements is particularly important in floodplain soils.

Inundation of floodplain soil alters soil redox status and consequently triggers a series of chemical, physical and biological changes that may affect Tl dynamics directly via changes of its speciation or indirectly through related changes in redox-sensitive ions and compounds. However, there is still insufficient knowledge of biogeochemical processes and of factors that govern Tl release.

Therefore, our objective was to determine the impact of redox dynamics from reducing to oxidizing condition and governing factors (i.e. pH, Fe, Mn, Cl⁻, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and sulfates (SO₄²⁻) on the (im)mobilization of Tl in an arable soil collected from the Velika Morava river valley (Serbia). The soil was selected due to several reasons: (i) it is representative for intensive field crops and vegetable production in the area (ii) it is occasionally flooded, thus subjected to rapid change of redox conditions; the last severe flood in the area was in May, 2014, and (iii) due to topography specifics, the area may be affected by sulfides released from Pb-Zn-Cu mining activities at Rudnik mine and transported to the Velika Morava river valley by erosion processes and/or flood-driven sediment deposition. In addition, Tl chemistry and associated environmental risk were evaluated by the means of its geochemical partitioning in the soil solid phases of differing reactivity.

MATERIAL AND METHODS

Study area and soil sampling

The study area is positioned at the northern part of the Velika Morava River valley, Serbia. Within the study area, one representative site (44°27'25'' N 21°06'05'' E, near Lozovik village) at the younger alluvial terrace was selected for soil sampling. Detailed map of the Velika Morava river catchment and position of the sampling site is provided by Antić-Mladenović et al. (2017a). At the study site, five soil samples were collected from the topsoil (0-25 cm) within a 25 x 25 m² square. The samples were bulked in the field to form a composite sample of about 1.5 kg. At the time of sampling, the soil was cropped with perennial alfalfa.

Soil pretreatment and analyses

The composite sample was air-dried; 250 g was crushed in a porcelain mortar to pass a 2-mm sieve for determination of basic soil properties and pseudo-total Tl content, whereas sub-sample of 25 g was ground to < 0.25 mm in an agate ball mill for the geochemical fractionation. The analytical procedures for the determination of the soil chemical and physical properties and the results (soil

reaction (pH), organic carbon content, cation exchange capacity (CEC), sand, silt and clay contents) can be found in Antić-Mladenović et al. (2017a). Pseudo-total Tl content was determined by inductively coupled plasma mass spectrometry (ICPMS) (Perkin Elmer Sciex) after digestion using nitric acid (HNO₃, 65%) + hydrogen peroxide (H₂O₂, 30%) (US EPA Method 3050b, 1996). Digestions and measurements were performed in triplicate.

Geochemical fractionation procedure

The modified BCR sequential extraction procedure (Rauret et al., 2000) was carried out for assessing Tl geochemical fractionation. The following fractions were determined: (F1) exchangeable/acid-extractable (0.11 M CH₃COOH-extractable); (F2) reducible (0.5 M NH₂OH·HCl-extractable); (F3) oxidizable (8.8 M H₂O₂/1 M CH₃COONH₄ (pH 2.0)-extractable); and (F4) residual (the residue from the three previous extraction steps was digested according to US EPA Method 3050b (1996)).

The extractions were performed in triplicate. Chemicals of analytical grade (Lach-Ner, Czech Republic) were used for the individual extraction steps. After each step, the suspension was centrifuged for 20 min at 5500 rpm. The supernatant was removed by a pipette, filtered through the Whatman 42 paper and analyzed for Tl by ICPMS. Before each next step, the residue was washed with 20 ml of deionized water (shaking for 15 min and centrifuging for 20 min). For the analytical quality control, the sum of Tl extracted in F1-F4 was compared to pseudo-total Tl content in the bulk soil; the average recovery was 92 %.

Biogeochemical microcosm experiment

Flooding of the soil was simulated in an automated biogeochemical microcosm (MC) system. Each MC consists of a glass vessel (2.88 L) equipped with a stirrer and an airtight lid. The system allows automatic control of redox potential (E_H) by flushing N₂ (to decrease the E_H) or O₂ (to increase the E_H) and automatic measurement of the E_H every ten minutes. In presented work, three independent MCs (MC1-MC3) were used as replications. Every MC was filled with 200 g of air-dried soil and tap water in a 1:8 ratio. After initial flooding, E_H was increased step-wise from reducing to oxidizing conditions in steps of about 100 mV. The soil slurry (55 mL) was sampled approximately 24 h after reaching each new E_H window and immediately centrifuged (15 min at 3,000 rpm). The supernatants were filtered under N₂ atmosphere through a 0.45-µm membrane and analyzed for total soluble Tl, Fe, Mn, DOC, Cl⁻ and SO₄²⁻. Total duration of the biogeochemical microcosm

experiment was 914 hours. A detailed description of the experiment and the analyses of the supernatant can be found in Antić-Mladenović et al. (2017a, b).

Statistical analyses

Statistical analyses (mean, maximum, minimum, standard deviation (SD), and Pearson's correlation coefficients (r)) were carried out using PASW Statistics 18. Microcal Origin 7.5 software packet was applied for the regressions equations and coefficients of determination (R^2). Before the statistical analyses, the measured E_H values were normalized to pH 7, since this pH is closest to the pH fluctuations during the sampling period (Tab. 1).

Table 1. Dynamics of E_H , pH, Tl and redox sensitive ions/compounds during the biogeochemical microcosm experiment

Parameters		n	Mean	Min	Max
E_H (all data)*	[mV]	5482	201	-205	530
pH (all data)*		5482	7.13	6.20	8.27
E_H^{**} (at sampling)	[mV]	30	148	-200	525
pH (at sampling)		30	6.94	6.21	8.02
Tl	[$\mu\text{g L}^{-1}$]	30	0.048	0.024	0.116
Fe		30	7.36	0.069	28.0
Mn		30	10.17	2.1	18.5
DOC	[mg L^{-1}]	30	217	46.6	395
DIC		30	22.0	1.0	78.4
SO_4^{2-}		30	9.63	1.22	26.9
Cl^-		30	126.0	85.1	234.4

* data measured every 10 min during the experiment

** E_H corrected to pH 7.0

RESULTS

Pseudo-total content and geochemical fractionation of Tl

Pseudo-total Tl content in the soil amounted $0.15 \pm 0.002 \text{ mg kg}^{-1}$. The residual fraction was the dominating binding form of Tl (85.5 %), followed by reducible (10.2 %), oxidable (3.8 %) and acid soluble (0.5 %) fraction (Fig. 1).

Dynamics and relations between E_H , soluble Tl and redox-sensitive compounds

Selected statistical values of the measured E_H , soluble metals (Tl, Fe, Mn), DOC, SO_4^{2-} , and Cl^- concentrations during the controlled E_H alteration from reducing to oxidizing conditions are

summarized in Table 1. Redox potential E_H (corrected to pH 7.0) of the slurry during the biogeochemical microcosm experiment ranged from -205 to 530 mV (all data, $n=5482$).

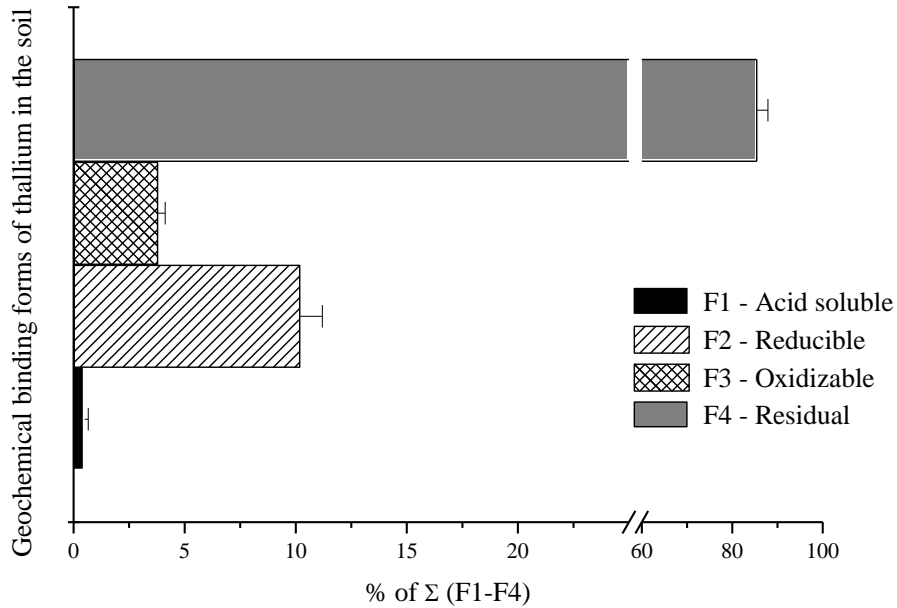


Figure 1. Geochemical fractionation of Tl (in % of Σ F1-F4) in the soil: (F1) exchangeable/acid-extractable, (F2) reducible, (F3) oxidizable, and (F4) residual fraction. Data shown are means \pm standard deviation ($n=3$).

Soluble concentrations of Fe, Mn and DOC decreased with E_H increase, which was reflected to significant negative correlations between Fe, Mn i DOC at one side and E_H at the other side ($r=-0.78$, $r=-0.73$ and $r=-0.91$, respectively, $p<0.01$, $n=30$). Soluble concentrations of sulfates and chlorides increased when E_H evolved from reducing to oxidizing conditions and correlated with E_H significant positive ($r=0.89$, $r=0.81$, respectively, $p<0.01$, $n=30$).

Soluble Tl concentrations varied in the range 0.024 – 0.116 $\mu\text{g l}^{-1}$, having an increase with increasing E_H ($r=0.75$, $p<0.01$, $n=30$). Correlation coefficients between Tl at one side and Fe, Mn, and DOC at the other side were significant negative ($r=-0.57$, $r=-0.67$, and $r=-0.74$, $p<0.01$, $n=30$, respectively). The correlations between Tl and sulfates and chlorides were significant positive ($r=0.75$, $r=0.71$, $p<0.01$, $n=30$, respectively).

DISCUSSION

Thallium content and geochemical fractionation in the bulk soil

The studied soil may be considered unpolluted, according to the determined pseudo-total Tl content (0.15 mg kg^{-1}) and Tl content in unpolluted soils in different countries (Kabata-Pendias and Mukherjee, 2007). This is also confirmed by dominance of residual fractions in Tl geochemical fractionation. This fraction mainly consists of silicates, which are considered to be the main pool of geogenic Tl (Gomez-Gonzalez et al., 2015; Vaněk et al., 2015).

Reducible fraction extracts element binds to Fe- and Mn- oxides and hydroxides. Thallium determined in this fraction in this study (Fig. 1) is consistent with previous findings (e.g. Yang et al., 2005; Grösslová et al., 2015), that Fe- to a lesser extend and Mn-oxides in particular were responsible for Tl retention/immobilization in soils. However, metal release upon the reductive dissolution of Fe-Mn oxides has often been reported (Shaheen et al., 2014; Frohne et al., 2015; Schuth et al., 2015). Thus, the reducing conditions in the soil might result in Tl release into soil solution, as suggested by Antić-Mladenović et al. (2017b) for soils from geographically close area in Serbia.

Oxidable fraction extract elements bind to soil organic matter and sulfides. Vaněk et al. (2016) assumed that soil organic matter has low ability to retain Tl. However, metallic sulfides are recognized as significant Tl-bearing phase (Laforte et al., 2005; Karbowska et al., 2014; Vaněk et al., 2015; Liu et al., 2016). Therefore, it is possible that part of the Tl extracted in the oxidable fraction (Fig. 1) could be related to unweathered sulfides. Further, Tl release into solution upon sulfides oxidation may occur in the soil.

Acid soluble (exchangeable) fraction of Tl in the soil is low due to its high proportion in the residual, reducible and oxidable fractions. Exchangeable metals are considered to represent most readily plant available forms in soil (Giacomino et al., 2010). Therefore, Tl geochemical fractionation in this study imply to a relatively low environmental risk in the soil in conditions common for arable soils.

Soluble Tl concentrations and interaction with redox-sensitive species

Intensity of soil redox status can be rapidly characterized by a measurement of soil redox potential (E_H). The E_H changes from high to low values when the redox status of a soil changes from aerobic to anaerobic conditions during flooding (Patrick et al., 1996). At low E_H redox-sensitive species

undertake a series of redox-reactions; major including reduction of Fe(III), Mn(IV, III), and sulphate (SO_4^{2-}) (e.g. Weber et al., 2009). This was verified in our study by the high concentrations of soluble Fe and soluble Mn measured at low E_H . The development of E_H from low to high in the microcosm experiment (Fig. 2) reflected the progressive oxygenation of the system. This, in turn, reversed the order of the redox-reactions. The successive decrease of soluble Fe and Mn concentrations and the final increase of SO_4^{2-} concentration measured in the slurry characterized soil redox conditions becoming more and more oxidative over time.

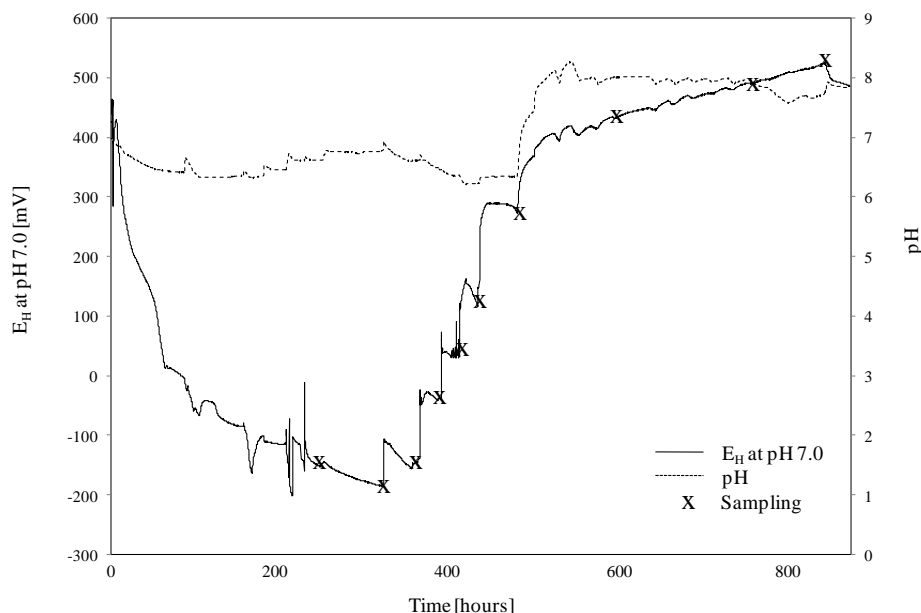


Figure 2. Temporal changes of redox potential (E_H) and pH in the soil slurry during the biogeochemical microcosm experiment. Data presented show dynamics measured in MC 3 replicate

Considering high standard reduction potential of the Tl(III)/Tl(I) couple and stability of Tl(I) (Lin and Nriagu, 1998), Tl(I) most probably represents a prevailing Tl species in the biogeochemical microcosm experiment from reducing to oxidizing conditions. Soluble Tl concentrations during low E_H (Fig. 3a) might be explained by their release upon reduction of reducible fraction (Fe-, Mn-oxides and hydroxides) which is additionally confirmed by the significant negative correlations between Tl at one side and Fe and Mn at the other side (Fig 3b, c). The temporal Tl dynamic during subsequent E_H increase was characterized by an increase of soluble Tl (Fig. 3a).

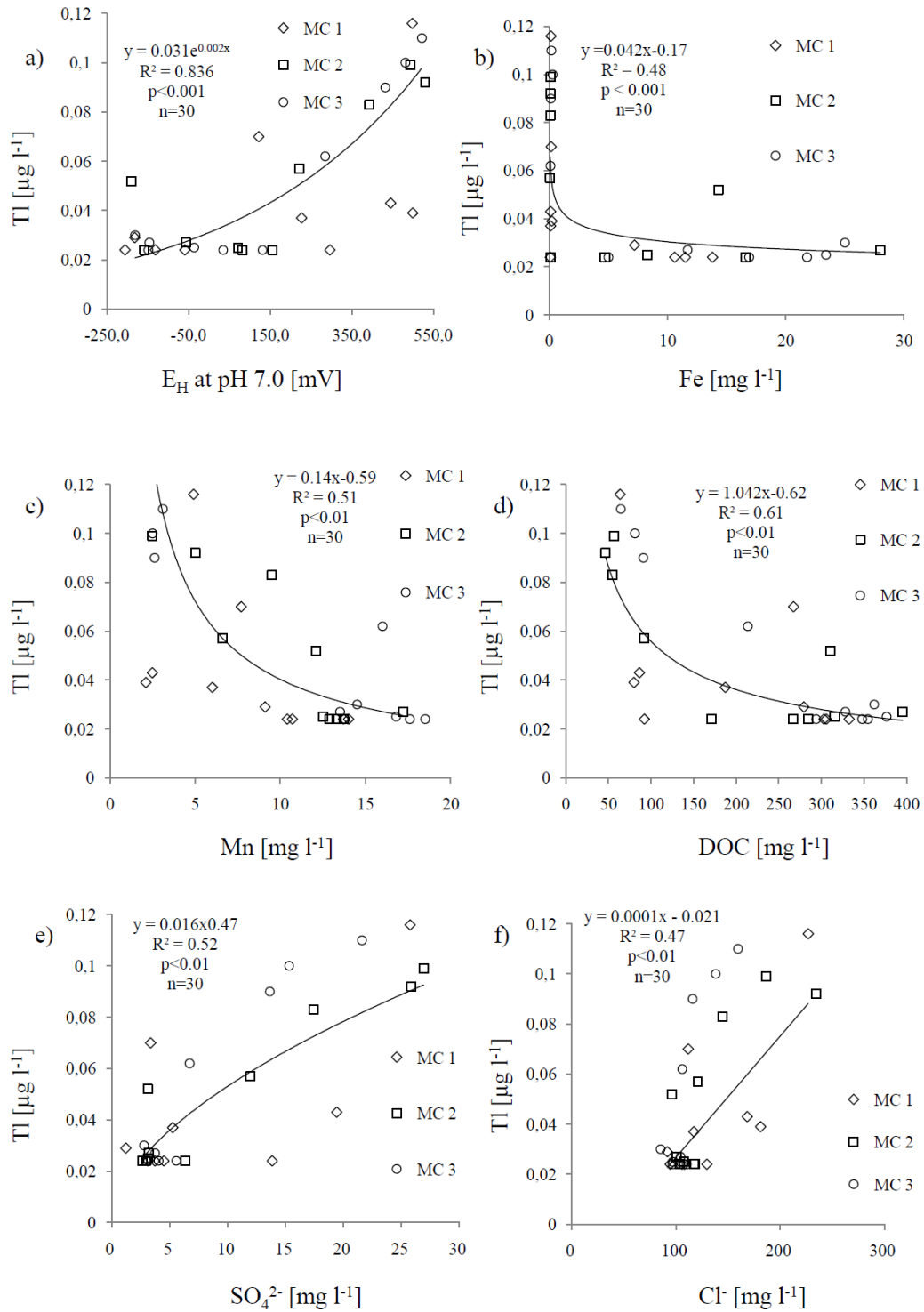


Figure 3. Concentrations of soluble Tl in the soil slurry during the biogeochemical microcosm experiment in a function of: a) redox potential (E_H), b) soluble Fe, c) soluble Mn, d) DOC, e) sulfates (SO_4^{2-}) and f) chlorides (Cl^-) in three independent MCs (MC1 – MC3) as replicates (n=30).

Thallium and E_H increase in our experiment coincide with an enhanced SO_4^{2-} concentrations (Fig. 3e) indicating that (i) sulfide oxidation occurred in our experiment and resulted in SO_4^{2-} increase in the slurry, and (ii) Tl was released into the slurry as a result of subsequent sulfide oxidation. This is in accordance with Karbowska et al. (2014), who estimated that the oxidable fraction is a major source of labile Tl.

Soluble Fe and Mn concentrations decreased with increases in E_H , confirming the precipitation of newly formed oxides at high E_H (see Antić-Mladenović et al., 2011). Based on Tl geochemical fractionation, its immobilization after Fe and Mn precipitation can be expected. However, soluble Tl concentration showed increasing tendency in oxidizing conditions (Fig. 3a). This points that several simultaneous processes might be involved in governing Tl solubility. Metallic sulfides (e.g. ZnS, PbS, FeS) differ in thermodynamic stability (Takeno, 2005), therefore, gradual oxidation of metallic sulfides might be a continuing source of soluble Tl with increasing E_H . Simultaneously, Tl sorption onto precipitated Fe- and Mn-oxides did not appear to cause complete Tl immobilization probably due to low Tl(I) affinity for sorption (Coup and Swedlund, 2015), which is the first step in immobilization process.

The opposite dynamic of Tl and DOC in our experiment (Fig. 3d) denotes the low tendency of Tl towards complexation with low molecular organic compounds Vaněk et al. (2012). Consequently, Tl extracted from the oxidable fraction was rather a product of sulfide oxidation than of organic matter decomposition.

Under oxic conditions, increase in soluble Tl concentrations coincided with an increase of Cl^- (Fig. 3f). Chlorides in the slurry probably occurred as a result of DOC breakdown via oxidation and/or microbial carbon consumption (Lee et al., 2001; Antić-Mladenović et al., 2011; Redon et al., 2013). Positive relation between Tl and chlorides indicate that soluble Tl at oxidizing conditions might partly be explained by formation of soluble Tl species, such as $TlCl_2^-$ (Evans and Barabash, 2010).

CONCLUSIONS

Based on the presented results, the following can be concluded:

- the largest part of Tl was bound to residual fraction in the soil, whereas the lowest proportion was found in the acid soluble (exchangeable) fraction, which directly denote a relatively low environmental risk;

- reducible and oxidable fractions were identified as a significant pool for Tl mobilization in dynamic redox changes in the soil;
- Soluble Tl concentrations and potential environmental risk might be higher in oxidizing than reducing conditions;
- Thallium mobilization in reducing conditions might be attributed to release upon reduction of Fe- and Mn- oxides;
- Thallium mobilization in oxidizing conditions might be associated with gradual oxidation of Tl-bearing sulfides;
- due to Tl toxicity at low doses and identified processes of mobilization in this research, monitoring of Tl contents in plants and ground water should be included in future research.

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UTICAJ RAZLIČITIH REDOKS USLOVA NA (I)MOBILIZACIJU TALIJUMA U ZEMLJIŠTE (SRBIJA)

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IZVOD: Talijum je veoma toksičan element i u niskim koncentracijama za razne organizme u okviru različitih delova životne sredine. Cilj rada bio je da se ispita (i) sadržaj talijuma u hemijskim frakcijama u zemljištu po modifikovanoj BCR proceduri i (ii) uticaj redoks potencijala (E_H) i glavnih faktora, kao što su gvožđe (Fe), mangan (Mn), rastvorljiv organski ugljenik (DOC), hloridi (Cl^-) i sulfati (SO_4^{2-}) na (i) mobilizaciju talijuma u povremeno plavljenom obradivom zemljište (Srbija). Plavljenje zemljište je simulirano u laboratorijskim uslovima, uz korišćenje automatskog biogeochemijskog zatvorenog sistema koji dozvoljava sistematsku kontrolu definisanih redoks uslova. Nakon toga, redoks potencijal zemljište je postepeno povećavan u okvirima od po 100 mV od redukcionih (-205 mV) do oksidacionih (530 mV) uslova. Redoks potencijal je automatski meren u intervalima od 10 minuta. Ukupno vreme trajanja oglada je bilo 914 sati. Hemijska frakcionacija je pokazala da se najveći deo ukupnog talijuma ($0,15 \text{ mg kg}^{-1}$) nalazi u rezidualnoj frakciji (85,5 %), a zatim u redukujućoj (10,2 %), oksidujućoj (3,8 %) i frakciji izmenljivo adsorbovanih elemenata (0,5 %). Redoks potencijal je značajno uticao na sadržaj rastvorljivog talijuma ($0.024\text{--}0.116 \mu\text{g l}^{-1}$), koji se povećavao sa njegovim povećanjem ($r=0.75$, $p<0.01$, $n=30$). Rastvorljivi sadržaji Fe, Mn, i DOC su pokazali značajnu negativnu korelaciju sa rastvorljivim sadržajem Tl ($r=-0.78$, $r=-0.73$ i $r=-0.91$, redom, $p<0.01$, $n=30$), dok su utvržene značajne pozitivne korelacije između Tl i sulfata i hlorida ($r=0.89$, $r=0.81$, $p<0.01$, $n=30$). Mobilizacija talijuma može se dovesti u vezu sa nekoliko procesa koji se istovremeno odvijaju, a to su, između ostalih, rastvaranje Fe- i Mn-oksida u oksidacionim uslovima i postepena oksidacija metalnih sulfida koji sadrže Tl. Naša istraživanja ukazuju da sadržaji rastvorljivog Tl mogu da se povećavaju u kada se redoks potencijal menja od redukcionih ka oksidacionim uslovima. Naša istraživanja upućuju na neophodnost sistematskog praćenja sadržaja Tl u biljkama i podzemnim vodama, s obzirom na njegovu visoku toksičnost u niskim dozama, kao i učestalu pojavu plavljenja obradivih zemljišta.