

Assessment of Extractants for the Determination of Thallium in an Accidentally Polluted Soil

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Abstract Thallium is a rare and easily dispersed element with high toxicity to organisms. Relatively high levels of thallium ($\sim 9.58 \text{ mg kg}^{-1}$) had been found in aqua regia soil extract of an accidentally polluted soil from south of Spain. To assess the available and leachable portions of thallium in the polluted soil, single and sequential extraction procedures have been utilized. Further, X-ray diffraction and scanning electron microscopic studies have also been used to find out the mineral phases. The amount of thallium extracted by the extracting agents in comparison to aqua regia, as well as the different phase associations are discussed.

Keywords Thallium · Single extraction · Sequential extraction · Accidentally polluted soil

Thallium (Tl) is a metal that has not been studied extensively. This element 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 (Peter and Viraraghavan 2005). Its chemical behaviour resembles the heavy metals (Pb, Au and Ag) on the one hand and the alkali metals (K, Rb, Cs) on the other. It occurs almost exclusively in natural waters as monovalent thallos cation. The solubility of thallos compounds is relatively high so that monovalent thallium is readily

transported through aqueous routes into the environment. Thallium can be transferred from soils to crops readily and accrues in food crops. Yet, there is relatively little literature available regarding the fate of this potentially hazardous element in terrestrial environments. Thallium is included in the United States Environmental Protection Agency list of priority toxic pollutants and fixed $2 \mu\text{g L}^{-1}$ as maximum contaminant level in the drinking water because of its acute toxicity. 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 \AA) is similar to that of the hard cation, potassium (K^+ ; 1.33 \AA), so that nondiscriminatory uptake of Tl^+ over K^+ has been suggested as a mechanism of its toxicity to biota (Tremel et al. 1997b). Thallium may also bind with sulfhydryl groups of proteins to inactivate many enzymatic reactions. In humans, one of the main symptoms of thallium poisoning is rapid (2–3 weeks) and often complete hair loss. Acute poisoning can lead to paralysis, coma, and death. Thallium also has mutagenic, carcinogenic and teratogenic effects (Leonard and Gerber 1997).

Worldwide, the thallium content of soils seems to depend largely on the geological origin of the parent material. In general, thallium concentrations in surface soils range from 0.1 to 2 mg kg^{-1} , with most reported concentrations being $<1 \text{ mg kg}^{-1}$ (Qi et al. 1992). There are exceptions, however as the clayey soils developed on the Sinemurian limestone in France with natural thallium contents as high as 55 mg kg^{-1} (Tremel et al. 1997a). Examples of soils contaminated with Tl include soils near cement plants in Germany with concentrations as high as 15 mg kg^{-1} and soils near old mines in Germany with

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concentrations up to 73 mg kg^{-1} , and mine tailings-impacted soils in China with thallium concentrations up to 61 mg kg^{-1} (Zhou and Liu 1985). Thallium is easily available to plants, and when concentrated in roots up to about 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. There is also an opinion that thallium is likely to be involved in microbial cycling by possible methylation (Weinberg 1977). As far as relatively high contents of Tl in soils, a potential risk for humans can arise at levels around 1 mg kg^{-1} . Especially growing of certain crops e.g. *Brassica-ceau* can pose a risk for the food chains because of elevated accumulation of Tl in plant tissues (Pavlickova et al. 2005). Although lot of literature is available on the leaching of several elements from soil by different extractants the information on thallium is very limited and due to its extreme toxicity it needs very immediate attention and utmost priority. Hence an attempt has been made in the present work to understand the leachability pathways of thallium and to find out the possible mode of its occurrence among different phases of a contaminated soil containing 9.58 mg kg^{-1} of thallium.

Thus the present investigation deals with the estimation of thallium in the above sample by utilizing different soil extractants like 0.1 M NaNO_3 , 0.01 M CaCl_2 , $1 \text{ M NH}_4\text{NO}_3$, 0.005 M Diethylenetriamine penta-acetate (DTPA), 0.05 M Ethylenediamine tetra-acetic acid (EDTA), 0.43 M acetic acid and 1 M HCl along with aqua regia to get a clear picture of the available and leachable portions of thallium due to operationally defined procedures. The above reagents have been chosen because NaNO_3 , CaCl_2 , NH_4NO_3 are unbuffered mild extractants which extract the exchangeable fraction of the elements; DTPA, EDTA are complexing agents which release the fraction of the elements mobilized by the complexation process; and acetic acid and HCl are acid reagents which allow the fraction of the elements remobilized by an acidification process. Finally BCR sequential procedure had also been applied to the sample to provide an estimation on the phase to which the thallium had been associated so that better understandability and interpretation of available thallium can be elucidated. X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies have also been carried out to find out the different mineral phases.

Materials and Methods

Soil sample had been collected from the site 20 km north of the Doñana National Park (South of Spain) which had

been contaminated by an accidental release of mineral waste which occurred in 1998 containing fine arsenopyrite and heavy metal-enriched sludge particles and acidic waters. The soil was collected with an auger down to 20 cm, placed in plastic containers and transported to the laboratory for preparation. The full details of sample preparation and characterization of the major elements by X-ray fluorescence method have been discussed by Pueyo et al. (2005).

All the reagents used to prepare the extracting solutions were products of analytical-grade quality (Merck pro-analysis). The concentrated acids (37% HCl and 70% HNO_3) used for the experiments were of Instra-Analyzed[®] quality from J.T. Baker. All solutions and dilutions were prepared using doubly de-ionised water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) obtained from an USF PureLaB Plus. All laboratory glassware and plastic ware were rinsed three times with double deionised water after being soaked in a HNO_3 (10%, v/v) bath overnight.

X-ray Diffractometer (XRD) studies were performed by preparing the sample by pressing some of the powder material in a cylindrical standard sample holder of 16 mm of diameter and 2.5 mm of height (PW1811/27). The instrument used was a PANalytical X'Pert PRO MPD Alpha1 powder diffractometer (radius = 240 mm) with Cu $K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a working power range from 45 kV to 40 mA. The qualitative phase analysis determination was carried out by means of the PDF (Powder Diffraction File) crystallographic data base from ICDD (International Centre for Diffraction Data, edition 2002).

Scanning Electron Microscope (SEM) investigations were carried using Stereoscan S-360 Scanning Electron Microscope (Cambridge Instruments Ltd., UK) equipped with an Energy Dispersive X-ray Microanalyzer (EDS) Inca series 200 (Oxford). The instrumental parameters used were, accelerating voltage 15 kV, beam current of 3 nA, working distance 24 mm and acquisition time of 300 s.

For ICP-MS measurements, Agilent 7500ce Model Inductively Coupled Plasma Mass Spectrometer (ICP-MS) equipped with an Agilent integrated auto-sampler and consisting of a radio-frequency source working at a power of 1550 W and a frequency of 40 MHz with a micromist Meinhard nebulizer, and a quartz spray chamber was used for thallium determination. Isotope ^{205}Tl was measured in helium gas mode to detect and control possible isobaric or polyatomic interferences.

The optimised BCR sequential extraction procedure was followed according to the procedure described fully by Rauret et al. (1999). Each extraction step was performed in triplicate, starting with 1 g of original material. The aqua regia step performed on the residue from Step 3 was based on ISO 11466 method (ISO 1995).

Soil extracts were obtained following the extracting conditions described as in the original procedures (Gupta and Aten 1993; Houba et al. 1996; DIN 1995; Lindsay and Norvell 1978; Quevauviller et al. 1997; Snape et al. 2004). The extracts were acidified with HNO_3 to prevent adsorption to the polyethylene of the storage vessel and to prevent growth of bacteria. The acidified supernatant was collected in polyethylene bottles and stored at 4°C until metal analysis. Three replicates were performed for each sample and each procedure and in independent working sessions. Blanks were measured in parallel for each batch of analysis using the extracting reagents described above.

Thallium content was determined in the extracts following the determination procedures described below. ICP-MS measurements were carried out by diluting 1:10 for all extracts except for aqua regia where 1:100 is employed (in 1% HNO_3) to minimise, interferences from the calcium and sodium present in the extracts. The calibration method used in all cases was an external calibration procedure (in 1% HNO_3) with ^{103}Rh as internal standard. No matrix matching was necessary due to sufficient dilution of the extracts. For all analytical measurements, the instrument was washed with HNO_3 (1%, v/v) between samples and standards during 30 s. Since a long series of samples were analysed, calibration after every ten samples was performed in order to control the sensitivity of the instrument.

Results and Discussion

Soil sample was characterised by XRD and SEM. The XRD results indicate that sample is comprised of mainly quartz, pyrites, calcite, gypsum, albite, with minor amounts of clinocllore, muscovite, Mg-hornblende, microcline or similar crystalline phases. Other trace crystalline phases may also be present in the sample. Due to its low concentration of around 10 mg kg^{-1} , thallium could not be identified as a separate phase although some possibility of occurrence as barium thallium oxide phase can exist. The SEM results reveal that the soil contains appreciable amounts of sulfur along with other usual major rock forming elements like Si, Al, Fe, Ca, Mg, Na, K, P, etc. It also shows significant concentrations of As, Pb, Zn and Cu. Hence most probably the sample comprise of pyrite with minor amounts of arsenopyrite, chalcopyrite and traces of sphalerite etc., along with other usual silicate matrix minerals.

The quantity of thallium extracted by the different extractant solutions are furnished in Table 1. A quantity of 9.58 mg kg^{-1} of thallium have been found in aqua regia soil extract (pseudo total content) of the contaminated soil. A perusal of the data given in Table 1 when following the standard conditions, indicate that out of the mild

extractants (0.1 M NaNO_3 , 0.01 M CaCl_2 , 1 M NH_4NO_3) 1 M NH_4NO_3 extract the maximum, and out of the strong extractants (0.005 M DTPA, 0.05 M EDTA, 0.43 M acetic acid and 1 M HCl) 1 M HCl extract the maximum being in all cases the extracted yield lesser than 5% with respect to pseudototal thallium content.

The interesting observation is that 1 M NH_4NO_3 which is a mild extractant and extracts generally only exchangeable portions of the elements could extract more thallium than other extractants with a priori stronger extracting capacity such as 0.005 M DTPA, 0.05 M EDTA and 0.43 M acetic acid. The possible reasons can be multifold: (a) ionic radius of Tl^+ (1.49 \AA) is similar to that of potassium (K^+ 1.33 \AA) and NH_4^+ (1.43 \AA); potassium depletion in the rhizosphere enhances the sorption of certain elements by clay minerals and the presence of ammonium ion (NH_4^+) may lead to the mobilization of thallium. (b) Presence of elevated levels of NH_4^+ could potentially compete with thallium for exchange sites on soil mineral and organic matter surfaces thereby releasing thallium. (c) Thallium forms weak complexation with most organic ligands ($\log k$ 0.5–2), fulvic acids ($\log k$, 3.32–4.83) and humic acids because the electronic configuration of Tl(I) ($[\text{Xe}] 4f^{14}5d^{10}6s^2$) and the two electrons in Tl(I) 's outer 6s orbital are σ -antibonding electrons and thus resist covalent bonding (Durrant and Durrant 1970; Lee 1971). (d) Thallium also binds to sulfide groups, but if specific metal complexing sites on organic matter are occupied by other cations, the slightly “harder” thallium is more likely to loosely associate with exchange sites on the soil organic matter. (e) Thallium is known to resist complex formation and most of its sorption has been attributed to simple exchange hence it would be expected to be more competitive for the monovalent cations such as NH_4^+ which is more similar in size etc.

Jacobson et al. (2005) in their studies of thallium sorption in soil solutions by DPASV technique indicate that all the thallium remaining in solution is labile. That is, all the thallium is present either as free Tl^+ , or as weak or small organic complexes that are readily converted to free Tl^+ . Considering the high total lability of thallium together with its suspected high bioaffinity based on observations of its indiscriminant uptake with K^+ , a noteworthy implication of these results is that the entire solution concentration of the highly toxic element meets the basic conditions for bioavailability as outlined by van Leeuwen (1999). High recovery of thallium by ammonium nitrate than the complexing reagents like EDTA obtained in the present study agrees with the earlier reported data by Zbiral et al. (2002) for some Czech republic soils samples.

Thus the present investigations indicate that 1 M NH_4NO_3 can be usefully utilized for the determination of mobile or exchangeable portion of thallium in soils which

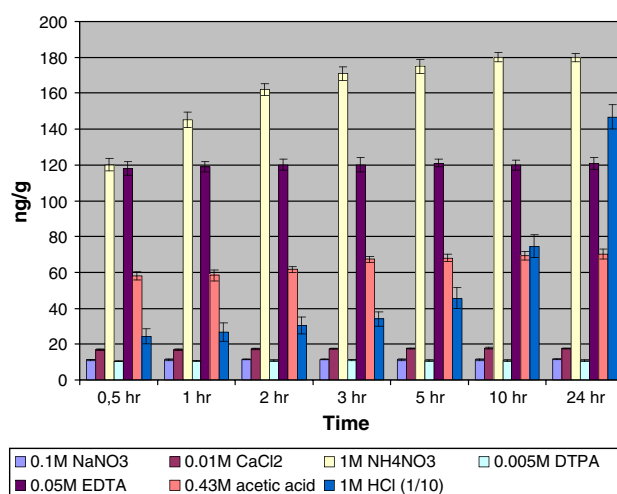
Table 1 Thallium values obtained with various procedures and the percentage of extraction in comparison to aqua regia value (considered as 100%)

Extracting reagent	Tl extractable amounts (ng g ⁻¹) (standard protocols)	% of extraction with respect to aqua regia
Single extraction procedures		
0.1 M NaNO ₃	11.25 ± 0.24	0.12
0.01 M CaCl ₂	17.52 ± 0.51	0.18
1 M NH ₄ NO ₃	162 ± 3.3	1.69
0.005 M DTPA	10.92 ± 0.45	0.11
0.05 M EDTA	119 ± 2.7	1.24
0.43 M CH ₃ COOH	70.5 ± 2.4	0.74
1 M HCl	415 ± 4.2	4.33
BCR sequential extraction procedure		
0.11 M acetic acid (Step 1)	40 ± 3	0.42
0.5 M hydroxyl amine hydrochloride (Step 2)	1040 ± 12	10.86
H ₂ O ₂ and 1 M ammonium acetate (Step 3)	250 ± 20	2.61
Aqua regia attack of the residue (Step 4)	8240 ± 96	86.01
Sum of 1 + 2 + 3 + 4 steps	9570 ± 105	99.89
Pseudo total content		
Aqua regia decomposition of the original sample	9580 ± 99	100

can help in identifying the extent of pollution and possible or potentially available concentrations to plants which can seriously effect the food chain so that remedial measures can be taken.

The BCR scheme results of the soil are also furnished in Table 1. It is evident from Table 1 that thallium is mainly associated to the residual phase (86.01%) and about 10.86% is released in the reducing step. The association of thallium with manganese and iron oxides have also been observed by Dahal and Lawrance (1996) and Smith and Carson (1977). Smith and Carson in their studies indicated that manganese oxides display an especially strong affinity for thallium as its enrichment in oceanic manganese nodules and ceratin US manganese deposits. Dahal and Lawrance (1996) observed that although the acidic character of δ -MnO₂ (S) may initiate this behaviour, the actual mechanism for the close association is believed to be the oxidation of Tl⁺ to Tl³⁺, which is then tightly sorbed to the manganese oxide surface or is precipitated on the manganese oxide surface as Tl₂O₃.

The extraction of thallium with various extracting reagents after shaking the soil sample for different times (from 0.5 to 24 h) had also been investigated to find out the quantity of thallium extracted with time. The results are shown in Fig. 1. It may be noted that the values of thallium obtained from 1 M HCl procedure have been divided by 10 to depict them suitably in the figure. It is evident from the Fig. 1 that there is no significant change in the extraction contents even after shaking for 24 h with reagents such as NaNO₃, CaCl₂, DTPA, EDTA and acetic acid. Whereas in the case of NH₄NO₃ a marginal increase is observed, with

**Fig. 1** Thallium recovery by various extractants at different extraction times

HCl there is an appreciable increase in the concentration of thallium with time. The higher recovery with HCl may be due to the more dissolution of Mn and Fe oxide phases with time which probably contains thallium as shown by the BCR sequential extraction procedure. It may also be noted that 1 M HCl extraction for 24 h could be utilized for finding out approximately maximum amount of leachable thallium levels of the samples as it approximately extracts the total amounts of thallium from all the combined steps of BCR 1, 2 and 3. Similar observations for some other elements have also been observed by Larner et al. (2006).

Thallium may pose high-potential health risks to humans through the food chain due to both natural

processes and human activities. In terms of geoenvironmental concern, proper planning and analysis would be far less costly to the well-being of the population. To do so, it is essential that the distribution pathways of thallium in different media and more specifically in contaminated soils are to be established. The present study underlines the fact that mild extractant like 1 M NH_4NO_3 can be utilized beneficially for the estimation of exchangeable and easily labile thallium content in soils. BCR sequential extraction scheme can be employed to understand the association of thallium to the relevant phase in the soil matrix. 1 M HCl extraction for 24 h can usefully be utilized to assess the maximum amount of leachable thallium as it extracts approximately total amount of thallium from all the combined steps of BCR 1, 2 and 3. XRD and SEM data can also be used further to substantiate the chemical data thereby improving the interpretation of the results on a more sound scientific basis.

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