Soil & Sediment Contamination, 13:25–36, 2004
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ISSN: 1058-8337 print
DOI: 10.1080/10588330490269769

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Thallium Behavior in Soils Polluted by Pyrite Tailings (Aznalcóllar, Spain)

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Thallium content and chemical speciation was studied at 91 sites contaminated by water and tailings spilled from the settling pond of a pyrite mine into the Agrio and Guadiamar rivers in Aznalcóllar (Spain). The contamination was highly heterogeneous, with 15% of the affected area seriously contaminated, 55% moderately contaminated and 30% uncontaminated. The total Tl content in the surface horizon increased with respect to the background level, more than 4-fold in the uppermost 10 cm of the soils, and clearly decreased with depth without contaminating either the subsoil or groundwater. Most of the Tl (approximately 75%) was in non-extractable forms, either as a component of the particles in the tailings or adsorbed to crystalline oxides. The remaining Tl was held on, or occluded in, amorphous or poorly crystallized oxides. In acidic soils, the adsorption of Tl was dominated by iron oxides (Feo) and, in neutral-alkaline soils, by aluminium oxides (Alo). A relatively high amount of the Tl adsorbed by amorphous oxides in the uppermost 10 cm of the soils was extracted with acetic acid, and was presumably bio-available (mean values approximately 15% of the Tlo). The EDTA is a strong extractant of inorganic forms of aluminium and, consequently, the quantity of Tl extracted by EDTA in neutral-alkaline soil (mean values more than 10% of the total Tl) could be higher than the truly bio-available fraction. Approximately 1% of the total Tl was extracted with calcium chloride, but only in the neutral-alkaline soil was the extraction significantly related to the cation-exchange capacity and, thus, adsorbed by the negative charges of the clay and organic matter. The Tl soluble in water (<0.1%) declined with the pH in the neutral-alkaline soils, and was unrelated to any soil property in the acid soils. Thus, the behavior of Tl is determined by climatic conditions, soils properties and time.

Keywords Pyrite tailings, soil pollution, thallium, speciation.

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Introduction

Thallium is a scarce element in nature but, because of its high toxicity (Sabbioni and Manzo, 1980; Douglas *et al.*, 1990), it is considered a potential environmental pollutant. Found mainly as an impurity in selenides, sulphides and sulphates (Sager, 1992; Sobott, 1993; Tremel and Baize, 1997; Pais and Benton, 1997; Kabata-Pendias, 2001), Tl is frequently associated with As, Sb, Cu, Pb, Fe, Au, Zn, Cd and Hg. The most dominant species in nature is Tl(I), while Tl(III) increases considerably under strongly acidic and oxidizing conditions (Lee, 1971). The latter species forms more stable complexes with organic matter (Tremel *et al.*, 1997) and precipitates in association with iron and manganese oxides (Smith and Carson, 1977). Geochemically, Tl(I) behaves as a heavy metal on the one hand and as an alkaline metal on the other (being related primarily to K and Rb; Pais and Benton, 1997; Kabata-Pendias, 2001). In this sense, Tl(I) is involved either in isomorphic replacements in feldspars and clays (Shaw, 1952) or in partial substitution of exchangeable K (Smith and Carson, 1977).

In sedimentary and metamorphic rocks, the Tl content is usually <0.6 mg kg^{-1} (Nriagu, 1998), whereas granites have been found to contain 0.35–3.60 mg kg^{-1} (Siedner, 1968), and basalts only 0.02–0.06 mg kg^{-1} (Heinrichs, 1975). The average concentration in soil is estimated to be 0.2 mg kg^{-1}, ranging from <0.01 to >5 mg kg^{-1} (IPCS, 1996). Soils developed on alluvial terraces, sandstones or limestones have a mean Tl concentrations of <0.4 mg kg^{-1} (Hofer *et al.*, 1990).

On 25 April 1998, a breach in the dam of a settling pond holding tailings from a pyrite mine in Aznalcóllar (Spain) spilled 45×10^5 m^3 of acidic waters and toxic tailings containing high concentrations of Zn, Cu, Cd, As, Pb, Sb, Bi and Tl into the basin of the Agrio and Guadiamar rivers, affecting some 43 km^2 (Grimalt *et al.*, 1999). The consequences were disastrous, where 60% of the land was agricultural (vegetables, sunflowers, rice, and fruit trees) and 20% was for grazing (pastures). The polluted waters reached the wetlands of the National Park of Doñana (proclaimed by UNESCO in 1994 as part of World Heritage), although the negative impact on fauna and vegetation was minor. As a result, cultivation, grazing and fishing were prohibited in the area by the Andalusian Regional Government.

The soils were polluted in two stages (Simón *et al.*, 1999). First, the toxic water (liquid phase) and tailings (solid phase) covered the soil. The water, having a far lower heavy-metal content (mean concentration of Tl was 0.7 ± 0.1 mg dm^{-3}) than the tailings had (mean concentration of Tl was 57.1 ± 24.0 mg kg^{-1}) penetrated more deeply into the soil. Meanwhile, the tailings only partially penetrated the soil through macropores. In the second stage, the drying, aeration and ageing processes of the tailings rapidly oxidized part of the sulphides to sulphates, forming an acidic solution with high concentration of heavy metals. With subsequent rainfall, this solution infiltrated and acidified the soils, sharply increasing the heavy-metal concentrations in the surface horizons. The lowest pH values were reached 25 days after the spill, and the total Tl concentration, at 90 days, doubled or tripled (depending on the soil type) the initial value of contamination in the upper 10 cm (Simón *et al.*, 2001).

In an extensive clean-up operation spanning eight months (May to December 1998) the tailings and part of the upper soil were removed. The present study provides an analysis of post-cleanup Tl concentrations in the affected soils, both in the surface area as well as in depth. The aim of the present work is to examine the behavior of Tl in contaminated soils, providing information to be taken into account for future remediation policies.

Materials and Methods

The climate of this area is typically Mediterranean (hot, dry summers; cold, wet winters; temperate autumns and springs with variable rainfall). The mean annual rainfall of 613 mm, the mean temperature of 17.7°C, and the potential evapotranspiration of 900 mm (taken from 7 weather stations near the spill, over 27 years). The affected soils were Typic Xerofluvents and Typic Xerothents (Soil Survey Staff, 1999) developed on alluvial deposits coming from the erosion of sedimentary and metamorphic materials of the Agrio and Guadiamar River basin, mainly gravels, sands, silts and clays from the Miocene and Plio-Quaternary.

After the removal of the tailings, the basin was gridded into 91 sectors of 400 × 400 m, and in the center of each sector a plot 10 × 10 m was laid out. In every plot, soils samples were taken at the four corners and center, at depths of 0–10, 10–30 and 30–50 cm. For each depth, 250 g of soil from the five sampling points per plot were mixed and homogenized, providing three samples per plot, for a total of 273 soil samples for the entire basin. All the samples were air dried and screened to 2 mm, and the percentages of gravels (>2 mm) and fine earth (<2 mm) were determined. The laboratory analyses were made with the fine-earth fraction.

Particle-size distribution was measured by the pipette method after eliminating organic matter with H_2O_2 and dispersion with sodium hexametaphosphate (Loveland and Whalley, 1991). The pH was measured potentiometrically in a 1:2.5 soil-water suspension, as recommended by the International Society of Soil Science, in a CRISON Digit 501 instrument. The $CaCO_3$ equivalent was determined manometrically by the Barahona method (1984). Total carbon and total sulphur were measured by dry combustion with a LECO mod. SC-144DR instrument. Organic carbon was calculated as the difference between total carbon and inorganic carbon from $CaCO_3$. The cation-exchange capacity (CEC) was determined with 1N Na-acetate at pH 8.2 (Rhoades, 1982), measuring the sodium in a METEOR NAK-II flame-photometer. The total concentration of iron (Fet) was measured by X-ray fluorescence in a Philips PW-1404 instrument equipped with a Rh tube and a generator of 3 Kw, from a disc of soil and lithium tetraborate in a ratio of 0.6:5.5. Total iron (Fed) and aluminum (Ald) oxides were extracted with citrate-dithionite (Holmgren, 1977), and the amorphous and poorly crystallized iron (Feo) and aluminum (Alo) oxides were extracted with oxalic-oxalate (Schwertmann and Taylor, 1977). Iron and aluminum in the extracts were measured by atomic-absorption spectroscopy.

Samples of air-dried soils, ground to <0.05 mm, were digested in open flasks by strong acids (HNO_3:HF in a ratio 2:3) at 160°C till dry, and 100 ml HNO_3 at 4% were added. In the digested samples, total Tl (Tl_t) was measured by ICP-MS with a PE SCIEX-ELAN 5000A spectrometer. A Multi-element Calibration Standard 4 (Perkin-Elmer) was used with Rh as the internal standard. The detection limit for Tl was 0.001 $\mu g\ L^{-1}$, and the accuracy of the method was corroborated by analyses (six replicates) of a standard reference material: SRM 2711 (soil with moderately elevated trace-element concentrations; Gills and Kane, 1993). For Tl, the mean certified value was 2.47 mg kg^{-1} with a standard deviation of 0.15; the mean experimental value was 2.57 mg kg^{-1} with a standard deviation of 0.08.

Soluble Tl (Tlw) was measured in the extract from a saturated soil paste. The Tl was extracted by 0.01 M calcium chloride (Tlc) using the method of Novozamsky *et al.* (1993), Tl extractable by 0.43 M acetic acid (Tla) following Ure *et al.* (1993), and Tl extractable by oxalic-oxalate pH 3 (Tlo) as in Schwertmann and Taylor (1977). For the 0.05 M EDTA extractable fraction (Tle), Quevauviller *et al.* (1998) were followed. The Tl of all the extracts was measured by ICP-MS.

For the statistical analysis, the SPSS 10.0.6 program was used. The areal distribution of the contamination was established by the algorithm of the least Euclidean, using the software Surfer 7.0.

Results and Discussion

Properties of the Affected Soils

According to the soil properties between 0 and 50 cm in depth, we assigned five different soil types with significant differences ($P < 0.05$) by a cluster analysis via the k-mean method (Table 1). Occupying roughly 20% of the affected area in the upper part of the basin, soil types 1 and 2 (hereafter Group A) were acidic and had little or no carbonate; type 1 had a loam texture while type 2 was dominated by gravel and sand. Soil types 3, 4 and 5 (hereafter Group B) were predominantly neutral or slightly alkaline and carbonate, the main differences between them being texture (type 3, clay loam; type 4, loam; and type 5, silty clay).

The variation in the soil properties with the depth was not significant in the cases of texture, calcium-carbonate content, organic-carbon content and cation-exchange capacity, indicating that these soils were quite homogeneous in depth. Nevertheless, other properties related to the contamination, such as total sulphur (St) and iron (Fet) content, all the soil types registered their highest values in the upper 10 cm, values declining progressively with depth (Figure 1), with statistically significant differences ($P < 0.001$). In addition, the contamination also affected the pH with progressively greater acidity towards the soil surface, differences between depths being significant. In the Group B soils, the presence of $CaCO_3$ caused more uniform pH values in depth, remaining higher, and rarely falling below 6.0.

The difference in Fet and St between the first 10 cm and the interval 10–30 cm was greater in Group A soils than in Group B, this being related presumably to the soil properties and climate. Under the acidic conditions of the Group A soils (usually below pH 5.0), Fe remained partially soluble and, due to the high evapotranspiration of the Mediterranean climate, rose to the soil surface, in places forming hard, thin crusts some 2 mm thick (Figure 2). Meanwhile, in Group B soils, where the pH generally exceeded 7.0, the Fe precipitated within the soil matrix without evidence of crust formation.

Total Tl Content

In uncontaminated soils next to the affected area the concentrations of the total Tl (Tlt) were between 0.2 and 0.9 mg kg^{-1}, with a mean value of 0.6 mg kg^{-1} (Simón *et al.*, 1999). Meanwhile, in contaminated soils, the mean Tl content in the uppermost 10 cm was 2.6 mg kg^{-1}, ranging between 0.3 and 19.3 mg kg^{-1}. This mean value significantly declined with depth in all soil types, with a distribution similar to that of St (Figure 1). Consequently, in the uppermost 10 cm of the soils, a highly significant linear relationship ($P < 0.001$) was found between Tlt and St (Figure 3).

In addition, the Tlt concentration in the 10–30 cm layer did not significantly differ from that of the 30–50 cm layer, and in fact had values approaching those of unaffected soils (Simón *et al.*, 1999; Cabrera *et al.*, 1999). Consequently, the pollution affected mainly the uppermost 10 cm of all the soils.

In any case, the pH range as well as the St, Fet and Tlt values in the upper 10 cm of the soils were very broad, indicating a highly heterogeneous contamination, as previously

Table 1
Mean and standard deviation (SD) of the particle size, pH, $CaCO_3$, organic-carbon (OC) content, and cation exchange capacity (CEC) in the uppermost 50 cm of the different soil types (*n* = number of samples in each soil type)

		Gravel (%)		Sand (%)		Silt (%)		Clay (%)		pH		$CaCO_3$ (%)		OC (%)		CEC ($cmol_c\ kg^{-1}$)	
Soil Type	*n*	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
1	36	5.2	3.5	50.7	18.4	30.8	14.1	18.5	6.9	5.8	1.9	1.7	3.5	1.0	0.4	15.5	5.8
2	33	37.2	24.5	76.2	17.1	13.6	9.3	10.2	8.6	5.9	1.8	0.8	1.7	0.4	0.3	7.7	3.7
3	63	6.9	9.4	19.6	11.2	49.4	9.7	31.0	11.2	7.7	0.5	10.0	5.0	1.1	0.5	18.1	5.2
4	87	4.8	8.5	48.8	12.6	32.5	9.4	18.7	6.0	7.8	0.7	6.9	6.3	0.9	0.4	12.1	4.2
5	54	8.2	9.6	4.9	7.1	47.7	11.2	47.4	14.0	8.0	0.3	13.6	4.9	1.3	0.5	22.9	4.9

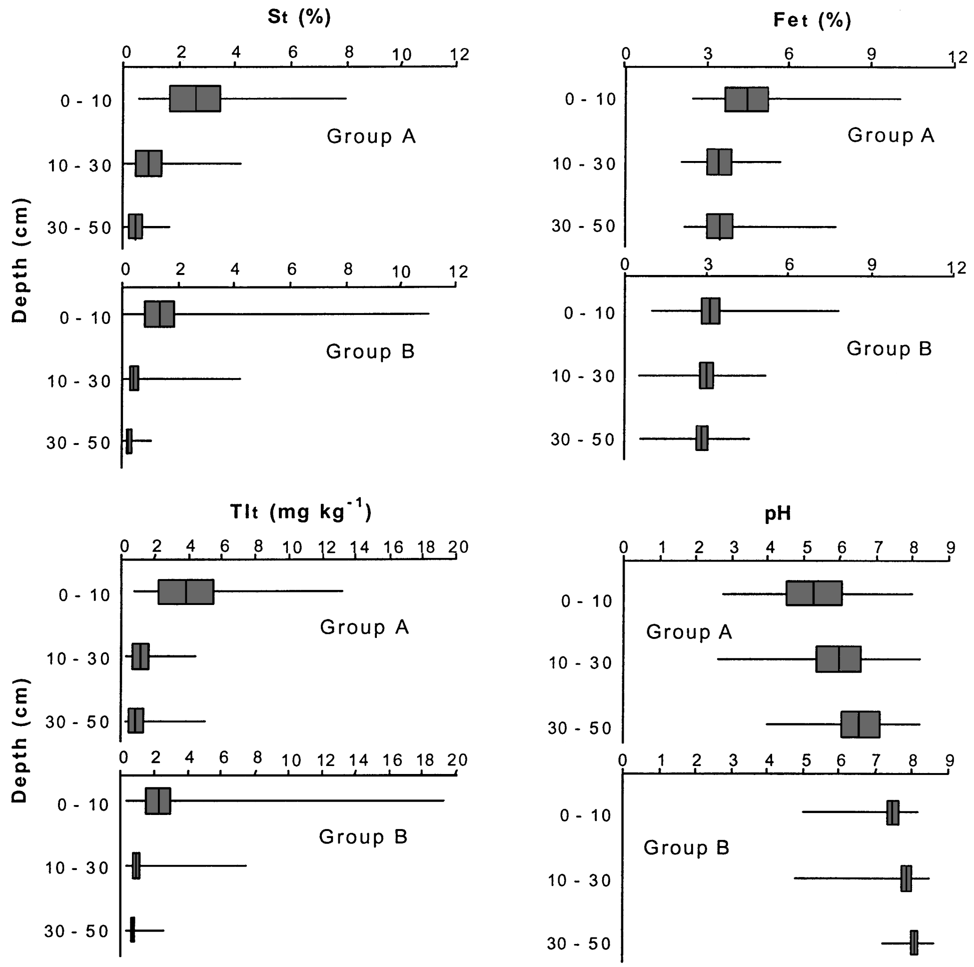

Figure 1. Total sulphur (St), iron (Fet), thallium (Tlt) content and pH in the two soil groups (horizontal lines goes from minimum to maximum values; boxes show the confidence interval at 95% for the mean; vertical lines mark the mean values).

reported by Simón *et al.* (1999). According to the reference and intervention levels for Tlt (1 and 5 mg kg^{-1}, respectively) established by the Andalusian Regional Government, 15% of the area proved to be seriously contaminated (>5 mg kg^{-1}), 55% was moderately contaminated (1 to 5 mg kg^{-1}), and 30% could be considered uncontaminated (<1 mg kg^{-1}).

Tl Speciation

For thallium speciation, selective extractants of different strengths were used, taking into account that most are not specific to a given soil phase (Ure, 1995). The following Tl extractions were used: water extracted constituted the soluble fraction (Viets, 1962; Sposito *et al.*, 1982); the $CaCl_2$ extracted was considered the exchangeable fraction (McLaren and Crawford, 1973; Iyengar *et al.*, 1981); acetic acid extracted was used as the bio-available

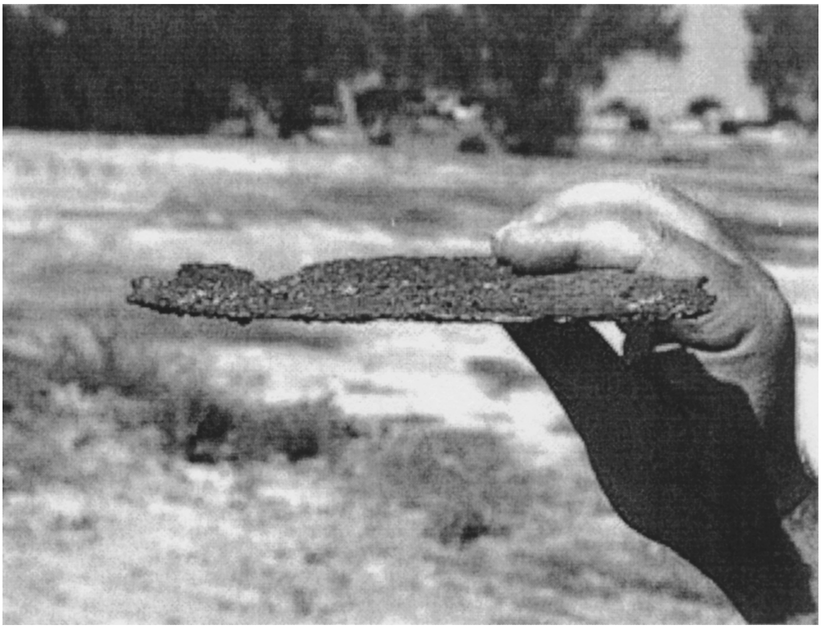

Figure 2. Iron-rich crust formed on the surface of acidic soils.

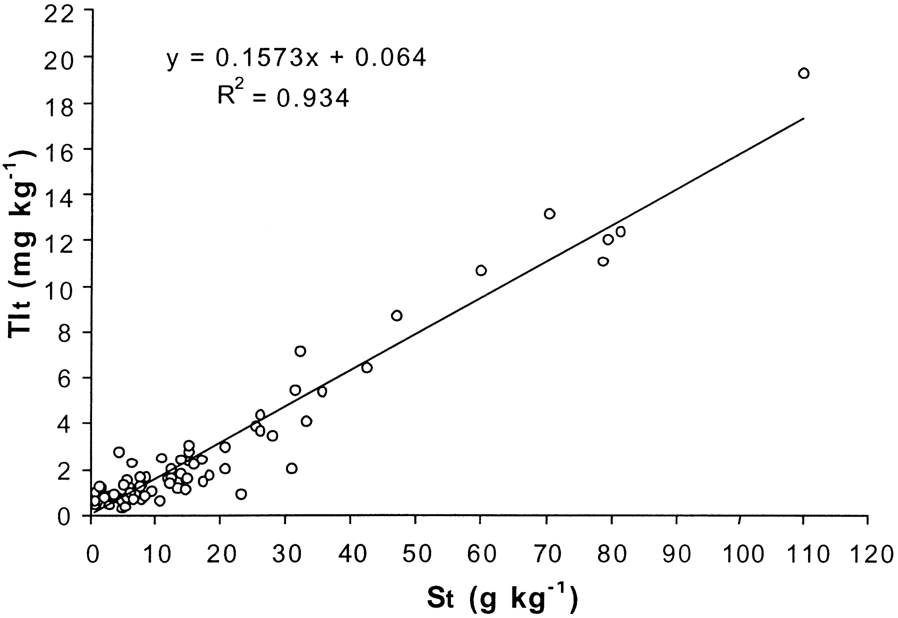

Figure 3. Regression plot between total thallium (Tlt) and total sulphur (St) content in the uppermost 10 cm of the soils.

Table 2

Mean content (mg kg^{-1}) and standard deviation (SD) in the A and B groups of soils for Tl extracted with oxalic-oxalate (Tl_o), EDTA (Tl_e), acetic acid (Tl_a), calcium chloride (Tl_c) and water (Tl_w)

Soil Group	Depth (cm)	Tl_o		Tl_e		Tl_a		Tl_c		Tl_w	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
A	0–10	0.48	0.29	0.06	0.04	0.06	0.04	0.010	0.007	0.001	0.001
	10–30	0.30	0.27	0.05	0.04	0.05	0.04	0.007	0.005	0.001	0.001
	30–50	0.22	0.21	0.03	0.03	0.03	0.03	0.005	0.003	0.001	0.001
B	0–10	0.34	0.14	0.13	0.08	0.05	0.03	0.036	0.041	0.002	0.002
	10–30	0.21	0.16	0.08	0.07	0.04	0.02	0.022	0.026	0.002	0.002
	30–50	0.19	0.15	0.07	0.06	0.04	0.02	0.016	0.019	0.002	0.002

fraction associated with carbonates and also specifically adsorbed by oxides as well as organic matter (McLaren and Crawford, 1973; Louma and Jenne, 1976; Stover *et al.*, 1976; Beckett, 1989); EDTA extracted was also considered to be the bio-available fraction associated with carbonates, inorganic precipitates, amorphous oxides and organic matter (Louma and Jenne, 1976; Stover *et al.*, 1976; Rendell *et al.*, 1980; Sposito *et al.*, 1982; Beckett, 1989); and the oxalic oxalate extracted were held on, or occluded in, amorphous or poorly crystallized iron, aluminium or manganese oxides (Chao and Zhou, 1983; Ure, 1995). The average concentration and standard deviation of the different extracted forms of Tl are shown in Table 2.

The reagent that extracted the significantly highest concentrations of Tl in the uppermost 10 cm of the soils was oxalic oxalate (mean ≈ 25% of the Tlt), indicating that a very high proportion of the Tl was adsorbed to amorphous or poorly crystallized iron and aluminium oxides. When all soils were pooled, the Tl extracted with oxalic oxalate (Tlo) was related to Feo and Alo, although with relatively low significance ($P < 0.05$). Nevertheless, when the soils were separated into acidic (Group A) and neutral alkaline (Group B), the former correlated significantly only with Feo and the latter only with Alo (Figure 4), in both cases with a far higher significance level ($P < 0.001$). These results could be attributed not only

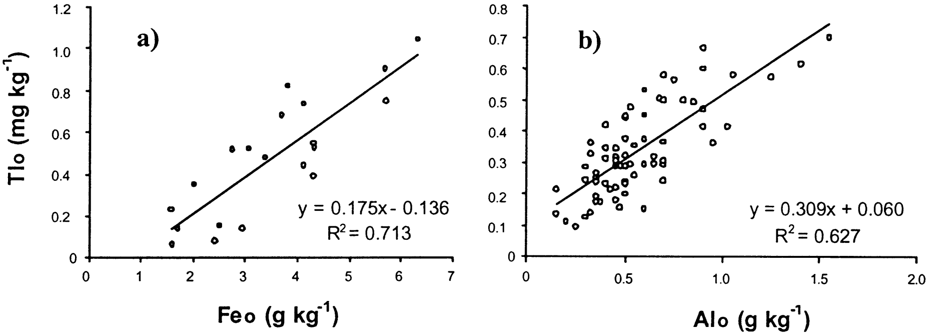

Figure 4. Regression plots between: a) amorphous iron oxides (Feo) and thallium extracted with oxalic oxalate (Tlo), and b) amorphous aluminum oxides (Alo) and thallium extracted with oxalic oxalate (Tlo).

to the higher pK1 of Al^{3+} in relation to Fe^{3+} (resulting in less extensive hydrolysis in acidic conditions and less adsorption of Tl), but also to a more negative surface charge of aluminium oxide than iron oxide at neutral-basic pH values.

In addition, the mean values of the ratio Tlo:Tlt was less than 0.2 in the uppermost 10 cm of the Group A soils, while between 10–30 cm in depth this value was around 0.4, this difference being statistically significant ($P < 0.01$). The decrease of this ratio in the upper soil layer may be related to the formation of surface crusts (Figure 2) in which amorphous and poorly crystallized iron oxides partially crystallized to form goethite, lepidocrocite or hematite (Schwertmann and Murad, 1983; Bigham and Nordstrom, 2000) and, thus, neither the crystallized Fe nor its adsorbed Tl would be extractable by oxalic oxalate. The lower Feo:Fed ratio in the uppermost 10 cm (mean 0.16) respect to the depth between 10–30 cm (mean 0.27), confirms the higher iron crystallization in the surface of the Group A soils. In the Group B soils, the mean values of the ratio Tlo:Tlt was between 0.20 and 0.25, and those of the ratio Feo:Fed between 0.26 and 0.30, without significant differences in depth. The adsorption of Tl by the amorphous aluminum oxides as well as the absence of crust formation in the neutral-alkaline soils must have been responsible for this behavior.

The Tl extracted with acetic acid (Tla) and EDTA (Tle) in the uppermost 10 cm of the soils, like that extracted with oxalic-oxalate, correlated significantly only to Feo in the case of the Group A soils ($P < 0.01$), and only with Alo in the Group B soils ($P < 0.01$). In the Group A soils the linear-regression equations are:

$$\text{Tla (mg kg}^{-1}\text{)} = -0.015 + 0.019\ \text{Feo (g kg}^{-1}\text{)} \tag{1}$$

$$\text{Tle (mg kg}^{-1}\text{)} = -0.004 + 0.018\ \text{Feo (g kg}^{-1}\text{)} \tag{2}$$

both with similar slopes, indicating that the quantities of Tl extracted with acetic acid and EDTA were equivalent. In the Group B soils the linear-regression equations are:

$$\text{Tla (mg kg}^{-1}\text{)} = 0.030 + 0.038\ \text{Alo (g kg}^{-1}\text{)} \tag{3}$$

$$\text{Tle (mg kg}^{-1}\text{)} = 0.065 + 0.119\ \text{Alo (g kg}^{-1}\text{)} \tag{4}$$

with clearly different slopes, indicating that in the neutral-alkaline soils the EDTA extracted higher quantities of Tl than did acetic acid, apparently due to the fact that EDTA is a strong extractant of inorganic forms of aluminium (Jarvis, 1986).

The Tl extracted with calcium chloride (Tlc) in Group A soils was significantly related only to the Feo ($P < 0.01$), according to the linear regression equation:

$$\text{Tlc (mg kg}^{-1}\text{)} = 0.002 + 0.0024\ \text{Feo (g kg}^{-1}\text{)} \tag{5}$$

This implies that in acidic soils Tl was adsorbed to iron oxides but not significantly held on inorganic or organic sites by electrovalent forces, presumably because, as noted by Lee (1971) as well as Smith and Carson (1977), the predominant form present would be Tl(III). On the contrary, in Group B soils, the Tlc was significantly related ($P < 0.01$) only to the cation-exchange capacity (CEC) and associated soil properties, such as the clay and organic-carbon content, presumably because the predominant form present was Tl(I) (Smith and Carson, 1977). The linear regression equation is:

$$\text{Tlc (mg kg}^{-1}\text{)} = -0.004 + 0.002\ \text{CEC (cmolc kg}^{-1}\text{)} \tag{6}$$

The Tl soluble in water (Tlw) was not significantly related to any of the properties studied in Group A soils, while in Group B soils proved to be negatively and significantly related to pH ($P < 0.001$), as in Tyler and Olsson (2001). The linear regression equation is:

$$\text{Tlw (mg kg}^{-1}) = 0.012 - 0.001 \text{ pH} \tag{7}$$

Conclusions

The behavior of thallium is controlled by the interaction of three factors: climatic conditions, soil properties and time. The high evaporation of the Mediterranean climate provokes the concentration of Tl on the soil surface in acid soils, in which this metal remains more soluble. Meanwhile, in neutral-alkaline soils Tl precipitates throughout the soil matrix. In both cases, the Tl accumulates in the top of the soil without contaminating the subsoil or groundwater. The amorphous oxides are the principal soil components in the adsorption of Tl, Feo in acidic and Alo in neutral-alkaline soil. The crystallization of these oxides reduces the bio-availability, which is best estimated by acetic acid (as EDTA is a strong extractant of the inorganic form of Al). Where pH values exceed 6.5, Tl solubility decreases, and the adsorption of Tl by clay and organic matter increases.

Acknowledgements

The authors express their gratitude to the Environmental Ministry of the Regional Government of Andalusia, Spain, for its financial support that made this work possible. David Nesbitt reviewed the English of the manuscript.

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