

Introduction

Thallium is a member of group 13 of the periodic table, which also includes B, Al, Ga and In. The element has an atomic number of 81, an atomic mass of 204, two main oxidation states (+1 and +3), of which the +3 state is most common, and two naturally occurring isotopes, ^{203}Tl and ^{205}Tl ; the latter is the most abundant at 70.5% of the total mass.

Thallium minerals are very rare and are formed exclusively during the epithermal stage of hydrothermal activity or under supergene conditions (Vlasov 1966). Examples of these minerals include lorandite TlAsS_2 , picotpaulite TlFe_2S_3 and vrbaita $\text{Hg}_3\text{Tl}_4\text{As}_8\text{Sb}_2\text{S}_{20}$ (Wedepohl 1978). Host minerals that provide a major source of Tl in igneous and magmatic rocks include plagioclase (up to 100 mg kg^{-1}), K-feldspar ($0.4\text{--}610 \text{ mg kg}^{-1}$), and mica minerals such as phlogopite, biotite ($0.8\text{--}380 \text{ mg kg}^{-1}$) and muscovite ($1\text{--}280 \text{ mg kg}^{-1}$) (Jović 1999b).

Thallium has both chalcophile and lithophile properties, and has an average abundance in the Earth's crust of 0.8 mg kg^{-1} (Jović 1999b). According to Kabata-Pendias (2001), the distribution of Tl in the Earth's crust shows that its concentration appears to increase from ultramafic to felsic rocks, and with increasing clay content of sedimentary rocks. Calcareous sedimentary rocks contain the least thallium. Ultramafic and mafic rock types contain very low concentrations of Tl, typically in the ranges $0.07\text{--}0.30 \text{ mg kg}^{-1}$ and $0.05\text{--}0.70 \text{ mg kg}^{-1}$ respectively. Intermediate rocks display a marked increase in Tl concentration ($0.15\text{--}1.4 \text{ mg kg}^{-1}$). Granitic rocks contain the highest Tl concentrations of all magmatic rocks ($0.6\text{--}3.5 \text{ mg kg}^{-1}$) (Wedepohl 1978). Late muscovite from replacement zones within pegmatite have been reported to contain up to 280 mg kg^{-1} Tl (Wedepohl 1978). Sulphide minerals from ore deposits often show increased concentrations of Tl, which is attributed to metal substitution brought about by metasomatic processes during ore formation. Galena PbS and sphalerite ZnS have yielded Tl concentrations in excess of 5000 and 1000 mg kg^{-1} respectively in polymetallic deposits from the Caucasus Region (Wedepohl 1978).

Average concentrations of Tl in sedimentary rock types are in the range 0.1 to 2 mg kg^{-1} . The

highest values are generally found in sandstone ($1\text{--}3 \text{ mg kg}^{-1}$) and coal ($2\text{--}3 \text{ mg kg}^{-1}$), although Tl in coal is thought to be associated with the sulphide phase, and not the coal itself (Wedepohl 1978). Calcareous sedimentary rocks contain very little Tl; Kabata-Pendias (2001) cite values in the range $0.01\text{--}0.14 \text{ mg kg}^{-1}$. The primary processes by which Tl becomes concentrated in sedimentary rocks are thought to be the chalcophilic tendencies of Tl (Voskresenskaya *et al.* 1962) and the adsorption of Tl to clay mineral surfaces (Canney 1953).

During weathering, Tl is readily mobilised and transported together with alkaline metals, but is most often fixed by Mn and Fe oxides and organic matter, the latter especially under reducing conditions (Kabata-Pendias 2001). The average concentration of Tl in soil is given as $0.02\text{--}2.8 \text{ mg kg}^{-1}$ (Jović 1999b).

In the aqueous environment, Tl^+ (aq) is the more stable cation, although Tl^{3+} forms complexes with carbonates, sulphates, chlorides, nitrates and fluorides of greater stability (CRC Press 1987, 2005, Ensafi and Rezaei 1998). A significant proportion of Tl^{3+} may also exist in colloidal form (Lin and Nriagu 1999). The dominant form of Tl in the aqueous environment is probably oxidised Tl^{3+} , but the proportion of Tl^{3+} to total dissolved Tl is highly variable (Lin and Nriagu 1999). River water Tl concentrations may be as low as 0.003 ng l^{-1} , whilst sea water is typically slightly higher at about 0.01 ng l^{-1} (Nielsen *et al.* 2004). In hydrothermal areas and geological formations that contain anomalously high Tl, stream water concentrations may be higher still; values up to $31 \text{ } \mu\text{g l}^{-1}$ have been reported in one anomalous area (Xiao *et al.* 2004).

The primary anthropogenic source of Tl is steel industry slag from blast furnaces, basic oxygen furnaces and electric arc furnaces. The slag may be used for fill, roadbase or landscaping (Proctor *et al.* 2002). Other significant sources are the cement industry, mining, and metal refining processes (Kabata-Pendias 2001). Thallium is also used in pesticides, although this has been banned in many industrialised countries, photocells, in the manufacture of glass and as an eutectic.

Thallium is extremely toxic, but little studied.

Thallium poisoning affects the central nervous system, causing visual disorders, such as failing eyesight or total blindness, hair loss and ultimately death (Xiao *et al.* 2004). In studies of Tl toxicity using the amphipod *Hyalella azteca*, an indicator of the health of the aquatic environment,

the toxicity of Tl was found to be similar to that of Cd, Hg and Pb (Borgmann *et al.* 1998).

Table 69 compares the median concentrations of Tl in the FOREGS samples and in some reference datasets.

Table 69. Median concentrations of Tl in the FOREGS samples and in some reference data sets.

Thallium (Tl)	Origin – Source	Number of samples	Size fraction mm	Extraction	Median mg kg⁻¹
Crust ¹⁾	Upper continental	n.a.	n.a.	Total	0.9
Subsoil	FOREGS	783	<2.0	Total (ICP-MS)	0.67
Topsoil	FOREGS	840	<2.0	Total (ICP-MS)	0.66
Soil ²⁾	World	n.a.	n.a.	Total	0.50
Water	FOREGS	807	Filtered <0.45 µm		0.005 (µg l⁻¹)
Water ³⁾	World	n.a.	n.a.		1 (µg l ⁻¹)
Water ²⁾	World	n.a.	n.a.		0.04 (µg l ⁻¹)
Water ⁴⁾	Barents region	1365	Filtered <0.45 µm		0.003 (µg l ⁻¹)
Stream sediment	FOREGS	848	<0.15	Total (XRF)	0.39
Floodplain sediment	FOREGS	743	<2.0	Total (XRF)	0.37

¹⁾Rudnick & Gao 2004, ²⁾Koljonen 1992, ³⁾Ivanov 1996, ⁴⁾Salminen *et al.* 2004.

Tl in soil

The median Tl content is 0.67 mg kg⁻¹ in subsoil and 0.66 mg kg⁻¹ in topsoil, with a range varying from 0.01 to 21.3 mg kg⁻¹ in subsoil and 0.05 to 24 mg kg⁻¹ in topsoil. The average ratio topsoil/subsoil is 0.982.

Low Tl values in subsoil (<0.44 mg kg⁻¹) occur in central and northern Finland and Norway, in the glacial drift area from the Netherlands to Poland, in northern Ireland, central Hungary, Crete, and eastern and southern Spain. The southern margin of the ice-age glaciation area is well marked on the Tl subsoil map, with low values north of it.

In subsoil, Tl shows high values (>0.97 mg kg⁻¹) in an area extending from northern Portugal to western and north-central Spain (crystalline basement of the Iberian Massif), from the Massif Central to Poitou (see Pb-Zn anomaly explanation above), in Brittany and Morvan (Copper mine of the Chessy district), and in the Italian alkaline magmatic province extending into Calabria. Some enrichment occurs locally in Greece (terra rossa in Kefallinia and Epirus, and

mineralised areas of central Macedonia), in karstic parts of Croatia and Slovenia (residual soil over carbonates), a large area in central Sweden around the Skellefte district, and smaller areas in south-east Sweden and southern Norway. This general pattern corresponds to enrichment over crystalline felsic rocks, with additional enrichment or even point anomalies in known Pb-Zn mining districts. Rapakivi granite in south-east Finland is known to be responsible for local Tl subsoil enrichment, which is faintly visible on the European scale. The highest Tl value in subsoil is an outlier (21.3 mg kg⁻¹), which occurs near Alès (Massif Central) in southern France and is due to mining contamination; this sample is also highly anomalous in As, Sb, Pb, Cd, I and Zn. The highest Tl value in topsoil (24 mg kg⁻¹) is also an outlier in France in the Dauphiné region (western Alps).

There is not much difference between the subsoil and topsoil Tl distribution maps. The average ratio topsoil/subsoil is 0.982. The continuous high Tl values in the Pyrenees are due

to Silurian black shale occurrences.

Thallium in subsoil shows a strong correlation (>0.6) with Be, Th, Rb, Cs, Ce, La, Pr, Nd, and a good correlation (>0.4) with U, Ag, As, Bi, Nb,

Ta, Al, Ga, In, K, Pb, Zn, Y and the remaining REEs. In topsoil, the correlations are similar, but Rb, Ta and U have a stronger correlation with Tl.

Tl in stream water

Thallium values in stream water range over two orders of magnitude, from <0.002 $\mu\text{g l}^{-1}$ to 0.22 $\mu\text{g l}^{-1}$, with a median value of 0.005 $\mu\text{g l}^{-1}$. Thallium data correlate, in many respects, with niobium, especially for the high values distribution.

Lowest Tl values in stream water (<0.002 $\mu\text{g l}^{-1}$) are predominantly found in southern and northern Spain, south-western and south-eastern France, western Switzerland, north-western and north-eastern Italy, southern England, south-western and northern Norway, at the border between Latvia and Lithuania, in north-eastern Germany, western Czech Republic, southern Hungary and eastern Croatia, in northern Albania and in central Greece.

Highest Tl concentrations in stream water (>0.02 $\mu\text{g l}^{-1}$) are found in southern Sweden, in central and southern Italy (including Sicily and Sardinia). Enhanced values Tl values in stream water (>0.01 $\mu\text{g l}^{-1}$) also occur in southern Norway, Sweden and Finland, in Denmark and in France (Brittany and Massif Central). Isolated enhanced Tl values in stream water occur in northern England (associated with the Durham Coalfield and local heavy industrial pollution), and in south-western France, near Bordeaux (no explanation, it is correlated with high dissolved Silica). In the southern branch of the Armorican shear zone, there are several pyrite-antimony-gold

occurrences and Tl is a potential pathfinder for this type of mineralisation). The isolated Tl anomaly in south-eastern Germany is related to pollution impact. The Tl anomalies in north-western Germany correlate with high DOC values. The high Tl values in stream water occurring in Italy (from northern to southern areas) are controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces and their accompanying hydrothermal activity; the ones in Sardinia are most probably related either to base metal deposits (Pb and Zn), widely occurring on the island, or to Tertiary volcanics, which also occur in the northern sector of the island. The high values in Sicily may also be related to volcanic layers that occur, interlayered with sedimentary evaporitic rocks.

The described Tl distribution in stream water of northern and western Europe (including Denmark and north Germany) is similar to the REEs and associated elements' pattern that is clearly climate-controlled. The geogenic anomalous patterns in the Erzgebirge, in Italy with Sardinia and Sicily, and in southern Spain, however, are closely related to the distribution of elements typical for Felsic and Alkaline rocks. Some of the patterns in stream water reflect the patterns in soils and sediments.

Tl in stream sediment

The median Tl content in stream sediment is 0.39 mg kg^{-1} , with a range varying from <0.02 to 7.90 mg kg^{-1} .

Low Tl values in stream sediment (<0.24 mg kg^{-1}) are mainly present in northern and central Norway and Finland, most of Poland, Denmark, northern Germany, western Ireland, southern England, eastern France, parts of western Switzerland, southern Austria, parts of southern and eastern Spain.

High Tl values in stream sediment (>0.59

mg kg^{-1}) appear in Variscan northern Portugal (vein-type hydrothermal Au mineralisation) extending into western Spain (crystalline basement of the Iberian Massif), an area from the Massif Central to Poitou and southern Brittany (mineralised shear zone), the Italian Roman and Neapolitan alkaline magmatic provinces, Sardinia (mineralisation), an area from the French Vosges to northern Bavaria, all of Croatia, Slovenia, north-eastern Italy, Scotland, Albania, north-east Greece, southern Norway and most of eastern

Sweden. A point Tl stream sediment anomaly in Sardinia is the result of mining and smelting activities; the point anomaly in Attica (Greece) is related to unknown base metal mineralisation or contamination by industrial activities (the sample is also anomalous in As, Cd, Cr, Cu, Hg, Pb, Sb and Zn). There is a point Tl stream sediment anomaly in north-easternmost Italy on the border with Austria, possibly associated with Pb-Zn

mineralisation.

The Tl stream sediment pattern is essentially natural, related to felsic or granitic geological associations, and mineralisation. Thallium in stream sediment has a strong positive correlation with K, Rb, Cs and Ta (felsic affinity), a good correlation (>0.4) with Li, Be, Al, Ga, Th and U, and a weak correlation (>0.3) with Nb, Pb, Sn, As, Y and the REEs.

Tl in floodplain sediment

Total Tl distribution in floodplain sediment, determined by ICP-MS, varies from <0.02 to 3.46 mg kg^{-1} , with a median of 0.37 mg kg^{-1} .

Low Tl values in floodplain sediment ($<0.24 \text{ mg kg}^{-1}$) occur in northern Finland and southernmost Sweden on metamorphic and partly felsic Precambrian rocks, in Scotland and north-east Ireland on mainly metamorphic Caledonian terrains; the glacial drift covered northern Europe extending from parts of northern Germany and almost the whole of Poland; on clastic rocks of the Paris Basin extending into Belgium and adjacent part of Germany; on mainly metamorphic rocks of Normandy, and over mostly clastic rocks of northern and southern Spain, in fluvial sediments of the Rhône estuary in France, and on clastic beds of the Jura Mountains in Switzerland.

High Tl values in floodplain sediment ($>0.58 \text{ mg kg}^{-1}$) extend across most of central Sweden on granite, gneiss and leptogneiss, partly also over the Skellefte and Bergslagen sulphidic ore provinces; in southern Finland on K-granite and clay, and in southern Norway on crystalline rocks, including the alkaline rocks of the Oslo rift; in both areas, sulphidic deposits are abundant. In addition, high Tl values in floodplain sediment are typical for Estonia on Early Palaeozoic beds (with phosphate deposits and black shale) and their glacial drift cover; in northern Norway over a variety of rocks in the Narvik and Sulitjelma mineralised areas; over predominantly calcareous rocks in Ireland; anomalous Tl values in floodplain sediment occur in the tin province of Cornwall in south-west England; the mineralised

Mendip Hills in southern England; in the southern, central and northern parts of Portugal extending into neighbouring Spain associated with granite and mineralisation; the mineralised Massif Central in France, Vosges and Black Forest; central Germany, from Sauerland to the Harz Mountains, Erzgebirge and Bohemian Massif; the border area of Austria, the Czech Republic and Slovakia and north-western Hungary, and the eastern Pannonian Basin in south-eastern Hungary with derived felsic volcanic and mineralised material from the Apuseni Mountains in Romania; in karstic soil of Slovenia and Croatia; in felsic rocks of Corsica and Sardinia, the Roman Alkaline Province; and in north-eastern Greece with granite intrusives and mineralisation.

Point anomalous Tl values in floodplain sediment occur in southern Norway (3.46 mg kg^{-1}), and in the Roman alkaline magmatic province (2.01 mg kg^{-1}); another two point anomalies are in the Pedroches and Valle de Alcudia Pb-Zn vein district (2.81 mg kg^{-1}) and the Iberian Pyrite Belt (1.7 mg kg^{-1}) in southern Spain (De Vos *et al.* 2005).

In floodplain sediment samples, correlations of Tl are strong (>0.6) with K, Rb, Ta and Th, and good (>0.4) with U, W, Y, Nb, Cs, Al and Ga. The REEs also have good to strong correlations with Tl.

It is concluded that the distribution map of Tl in floodplain sediment reflects the geochemical differences of the lithology quite well, and especially the high values show areas with felsic rocks and mineralisation.

Tl comparison between sample media

In general, there are broad similarities between all solid sample media; patterns in topsoil and

subsoil are very closely related. In stream and floodplain sediments, Tl levels are much lower

than in soils over the Pyrenees and in southern Italy. Thallium levels are enhanced in stream sediment compared to soil in Albania and Scotland. In floodplain sediment, Tl is enhanced in Ireland and south-west England. A boxplot comparing Tl variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 49.

Patterns in stream water Tl are complex, and quite often opposite to those observed in all solid

sample media. Thallium is strongly controlled by pH, and tends to low concentrations in the alkaline environments of central Spain, Greece and Albania, and higher concentrations in the more acidic environments of southern Sweden and Finland, Denmark (also associated with high DOC) and Brittany. Corsica and Sicily also have high Tl in stream water, which may be related to high DOC and hydrothermal activity respectively.

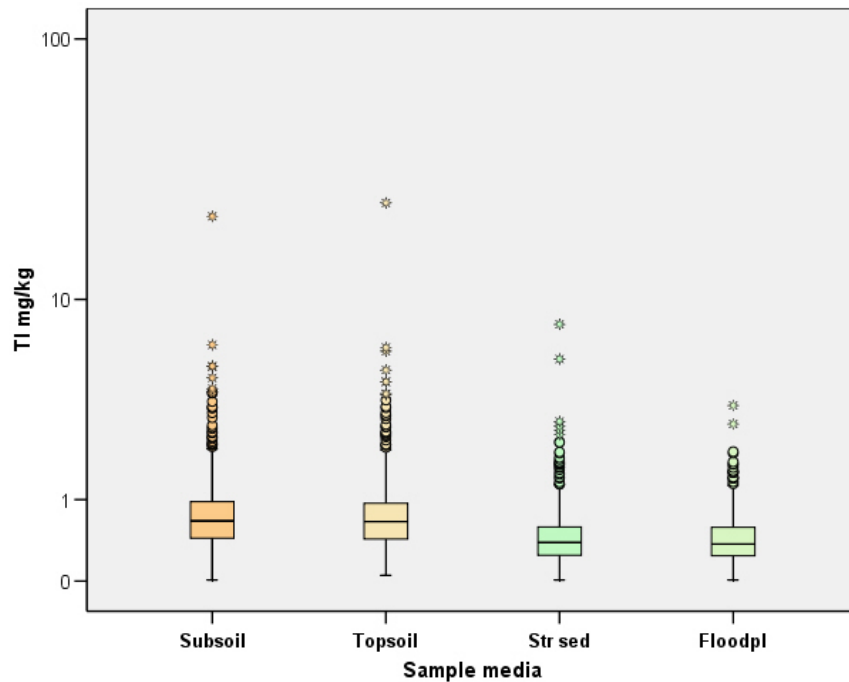


Figure 49. Boxplot comparison of Tl variation in subsoil, topsoil, stream sediment and floodplain sediment.