

Environmental levels of thallium

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Environmental levels of thallium

– Influence of redox properties
and anthropogenic sources

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Abstract

Thallium is a highly toxic element that humans are exposed to mainly by consumption of drinking water and vegetables grown in soil with high thallium content but also through inhalation of particles in the air. Thallium is also present in fossil fuels, alloys, and in electronic utilities. The increasing use of the element and emissions from notably energy production has lead to a higher load on the surface of the Earth. This study aims at increasing the knowledge about the behaviour of thallium in aquatic environments. Focus has been on the redox chemistry of thallium in relation to its mobility, which is of great importance because Tl(I) and Tl(III) have very different properties in this respect.

The relationship between Tl(I) and Tl(III) in surface waters from contaminated and uncontaminated environments was examined by ion chromatography connected on line to ICP-MS (inductively coupled plasma mass spectrometry). It was found in controlled systems that even though Tl(III) is thermodynamically unstable under fresh water conditions Tl(I) was oxidised in the presence of light and iron(III). This was also confirmed in field studies. When lake water samples were exposed to light, Tl(I) was oxidised and thallium was lost from the solution. The most likely explanation for this was adsorption of thallium to particle surfaces.

The concentration of thallium in Swedish lakes and soil was measured. In unpolluted lakes the concentration ranges between 4.5-12 ng/l, the sediment concentration was 0.07-1.46 mg/kg. The anthropogenic load was found to have increased since the end of the Second World War although concentrations above background were found since the early industrialisation. In contaminated areas the concentration in soil ranges from 0.64-88 mg/kg, high concentrations were found in systems with alum shale and in soil exposed to runoff from a lead and zinc enrichment plant.

The mobilisation of thallium from solid phases in contaminated areas was dependent on pH and about 50% of the leachable content was mobilised already at pH 5-6. Once it had been released to water it was highly mobile. These conditions suggest that in a large part of the Swedish environment a high mobility of thallium can be expected.

Keywords: thallium, Tl(I), Tl(III), separation, ion chromatography, fresh water, sediment, mine waste, fly ash, redistribution, ICP-MS

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Thallium – can't live with it, can't bury it in the backyard.

List of included papers

This thesis is based on the following papers, which are referred to in the text by their roman numbers.

- I Grahn, E., Karlsson, S., Karlsson, U., Düker, A. (2006). Historical pollution of seldom monitored trace elements in Sweden - Part B: Sediment analysis of silver, antimony, thallium and indium. *Submitted to J. Environ. Monit. (February 2006).*
- II Karlsson, U., Karlsson, S., Düker, A. and Bäckström, M. (2006). Assessing the release of thallium, cadmium, lead, copper and zinc from deposits with mixed wastes – A case study. *manuscript.*
- III Bäckström, M., Karlsson, U. and Karlsson, S. (2006). Hydrogeochemical interpretations of a fly ash/municipal sludge covered sulphidic mine waste deposit – A case study of alkaline leachates in an acidic water environment. *manuscript.*
- IV Karlsson, U., Düker, A. and Karlsson, S. (2006). Separation and quantification of Tl(I) and Tl(III) in fresh water samples.
J. Environ. Sci. Heal. A., scheduled for Vol. A41, No.7.
- V Karlsson, U., Karlsson, S. and Düker, A. (2006). The effect of light and iron(II)/iron(III) on the distribution of Tl(I)/Tl(III) in fresh water systems.
Submitted to J. Environ. Monit. (November 2005).

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1 Introduction

Thallium was discovered in 1861 by Sir William Crookes and independently by Claude-Auguste Lamy in 1862. The element has two dominant redox states, monovalent (thallous, Tl(I)) and trivalent (thallic, Tl(III)). It was introduced as a therapeutical drug in the 1880s against syphilis, ringworm and for depilation, but this usage ceased in the beginning of the 20th century due to the high toxicity of thallium. During the 1920s commercial thallium-based hair removal cream was used during a limited time period. In more recent years the use of thallium in pesticides has been banned in many countries since they were considered too toxic to be handled by the public (Schoer, 1984; IPCS, 1996; Nriagu, 1998). The use of thallium in alloys has increased with the electronic revolution (Nriagu, 1998) why there are reasons to assume that it is accumulating in the society at present. Thallium is also used in laser and acousto-optic equipment, optical glass with high refractive index, as catalyst etc. see further in ICPS (1996) and Nriagu (1998). The emission (both airborne and aqueous) of thallium has increased along with the industrial development in central Europe and North America, as evidenced from sediment and peat bog cores (Gélinas et al., 2000; Müller et al., 2000; Shotyk and Krachler, 2004; Laforte et al., 2005; Yang et al., 2005).

Thallium is highly toxic, the average lethal dose of thallium for humans ranges from 4 to 60 mg/kg, with an average between 10 to 15 mg/kg (IPCS, 1996). Monovalent thallium is considered the more toxic species for humans (see Galvan-Arzate and Santamaria, 1998) because of the ability to replace K^+ . The toxicity of Tl(III) is difficult to estimate because it is easily reduced in biological systems (Repetto et al., 1998). Recent studies have proposed that Tl(III) is 50,000 times more toxic than Tl(I) (Ralph and Twiss, 2002) and similar in toxicity to Hg(II) but much more toxic than Cd(II), Cu(II) and Ni(II) (Lan and Lin, 2005).

Human exposure to thallium occurs mainly through inhalation of air-borne particles and food (Peter and Viraraghavan, 2005). Consumption of vegetables and fruit grown in regions with high levels of thallium in soil has been the main source for human exposure (Brockhaus et al., 1981; Ewers, 1988; Zhang et al., 1998; Xiao et al., 2004a, b). Plant uptake of thallium increases with increasing soil acidity (Kazantzis, 2000) why acidification of the environment might be critical. Thallium in emissions of airborne dust particles from cement production are more available than the thallium content in the soil why the origin and chemical form are important parameters. High concentrations of thallium have been found in the vicinity of cement plants in Poland (Wierzbicka et al., 2004) and Germany (Schoer and Nagel, 1980; Scholl and Metzger, 1981; Lehn and Schoer, 1987; Ewers, 1988) where increased concentrations of thallium has been found in the population in these areas. Chronic occupational exposure by thallium-containing dust in a glass manufactory facility has been reported in Japan (Hirata et al., 1998). In Taiwan analysis of whole blood from college students revealed elevated concentrations around 1.90 µg/l (Lin and Chang, 2005) to be compared with 0.15-0.63 µg/l for the general population of the world (Repetto et al., 1998). The most possible reason was an every day use of incense sticks, and candles and mosquito coils in their homes along with a high consumption of fish. Fish is a known bioaccumulator of thallium (Zitko, 1975; Lin et al., 2001).

Few studies have been done on thallium uptake in the Swedish population. Bárány et al. (2002) studied a population of fifteen year old Swedes and found that the thallium concentration in whole blood ranged between <0.06 and $0.15 \mu\text{g/l}$ which is lower than the range presented previously for the general population of the world. Atmospheric deposition of thallium in Sweden has been noticed on wild berries. Rodushkin et al. (1999) found in lingonberry and blueberry a thallium content of 0.11 and 0.009 ng/g in low-contaminated areas and 0.47 and 0.11 ng/g near mining areas, respectively. Rinsing the berries with water decreased the concentration by half which indicates external pollution, probably through deposition from particles in the air.

In many regions the load of thallium on the Earth's surface has increased as a result of atmospheric deposition from combustion of fossil fuels, notably coal, and industrial emissions (Fergusson, 1990; Müller et al., 2000; Pacyna and Pacyna, 2001; Shotykh and Krachler, 2004). Locally also effluents from mining and mine waste have contributed to increased loading (Lis et al., 2003; Yang et al., 2005). About 15 tonnes of thallium is produced annually in the world, and it is estimated that 2,000-5,000 tonnes are mobilised through industrial processes (Kazantzis, 2000). In the US about 1,000 tonnes of thallium is estimated to be released to the environment annually (Kazantzis, 2000). These amounts are released as dust and vapours (35 tonnes), bound to non-ferrous metals (60 tonnes) and in fluids and solid wastes (>500 tonnes). This can be compared to the estimated worldwide emission of thallium in the mid-1990s of 1824 tonnes/year from combustion of fuels in power plants, about 73% originating from Asia and North America (Pacyna and Pacyna, 2001). In Sweden the estimated annual total consumption of thallium is 10-24 kg but the true amount is not known. The disposal of thallium-containing goods also remains unknown; no recycling of thallium containing wastes takes place in Sweden. The annual emissions from coal fuelled power plants in Sweden are between 700-3,500 kg, for oil combustion no data is available. The natural weathering of bedrock and mine wastes are expected to contribute with an additional 250-1,700 kg/yr (Sternbeck and Östlund, 1999).

Thallium emissions can be traced from atmospheric deposition in the Canadian Arctic ice and snow (Cheam et al., 1996a), which show that there is a global transport. No reports on the thallium content in rain have been found but several snow and ice measurements, mainly from the Canadian Arctic, show a concentration range of 0.03 - 1.32 pg/g (Cheam et al., 1996a, 1998; Cheam, 2001; Krachler et al., 2005). Since these measurements are made far from urbanised regions there are reasons to assume higher concentrations in precipitation close to the release points. The flux of thallium in the Canadian Arctic was determined by Cheam et al. (1998) to $0.05 \pm 0.01 \mu\text{g m}^{-2} \text{ yr}^{-1}$, which is considerably lower than the bulk mass flux in North America of $5 \pm 1.9 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (Gélinas et al., 2000). The large difference in mass fluxes can be explained by the relative non-contaminated environment of the Arctic and thus a clear evidence for the societal release. In Antarctic snow at heights above 700 m 0.18 - 0.45 pg/g has been measured (Baiocchi et al., 1994). This range is slightly lower than for the Arctic which is consistent with its distance from heavily industrialised regions and another circumstantial evidence for the importance of the societal release of thallium.

In Sweden the atmospheric deposition of thallium in moss (*Pleurozium schreberi*), the content in fresh water sediments and sea sediments (the Baltic) all show the same trend with decreasing concentrations towards the north (Table 1; Lithner and Holm, 2003). A similar geographical trend has been reported from measurements in moss (*Hylocomium splendens*) from Norway (Berg et al., 1995). The highest concentrations (0.1-0.5 µg/g dry weight) were found in the south and they decreased towards the north (0.05 µg/g dry weight) (Berg et al., 1995). The south to north gradient of thallium infers that the element is associated with long-range atmospheric transport in Scandinavia as well. Consequently, large areas are possibly affected with increased concentrations of thallium. Recent investigation of moss in the south of Sweden showed that the concentration of thallium in *Pleurozium schreberi* has decreased between 1975 and 2000 by a factor of 2.3 (Rühling and Tyler, 2004), attributed to lowered emissions.

Table 1. Concentrations of thallium in southern and northern Sweden in the south and north (after Lithner and Holm, 2003). All concentrations in µg/g dry weight.

	South	North
Moss (<i>Pleurozium schreberi</i>)	0.14	0.06
Fresh water sediments	0.44-0.65	0.29-0.30
Sea sediments (the Baltic sea)	0.82-1.61	0.42-0.77

Aims of study

In this thesis the aim has been to enhance the knowledge about the behaviour of thallium in aquatic environments. Focus has been on the redox relationship between Tl(I) and Tl(III) in relation to the mobility of the element.

Specific aims are:

- To develop and apply an analytical scheme that allows for reliable determinations of Tl(I) and Tl(III) in fresh waters.
- To quantify thallium in solid and aqueous phases from various field sites in order to estimate reference concentrations in different geological settings.
- To estimate the chronology and redistribution of the anthropogenic release of thallium in Sweden as it is reflected by fresh water sediments from lakes exposed only to atmospheric deposition.
- To elucidate the general mechanisms for the mobilisation of thallium from soil and contaminated solids.
- To increase the knowledge on the distribution of Tl(I) and Tl(III) in natural water systems and mechanisms controlling the distribution.

2 Thallium in the environment

2.1 Occurrence in geologic materials

The average thallium concentration in the Earth is estimated to 0.004 mg/kg (Nriagu, 1998), whereas the average content in the Earth's crust varies between 0.3 and 3 mg/kg (Shaw, 1952; Lepp et al., 1995; IPCS, 1996; Kaplan and Mattigod, 1998; Nriagu, 1998; Zbiral et al., 2000). Wedepohl (1995) reported an average concentration of 0.75 mg/kg in the upper continental crust.

The variation of the thallium content is high among geological materials. Thallium is enriched in potassium feldspars (0.5-50 mg/kg) and sulphides, i.e. pyrite (5-23 mg/kg) (Kaplan and Mattigod, 1998; Nriagu, 1998; Lis et al., 2003) sphalerite and marcasite (8-45 mg/kg and 5-23 mg/kg, respectively; Kaplan and Mattigod, 1998; Lis et al., 2003). Also, igneous shales (0.5-2.5 mg/kg; Heinrichs et al., 1980), galena (0.27 mg/kg; Shaw, 1952), granites and carbonaceous minerals (0.7-1.3 mg/kg and 1.9-2.5 mg/kg, respectively; Shaw, 1952; Kaplan and Mattigod, 1998). Production of thallium is done from flue dusts from roasting of zinc and lead sulphides but also when sulphides are used for production of sulphuric acid (Fergusson, 1990). Such operations are of course potential release points for atmospheric pollution, unless measures are undertaken. Direct emissions to water have also been documented in regions with thallium processing (Schoer, 1984; IPCS, 1996; Zhang et al., 1998; Xiao et al., 2003, 2004b). Other industries where there is a risk for local aquatic thallium pollution are compiled in Table 2 along with a selection of concentrations.

Table 2. Examples on concentration of aqueous thallium close to some selected emission sources.

Matrix, source	Concentration	Reference
Waste water, cement industries	Up to 20 µg/l	(Schoer, 1984)
Waste water, oil field	13-672 µg/l	(IPCS, 1996)
Waste water, mining	Up to 2,400 µg/l	(IPCS, 1996)
River water, mining	<1-80 µg/l	(IPCS, 1996)
Seepage water, waste rock dump	250 ng/l	(Plessow and Heinrichs, 2000)
River Rhine, multiple industrial sources	102 ng/l	(Cleven and Fokkert, 1994)
Waste water, Al-plant	86 µg/l	(Deb et al., 1998)
Surface water, Kankali tank	166 µg/l	(Deb et al., 1998)

2.2 Abundance in water

Lin and Nriagu (1998b) considered concentrations in fresh waters at 5-10 ng/l to be uncontaminated and concentrations of 20-50 ng/l to be polluted. These values are low since according to WHO the concentration in non-contaminated river water is <10-1,000 ng/l (IPCS, 1996). Concentrations in the Great Lakes range from 0.9-18 ng/l (Cheam et al., 1995,

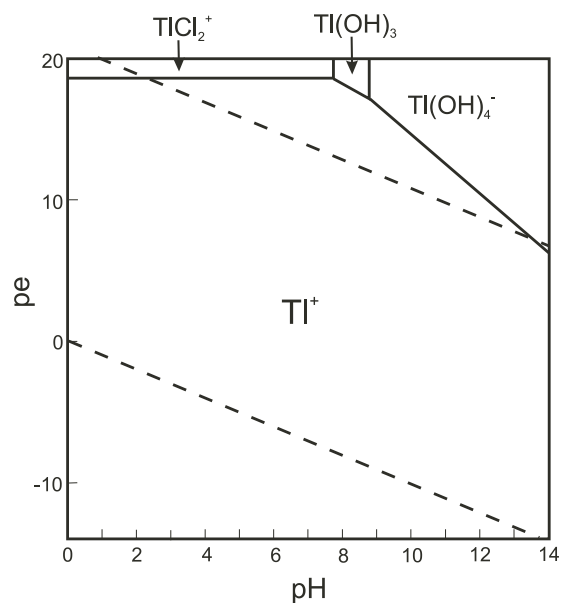


Figure 1. pe-pH diagram for a natural water calculated with the computer program Solgaswater, constants from Lin and Nriagu (1998b), Table 3. Complexes formed with SO_4^{2-} , Cl^- and water are taken under consideration, carbonate had to be excluded due to uncertainties of the correctness of available association constants. Concentrations used in the model $[\text{Ti}^{3+}] = 0.5 \text{ nM}$, $[\text{SO}_4^{2-}] = 0.1 \text{ mM}$, $[\text{Cl}^-] = 0.28 \text{ mM}$.

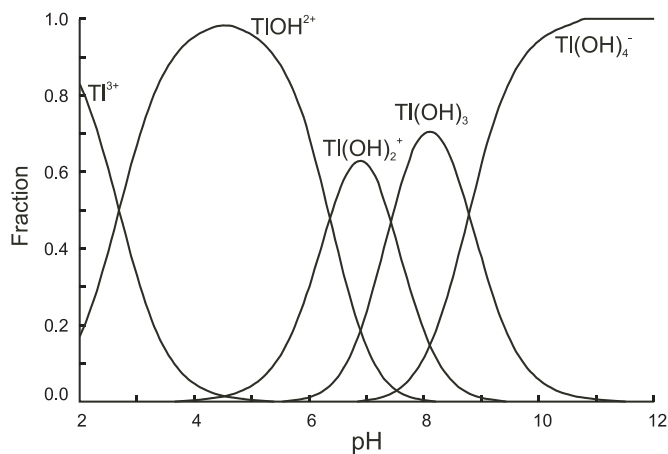


Figure 2. The distribution of Ti(III) hydroxide complexes as a function of pH. Hydrolysis constants from Lin and Nriagu (1998a, b), Table 3.

1996b; Lin and Nriagu, 1999b) but they increase nearby industrialised regions. In Hamilton Harbor Cheam et al. (1995, 1996b) reported concentrations between 23 and 36 ng/l. Also the Rhine River appears to be influenced by anthropogenic release; the thallium concentration at Lobith is 71.5 ng/l (Cleven and Fokkert, 1994).

In Sweden the number of studies that include thallium in natural systems is low. In seawater an average concentration of 13 ng/l has been measured (Sternbeck and Östlund, 1999), while the average for lakes is 5.3 ng/l, with a concentration range of 0.65-13 ng/l (SEPA, 1999). This agrees with results of Grahn et al. (2006) who found an average of 6.4 ng/l in four Swedish lakes without any known point sources of pollution. For comparison, in a catchment in northern Sweden the stream water had an average concentration of 11.4 ng/l (Temnerud, unpublished data). Axner et al. (1993) reported 8 ng/l for drinking water in Göteborg and 46 ng/l in the river Viskan (150 km from Göteborg). This can be compared with groundwater where the average concentration in Swedish granitic bedrock is 14 ng/l (Bäckström, 2002), and in Norway 7 ng/l (Frengstad et al., 2000). Both studies show that thallium is released even from this chemically inert mineral matrix. The highest concentrations reported in the studies were 120 ng/l in Swedish granites and 250 ng/l in Cambro-Silurian meta sediments.

In Sweden there are no legislative or technical limits for admissible concentrations in drinking water. The MCL (maximal contamination level) from USEPA for drinking water is 2 µg/l and MCLG (maximum contaminant level goals) 0.5 µg/l (USEPA, 2005b). This can be compared to arsenic which has a new MCL value of 10 µg/l since January 2006 (USEPA, 2005a). A problem with assigning quality limits is the analytical constraints. Lower permissible levels require analytical methods with sufficiently low and reliable detection limits. Preferably they shall also be able to distinguish between different forms as inorganic Tl(I) and Tl(III) as well as organometallic compounds etc. because of the differences in toxicity and mobility. As noted previously, the speciation of thallium has an impact on the toxicity and mobility but regulations do not account for this.

2.3 Distribution of aqueous Tl(I) and Tl(III)

The chemical and physical properties differ between Tl(I) and Tl(III). Tl⁺ has an ionic radius similar to that of K⁺ and can replace K⁺ in minerals and biological systems. Substitution of Rb⁺ and Ag⁺ by Tl⁺ in mineral systems has also been reported (Kaplan and Mattigod, 1998). In a general sense Tl³⁺ behaves similar to Al³⁺ and Fe³⁺ with respect to chemical and physical properties.

Early studies performed by Shaw (1952) and Lanford (1969) (ref. from Kaplan and Mattigod, 1998) indicate that dissolved thallium in the aquatic environment is present as Tl(I). This is also supported by available thermodynamic data (Figure 1), the only ligands of importance are carbonate, sulphate and phosphate species, and their complexes with Tl⁺ are relatively weak (Table 3). Hydrolysis is quite insignificant for Tl(I), in similarity with the alkaline elements. Formation constants (log K) of 2.3 (Lin and Nriagu, 1998a) and 0.9 (Laforte et al., 2005) for the hydroxide complex have been reported. For Tl(III) the impact of hydrolysis on its chemical behaviour in aqueous systems is evident (Figure 2). A formation constant (log K) of 11.31 (Lin and Nriagu, 1998b) for the first hydroxide complex indicates that even the anionic complex (Tl(OH)₄⁻) can exist at high pH which would make the presence of this redox form possible.

Table 3. Stability constants for aqueous thallium complexes compiled by Lin and Nriagu (1998b).

Ligand	Number of ligands	Tl(I) log K	Tl(III) log K
Citric acid	1	1.04	12.02
NTA	1	3.44	16.81
Acetate	1	0.79	8.42
Br ⁻	1	0.93	9.70
Br ⁻	2		16.60
Br ⁻	3		21.20
Br ⁻	4		23.90
Cl ⁻	1	0.52; 0.51 ^c	8.14
Cl ⁻	2	0.28 ^c	13.60
Cl ⁻	3		15.78
Cl ⁻	4		18.00
EDTA	1		22.50
F ⁻	1	0.10	6.44
DTPA	1	5.97 ^d	46.0 ^d
I ⁻	1	0.72	11.42
I ⁻	2		20.88
I ⁻	3		27.60
I ⁻	4		31.82
OH ⁻	1	2.3; 0.9 ^c	11.31
OH ⁻	2		18.95
OH ⁻	3		25.53
OH ⁻	4		30.75
Nitrate	1	0.33	0.92
HPO ₄ ²⁻	1	3.31	17.66
SO ₄ ²⁻	0.5	3.787 ^c	
SO ₄ ²⁻	1	0.95; 1.37 ^c	9.02
SO ₄ ²⁻	2	1.02	9.28
NO ₃ ^{-a}	1	0.45	7.20
CO ₃ ²⁻	0.5	3.837 ^c	
CO ₃ ²⁻	1	0.51 ^c	
CO ₃ ²⁻	2	2.79	15.76 ^c
HCO ₃ ⁻	1	3.42	18.07 ^c
Sorption-natural particle	1	2.50	14.68
≡S-OH _{weak}	1	0.24	6.41
≡S-OH _{strong}	1	1.31	10.35
Biosorption-S-site	1	1.25	10.83
Biosorption-C-site	1	1.62	12.10
-Ful1 (COOH-site) ^b	1	4.83	
-Ful2 (OH-site) ^b	1	3.32	

^a This may be an error in the original table, probably the ligand is NO₂⁻ instead.

^b The association constants for fulvic acid are described as complexation to two different sites, carboxylic functional groups (Ful1) and hydroxyl (Ful2) (Kaplan and Mattigod, 1998)

^c (Laforte et al., 2005)

^d (Anderegg and Bottari, 1967)

^e The stability constants are very high and some concern about their accuracy have been raised.

The only solubility-limiting stoichiometric Tl(I) phase under fresh water condition is the sulphide, while for Tl(III) they include $\text{Tl}(\text{OH})_3(\text{s})$ and Tl_2O_3 (Lin and Nriagu, 1998a, b).

According to the different properties of Tl(I) and Tl(III) the behaviour of thallium in the environment is largely determined by the distribution of its redox forms. An E^0 -value of 1.28 V ($\text{Tl}^{3+}_{(\text{aq})} + 2\text{e}^- \rightarrow \text{Tl}^+$) has been reported (Kaplan and Mattigod, 1998; Lin and Nriagu, 1998b). The uncertainty of the E^0 -value is, however, rather large and reported values range from 1.12 V to 1.28 V, which has a large impact when estimating the speciation in different aqueous systems (IPCS, 1996; Kaplan and Mattigod, 1998; Lee et al., 2002). Tl(I) can also be reduced to the metallic state ($E^0 = -0.33$ V; Lin and Nriagu, 1998b), such as in carbon-rich sediments. With respect to the redox conditions in fresh water systems in relation to the E^0 -value it is unlikely that Tl(III) would be stable. The Tl(III) would dominate only under extreme conditions like in highly acidic environments that contain strong oxidising agents such as MnO_4^- and Cl_2 (Kaplan and Mattigod, 1998; Vink, 1998) or in alkaline environments. Field measurements reports however the presence of Tl(III) in lake waters (Lin and Nriagu, 1999a, b; Li et al., 2005). Other theoretical considerations indicates that Tl(III) is feasible in oxic waters (Batley and Florence, 1975; Laforte et al., 2005) which infers that the environmental chemistry of thallium is inadequately known.

The imperfect knowledge of the environmental geochemistry of thallium has also been highlighted by the recent debate from field measurements of its redox species. In a field study by Lin and Nriagu (1999a, b) they reported that Tl(III) dominated in the natural water system studied. Cheam (2000) argued that the conclusion was an overestimate and advocated that Tl(I) is the principal redox form, in accordance with thermodynamic predictions. The main point of difference in the debate was the use of nitric acid by Lin and Nriagu (1999b, 2000) in their analytical scheme since it might oxidize Tl(I). Thus, it is important to develop analytical procedures that efficiently separate the redox species of thallium. It is also of high relevance to establish a field sampling and sample treatment protocols that preserve the original distribution of thallium species.

2.3.1 Adsorption

When studying the speciation of thallium in natural waters, any surfaces onto which Tl(I) and Tl(III) can adsorb must be considered as they can serve as sinks and induce associations that are non-predictable from common equilibrium modelling. Interactions with organic ligands influence this process in several ways. Although the number of available stability constants is rather low it seems like Tl(I) forms weak complexes with low molecular weight organic substances (Table 3; Kaplan and Mattigod, 1998), while the complexing properties of Tl(III) is not fully understood. Association with humic substances is known but information is very scarce and available stability constants are highly uncertain (Bidoglio et al., 1997; Kaplan and Mattigod, 1998; Il'in and Konarbaeva, 2000).

Adsorption to ferric oxides is environmentally important from quantitative as well as qualitative aspects. Lin and Nriagu (1998b) used the software MINEQL to model the adsorption of thallium to these surfaces. Stability constants compiled in Table 3 represent a two-layer adsorption model. It was found that Tl(I) adsorption to the ferric oxide surface can be approximated to $\equiv\text{S-OH} + \text{Tl}^+ \rightarrow \equiv\text{S-OTl} + \text{H}^+$. Below pH 3 no adsorption was noticed while at a pH about 6.5 all Tl^+ had adsorbed to the surface. Assuming that the

adsorption of Tl(III) follows a similar mechanism $\equiv\text{S-OH} + \text{Tl}^{3+} \rightarrow \equiv\text{S-OTl}^{2+} + \text{H}^+$ the Tl(III) concentration in solution is significantly decreased at pH 4.6 and at pH 6.5 aqueous Tl^{3+} is quantitatively adsorbed. Compared to Cu^{2+} , Pb^{2+} , Cd^{2+} and Zn^{2+} as well as Tl^{3+} , the adsorption of Tl^+ takes place at a lower pH range (Lin and Nriagu, 1998b) which is important to consider in natural systems exposed to acidification.

In contrast to these results Koschinsky and Hein (2003) reported that the Tl^+ ion was preferentially sorbed to the negatively charged surface of $\text{MnO}_2(\text{s})$ in a study on thallium adsorption to ferromanganese crusts in seawater. The Tl(III) hydroxide and chloro-complexes were found on the nearly neutral surface of FeOOH . The strong association of thallium to the MnO_2 surface was explained by surface oxidation of Tl(I). This mechanism is supported by the findings of Bidoglio et al. (1993) who reports on surface precipitation of $\text{Tl}_2\text{O}_3(\text{s})$ on $\delta\text{-MnO}_2(\text{s})$. Thus, the redox state appears to have both quantitative and qualitative implications for thallium in natural water systems. Even in a more complex system Jacobson et al. (2005b) found that manganese oxides influence the retention of thallium in soil, whereas iron oxides had little or no effect on the sorption efficiency. These reports clearly illustrate that the redox state of thallium can be influenced by interactions with oxide surfaces, accompanied by the formation of surface complexes. Since at least ferric hydrous oxides are very common in boreal fresh water systems this is one potential mechanism behind field observations of Tl(III) in lakes. Thallium is not unique in this context since other elements such as antimony is oxidized upon contact with iron and manganese oxide surfaces under certain conditions (Belzile et al., 2001).

Although oxidation/adsorption has been demonstrated to influence the aqueous speciation of thallium the results from several field studies are diverse with respect to the presence of particle bound thallium. In Lake Ontario, Hamilton Harbour and Lake Erie the dissolved (filtered through $0.4\ \mu\text{m}$) thallium was found to be 80-90% of the total concentration (Cheam et al., 1995) which indicates a low affinity for surfaces. Also Lin and Nriagu (Lin and Nriagu, 1999a, b) reported a high fraction of dissolved thallium in the Lake Michigan, Huron and Erie, on average 90% of the total thallium concentration. However, in the dissolved fraction 64-68% was in the form of Tl(III). The results from Lake Erie were supported by Twining et al. (2003) who found that 74% of total dissolved thallium was present as Tl(III). Considering the high affinity of Tl(III) for oxide surfaces it is surprising that such a high amount was present in the dissolved fraction. However, there is a possibility that the Tl(III) was not truly dissolved but associated with surfaces in the colloidal size range. Such an association, if it is stable, infers that Tl(III) also can be transported over long distances i.e. as long as the colloidal phase is stable.

2.4 Thallium in soil

Information about the adsorption of thallium to environmentally common solids is scarce, except for ferric hydrous oxides, as previously mentioned. Some studies have revealed that the thallium fraction in soil that has been released by weathering of soil minerals is easier to extract/desorb than the original mineral fraction (Lehn and Schoer, 1987; Sager, 1992; Kaplan and Mattigod, 1998; Yang et al., 2005). Natural weathering would therefore lead to an adsorbed fraction of thallium in the soil. Its mobility and availability would therefore be highly influenced by the composition of the soil water. There are some

indications that thallium binds strongly to organic material in soil (Heinrichs and Mayer, 1977) but its influence on the redox state is not documented. Kaplan and Mattigood (1998) and Schoer and Nagel (1980) reported that thallium accumulated in the organic horizon in forest soils and in those systems no transport of the element through the lower soil horizons was noticed. This observation might infer that organic matter, at least partially, lowers the thallium mobility in soils.

In uncontaminated sediment thallium is found in the organic or residual (insoluble) fractions (Lehn and Schoer, 1987) but it is also often associated with sulphides (Thomson et al., 1995; Laforte et al., 2005). Allochthonous thallium additions to sediments have been suggested to adsorb to weakly binding sites on the solid sediment mineral matter (Lehn and Schoer, 1987; Sager, 1992; Yang et al., 2005). The mobility of thallium in sediments is pH dependent; Günther et al. (1987) found in a study of river sediments that thallium was mobilised at $\text{pH} < 2$. In summary, the mobility is largely controlled by adsorption, and the principal mechanism appears to be cation exchange (Kaplan and Mattigood, 1998). It is likely that Tl(I) can replace potassium and rubidium, whose adsorption is also controlled by cation exchange (Kaplan and Mattigood, 1998).

2.5 Photoreduction

Humic substances are known to influence the redox state of several elements. For instance, reduction of Fe(III) , Mn(IV) and stabilisation of Fe(II) have been reported from field studies of water systems as well as laboratory experiments. External energy input to the systems, such as light in the ultraviolet and visible regions increases the rate of reduction, even in systems that are in equilibrium with atmospheric oxygen. According to the E^0 -value for thallium it might be possible that humic substances could influence its speciation but no reports are however available on this phenomenon (Plavšić and Cosovic, 1994).

The photochemistry of manganese and iron in natural waters is well documented (see Oster and Oster, 1959; McKnight et al., 1988; Sulzberger et al., 1990; Waite and Szymczak, 1994; Karlsson et al., 1995; Kieber et al., 2005). In systems saturated with oxygen the process is at least partly reversible and oxidation of Fe(II) begins when the solar energy is lower than some 1 W/m^2 (Karlsson et al., 1995). As a consequence, reduction takes place during the day, followed by oxidation and precipitation of particulate/colloidal hydrous oxides at night (Helz et al., 1994; Karlsson et al., 1995; Kieber et al., 2005). The process has a large impact on the mobility and transport of iron but it also influences the speciation of elements that adsorb to the hydrous oxides. Possibly it might also have an impact on redox reactions at the surface of the hydrous oxides, such as oxidation of organic matter etc.

Several other electron donors than humic substances have been proposed to take part in the redox cycling of iron in natural waters why the process is feasible in systems with low humic concentrations. The potential electron donors range from simple inorganic ions such as bisulphite, low molecular weight organic acids to complex organic molecules like proteins and humic (Deng, 1992; Faust, 1994; Kieber et al., 2005). From studies in oceans and laboratory experiments oxidation of Tl(I) has been observed through formation of dimethylthallium (Huber and Kirchmann, 1978; Schedlbauer and Heumann, 1999, 2000).

As stated previously, the impact of photochemical processes on biogeochemical cycles is inadequately understood. Li et al. (2005) showed that oxidation of Tl(I) in an aqueous

solution can take place when it is exposed to UV irradiation or sunlight. They suggested that formation of $\text{Tl}(\text{OH})_3(\text{s})$ stabilised the system and controlled the dissolved thallium concentration in the solution phase. These experiments were, however performed at thallium concentrations by far exceeding the natural range for fresh waters. In the latter systems the total concentration of thallium is generally so low that precipitation of $\text{Tl}(\text{OH})_3(\text{s})$ is unlikely according to available stability constants. Oxidation of $\text{Tl}(\text{I})$ in undersaturated systems would nevertheless have a great impact on the speciation of the element since $\text{Tl}(\text{III})$ has a much higher affinity for surfaces, hydrolyses etc. Electron transfer processes have also been reported to occur with lead ions. Kamenov et al. (2004) observed oxidation of $\text{Tl}(\text{I})$ in an aqueous system that contained $\text{Pb}(\text{II})(\text{aq})$ when it was exposed to sunlight. As for the previously mentioned iron-humic systems the equilibrium was reversed when the sample was kept dark. To summarise, it is possible that several common constituents in fresh waters have the potential to influence the redox state of thallium. As discussed earlier also (oxide) surfaces influence the redox speciation. If the impact of light is added these processes would be highly variable and their rates vary from a stochastic manner to large scale seasonality. Thus, it is essential to include their impact on thallium chemistry in terms of rates and reversibility.

3 Materials and methods

3.1 Analytical

3.1.1 Chemicals

In all studies the water that was used for dilution, preparation of solution and washing was produced by reversed osmosis, ion-exchange and UV-irradiation giving an 18.2 MΩ quality. Metal contamination was checked routinely by ICP-MS. Nitric acid was bought from Scharlau and further purified by sub-boiling distillation when used for trace analysis. HCl was bought from Merck and used without further purification. Chemicals and calibration solution were of analytical quality or equivalent unless other stated.

Stock solutions with 1000 mg/l thallium for experiments were prepared from $\text{TiNO}_3(\text{s})$ (p.a.) and $\text{Ti}(\text{NO}_3)_3 \times 3\text{H}_2\text{O}(\text{s})$ (purum), respectively, in 0.14 M HNO_3 (both salts were purchased from Sigma-Aldrich). DTPA (diethylenetriaminepentaacetic acid) was purchased from Merck.

3.1.2 ICP-MS

Metal analysis was performed by ICP-MS (Agilent 4500), using a V-groove nebuliser or an ultrasonic nebuliser (USN, CETAC). External calibration was used routinely with dilutions of the Merck VI multielement standard solution and ^{103}Rh at 1 µg/l as internal mass standard. Precision and accuracy were monitored continuously using in-house quality-control solutions validated against certified reference materials (SLRS-4 and/or NCS DC 73310). Both semiquantitative and quantitative evaluations were performed.

3.2 Field studies

The field studies were conducted in different fresh water systems and solid waste to include a wide range of concentrations and chemical conditions (Figure 3). Reference concentrations in sediments were studied in four lakes in a northern gradient, starting nearby Örebro. These lakes are all oligotrophic, on granitic bedrock, dominated by boreal forests and without thallium point sources in their catchments (Paper I). The sediment cores from these lakes were also evaluated with respect to potential diagenetic redistribution and its impact on the chronological interpretation of the concentration profiles (Paper I). A more detailed description of the lakes is presented in Grahn et al. (2006), and the procedures for dating of the sediment cores are found in Karlsson et al. (2006).

The impact of solid waste on the release, environmental levels and chemical redistribution of thallium was studied at three historical deposits with different mining waste (Paper II & III). The deposits have in common that they are no longer in operation and restoration have been performed or is under consideration.

Kvarntorp – This deposit originates from 1941-65 when alum (black) shale was mined extensively for oil production through pyrolysis. When the mining ceased in 1965 the deposit was about 100 meter high and contained 40 million m³ solid waste material. Soil around the deposit is influenced by leachates and waste products from the shale oil production (Bäckström et al., 2003).

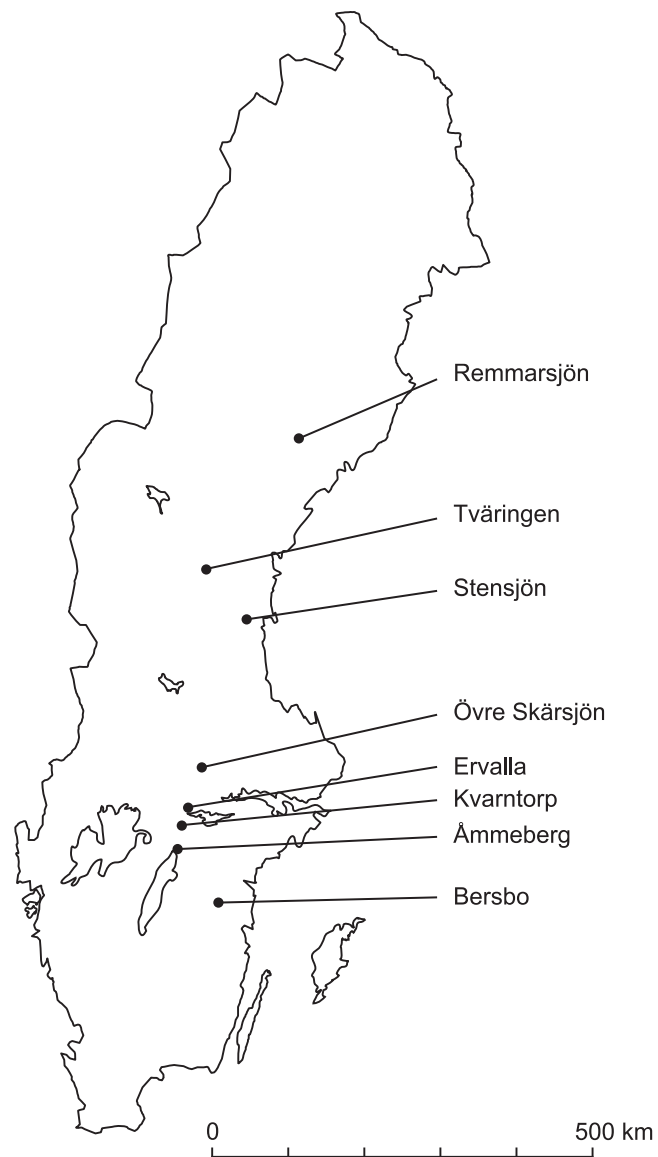


Figure 3. Map over Sweden with field sampling locations.

Ämmeberg – A mine waste deposit from mining of lead and zinc (mainly sphalerite and galena) between 1862 and 1976. The ore has a natural high content of calcite (about 8%_{w/w}), and the waste produces a leachate with a pH close to 7. At the same site soil exposed to runoff from the enrichment plant containing high concentrations of zinc was sampled (Karlsson and Karlsson, 2003).

Ervalla – A deposit with a mixture of weathered sulphidic mine waste covered with municipal sludge and wood fly ash. As weathered mine waste is present outside the deposit pH in the area is low (between 3-4). The effluents from the cover material are alkaline due to the presence of fly ash. Mixing zones between alkaline and acidic water are present both on and below ground surface (Bäckström and Karlsson, 2006).

The study also contains water samples from leachates of the black shale deposit in Kvarntorp and from sulphidic mine waste in Bersbo (Sweden) (Paper IV). Uncontaminated fresh water samples were also taken from Lake Listresjön, a boreal forest lake located about 5 km south of Ervalla (Paper IV-V).

3.2.1 Sample treatment

Preparation of water samples

At arrival to the laboratory pH, alkalinity, electrical conductivity and dissolved oxygen were measured. Principal anions (SO_4^{2-} and Cl^-) were analysed by capillary electrophoresis (Agilent ^{3D}CE) (Jones and Jandik, 1991; Romano et al., 1991) in samples that were filtered through 0.4 μm polycarbonate membranes. Total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) were analysed by a Shimadzu TOC-V. Water samples for metal analysis with ICP-MS were acidified with HNO_3 to a final concentration of 0.3 M.

Radiometric determinations of ²¹⁰Pb as well as ICP-MS measurements of ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were used as chronological markers (Paper I). The common lead reference from NIST (SRM 981) was used for mass bias correction of stable lead isotope readings.

Sediment cores

Sediment cores (Paper I) were sliced in 1 cm subsamples under nitrogen, and pore water was recovered by centrifugation at 20,000 g for 30 minutes. Size fractionation of the solid phase was not included. The solid phase was freeze dried, homogenised in a mortar and digested with concentrated nitric acid on a hot plate for 1 hour (see Grahn et al., 2006). Metal analysis was made by ICP-MS as described above.

Soil samples

Acid soluble metals in Paper II were quantified by ICP-MS after digestion of the samples in concentrated nitric acid as described above. Microwave digestion was made in open (Prolabo Microdigest 3.6) or closed vessels (CEM MARS 5) in accordance with EPA 3051.

To evaluate the metal release from the soil (Paper II & III) parallel leachings were performed (Table 4). In each treatment 1 g (w.w.) of soil at original water content was leached with 20 ml of solution in a batch fashion. Separation of phases was done by centrifugation (20,000 g, 30 minutes, 20°C). Three leaching steps included water, ammo-

nium acetate at pH 5 and acidic hydroxyl ammonium chloride. These treatments intend to mimic the original pore water, ion exchangeable and carbonate bound elements and finally metals bound to reducible manganese and ferric hydrous oxides (Tessier et al., 1979).

The pH-dependent distribution of the metals was further examined (Paper II) by equilibrating soil samples for 24 hrs at pre-defined pH in the range 3.0-9.3. Similar pH-stat distribution studies have been performed by Polyák and Hlavay (2001) and Brunori et al. (2001) on fly ash samples. Polyák and Hlavay (2001) showed that the results of pH-stat leaching at pH 3 was comparable to the sum of the exchangeable and carbonate bound fractions for Cd, Cu and Zn. After equilibration the samples were filtered through 0.4 μm polycarbonate filters and acidified with nitric acid to a final concentration of 0.3 M prior to metal analysis by ICP-MS. The pH control was made with a half-cell-glass electrode and a sleeve-junction Ag/AgCl electrode connected to an automatic titration unit (Radiometer TIM900 + ABU93) operated in pH-stat mode.

Table 4. The leaching procedures used in the mobility study (after Bäckström, 2002).

Leaching step	Procedure
Water	water, 1 hr in a shaker, room temperature
Acetic (decrease of pH and change of ionic strength)	1 M NH_4Ac , pH 5, 5 hrs at 90°C
Reducible (hydroxyl ammonium chloride solution)	0.043 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HAc, pH 2, 5 hrs at 90°C

3.2.2 Data evaluation

Statistical analysis

Principal component analysis (PCA, The Unscrambler® v8.0, Camo ASA, Norway) was used to discriminate between soil samples with mixed compositions in Paper II and to identify contamination sources in Paper III. In all multivariate models the data were autoscaled, the results were validated by "leave-one-out" cross validation.

To validate the grouping from the multivariate models conventional bivariate correlation analysis (SPSS) of the analytical data was used. Both the concentrations of principal elements and the trace metals were included in the comparison. The criteria for difference between the groups were set to a 95% difference in order to be significant.

Speciation estimates

Speciation estimates were mainly performed to provide information about the saturation state in the systems (Paper III). The calculations were performed with the software PHREEQC-2 (Parkhurst and Appelo, 1999) and the MINTEQ database (Ball and Nordstrom, 1991). The level of saturation is presented as the saturation index (the logarithm of the ion activity product divided by the solubility product). Equilibrium between the solid and the aqueous phase is considered to prevail when the saturation index (SI) is between -0.5 and 0.5.

3.3 Quantification of Tl(I) and Tl(III)

Several methods for measurements of Tl(I) and Tl(III) have been published but most of them have too high limits of detection in order to be useful for the analysis of most fresh water systems. Another frequent disadvantage is that many methods are selective to only one of the two oxidation states and reduction or oxidation of the other oxidation state is necessary.

Spectrophotometric determination is a traditional way of determining metal concentrations and a ligand that forms a light-absorbing complex with either Tl(I) or Tl(III) can be used (Pérez-Ruiz et al., 1996; Deb et al., 1998; Ensafi and Rezaei, 1998). A compilation of methods is provided in Table 5. Most of these methods are also time consuming why the risk for system changes increases and the limits of detection are relatively high.

Table 5. Methods to measure Tl(I) and Tl(III) separately.

Measured redox state	Method description	Reference
Tl(III) in soil	Extraction with toluene/N,N'-diphenylbenzamidine/HCl, reaction with crystal violet/HCl, det. Limit 20 ng/ml with spectrophotometry.	(Patel and Agarwal, 1992)
Tl(III)	Extraction of Tl(III) in an hydrochloric acid solution to a N,N'-diphenylbenzamidine/toluene solution, reaction with brilliant green, spectroscopic determination at 640 nm, concentration range 0.2-2.5 µg Tl/ml toluene. Present Tl(I) oxidised with Br ₂ .	(Agarwal and Patel, 1991)
Tl(III)	Chlorothallate(III) complexes are extracted in the presence of ceptylpyridinium chloride and N,N'-dipenylbenzamidine in toluene as brilliant green is added the colour complex Tl(III)-Cl ⁻ -N,N'-diphenylbenzamidine-cetylpyridinium/-brilliant green is formed and measured at 640 nm, det. limit 5 µg/l Tl in water. Tl(I) is oxidised to Tl(III) by Br ₂ .	(Deb et al., 1998)
Tl(I)	Oxidation of Tl(I) at a platinum electrode in a solution of H ₂ SO ₄ /formic acid. In the dark only Tl(I) is measured, in light Tl(III) is reduced to Tl(I) and the total conc. can be measured, det. limit 10 ng/ml at a flow of 0.5 ml/min.	(Barisci and Wallace, 1992)
Tl(I)	Tl(I) (TlCl ₃ ²⁻) is measured with fluorescence (λ _{ex} =227nm, λ _{em} =419nm) in an HCl medium, Tl(III) is reduced to Tl(I) by thiourea. Operational range 10.2- 2044 µg/l.	(Pérez-Ruiz et al., 1996)
Tl(I)	Tl(I) is measured by fluorescence as (TlCl ₃ ²⁻ , λ _{ex} =227nm, λ _{em} =419nm) in an HCl medium. Tl(III) is reduced by hydrazine. The method is useful down to 20 µg Tl/ml with a flow injection system.	(Ensafi and Rezaei, 1998)
Tl(I)	Tl(I) is measured by fluorescence (λ _{ex} =227nm, λ _{em} =419nm).	(Li et al., 2005)

3.3.1 Ion exchange

Ion exchange can normally handle low concentrations, as pre-concentration of the analyte on the exchange material is possible. The procedure with ion exchange normally follows the following steps: activation of the resin, adsorption of the analyte to the resin, and a desorption step, where a strong acid is normally used.

The eluate from the adsorption step is either analysed for non-exchangeable thallium or, if a pre-concentration is desired, the remaining thallium is converted to an adsorbing form and collected on the resin in a second process. In Table 6 some different ion exchange methods are summarised. Most ion exchange resins bind trivalent ions and in order to adsorb Tl(I) it is often oxidised to Tl(III) using additions of bromine as oxidising agent. A serious drawback of bromine is that it is difficult to remove from the sample and can have an adverse effect on the analysis, particularly when ICP-MS is used since it adheres to the sample introduction system.

A separation between the redox species is possible by controlling the pH of the sample solution. This has been done with Dowex A-1 (Ganapathy Iyer and Venkateswarlu, 1976), for which Tl(III) has an almost constant K_d ($10^{3.1}$) in the pH range from 1 to 6 whereas for Tl(I) the K_d value increases from $10^{0.25}$ to $10^{1.5}$ as pH is raised from 3 to 4.

Table 6. Separation methods for Tl(I) and Tl(III).

Resin	Adsorbing form (det. limit)	Sample matrix	Oxidising agent	Eluent	Reference
Bio-Rad AG 1-X8 (100-200 mesh) Cl ⁻ -form	Tl(III) (0.6 ng/l)	Acetate buffer pH 4.6 + EDTA	Br ₂ (aq)	H ₂ SO ₄	(Batley and Florence, 1975)
Quinolin-8-ol (8Q) immobilised on pore glass beads	Tl(III) (3 µg/l)	Acetate-ammonium chloride buffer, pH 10 or maleate pH 4-10	Br ₂ (aq)	HNO ₃ or HCl	(Mohammad et al., 1994)
Dowex 1×8 (200-400 mesh) Cl ⁻ -form	Tl(III) (0.04 µg/g)	Digest solution (HF/HNO ₃)	Br ₂ (aq)	Ascorbic acid (2%, w/w)	(Tsakovski et al., 1994)
Dowex 1×8 (200-400 mesh) Cl ⁻ -form	Tl(III) in soil (0.04 µg/g)	1 M HCl	Br ₂ (aq)	Ascorbic acid (2%, w/w)	(Ivanova et al., 1996)
Dowex 50-8X	Tl(I) & Tl(III) (0.7 ng/l)	Sampled acidified with HNO ₃ to pH 1.8.	-	14% HNO ₃	(Lin and Nriagu, 1999b)
Dowex A-1 (H ⁺)	Tl(III) & Tl(I), differ in pH of adsorption	-	-	-	(Ganapathy Iyer and Venkateswarlu, 1976)
Chelex-100 (100-200 mesh) Na ⁺ -form	Tl(III) (1 ng/l for both Tl(I) and Tl(III))	Sampled acidified with HNO ₃ to pH 1.8.	Br ₂ (aq)	14% HNO ₃	(Lin and Nriagu, 1999a)
Duolite G-73	Tl(I) & Tl(III) in soil				(Jacobson et al., 2005a, b)
IC-ICP-MS (cation column, CG12A)	Tl(III) & Tl(I) (Tl(I): 25 ng/l, Tl(III): 70 ng/l)	Tl(III) complex with DTPA, Tl(I) is eluted unaffected	-	HNO ₃ (gradient)	(Coetzee et al., 2003)
IC-ICP-MS (anion column, Hamilton PRP-X100)	Tl(III) & Tl(I) (0.3 µg/l for both)	Tl(I) was not retained but the complex of Tl(III) and DTPA was	-	NH ₄ Ac (100 mM, pH 6.2)	(Nolan et al., 2004)

Chelex-100

Lin and Nriagu (1999a) used a Chelex-100 resin to consecutively separate Tl(III) from Tl(I) in a solution by first sorbing Tl(III) at pH ~1.8 and then Tl(I) at pH ~4 (Lin and Nriagu, 1999a). These conditions recovered >90% of both Tl(I) and Tl(III) from the sample solution. Separation of Tl(I) and Tl(III) with Chelex-100 was evaluated with this method (Lin, 1997; Lin and Nriagu, 1999a). The resin consisted of a styrene divinylbenzene copolymer with paired iminodiacetate groups that chelate the thallium. An aliquot (3.5 g) of Chelex-100 (analytical grade, 100-200 mesh, Na⁺ form, Bio-Rad) was added to a beaker. Water was added and the slurry transferred to a disposable column (3 ml, PP (polypropylene), Supelco) equipped with PE (polyethylene) frits in both ends. The column was first rinsed with 150 ml water and then 100 ml 2 M HCl, 150 ml 3 M HNO₃ and finally 50 ml water. At analysis first, Tl(III) was adsorbed at pH 1-2, followed by immobilisation of Tl(I) on the column in a second step, where pH was increased to 4. Elution of the adsorbed species was done after each step. Metal analysis was performed by ICP-MS. The sample was allowed to pass through the column and the adsorbed species were eluted with 50 ml 3 M HNO₃. Between runs the resin was regenerated with 60 ml water, 40 ml 0.5 M NaAc and 40 ml water. The flow rate was kept below 2 ml/min.

In order to increase the speed of the procedure, the activation, adsorption and elution were made in a batch design. Resin (about 1 g) was added to a 50 ml PP tube and activated with 2×50 ml water, 2×30 ml 2 M HCl, 3×30 ml 3 M HNO₃. Before the sample was added the resin was washed with 2×30 ml water. The tube was shaken for 5 minutes between each step to ensure contact between the resin and the solutions. After about 5 minutes of settling, the supernatant was decanted or removed with a pipette and the resin was transferred to the sample beaker/flask and left for about 1 hour with intermediate agitation/shaking to equilibrate with the sample. The supernatant was removed and either discarded or saved for further treatment, and the resin was rinsed with 20 ml water. Thallium was desorbed with 3×15 ml 3 M HNO₃ with 30 minutes contact time for the first aliquot and 10 minutes for the following two.

Duolite GT-73

No data on the suitability of using Duolite for aqueous samples was found but Jacobson et al. (2005a) used the resin to determine the desorption of thallium from soil. Their procedure was modified to suite aqueous solutions.

The resin was activated by adding 0.3-0.5 g resin to a 50 ml PP tube, rinsing with 2×30 ml water and then transferring the resin to the sample vessel. After equilibration for 24 hrs under slow agitation, the solution phase was decanted and the resin collected, rinsed with 20 ml water before thallium was desorbed with 3×15 ml 8 M HNO₃ and analysed as previously described.

3.3.2 IC-ICP-MS

Ion chromatography (IC) combined with ICP-AES/MS has proven to be a useful combination for speciation of many elements (Seubert, 2001). The ICP-MS is highly suitable for detection of thallium as it has good sensitivity for elements with high atomic mass and there are virtually no interfering ions in fresh water samples. Coetzee et al. (2003) and

Nolan et al. (2004) have both used this technique to separate Tl(I) and Tl(III). The limit of detection is 25 ng/l for Tl(I) and 70 ng/l for Tl(III) according to Coetzee et al. (2003).

In Paper IV & V the method developed by Coetzee et al. (2003) was optimised and used to separate and quantify Tl(I) and Tl(III) by IC-ICP-MS. In the experimental set up in these studies, a Dionex ion chromatograph (4000i) was equipped with a CG12A cation exchange guard column with carboxylic functional groups. The ion chromatograph was connected to the ICP-MS that was operated with either a V-groove nebuliser or an USN. The eluent consisted of 15 mM HNO₃ at a flow rate of 1.0 ml/min for both nebulisers.

By addition of DTPA, the strong complex [Tl(DTPA)]²⁻ is formed. The formation constant for deprotonised DTPA and Tl³⁺ is 10⁴⁶ at 1 M ionic strength and 20°C (Anderegg and Bottari, 1967). Separation is then possible on a cation column as Tl⁺ does not react with DTPA and is retained by the column. DTPA and HNO₃ were added to the sample to a final concentration of 1 mM and 0.14 M, respectively.

3.3.3 Experimental design

The IC-ICP-MS method was used to study the stability of Tl(I) and Tl(III) in various aqueous matrices, light conditions (fluorescent tube UV, sunlight, and darkness) and presence of both dissolved and colloidal trivalent iron at different concentrations. The sorption of thallium to silica-stabilised ferric hydroxide was studied as well as preservation and storage of field sample. The silica-stabilised ferric hydroxide (denoted ferrihydrite) was produced in accordance with (Anderson and Benjamin, 1985).

All experiments were carried out in a 100 class clean-room with the exception of the sunlight exposure which was performed outdoors. The samples were open to the atmosphere and exposed to ordinary laboratory light unless kept in the dark.

The efficiency and long-term stability of HNO₃ and HCl as eluents were evaluated in terms of retention times (t_R) and peak symmetry. Both isocratic and gradient elution in the range 1-20 mM were included and the hold-up time was determined with H₃BO₃. Optimisation of the DTPA concentration was made in the range 1 nM to 1 mM.

Stability of Tl(III) solutions

Solutions with either 0.1-10 µg/l Tl(III) in 0.14 M HNO₃ or a 1:1 mixture of Tl(III) and Tl(I) in the concentration range 0.2-1 µg/l in the experiments that evaluated the stability of Tl(III). The impact of DTPA (1 mM) was included. The solutions were stored in PE (polyethylene) bottles under normal laboratory conditions with intermittent exposure to fluorescent light. For comparison, a separate solution with 1 µg/l Tl(III) (without DTPA) was stored in darkness at room temperature.

A separate series of experiments were made to elucidate the impact of high ionic strength and low pH on the stability of Tl(III). Here a 5 mM ammonium acetate buffer at pH 3 was used as solution phase. Sample solutions with 1 µg/l Tl(III) were stored in the dark in PE bottles (500 ml) as well as in two 15 ml PP tubes, one stored dark and the other in light in order to study the impact of sample volume/vessel surface area. DTPA was not present in the solutions.

UV exposure

The relationship between Tl(I)/Tl(III) and Fe(III)(aq) (0-60 mg/l) was evaluated in batch experiments with 1 µg/l Tl(I). The experiments were made at pH 3 (0.5 mM NaNO₃) and 7 (0.5 mM NaHCO₃) to include the common range of Swedish fresh waters. Each sample had a volume of 20 ml and it was kept in a 50 ml PP test tube with screw cap. The samples were irradiated with UV-light (Philips TL40/12UV) for 2 hrs, unless otherwise stated. The impact of solid Fe(III) as ferrihydrite (0-40 mg/l) was evaluated under identical conditions.

After irradiation the samples were filtered through 0.05 µm polycarbonate filters and the filtrates were analysed for pH, Tl(I)(aq) Tl(III)(aq) and Fe(II)(aq) as well as the total concentrations of thallium and iron in the solution. The total concentrations of thallium and iron were determined with ICP-MS, Tl(I) and Tl(III) with IC-ICP-MS while Fe(II)(aq) was quantified with capillary electrophoresis (Dahlén and Karlsson, 1999). The time between termination of the experiment until analysis or preservation of the sample was less than 5 minutes.

Adsorption to ferrihydrite.

Adsorption of 1 µg/l Tl(I) to 40 mg/l ferrihydrite was determined at pH 3 and 7 (20 ml 0.5 mM NaNO₃/NaHCO₃ in 50 ml PP test tubes). At the end of the experiment the solid phase was recovered by filtration through 0.05 µm filters and dissolved in acid. The total thallium content was determined by ICP-MS in both the solid and aqueous phase. The contact time was either 23 hours in the dark or 2 hrs of UV-irradiation followed by 20 hours in the dark. The samples were intermittently agitated and sub-samples withdrawn after each treatment.

Field samples

Water samples were collected at three field sites with different hydrogeochemical properties. 1) A lake receiving leachates from weathering sulphidic mine waste provided samples with thallium levels above background and high concentrations of iron. Samples were taken where the leachates entered the lake and at the outlet. 2) Reference samples for estimation of the background levels of thallium were sampled in a boreal forest lake, Listresjön, (20 km north east of Örebro). 3) A more complex matrix with high thallium levels was collected from the leachates from partially pyrolysed black shale, Kvarntorp (20 km south of Örebro). General properties of the samples are found in Paper IV & V.

The field samples were stored in a refrigerator and analysed within 24 hrs after sampling. The impact of acidification and addition of DTPA at the time of sampling was evaluated. As well as exposure of sunlight, UV and the absence of light was evaluated with field samples spiked to 1 µg/l Tl(I). Between each step, sub-samples were removed for analysis as above, but without measurements of pH.

4 Results and discussion

4.1 Thallium in solid and aqueous phases at selected field locations

Five of the field locations included in this thesis were considered to be unpolluted, the Lakes Övre Skärsjön, Stensjön, Tväringen, Remmarsjön and Listresjön. The thallium concentrations in the lake water were 4.5-12 ng/l (Table 7). This range agrees with previously presented concentration levels by the Swedish EPA (1999), Sternbeck and Östlund (1999) and Grahn et al. (2006). Porewater concentrations in Lakes Övre Skärsjön, Stensjön, Tväringen and Remmarsjön were higher than in the lake water (0.97-260 ng/l; Table 7). Decreasing concentrations towards the north was interpreted as a result anthropogenic release, notably deposition from air. The sediment concentrations were 0.07-1.46 mg/kg (Table 8), similar to the average concentration in the upper continental crust reported by Wedepohl (1995). Sediment concentrations at the same order of magnitude has also been reported by Lithner and Holm (2003) and Sternbeck and Östlund (1999). Although thallium concentrations in the solid sediment appear to decrease further below the sampled 30 cm the reference concentrations at this depth in the northern transect were increasing most likely due to the geological conditions.

Table 7. Concentrations of thallium in water samples.

Location, matrix	Tl (ng/l)	Paper
Lake Övre Skärsjön, lake water	7.3-9.0	I
Lake Stensjön, lake water	4.5-8.0	I
Lake Tväringen, lake water	4.9-6.4	I
Lake Remmarsjön, lake water	6.5-7.9	I
Lake Övre Skärsjön, porewater	19-260	I
Lake Stensjön, porewater	0.97-184	I
Lake Tväringen, porewater	6.90-55	I
Lake Remmarsjön, porewater	2.12-34	I
Ervalla, surface water (min-max)	40-1200	II-III
Ervalla, groundwater (min-max)	40-2000	II-III
Åmmeberg, surface water	266	II
Åmmeberg, groundwater	280	II
Kvarntorp, leachates	594	IV
Bersbo, inlet	259	IV
Bersbo, outlet	b.d.	IV
Lake Listresjön	12	IV

b.d. = below limit of detection

As thallium is present in lead and zinc ores (Fergusson, 1990) high levels can be expected in areas rich in such ores. In Örebro county the concentration of thallium is higher in silty and sandy-silty till compared to the Swedish average (0.50 mg/kg versus 0.18 mg/kg; Holmberg, 2005). The elevated concentration is attributed to the presence of alum shale.

Table 8. Thallium in solid samples.

Location, matrix	Tl (mg/kg)	Paper
Lake Övre Skärsjön, sediment	0.07-1.04	I
Lake Stensjön, sediment	0.11-0.66	I
Lake Tväringen, sediment	0.12-0.78	I
Lake Remmarsjön, sediment	0.12-1.46	I
Ervalla, sulphidic mine waste	0.38	II
Ervalla, fly ash	1.90	II
Ervalla, mixed sample, influenced by mine waste	0.46	II
Ervalla, mixed sample, influenced by fly ash	0.77	II
Åmmeberg, mine waste	635	II
Åmmeberg, contaminated soil	88	II
Kvarntorp, alum shale	8.48	II
Kvarntorp, background	0.64	II

In Kvarntorp the presence of alum shale gave thallium concentrations of 8.48 mg/kg (Table 8) in soil samples and 594 ng/l in the leachates from the deposit. High concentration in samples with alum shale agrees with its content in Norwegian black shale of 13 mg/kg (Lipinski et al., 2003). The soil background concentration in this area was 0.64 mg/kg, which is in agreement with the results of Holmberg (2005). A strong relationship between thallium and sulphur has been shown in Australian coal (Ward et al., 1999) and this was also the case for samples from Kvarntorp ($r^2 = 0.86$). It is highly likely that the elevated thallium concentrations in the Kvarntorp area are caused by the presence of sulphides in the alum shale. Exposure of the shale to oxygen would accordingly increase the mobility of thallium, thereby posing as an even more prominent environmental threat than at present.

In Åmmeberg the residues from sphalerite and galena processing have a high concentration of thallium (635 mg/kg) but the concentration in the leachates (266-280 ng/l) is lower compared to Kvarntorp. This is most likely due to a higher content of carbonaceous minerals leading to a higher pH in Åmmeberg (> 7 ; Paper II) preventing metal release and enhancing adsorption of mobilised thallium. The impact of the properties of the solid material as well as distribution caused by pH is even more evident from the study of the mixed waste deposit in Ervalla. The local background concentrations of thallium in surface water range from 40 ng/l to 300 ng/l and in groundwater from 90 ng/l to 800 ng/l. This rather high background is at least 9 times above the concentrations in groundwater from granitic bedrock and attributed to the presence of several diffuse release points in the old mining area. It is also evident that release from the waste results in very high concentrations in the surface water being 500 ng/l - 2,000 ng/l. The highest concentrations of thallium within the deposit were attributed to the fly ash fraction in the deposit.

4.2 The anthropogenic load of thallium in Swedish fresh water sediments

The acid leachable thallium concentrations in the cores from Lake Stensjön decrease from 0.29-0.42 mg/kg at the sediment water interface (SWI) to 0.13 mg/kg at 30 cm (Figure 4). A subsurface maximum (0.42-0.49 mg/kg) appear at 2-4 cm. The porewater profiles differ slightly from the solid phase. The concentration at SWI is 0.006 µg/l followed by a subsurface maximum (0.01 µg/l) at 4-6 cm and at 15 cm the concentration is

0.006 $\mu\text{g/l}$. This is followed by increasing pore water concentrations with depth and at 25-30 cm maxima of 0.015 $\mu\text{g/l}$ and 0.025 $\mu\text{g/l}$, respectively, are found in the two cores. The $\log K_d$ for Lake Stensjön shows a continuous decline from 4.5 at the SWI to 4 at the 30 cm level (K_d : solid/solution distribution coefficient, l/kg). Although Gélinas (2000) considered thallium to be enough immobile to allow for a chronological evaluation the results presented here indicate that diagenetically induced redistribution might be present. Laforte et al. (2005) concluded that thallium is mobilised in the anoxic parts of the sediment they studied but it was immobilised by adsorption/occlusion to precipitating sulphide phases in reducing environments and iron/manganese hydrous oxides in oxic zones. The conditions in Lake Stensjön are apparently different since the porewater thallium increases with depth. One possible explanation for the different behaviour might be that formation of sulphides is limited in Lake Stensjön why thallium is more mobile in the reducing sediment environment.

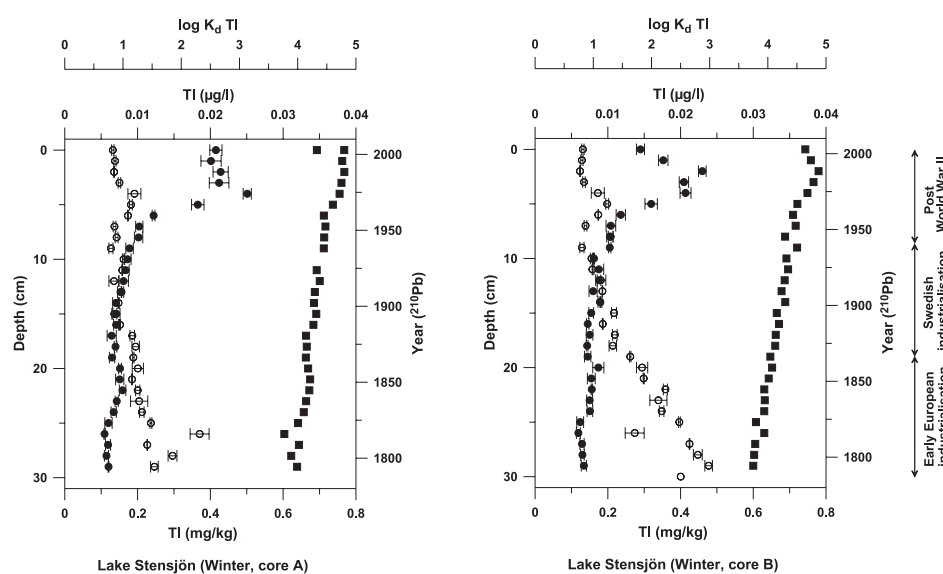


Figure 4. Concentrations of acid leachable thallium (●) and its pore water concentrations (○), as well as the solid/solution distribution coefficient (l/kg) (■).

In the solid phase the correlation (r^2) between lead and thallium is 0.93 and 0.94 in the two cores. This resemblance indicates either synchronous chronological deposition or identical diagenetic redistribution, or possibly both. Gallon et al. (2004) showed recently that that diagenesis has an impact on lead concentration profiles in sediments. The quantitative impact at the resolution in this study would however be minor why comparisons between lead and thallium in the solid phase seem feasible. Chronological interpretations of the thallium profile should however be made with care and limited to the general patterns until its diagenetic behaviour has been elucidated in detail.

The dating from the combination of ^{210}Pb , $^{206}\text{Pb}/^{207}\text{Pb}$ ratios and the acid leachable concentration of lead in Lake Stensjön revealed at least three periods with different metal accumulation rates and sources (Paper I). The Post-Second World War period (3-8 cm below the SWI), the Swedish industrialisation (8-18 cm) and the industrialisation in central Europe and the British Isles (19-30 cm). Between 19-23 cm the acid leachable concentration of lead was almost constant which indicates a constant input from the European sources. For lead, historical deposition in this part of Sweden has been present for 4000 years (Renberg et al., 2002). This is consistent with the declining concentrations in the solid phase towards the bottom of the cores from Lake Stensjön which indicate that a true geological background concentration was not reached at 30 cm.

There are increasing acid leachable thallium concentrations in both cores from the mid 1800s although the most prominent increase took place after the Second World War (Figure 4). The high deposition rate observed in this study during the first half of the 19th century is attributed to foreign sources since the Swedish industrialisation had only just begun to develop. In similarity with lead the most likely sources are central Europe and the British Isles where the industrial development preceded that in Sweden. Pre-industrial deposition of thallium was minor in peat profiles from Switzerland presented by Shotyk and Krachler (2004), as the concentrations of thallium in the Medieval and Roman layers were 0.01 mg/kg, not different from background. Consequently, the environmental pollution from atmospherically deposited thallium seems to have a similar history in both central and northern Europe since it begins during the industrialisation. An ancient release of thallium to the atmosphere seems however highly likely due to processing of sulphide ores notably for silver and lead for thousands of years.

The anthropogenic load of thallium in Lakes Övre Skärsjön, Stensjön, Tväringen, Remmarsjön can be illustrated by ratios of the acid leachable concentration in recent and reference strata (see Paper I or Grahn et al., 2006). The recent strata corresponds to the time period from the 1950s to present, and the reference strata cover the time between the end of the First World War until the 1950s, as estimated from sediment dating. The ratios are 2.3, 2.6, 1.2 and 1.0 from south to north, indicating that the anthropogenic load is larger in the southern part of the studied area where it has doubled. In the porewater the similar concentration gradient to the north has been observed (Paper I). This geographical pattern illustrates that significance of societal sources for the thallium content in the studied lake sediments.

4.3 Mobilisation of thallium from solid phases

The mobility of thallium was found to be higher from secondary metal sources like soil exposed to metal rich run-offs compared to primary sources which has a natural content of thallium (e.g. mine waste) Paper II-III. The leaching tests with soils from Ämmeberg revealed that the mobility of thallium was strongly influenced by the composition of the aqueous phase and properties of sorbents present in the system. The pH leachings of contaminated soils showed that the desorption edge (pH where 50% of the leachable content was mobilised) for thallium was at pH 5-6. This finding indicates that thallium is readily mobile in a large part of the Swedish environment. Exposing soils from Kvarntorp to slightly acidic and reducing solutions dramatically increased the mobility compared

to leaching with pure water. In analogy with these results seasonal variations in soil redox conditions as a response to fluctuations of the groundwater table might influence the environmental transport of thallium why this possible mechanism should be elucidated.

In Ervalla it has been possible to study the total thallium content in the solids (mine waste and cover material consisting of fly ash and municipal sludge) in relation to its presence in surface and groundwater. The mobility was also evaluated by leaching testes (L/S 10) and proportional mixing of acid and alkaline waters from the deposit within a pH range from 3.5 to 11.5. Multivariate analysis was used to identify the source of thallium in the solids and also in each aqueous phase. The highest amounts of thallium were found in the fly ash (Paper II). However, in the water leachings most thallium was released from the mine waste (Paper III). This is probably a response to the significantly lower pH of the aqueous phase after contact with the mine waste samples. In the groundwater thallium correlates with aluminium ($r^2 = 0.74$). Considering the low pH of the system the source for thallium would be of mineral origin, e.g. mine waste and parent rock. In the surface water occasional additions of thallium from the cover material was likely, as supported by the multivariate analysis (see Paper III). The distance of impact for thallium downstream was controlled by dilution since it was equal to sodium and potassium. In spite of massive precipitation of aluminium and iron solid phases the scavenging of thallium was minor. The mixing tests indicate that a maximum of 30% of the thallium content in the aqueous phase was adsorbed/occluded at pH 9.

In Ämmeberg the high pH is the most evident reason for the low water leachability of thallium even though the total concentration is high (Paper II). At Kvarntorp pH of leachates were very low as was the leachability of thallium despite high total concentrations (Paper II). This would induce that the thallium present in these samples are incorporated in the crystal lattice. However as the mobility of thallium was highly affected by the leaching medium (acetic and reducing leaching solutions increased the mobility) the readily mobile fraction of thallium was found to be above 20%. Comparing these results with those from Ervalla (Paper III) the surface water seems to be the water most influenced by both the acidic mine waste and the alkaline cover material.

4.4 Quantitative determination of Tl(I) and Tl(III) in natural waters

4.4.1 Application of ion exchange resins

As presented before the concentration of thallium in uncontaminated waters is low (<20 ng/l) which requires sensitive and accurate analytical methods. Ion exchange resin techniques were chosen because of the possibility for pre-concentration. Both Chelex-100 and Duolite GT-73 were evaluated.

The Chelex-100 was used in batch experiments, as the resin swells and shrinks during these treatments. Despite this problems about 80% of a freshly prepared aqueous solution with 1 µg/l Tl(III) at pH 1-2 was recovered. It was noted that when the 1000 µg/l Tl(III) stock solution (0.14 M HNO₃) was left for several weeks, the recovery decreased. However, the recoveries for Tl(I) were only 50% or less, for a solution with pH 4. The reason for the low recoveries was not fully understood although the impact of the principal aqueous components was evaluated. The low and highly variable recoveries made this technique unsuitable for these studies.

The evaluation of Duolite GT-73 showed a quantitative recovery of both Tl(I) and Tl(III) regardless of pH. The use of this resin seems highly suitable when a general pre-concentration is desired for the total determination of thallium, since the resin does not discriminate between the redox species. For these purposes the detection limit of the ICP-MS was sufficient why the lack of preference for the different redox species made the resin unsuitable for these purposes.

4.4.2 Application of IC-ICP-MS

As both ion exchange resin methods are time consuming and requires large sample volumes, the performance of ion chromatography (IC) combined with ICP-MS was evaluated (Paper IV). Separation of Tl(I) and Tl(III) was successful and the total time of analysis was only about 5 minutes. In the method developed by Coetzee et al. (2003) the eluent consisted of 15 mM HNO₃. After several months of use and storage of the column in HNO₃ the resolution between Tl(III)-DTPA and Tl(I) decreased substantially and eventually the species co-migrated. By changing the isocratic HNO₃ elution to a gradient with HCl (30 sec with 1 mM ramp (6 sec.) to 20 mM) this problem was avoided without loss of either resolution or sensitivity. The flow rate could be increased from 1 ml/min to 1.5 ml/min which decreased the run time and improved the peak shape of Tl(I) (results not published).

The LOD (limit of detection) with the ultrasonic nebuliser (USN) was 9.0 ng/l and 0.7 ng/l for Tl(I) and Tl(III), respectively. For Tl(I) this LOD is slightly too high in order for the method to be applicable to all fresh water systems. It covers however most of the surface waters while some groundwater will have concentrations below the LOD. Due to the high sensitivity, memory effects and contaminations in the chemicals were detected and had to be corrected for. With the V-groove nebuliser the LOD was 25 ng/l and 3 ng/l for Tl(I) and Tl(III), respectively. This is considerably higher than those reached with the USN but memory effects and contaminates in chemicals made the USN time consuming to work with.

Solution stability

The stability of Tl(I) and Tl(III) solutions at different concentrations when they are stored in 0.14 M HNO₃ was examined to ensure that the reference solutions maintained the original concentrations. This study showed that solutions with Tl(I) was stable within the accuracy of the analytical method while Tl(III) was rapidly reduced in dilute solutions. Solutions containing 0.14 M HNO₃ and high concentrations of Tl(III) (≥ 1000 mg/l) were stable up to one year without any detectable reduction. In 0.14 M HNO₃ (pH <1) the rate of reduction in solutions with 1-10 μ g/l Tl(III) was 0.12 nM/hr during the initial 24 hours, independent of light exposure. At pH 3 the reduction rate was lowered to 0.03 nM/hr.

The stability of Tl(III) solutions at low concentrations was improved by addition of DTPA. A concentration of 10 nM DTPA stabilised the Tl(III) for up to a minimum of one week. This approach was also evaluated for the preservation of field samples with different hydrogeochemical signatures. For this kind of samples the recommended procedure includes acidification with nitric acid to a final concentration of 0.14 M and addition of a minimum of 10 nM DTPA, in this order.

Field sample application

Applying the recommended preservation scheme on natural fresh water samples in combination with IC-ICP-MS proved to be useful. This is indicated by a close agreement between the concentrations determined with IC-ICP-MS and the total thallium concentration, Table 9. The sum of the concentrations of the two redox forms was not different when the total concentration was determined with two different methods. Quantification of Tl(I) and Tl(III) is recommended to be performed using an internal standard (^{11}B or ^{103}Rh) in combination with standard addition to minimize interferences of sample matrices. This is especially important from sample series with varying solution matrices.

Table 9. Results from the field samples (average values, n=3).

	pH	Cond. ($\mu\text{S}/\text{cm}$)	Total Tl (ng/l)	Tl(I) (ng/l) ^c		Tl(III) (ng/l) ^c	
				Ext. cal.	St. add.	Ext. cal.	St. add.
Bersbo, inlet	3.34	670	259	209 ^a	n.d.	1.2 ^a	n.d.
Bersbo, outlet	6.42	168	b.d.	5.4 ^a	n.d.	4.5 ^a	n.d.
Lake Listresjön	7.09	114.7	12	47 ^a	18 ^a	0 ^a	0 ^a
				38 ^b	16 ^b	0 ^b	0 ^b
Kvarntorp, leachates	7.49	2362	594	739 ^a	513 ^a	2.4 ^a	46 ^a
				(53.5 ^b)	526 ^b	(14 ^b)	35 ^b

b.d. = below the detection limit of the ICP-MS measurement.

n.d. = not determined.

Values in parenthesis are underestimated due to the presence of boron in the samples.

^a peak area used

^b ratio between ^{11}B and ^{205}Tl used

^c calibration done with external calibration (Ext.cal.) and standard addition (St. add.)

4.5 The effect of iron and light

The distribution of Tl(I)/Tl(III) was influenced by light and the presence of Fe(III), both as the aqueous ion and as silica-stabilised amorphous ferric hydroxide (denoted ferrihydrite). In the reference systems that were kept in the dark the initial Tl(I) concentration at 1 $\mu\text{g}/\text{l}$ at pH 3 remained constant. Addition of Fe(III)(aq) to systems kept in the dark did not alter the Tl(I) concentration from the initial level. Reduction of Fe(III) was low under these conditions, some 0.6 mg/l Fe(II) was found in systems with initially 40 mg/l Fe(III)(aq). Reduction of Fe(III) was also low in systems without any thallium additions, only 0.4 mg/l Fe(II) was formed in a solution with 40 mg/l Fe(III)(aq). When exposing the same system to UV-light oxidation of Tl(I) was observed since measurable concentrations of Tl(III) appeared in the solution (Figure 5). About 90% of the initial Tl(I) content was retrieved as Tl(III) above a concentration of 5 mg/l Fe(III)(aq). The oxidation of thallium was almost quantitative at higher concentrations of Fe(III)(aq). The simultaneous reduction of Fe(III) reached a plateau of about 3 mg/l Fe(II) at 15 mg/l Fe(III)(aq). Higher concentrations of Fe(III)(aq) did not increase the Fe(II) concentration. The external light energy was evidently required to maintain thallium in the oxidized state since it returned to Tl(I) when the irradiated solution was put in the dark. Thus, the experiment also demonstrated that the light dependent oxidation is reversible.

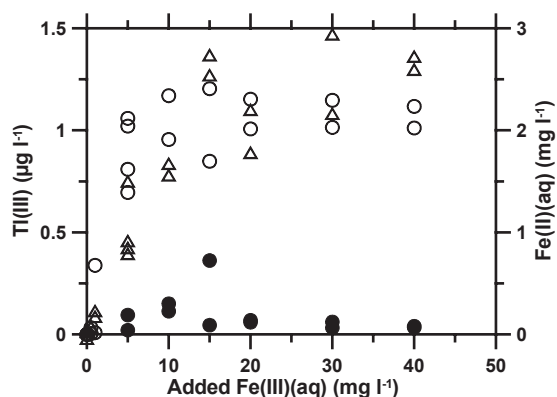


Figure 5. Concentrations of Tl(III)(aq) (○) and Fe(II)(aq) (△) as a function of added Fe(III)(aq) at pH 3 after 2 hours UV irradiation and Tl(III)(aq) (●) after keeping the irradiated samples dark for 2 hrs.

Oxidation of Tl(I) was also noted in systems with pH 7 but to a lower extent than in the acidic ones (Figure 6). There was also a loss of thallium from the systems analysed with IC-ICP-MS, most likely caused by adsorption of Tl(III) (Figure 7). These results agree with Li et al. (2005) who found a quantitative oxidation of 0.2 mg/l Tl(I) at pH 2 after 10 min of UV-irradiation, but only 17% at pH 9 after 1 hour of irradiation.

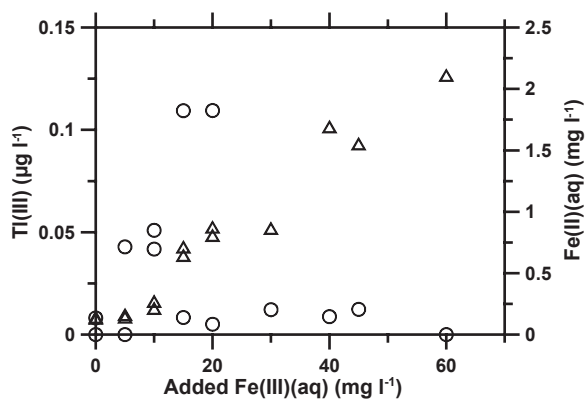


Figure 6. Concentrations of Tl(III)(aq) (○) and Fe(II)(aq) (△) as a function of added Fe(III)(aq) at pH 7 after 2 hours of UV irradiation.

With ferrihydrite present in the systems the degree of oxidation was lower, compared to systems with Fe(III)(aq). At pH 3 maximum concentrations of Tl(III) and Fe(II) were 0.03 µg/l and 0.22 mg/l, respectively (Figure 8). At pH 7 the concentrations of both Tl(III) and Fe(II) were below the limits of detection. Under these conditions the loss of

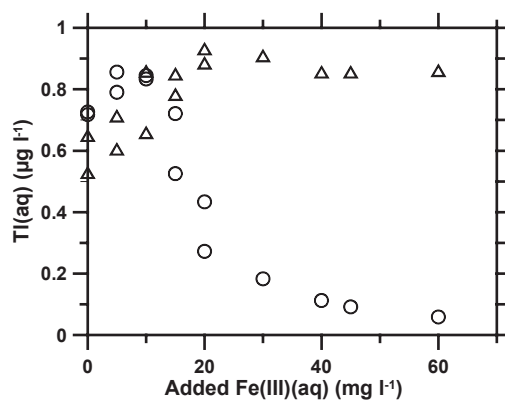


Figure 7. Concentrations of total thallium (Tl(aq)) in samples at pH 7 as a function of added Fe(III)(aq) measured by both IC-ICP-MS (○) and ICP-MS (△).

thallium from the solutions occurred at both pH 3 (Figure 8) and pH 7 (Figure 9). Evidently thallium adsorbs quite efficiently to ferrihydrite at these pH but the mechanisms appear to be different. At pH 3 thallium was desorbed from the ferrihydrite when the external light energy ceased whereas at pH 7 it remained adsorbed to the solid phase. Applying these findings to surface waters it is evident that Tl(III) would be possible to detect if the system is circumneutral, contains a suitable adsorbent and that it has been exposed to enough sunlight. In more acidic systems the major part of oxidised thallium during the day is reduced during the darkness of the night. It is also obvious that pH has a major impact on the solid/solution distribution of thallium not only through adsorption but the combined effect of oxidation/reduction and surface interactions.

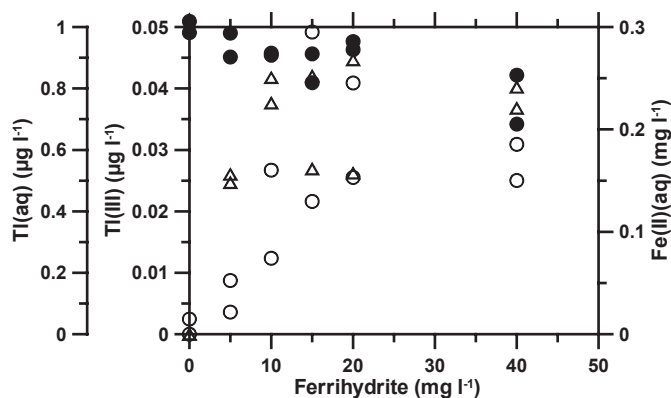


Figure 8. Concentrations of total thallium (Tl(aq)) (●), Tl(III)(aq) (○) and Fe(II)(aq) (△) as a function of added silica stabilised ferrihydrite at pH 3 after 2 hours irradiation with UV.

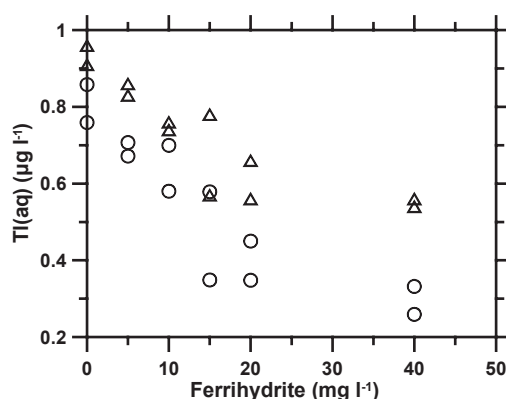


Figure 9. The concentration of total thallium (Tl(aq)) in samples at pH 7 as a function of added silica stabilised ferrihydrite measured with IC-ICP-MS (○) and ICP-MS (Δ).

The results from the controlled systems were extended to a natural water sample at pH 7 where 1 µg/l Tl(I) had been added. These systems were exposed to both UV and sunlight, respectively, with periods of darkness in-between to mimic the daily light cycle. In similarity with the controlled systems Tl(I) was oxidised but it remained at some 0.2 µg/l throughout the experiment. Consequently, thallium was lost from the solution phase in a manner that resembled the irreversible process mentioned previously. Although no unambiguous conclusions can be made these results infer once again that the aqueous geochemistry of thallium is heavily influenced by the redox properties of the element. These findings would also explain why several studies (Batley and Florence, 1975; Deb et al., 1998; Lin and Nriagu, 1999a, 1999b) have reported the presence of Tl(III) in lake systems.

The study demonstrates that Tl(I) is oxidised to Tl(III)(aq) in systems where Fe(III) is reduced when exposed to light. The oxidation is almost quantitative in the presence of Fe(III)(aq) and occurs to a lower extent in systems with Fe(III)(s). At low pH Tl(III) remains dissolved whereas at circumneutral or alkaline conditions thallium adsorbes to the ferrihydrite. In the lake water studied, proportionally higher fractions of Tl(III) that was formed upon irradiation remained in solution, possibly because of complexing agents. Both sunlight and artificial UV-light were able to oxidise Tl(I) to Tl(III).

5 Conclusions

Separation and quantification of Tl(I) and Tl(III) at natural levels was accomplished by IC-ICP-MS in combination with complexation of Tl(III) with DTPA.

The distribution of Tl(I) and Tl(III) was highly dependent on the presence of iron(III)(aq), iron(III)(s), pH and light. Exposing a Tl(I) solution with Fe(III)(aq) to sunlight gave a rapid formation of dissolved Tl(III). In the presence of Fe(III)(s) a decrease in total concentration of thallium occurred, most likely due to adsorption of Tl(III) on the iron(III)(s) surfaces. When exposing a lake water sample spiked with Tl(I) to light oxidation to Tl(III) and adsorption to the dispersed solids lowered the dissolved thallium concentrations.

The thallium concentration in the Swedish environment was found to be related to the geological conditions. As a consequence of the thallium speciation it was found that it was mobilised from contaminated soil and solid wastes in the pH 5-8, often enhanced by reducing conditions. These findings indicate that thallium is readily mobile in a large of the Sweden environment. In unpolluted fresh water lakes the concentration of thallium was 4.5-12 ng/l whereas close to mine waste deposits it could reach up to 594 ng/l due to the mineralogy. The impact of the geological form of thallium on its mobility was also evident by the presence of alum shale.

The anthropogenic atmospheric deposition of thallium to the Swedish environment can be dated back to the industrialisation in central Europe and the British Isles. The largest increase has been after the Second World War. The anthropogenic load is lowered towards the north.

From this study it is evident that the geochemistry of thallium has to be studied further. The highly different properties of Tl(I) and Tl(III) with respect to mobility in the environment, toxicity etc. necessitates a closer investigation on the mechanisms behind the distribution. Particularly the influence of humic substances, iron, manganese and light are important to include. Since the element is highly toxic a closer look on thallium concentrations in the environment as well as the technosphere is required since its direct use has increased as well as it is emitted as a trace contaminant in many compounds.

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