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THALLIUM PROPERTIES AND BEHAVIOUR - A Litterature Study

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Contents

Documentation page

1	PHYSICAL AND CHEMICAL PROPERTIES	1
2	NATURAL SOURCES: THALLIUM IN ROCKS AND MINERALS	3
3	ANTHROPOGENIC SOURCES	7
4	USES OF THALLIUM	7
5	EMISSION FROM INDUSTRIAL SOURCES	8
	5.1. Metal production industries	8
	5.2 Power - generating plants	9
	5.3 Brickworks and cement plants	11
	5.4 Sulphuric acid plants	12
	5.5 Fertilizers	12
6	TRANSPORT AND DISTRIBUTION BETWEEN ENVIRONMENTAL MEDIA	12
	6.1 Transport and distribution in air, water and soil	12
	6.2 Soil-vegetation transfer	13
	6.3 Absorption by plants	15
	6.4 Distribution in plants	15
7	RELEASES TO THE ENVIRONMENT	16
	7.1 Air	16
	7.2 Water	16
	7.3 Soil	17
	7.4 Plants	17
8	ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE	17
	8.1 Air	18
	8.2 Water	18
	8.2.1 Areas not contaminated by thallium	18
	8.2.2 Areas contaminated by thallium from industrial sources	18
	8.3 Rocks, soil and sediment	20
	8.3.1 Areas not contaminated by thallium	20
	8.3.2 Areas contaminated by thallium from industrial sources	20
	8.4 Plants	22
	8.4.1 Areas not contaminated by thallium	22
	8.4.2 Areas contaminated by thallium from industrial sources	22
	8.5 Animals	26
	8.5.1 Areas not contaminated by thallium	26
	8.5.2 Areas contaminated by thallium from industrial sources	26
9	DISTRIBUTION IN HUMANS	28

9.1 Increased concentrations after lethal poisoning	28
9.2 Increased concentrations after long-term sublethal poisoning	28
4 10 HAZARD EVALUATION AND LIMITING CONCENTRATIONS	31
11 REFERENCES	33

GEOLOGICAL SURVEY OF FINLAND DOCUMENTATION PAGE

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Abstract Properties and behaviour of thallium, one of the most poisonous element, were compiled based on publications written during past 30 years. Altogether 156 articles and other publications were reviewed. The geochemistry of Tl is known quite well, but the behaviour of Tl in geological processes and its cycle from lithosphere to hydrosphere and biosphere is still unclear and includes many open questions. The distribution of Tl in different natural materials also needs improvement.			
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Abstract

Properties and behaviour of thallium, one of the most poisonous element, were compiled based on publications written during past 30 years. Altogether 156 articles and other publications were reviewed.

The geochemistry of Tl is known quite well, but the behaviour of Tl in geological processes and its cycle from lithosphere to hydrosphere and biosphere is still unclear and includes many open questions. The distribution of Tl in different natural materials also needs improvement.

1 PHYSICAL AND CHEMICAL PROPERTIES

Thallium is a typical metal and belongs to Group 13 of the Periodic Table of Elements (according to the IUPAC proposal 1986); atomic number, atomic mass and density are 81, 204.37 and 11.85 g/cm³, respectively. Due to its high specific gravity of 11.85 g/cm³, Tl belongs to the heavy metal group. It is very heavy and soft, and the colour of a freshly cut surface is silvery-white, rapidly developing characteristic bluish oxidation films.

At room temperature, Tl occurs in a hexagonal close-packed structure (alpha-Tl) which transforms at 232°C into a cubic body-centred modification (beta-Tl). Thallium begins to volatilize at 174 °C, the melting point is at 302 °C, and the boiling point is at 1457 °C.

The electron configuration is 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰4s²3d¹⁰4f¹⁴5s²3d¹⁰6s²6p¹. Thallium is a very reactive metal. When exposed to air and moisture, it is superficially oxidized, forming a coating of Tl(I) oxide (Tl₂O). At higher temperatures it reacts with a lovely green flame to form Tl(III) oxide (Tl₂O₃). Thallium carbonate (Tl₂CO₃) is the only heavy metal carbonate that is very soluble in water (Micke et al., 1983; Stokinger, 1987).

Corresponding to the place in the Periodic System of Elements, in compounds formed under natural conditions the metal chiefly occurs in the monovalent oxidation state due to the high oxidation potential from Tl (I) to Tl (III) of +1.25V.

Monovalent (thallous) compounds behave like alkali metals, e.g. potassium, whereas the trivalent (thallic) compounds are less basic, resembling aluminium. In contrast to inorganic compounds in which the Tl (I) ion is more stable in aqueous solutions than the Tl (III) ion, the latter is more stable in organic compounds (Kemper et al., 1991; Sobott, 1993; EHC 182, 1996).

The ionic radii and the electronegativity constant of monovalent Tl are very similar to those of other alkali metals. Tl (I) hydroxide, carbonate and sulphate, like the corresponding potassium compounds are very soluble in water. With respect to their physical and chemical properties, e.g., poor water solubility, Tl (I) oxide, sulphide and halides show similarities to the corresponding compounds of silver, mercury and lead (Trotman-Dickenson, 1973). In contrast to inorganic Tl compounds, covalent organoTl compounds are only stable in the trivalent form (McKillop & Taylor, 1973). Tl (I) is not strongly complexed by humic acids, whereas Tl (III) forms stable complexes of the [TlX₄]- or [TlX₆]³⁻ type (Schoer, 1984).

An overview on the properties, and chemical formulae of pure Tl and some of its compounds is given in Table 1.

Thallium is a non-volatile heavy metal, and if released to atmosphere from anthropogenic sources, may exist as an oxide (Tl₂O), hydroxide (TlOH), sulfate (Tl₂SO₄), or sulfide Tl₂S (EPA, 1988). These Tl compounds are not volatile (EPA, 1983). It has been speculated that Tl sulfate and hydroxide will partition into water vapor (such as clouds and rain drops) because they are soluble in water and thus precipitation may remove these forms of Tl from the atmosphere (EPA, 1988). Thallium oxides are less soluble in water, and may be subject to only atmospheric dispersion, and gravitational settling. The atmospheric half-life of suspended Tl particles is unknown.

Thallium exists in water primarily as a monovalent ion Tl (I); Tl may be trivalent in very oxidizing water (Callahan *et al.*, 1979). Tl (I) forms complexes in solution with halogens, oxygen, and sulfur (Lee, 1971). Thallium may precipitate from water as solid mineral phases. However, Tl chloride, sulfate, carbonate, bromide, and hydroxide are very soluble in water (Table 1). For example, the solubility of Tl sulfate at 0°C is about 27 g/l (EPA, 1980). In extremely reducing water, Tl may precipitate as a sulfide (Tl₂S), and in oxidizing water, Tl³⁺ may be removed from solution by the formation of Tl(OH)₃ (Lee 1971).

Table 1. Physical and chemical properties of Tl and some selected Tl compounds. From: Stokinger (1987); Budavari (1989); Lide (1990).

Name	Chemical formula	Relative atomic/molecular mass	Specific gravity (g/cm ³)	Melting point (°C)	Boiling point (°C)	Solubility in water (g/litre)
Thallium	Tl	204.38	11.85	303.5	1457	insoluble
Thallium(I) acetate	TlC ₂ H ₃ O ₂	263.43	3.765	131	-	very soluble
Thallium aluminium sulphate	TlAl(SO ₄) ₂ *12H ₂ O	639.66	2.306	91	-	117.8
Thallium(I) bromide	TlBr	284.29	7.557 (17.3°C)	480	815	0.5 (25°C)
Thallium(I) carbonate	Tl ₂ CO ₃	468.78	7.110	273	-	40.3 (15.5°C)
Thallium(I) chloride	TlCl	239.84	7.004 (30°C)	430	720	2.9 (15.5°C)
Thallium(III) trichloride	TlCl ₃	310.74	-	25	decomposes	very soluble
	TlCl ₃ *4H ₂ O	382.80	-	37	100 (-H ₂ O)	862
Thallium ethylate	TlOC ₂ H ₅	249.44	3.493 (20°C)	-3	130 (decomposes)	-
Thallium(I) fluoride	TlF	223.38	8.23 (4°C)	327	655	786 (15°C)
Thallium(III) trifluoride	TlF ₃	261.38	8.36 (25°C)	550 (decomposes)	-	decomposes to TlOH
Thallium hydroxide	TlOH	221.39	-	139 (decomposes)	-	259
Thallium(I) iodide (alpha)	TlI	331.29	7.29	440 (β)	823 (β)	0.006 (20°C)
Thallium(I) nitrate (alpha)	TlNO ₃	266.39	-	206	430	95.5 (20°C)
Thallium (III) nitrate trihydrate	Tl(NO ₃) ₃ *3H ₂ O	444.44	-	105-107 (decomposes)		decomposes
Thallium(I) oxide	Tl ₂ O	424.77	9.52 (16°C)	300	1080 (-O)	decomposes to TlOH
Thallium(III) oxide	Tl ₂ O ₃	456.76	10.19 (22°C)	717 ± 5	875 (-O ₂)	insoluble
Thallium(I) sulphate	Tl ₂ SO ₄	504.82	6.77	632	decomposes	48.7 (20°C)
Thallium(I) sulfide	Tl ₂ S	440.85	8.46	448.5		0.2 (20°C)

Thallium may partition from water to soils and sediments. Partition coefficients such as adsorption constants describe the tendency of a chemical to partition to solid phases from water. Adsorption constants for inorganic ions such as Tl (I) cannot be predicted a priori, but must be measured for each adsorbent.

The two naturally occurring isotopes ^{203}Tl (~ 30%) and ^{205}Tl (~ 70%), and 26 artificial isotopes are known: mass range 191-210, half-life range 2.1 ms ($^{201\text{m}}\text{Tl}$) to 3.8 years (^{204}Tl). With its high density of 11.85 g/cm^3 Tl is an heavy metal (Kemper & Bertram, 1991).

Many of its physical properties such as density and ductility are similar to those of lead, the immediate neighbour in Group 14, whereas the chemical behaviour is comparable to that of silver, mercury, lead and larger alkali elements.

Thallium is very soluble in HNO_3 and H_2SO_4 , but only slow dissolution takes place in HCl , because of the low solubility of the halides. It is insoluble in alkali bases. Thallium combines with fluorine, chlorine and bromine at room temperature, and reacts with iodine, sulphur, phosphorus, selenium and tellurium after heating. The metal does not react with molecular hydrogen, nitrogen or carbon. It forms alloys with other metals and readily amalgamates with mercury (Micke *et al.*, 1983).

2 NATURAL SOURCES: THALLIUM IN ROCKS AND MINERALS

Thallium occurs in small amounts in the Earth's crust. During the process of magmatic differentiation the large Tl^+ ion (1.47 Å) is enriched in the fluids of the late pegmatitic and hydrothermal stages. For this reason in the igneous rocks generally Tl is strongly enriched in pegmatites. Mafic and ultramafic rocks containing mafic minerals are poor in Tl; on the other hand, acid and intermediate magmatic rocks consisting of K-feldspar, plagioclase, biotite or muscovite are characterized with higher Tl content (V. Jović, 1993). Much higher values have been found in organic rich shales and coals of the Jurassic period with values of up to 1,000 mg/Kg (Kazantzis, 2000).

In table 2 are shown the average Tl concentrations (mg/Kg) in different constituents of the Earth's upper crust and in some rocks.

Table 2. The average natural content of Tl in selected rocks (all in mg/Kg, except stream water and sea water in µg/l). From: 1) Vlasov, 1966; 2) Koljonen, 1992; 3) Wedepohl, 1991; 4) Ivanov, 1996; 5) Kabata-Pendias, 2001.

Continental crust	Oceanic crust	Acid rocks	Alkaline rocks	Intermediate rocks	Basic intrusive and effusive rocks	Ultrabasic rocks	Peridotites	Gabbros & basalts	Granites & granodiorites	Shales & schists	Sandstones	Limestones	Stream water	Sea water
0.700 ³⁾	0.010 ³⁾	1.6 ¹⁾	1.5 ¹⁾	0.83 ¹⁾	0.27 ¹⁾	0.1 ¹⁾	0.150 ³⁾	0.300 ³⁾	1.300 ³⁾	0.900 ³⁾	1.000 ³⁾	0.050 ³⁾		0.01 ³⁾
	0.49 ²⁾							0.08 ²⁾	1.1 ²⁾	0.45 ²⁾		0.03 ²⁾		
		1.9 ⁴⁾		0.5 ⁴⁾	0.25 ⁴⁾	0.18 ⁴⁾				1.3 ⁴⁾	1.5 ⁴⁾	0.1 ⁴⁾	1 ⁴⁾	0.01 ⁴⁾
		0.5-1.8 ⁵⁾		0.5-1.4 ⁵⁾			0.05-0.2 ⁵⁾	0.1-0.4 ⁵⁾	0.6-2.3 ⁵⁾	0.5-2.0 ⁵⁾	0.4-1.0 ⁵⁾	0.01-0.14 ⁵⁾		

As it is possible to note, Tl content in rocks depends mostly on their mineral composition and its accumulation, no matter whether the rocks are of magmatic, metamorphic or sedimentary origin, is on ppm level.

The more common Tl host minerals are K-minerals (e.g. micas, feldspars) and many sulphides. In silicates such as K-feldspar, biotite and muscovite, due to a similar ionic radius and identical electric charge, it can substitute isomorphously K^+ (1.33 Å) and Rb^+ (1.48 Å).

In sulphides, Tl is preferably associated with arsenic, antimony, copper, lead, iron, gold, mercury and zinc and forms either independent minerals (Sobott *et al.*, 1987; Kemper, 1991) or, more frequently, occurs as trace element in galena, sphalerite and pyrite (Sobott, 1993) (Table 3).

Thallium can be associated with As, Ag, Au, Cu, Fe, Hg and Sb also, but the Alšar ore deposit (Greek-Macedonian border) is the unique known containing economic concentrations of Tl, arsenic, antimony and gold (Slobodan, 1993). Totally, Tl reserves in ore deposits are estimated about 1.4×10^3 ton a worldwide basis (Gocht, 1974; Global 2000, 1980; Haefs, 1986).

In contrast to the occurrence of Tl as trace element, Tl minerals are very rare. Crookesite (from Skikerum/Sweden) is a mixture of the selenides of copper, Tl and silver ($(\text{Cu, Ag, Tl})_2\text{Se}$); similar chemical compositions have been found in berzelianite (Germany) and lorandite (Macedonia). Other minerals with high Tl-content are located in the USA and Brazil (Kazantzis, 1986; Schoer, 1984); in lorandite and crookesite Tl can reach levels up to 60%, but usually they are not used for Tl production (Kazantzis, 2000).

Tables 3, 4 and 5 show the average Tl content (mg/kg) in some minerals in different rocks and in ore deposits. In fact in order to determinate the fate of Tl in soils formed by weathering of rocks, it is necessary to establish in which rock-forming minerals and which concentrations Tl can appear.

Table 3. Average Tl concentrations in some silicates and sulphides minerals (Ivanov, 1996).

Mineral	Concentration	Mineral	Concentration		
Biotite	3.3 – 389	Chalcopyrite	0.00 – 33		
K-feldspars	0.5 – 610	Pyrite	≤ 8500		
Muscovite	1.5 – 145	Sphalerite	≤ 1057		
Amphibole	0.00 – 2.6	Pyrrhotite	≤ 20		
				Plagioclase	≤ 10
Silicates	0.044 – 0.50	Sulphides	≤ 700		
				Pyroxene	0.23 – 27
				Garnet	

Nevertheless, the availability of Tl in all the environmental matrices depends on its solubility and mobility in the different conditions; moreover it depends on the characteristics of the elements with which it is associated.

Thallium concentrations in uncontaminated soils are generally of the order of 0.01 to about 3.0 mg/kg, but most soils contain Tl at concentrations of less than 1 mg/kg (Kazantzis, 2000; Xiao, 2003). Table 6 shows soil Tl contents in various countries.

Marine sediments from different areas have shown Tl concentration varying from 0.14 to 1.13 mg/kg, and in small rivers and streams of the order of 0.01 to 0.07 mg/kg dry weight (Smith & Carson, 1977; Bowen, 1979). Data summarized by Smith & Carson (1977) show a concentration up to 614 mg/kg in manganese nodules.

The behaviour of Tl in the weathering processes is relatively little known. Tl can be easily released during weathering and transported together with alkaline metals, but its great ionic radius causes fast fixation by oxides of Fe and Mn, clay minerals and some gels (Kabata-Pendias & Pendias, 2001). Particularly, Tl shows a tendency of enrichment in illitic clays (Table 2). So, it gradually enriches in the weathering products of various rocks; moreover, Tl content in elluvial-

deluvial deposits are higher than in the primary rocks and it can be explained by clay sorption (Butler, 1962; Kurbanayev, 1966; Jović, 1993). Tl is retained in the upper layers of soil, retention being less effective in acid soils (Kazantzis, 2000).

Tl is mostly soluble in water, but when it enters in soils it becomes immobile (Jović, 1993). Tl is characterized by low mobility in oxidized, acid and neutral to alkaline conditions. In reducing conditions it is of very low mobility or even immobile (Jović, 1993). It was found that increasing pH decrease Tl-inorganic interactions (Kazantzis, 2000). Increases in pH, however, produce extensive Tl-humic acid interaction. It appears that Tl-organic interactions may be important in most natural water systems. In reducing environments, thallos species may precipitate as a sulfide; otherwise, it will remain in solution (EPA, 2004).

Table 4. Average Tl concentrations in some minerals in different rocks (Jović, 1993)

	Granotoid rocks	Alkaline rocks	Granite pegmatites	Gabbroid rocks	Granulite	Basaltic rocks	Ultramafic rocks	Gneisses
Biotite	3 - 15	3.2 - 7.6	3 - 15					
K-feldspars	0.7 - 30	1.2 - 3.4	0.5 - 50 (600)		< 1			0.7 - 30
Muscovite	1.5 - 3.7		1.5 - 3.7					
Hornblende	0.8 - 2.6	0.7						
Plagioclase				0.05		0.030 - 0.052		
Pyroxene						0.003 - 0.045		
Olivine				0.05		0.008		
Magnetite	0.4			2.20		0.036 - 0.097		
Phlogopite							3	
Ilmenite				1.60				

Table 5. The main types thallium-containing deposits (Ivanov, 1996)

Deposit	Mineral-carrier	Average abundance (ppm)
Pb-Zn strata bound in silicate	Sphalerite	10
	Pyrite	120
	Galenite	7
Pb-Zn veined in metamorphic rocks	Galenite	10
	Galenite	7
Skarnic deposits and veins in metamorphic rocks	Galenite	7
	Galenite	14
	Sphalerite	8
Cu-Pb-Zn	Pyrite	5
	Galenite	5
	Sphalerite	8
Cu-Zn and sulphuric-pyrite	Galenite	5
	Sphalerite	8
	Chalcopyrite	5
Rare-metal granite, pegmatite and greisens	Feldspars and common minerals	10 - 48

Table 6. Tl-content (mg/Kg) in the upper soil layers of various countries, n indicating the number of samples. ¹⁾ Tremel *et al.* (1997), ²⁾ Kabata-Pendias *et al.* (2001), ³⁾ Xiao *et al.* (2004).

Country	n	Median value	Mean value
Thüringen (FRG) ¹⁾	51	0.460	
Upper Austria ¹⁾	460		0.300
Switzerland ¹⁾	369	0.050	
Great Britain ³⁾		0.03 - 0.99	
France ¹⁾	244	0.292	1.513
Canada ²⁾		0,25 - 0,71	
China ³⁾	853	0.580	
World ^{1),3)}		0.200	

Table 7 shows an example of Tl average content (mg/kg) in fresh rocks and in their weathering products. In the oxidation zone of ore deposits the extremely insoluble sulphide minerals are transformed into soluble sulphates and Tl can be set free and migrate with mine waters. Comparable processes take place on mine dumps and Tl, among other minerals, will be leached by percolating water. Mobile Tl will soon be fixed again, either by co-precipitation with flocculated iron and/or manganese oxihydroxide or adsorption by clay minerals or organic matter (Sobott, 1993). In fact, generally, in the oxidation zone of ore deposits Tl is mostly dispersed and its content is lower than in the sulphide zone. There are some cases in which Tl is concentrated in the secondary minerals of the oxidated zone, as Mn-oxides (Jović, 1993).

Table 7. Thallium content (mg/Kg) in fresh and weathered rocks (Jović, 1993).

Bedrock	Weathered rock and shingle	Weathered mantle	Clays	Loam and silt
Granodiorite	0.2	0.26	0.3	0.33
Andesite	0.22	0.03	0.32	0.77
Silty shale	0.04	0.10	0.13	0.28

Investigating an area where lead and zinc with sometimes appreciable amounts of Tl were mined (Rehrauer, 1991) has been found out that the highest contents of cadmium, zinc, arsenic, copper and Tl occur in soils either overlying outcropping ore bodies, or containing slags and/or waste material or lying within the flooding area of a rivulet cutting through the mining area. Has been demonstrated that about 60% of the binding types, in the case of Tl, are concentrated in the insoluble residual fraction. The remaining 40% are distributed fairly even over the exchangeable, carbonatic, oxidic and organic fractions. About 10% of the total Tl concentration is disposable for the uptake by plants (Schoar & Nagel, 1980).

Very high Tl concentrations can occur in organic-rich shales such as the Pierre Shale in the USA (25 mg/kg) and in coals of the Jurassic period in Tadzhikistan (100 to 1000 mg/kg) (Smith & Carson, 1977).

3 ANTHROPOGENIC SOURCES

Since Tl is used only in small amounts by industry, worldwide production of pure Tl is low. In 1975 about 8 tonnes were produced in Germany and 2 to 3 tonnes in the USA (Zitko, 1975), while in 1987 and 1988 worldwide production was about 17 tonnes (US BM, 1992). Sources for the production of Tl are zinc, lead and sometimes copper or iron smelters and sulfuric acid plants. Flue dust in particular is used as a Tl source (Zitko, 1975; Smith & Carson, 1977; Micke *et al.*, 1983; Briese *et al.*, 1985). Procedures for the separation of Tl from other metals depend on the proportions of the different minerals and, therefore, vary considerably between the different smelters (Sanderson, 1952; Smith & Carson, 1977; Micke *et al.*, 1983; Kemper & Bertram, 1984; Briese *et al.*, 1985b).

4 USES OF THALLIUM

Thallium(I) sulphate was once used in medicine to reduce sweating and to cure various infections, e.g., venereal diseases, ringworm of the scalp, typhus, tuberculosis and malaria, and as a depilatory agent, which caused many intoxications (Munch, 1934; Smith & Carson, 1977; Em- sley, 1978; Briese & Nessler, 1985a). However, therapeutic uses of Tl have been discontinued despite of its toxicity.

Since 1920, Tl(I) sulphate has been used as a rodenticide, in Europe chiefly against rats and in the USA chiefly against ground squirrels (Howe, 1971; Smith & Carson, 1977). Formerly it was used as an insecticide (against ants and cockroaches). However, Tl is no longer on sale as a ro- denticide in most industrial countries (Bruère *et al.*, 1990), but is still used in developing coun- tries because of its cheapness.

Other areas in which Tl is used (Howe, 1971; Smith & Carson, 1977; Micke *et al.*, 1983; Briese *et al.*, 1985; Sharma *et al.*, 1986; Kazantzis, 1986; Manzo & Sabbioni, 1988; ATSDR, 1992; Sobott, 1992) are as follows:

- Llow temperature thermometers (down to -59°C) made from a mixture of Hg and Tl (Sobott, 1992);
- Sspecial glasses with a high resistance and a low melting point, containing Tl and Se (Sobott, 1992);
- Mmixed crystals for infrared instruments, composed of As or Tl(I) salts and halogenides (TlI - TlBr), and Tl_3VS_4 , Tl_3NbS_4 , and Tl_3PSe_4 for acusto-optic and laser equipment (Sobott, 1992);
- Eelectronic devices, e.g. Tl(I) sulphide for semiconductors and scintillation counters (Sobott, 1992);
- M mercury lamps (addition of Tl(I) halogenides increases the yield of light and changes its spectrum) (Sobott, 1992);
- A alloys with Pb, Zn, Ag and Sb enhance resistance to corrosion (Sobott, 1992);
- C catalyzing organic reactions, e.g., oxidations of hydrocarbons and olefins (Tl compounds are be- ing increasingly used for organic synthesis) (Smith & Carson, 1977);
- R radioactive isotopes, used in physics for measurement of exact time periods (^{205}Tl), in industry for measuring the thickness of material (^{204}Tl), and in medicine for scintigraphy of heart, liver, thyroid and testes, and for the diagnosis of melanoma (^{201}Tl) (Rao *et al.*, 1983; Müller-Brand *et al.*, 1984; Urbain *et al.*, 1986);
- O other uses, e.g., in the production of imitation jewellery, fireworks, pigments and dyes, the im- pregnation of wood and leather against bacteria and fungi, and in mineralogical analysis;

- Minor amounts of Tl are used in biochemistry, e.g., arylTl(III) compounds for modification of proteins and tRNA (Douglas *et al.*, 1990).

Worldwide industrial consumption in 1991 was estimated to be 10 to 15 tonnes. Between 1940 and 1980 consumption in the USA varied considerably between 0.5 and 11 tonnes/year (Schoer, 1984), and between 1984 and 1988 it was 1.1-1.5 tonnes/year (US BM, 1985, 1989).

In the USA it is used mainly in the electrical and electronic industries and the 650 kg used in 1983 in the German Democratic Republic was mainly for making special glass (Smith & Carson, 1977; Micke *et al.*, 1983; Briese *et al.*, 1985; Kazantzis, 1986; Kemper & Bertram, 1991).

Nevertheless, anthropogenic accumulations of Tl are caused mostly by industrial plants processing continuously large quantities of raw material containing Tl as trace element such as fossil fuels, oils, sulphide ores (Cu, Pb, Fe, Zn) or cement (Kazantzis, 2000). Volatile Tl compounds escape through chimneys without proper filter installations and subsequently fall out on rural and urban areas (Kemper & Bertram, 1991; Sobott R.J.G, 1993; Kabata-Pendias & Pendias, 2001).

5 EMISSION FROM INDUSTRIAL SOURCES

There is an enormous difference between the amount of Tl mobilized (released into air, water or disposed of on land) and the Tl consumption of about 12 tonnes/year. Worldwide a total of 2000-5000 tonnes of Tl is estimated to be mobilized per year, especially through the combustion of fossil fuels, refinement of oil fractions, the smelting of ferrous and non-ferrous ores, and also by some other industrial processes such as cement production (Gorbauch *et al.*, 1984; Ewers, 1988; Nriagu & Pacyna, 1988). Smith & Carson (1977) estimated that about 15% (240 tonnes) of total mobilized Tl is transferred annually to the atmosphere. However, only a small fraction is released into the atmosphere or wastewater during production processes or from waste materials (Table 8). Summarizing estimations for the USA by Smith & Carson (1977), Schoer (1984) emphasized that in the USA each year nearly 1000 tonnes of Tl are released into the environment, of which 350 tonnes are emitted in vapours and dusts, 60 tonnes bound to non-ferrous metals, and more than 500 tonnes contained in fluid and solid wastes.

5.1. Metal production industries

In residues of ore smelting and metal processing Tl is enriched. Smelting of chalcogenic ores, especially lead and zinc sulphides, yields Tl emissions. The annual demand of Tl (about 10-15 t; Kemper & Bertram, 1991) is easily met by the production of the metal by leaching it with sulphuric acid from the flue dusts of roasting and smelting of lead, copper, iron and zinc sulphide ores. This is done by dissolving in dilute acid, precipitating out lead sulphate, and then adding HCl to precipitate the poor soluble Tl chloride, TlCl. Further purification can be achieved by electrolysis of soluble Tl salts (Micke *et al.*, 1983; Schoer, 1984). In contrast to the small world production Tl per year, it has been estimated that worldwide over 600 tonnes of Tl are processed per year during the smelting of lead, copper and zinc ores (Micke *et al.*, 1983).

Thallium emissions from smelters can vary greatly from plant to plant, depending upon the Tl content of the raw materials and the technology used. For this reason, and because of the lack of recent emission data, global releases can be only roughly quantified. On the basis of the data in Table 8, a total of about 90 tonnes of Tl may be released each year into the atmosphere from non-ferrous metal production operations in the USA, Canada and Germany. Dust in one zinc smelter was reported to contain 380-3700 mg Tl/kg before and 60-9700 mg Tl/kg after starting the production of Tl (Briese *et al.*, 1985). Although it is not possible to estimate the losses of Tl from mineral waste materials, releases from these materials are generally expected to be small.

Data from the USA (Smith & Carson, 1977) indicate that relatively large amounts of Tl are present in waste materials from non-ferrous metal (mainly copper) and iron and steel production (Table 8). Although no precise data were available on Tl levels in waste from ferroalloy production using manganese ores, Smith & Carson (1977) suggested that emissions from this source could be significant. Atmospheric releases resulting from the production of iron and steel in the USA were estimated to be relatively small (about 5 tonnes from steelmaking and 1 tonne in iron blast furnace gases). In the main area of iron and steel production in Germany, annual Tl emissions into air have been estimated to be about 0.8 tonnes (Ewers, 1988).

5.2 Power - generating plants

Thallium in coal (with high sulphidic portion) has been determined in 1968 by Voskresenskaya, and he found that Tl is not firmly bound in coal, but it forms soluble compounds of humic and fulvic types (humates and fulvenes) with organic coal components; moreover pyrite from coal was richer in Tl than pyrite from the neighbouring sedimentary rocks. Tl came into the coal-forming basins during sedimentation or in the early diagenesis; its contents are not controlled by the petrography of coal and its contents in pyrite are constant throughout the vertical profile of the seam (Bouška, 1981). Table 9 shows Tl contents in pyrites from some coals deposits (Voskresenskaya, 1968).

Ewers (1988) states that worldwide 600 t/y of Tl are emitted by coal burning power plants (Tab. 8). Of all the elements Ag, As, Bi, Cd, Pb, Se, Tl and Zn are accumulated to high levels in the finest fraction of particulate aerosols which leave the stacks of coal firing power plants (Brumsack *et al.*, 1984). According to balance computations on the behaviour of numerous metals during the combustion of hard coal in West-German power plants Brumsack *et al.* (1984) concluded that the fly-ash from the stacks contains about 10 to 60 mg/kg Tl. The volatility of Tl and of the other listed elements is caused by the relatively high concentration of chlorine in the firing process (0.6 to 1.2 % Cl in stack fly-ash). Large amounts of volatile elements in particulate aerosols are transported by wind over large distances. The yearly firing of coal probably causes the worldwide emission of 1.5×10^2 t Tl, if the data computed by Brumsack *et al.* (1984) on emissions in West Germany are extrapolated (Wedepohl, 1991).

Power-generating plants represent a major source of Tl emissions, especially those using some brown coal or coal of the Jurassic period. Most coals contain only about 0.5 to 3 mg/kg, mainly incorporated in sulphide inclusions. Some of these impurities can be removed by washing and mechanical cleaning. It has been estimated that about half of the Tl content of coal is emitted into the atmosphere and represents the biggest anthropogenic source (Smith & Carson, 1977) (Table 8). In such estimations, losses from collected fly ash are not taken into consideration, because its use may vary. Only a minor amount is used in cement making. If it is used as a soil stabilizer, contamination of the environment is much higher (Smith & Carson, 1977).

Natusch *et al.* (1974) found that coal-fired power-generating plants emitted about $700 \mu\text{g Tl/m}^3$ flue gases, resulting in a local level of air emission of about 700 ng/m^3 . This would result in an estimated daily absorbed amount of $4.9 \mu\text{g}$ airborne Tl per person (US EPA, 1980). In the European Union, coal-fired power-generating plants were estimated to have caused a total mobilization of 240 tonnes of Tl during 1990, about one third of this being concentrated in the smallest particles, and atmospheric emissions of 7 tonnes (Sabbioni *et al.*, 1984b).

Table 8. Estimated emissions of thallium (tonnes/year) into the environment. From: ¹⁾ Smith & Carson (1977), ²⁾ Brumsack (1977), ³⁾ Sabbioni *et al.* (1984b), ⁴⁾ Bowen (1979), ⁵⁾ Schoer (1984), ⁶⁾ Brumsack *et al.* (1984), ⁷⁾ Davids *et al.* (1980), ⁸⁾ Ewers (1988), ⁹⁾ Nriagu & Pacyna (1988), ¹⁰⁾ Kogan (1970).

Emission source	USA	Canada	Germany	Europe	World
Coal combustion					
into air	180 ¹⁾ 140 ⁵⁾		7.5 ²⁾ 4 ⁶⁾ 6 ⁷⁾	7 ³⁾ 80 ⁵⁾	54 ⁴⁾ 600 ⁵⁾
into soil/water	170 ¹⁾				
into total environment				240 ³⁾	
Coal combustion (into air)					
from electric utilities					155-620 ⁹⁾
from industry and domestic					495-990 ^{8, 9)}
Ferroalloy production using manganese ores					
into air	140 ¹⁾				
into soil/water	220 ¹⁾				
Raw iron production and related coal combustion					
into air	6 ¹⁾		35 ⁷⁾		30 ⁴⁾
into total environment	205 ¹⁾				
Production of nonferrous metals					
into air	38 ¹⁾	44 ¹⁰⁾	11 ⁷⁾		
total emission	496 ¹⁾				
Potash-derived fertilizers					
into total environment	5 ¹⁾				
Cement plants					
into air			25 ⁷⁾		2670-5340 ⁹⁾
Brick works					
			28 ²⁾		
Oil fuel combustion, mining and processing of oil shales					
into soil/water	8 ¹⁾				
total emission	8 ¹⁾				
Waste combustion			< 1 ⁷⁾		

Table 9. Thallium contents in pyrite from coal (Bouška, 1981). In parenthesis the number of samples.

Coal deposit place (sample number)	Average content (mg/Kg)
Central Asia (30)	34
Moscow Basin (14)	3.3
Transcarpathian Basin (5)	11
Dnieper Basin (23)	<0.5

In coal burners, Tl volatilizes and recondenses onto the surface of ash particles in cooler parts of the system. As a result, 2 to 10 times higher concentrations of Tl may occur in the fly-ash than was present in the coal (Galba, 1982). Fly-ash Tl content is negatively correlated with particle size (Manzo & Sabbioni, 1988). Thus, Tl and other toxic trace elements are concentrated in the smallest particles, which pass through conventional power-generating plant filters, remain suspended in the atmosphere for long periods and are respirable. For instance, particles with a diameter of 1.1-2.1 μm contain 76 mg Tl/kg fly-ash, those with a diameter of 2.1-7.3 μm contain 62-67 mg/kg and those with a diameter of 7.3-11.3 and $> 11.3 \mu\text{m}$ contain 40 and 29 mg/kg, respectively. Particles with a diameter of less than 74 μm contain only 7 mg Tl/kg (Natusch *et al.*, 1974). These particles are highly toxic, since Tl and other heavy metals are preferentially concentrated on the particle surfaces and therefore are relatively bioavailable (Linton *et al.*, 1976; Natusch, 1982).

5.3 Brickworks and cement plants

Total Tl emissions from brickworks in Germany have been estimated to be 28 tonnes/year. This compares with emissions of 7.5 tonnes/year from the burning of coal (Brumsack, 1977).

The emission potential of cement plants was not recognized until 1979. The first effects on vegetation around a cement plant in Lengerich, Germany were observed in 1977 (Pielow, 1979; LIS, 1980), but only the gradual hair-loss in a rabbit led to the suspicion that Tl was the cause of the toxic effects (LIS, 1980; Brockhaus *et al.*, 1981; Dolgner *et al.*, 1983). The source of Tl was found to be residues of pyrite roasting added as a ferric oxide additive to powdered limestone in order to produce special qualities of cement and the addition of the filter fly-dust (LIS, 1980). Studies at other plants showed much lower emission levels, so that the emission at Lengerich was caused by the exceptional circumstances. Production alterations in Lengerich caused a reduction in the emissions of more than 99% (Pielow, 1979; Prinz *et al.*, 1979; LIS, 1980).

Like power-generating plants, cement plants emit Tl mainly bound to particles with a diameter of 0.2-0.8 μm (LIS, 1980).

Cement is produced from a mixture of limestone and shale or clay (Table 2). The heating of clay materials up to 1000°C causes a partial volatilization of Bi, Cd, Pb, Tl and Zn which ranges from about 40 to 80 % of the original metal concentration (Wedepohl, 1991). Polluted soils around a cement plant at Leimen (SW Germany) have 3.6 mg/kg Tl in surface parts (0-10 cm), 0.7 mg/kg at depth 40-50 cm and 0.1 mg/kg at depth 60-70 cm (Schoer, 1984).

Thallium concentrations in fly-dust emitted by the cement plant in Lengerich were about 2.5 mg/m³ air, of which nearly all was water-soluble Tl(I) chloride. Whereas the filter efficiency was 99% with respect to cement dust, it was only 50% with respect to the Tl-containing particles. As a result, about 140 to 200 g Tl/hour was emitted (Pielow, 1979; Prinz *et al.*, 1979; Weisweiler *et al.*, 1985). Changing the production process reduced the Tl content to less than 25 $\mu\text{g}/\text{m}^3$ (< 200

mg/kg dust). In other cement plants the concentrations in the filter dust were reduced from 3066 mg/kg to about 100 mg/kg, and after this reduction only 13% of the Tl was soluble in water (LIS, 1980).

5.4 Sulphuric acid plants

The sulphuric acid plant that had been the source of the roasted pyrite used in the cement plant in Lengerich used pyrite containing about 400 mg Tl/kg. However, in the roasted pyrite about 7% of the Tl was water-soluble. During production of sulphuric acid, a 100-fold enrichment of Tl was found (LIS, 1980). As a consequence, increased levels of Tl were found in Duisburg, Germany around the sulphuric acid plant but never such high concentrations as around the cement plant (Gubernator *et al.*, 1979).

5.5 Fertilizers

In arable soils Tl input from potassium fertilizers is reported to be very low. Some phosphorus fertilizers seem to contain high Tl concentrations, up to 2 mg/kg. But in general, input from agricultural practices are especially difficult to detect because they are diffuse and the Tl concentration of agricultural additives is not well known (Tremel *et al.*, 1997).

6 TRANSPORT AND DISTRIBUTION BETWEEN ENVIRONMENTAL MEDIA

6.1 Transport and distribution in air, water and soil

Near point sources such as coal-fired power-generating stations, cement plants using pyrite and some metal smelting operations, the major source of Tl in air is emission of fly-ash. Although data on the forms of Tl in these emissions are limited, results of one study indicate that nearly all of the Tl in fly dust from a cement plant (in Lengerich, Germany) was present as soluble Tl(I) chloride (LIS, 1980).

Assuming that 4×10^{12} kg of crustal rocks weather each year, Bowen (1979) calculated that 2.4×10^6 kg Tl/year become available to plants. However, as Jović (1993) has noted, Tl tends to be retained during rock weathering, and concentrations in soils tend to be somewhat enriched in soils compared to the original bedrock (Tab. 7).

The fate of Tl added to soil in deposited fly-ash probably depends greatly on soil type (Crössmann, 1984). The retention should be greatest in soils that contain large amounts of clay (Wedepohl, 1991; Ivanov, 1996), organic matter and iron/manganese oxides (Kabata-Pendias & Pendias, 2001). Thallium can also be incorporated into stable humus complexes (Crössmann, 1984), which are resistant to rapid "wash-out" (Schoer, 1984).

Results of studies in several areas indicate that Tl deposited from the atmosphere tends to accumulate in the surface layers of soils (Smith & Carson, 1977; Heinrichs & Mayer, 1977; LIS, 1980; Schoer, 1984). Retention processes will, however, be less effective in acidic soil (Heinrichs & Mayer, 1977).

Elevated concentrations of Tl in groundwater (up to 40 µg/litre) and in an irrigation canal (up to 96 µg/litre) in China, near a site where waste materials from the mining of mercuric ore and coal containing 25 to 106 mg Tl/kg were deposited (Zhou & Liu, 1985), indicate that under some circumstances significant amounts of Tl can move from soil into local water.

Although there is little information on the forms of Tl in natural water, most dissolved Tl in fresh water is expected to be present as the monovalent Tl^+ ion (Smith & Carson, 1977). In strongly oxidizing fresh water and in most seawater (Sager & Tölg, 1984), however, trivalent Tl is probably the predominant dissolved form. Both forms of Tl can be removed from solution by exchange and complexing reactions with suspended solid phases.

Trivalent Tl is also susceptible to reduction and precipitation processes. According to Cotton & Wilkinson (1988), trivalent Tl is extensively hydrolysed to form the colloidal oxide over the pH range of natural water. Depending upon the relative kinetics of reduction and hydrolysis, precipitation of Tl(III) hydroxide may be an effective mechanism for removing Tl from solution. When Tl(III) (precipitated as the oxide or hydroxide) settles into organic-rich anaerobic sediment, it will be reduced to the monovalent form, which can in turn be fixed in the sediment by reaction with sulphide to form insoluble Tl_2S (US EPA, 1978). Thallium is thus relatively depleted in seawater where Tl(III) predominates and can be enriched in sediments where organic matter accumulates under undisturbed, anaerobic conditions (Smith & Carson, 1977).

The partitioning of Tl among the water, sediment and biotic compartments of aquatic systems has rarely been investigated. In one study, however, in which Tl (100 $\mu\text{g/litre}$ as Tl(I) nitrate) was added to a 7-litre glass aquarium containing washed sea sand, goldfish and submergent aquatic angiosperms, Tl was distributed among all of the compartments. Concentrations in water decreased gradually, while those in the fish and vegetation increased, throughout the 9-day duration of the experiment, indicating that Tl was being exchanged among these media (Wallwork-Barber *et al.*, 1985). Concentrations in the sand increased rapidly to a relatively low value (0.05 mg Tl/kg), and remained relatively stable thereafter, suggesting that there was little exchange between the sediment and the other compartments. The limited accumulation of Tl in the sediment was attributed in part to the short duration of the study and to the absence of organic matter and clay in the sand.

6.2 Soil-vegetation transfer

In general, the solubility of Tl compounds governs the availability of the metal to vegetation (discussed in detail by Cataldo & Wildung, 1978). Crössmann (1984) mentioned that so far no method had been developed to quantify the amount of Tl in soil that is easily available for plants. However, Schoer & Nagel (1980) emphasized the good correlation between soil-vegetation transfer and the concentration determined following ammonium acetate extraction from soil. Other authors favour an EDTA/ammonium acetate extraction (Scholl & Metzger, 1982).

Transfer is influenced by various factors, e.g., pH and the type of the contaminated soil. Green rape, bush beans and rye grass were found to take up less Tl from weakly acidic soil (pH 6.2) than from more acidic soil (pH 5.6), and Tl supplied by cement factory dust was more available to plants than Tl in soil (Makridis & Amberger, 1989). Rape plants grown on two samples of soil from a contaminated area, one sample (A) containing a 3-fold higher concentration of Tl than the other, showed identical concentrations of Tl, while other vegetables grown on sample A even showed a lower Tl content. It was concluded, that plant availability cannot be correlated to total soil Tl content as determined after extraction with concentrated nitric acid (Hoffmann *et al.*, 1982). Only 4.4% ($\pm 2.7\%$) of the Tl content of soil from a lead-zinc mining waste material area was available to vegetation, compared to 17.5% ($\pm 10.7\%$) in soil from a cement plant area (Schoer & Nagel, 1980). In a similar study with soil from a cement plant and with stream sediments from a mining district (Wiesloch, Germany), rape plants took up about 20% of soil Tl from the cement plant sample but only 1.4 to 5.1% from the stream sediments, although the latter contained 2- to 3-fold higher Tl concentrations; 8- to 80-fold higher concentrations of plant-available Tl were calculated for the soil from the cement plant (Scholl & Metzger, 1982). Com-

paring the uptake of Tl by rape seedlings from soil contaminated by emissions from a cement plant (mainly with Tl(I) chloride or iodide) with that from uncontaminated soil (traces of Tl(I) sulfide), a 7.5-fold higher uptake from the contaminated soil was found (Lehn & Bopp, 1987).

At lower Tl concentrations, some plant species took up a higher percentage of the available Tl than at higher concentrations, perhaps in part because of the stronger toxic effects at higher concentrations. However, the total amount of Tl found in the plants and the Tl content of the artificial soil solutions were correlated, reaching up to 1000 mg/kg dry weight in green kale following one week's exposure to a concentration of 10 mg/litre (Schweiger & Hoffmann, 1983).

The transfer from soil to plant also depends on a number of factors relating to the plant, e.g., root system, kinetics of membrane transport, metabolism of Tl (Cataldo & Wildung, 1978), so that the total amount of Tl taken up is species-specific. This is shown by the bioconcentration factor (concentration of Tl in the plant (fresh or dry weight) in relation to its concentration in dry soil) found for different plants grown in soil contaminated by mining waste materials or collected from sites with naturally high concentrations (Table 10) (Schoer & Nagel, 1980; Lehn & Bopp, 1987). Calculations based on the concentrations in plant ash and dry soil show that the concentration factor is usually less than 20 (Smith & Carson, 1977). The concentrations of Tl in vegetables reported by these authors are one to two orders of magnitude higher than those found by Geilmann *et al.* (1960) in vegetation grown on uncontaminated soil (Schoer & Nagel, 1980). Trees can be a long-term reservoir of Tl. As a result of emission by cement plants, the bark and lichens of several trees contained 2-23.8 mg Tl/kg dry weight.

The use of ground-up bark from these trees for mulching can lead to considerable uptake of Tl by other plants (Arndt *et al.*, 1987).

Table 10. Concentration of thallium in fresh or dry weight of the plant in relation to its concentration in dry soil (bioconcentration factor) for plants grown on contaminated soils. From: ¹Lehn & Bopp, 1987; ²Maier *et al.*, 1987; ³Schoer & Nagel, 1980.

Plant	Bioconcentration factor ^{a)}	
	Fresh weight	Dry weight
Barley (<i>Hordeum vulgare</i>)		0.14 ¹⁾
Green kale	< 0.1 ²⁾	
Brussels sprouts	< 0.1 ²⁾	
Celeriac (<i>Apium graveolens</i>)	< 0.1 ²⁾	
Cress (<i>Lepidium sativum</i>)	0.45-0.59 ²⁾	33 ¹⁾
Horse-radish (<i>Armoracia</i>)	0.33 ²⁾	
Maize (<i>Zea mays</i>)		0.05 ¹⁾
Mushrooms	2.9 ²⁾	
Mustard (<i>Sinapis alba</i>)		1.07 ¹⁾
Parsley (<i>Petroselinum crispum lapathifolia</i>)	0.15-0.21 ²⁾	
Rape (<i>Brassica napus</i>)	0.26-0.29 ²⁾	66 ¹⁾
Spinach		594 ²⁾
Wheat (<i>Triticum aestivum</i>)		0.05 ¹⁾

6.3 Absorption by plants

Uptake of Tl(I) ions occurs via all parts of the plant, presumably by using the uptake mechanisms for K. However, uptake of fly-dust by the leaves of sunflowers is minimal (Schweiger & Hoffmann, 1983). Although the majority of the Tl-containing particles have a diameter less than 2 μm , they cannot be absorbed by transpiration through the stomata (Pallaghy, 1972; LIS, 1980). In numerous laboratory studies using nutrient solutions, a positive correlation between plant uptake and Tl concentration in the solution has been demonstrated (*e.g.*, Al-Attar *et al.*, 1988).

Comparable results have been obtained from the cultivation of mycelium of higher fungi in Tl-enriched agar medium (Seeger & Gross, 1981).

According to Cataldo & Wildung (1978), absorption of Tl by plants seems to be under metabolic regulation, and K is a non-competitive inhibitor. Sunflowers with a deficiency of K and supplied with 1 or 10 mg Tl nitrate/litre possessed a 2 to 3 times higher concentration of Tl per gram dry weight than those supplied with K (Schweiger & Hoffmann, 1983). Metabolically controlled uptake seemed to occur only with Tl(I), supplied as the acetate, while Tl(III), supplied as the chloride, was presumably taken up by passive processes such as cation exchange (Logan *et al.*, 1983, 1984). Since increasing concentration of K decreases the uptake of Tl(I), this uptake was postulated to be mediated by the (Na^+/K^+) ATPase system. During a 3-h exposure to a solution concentration of 5 mg/litre, excised barley seed roots took up about 6009 (± 185) mg Tl(I)/kg dry weight and only 870 (± 44) mg Tl(III)/kg. Thallium(III) ions were easily desorbed, presumably because of a large extracellular component, whereas the Tl(I) ions were unavailable for exchange. The different uptake mechanisms are also reflected in the sensitivity of Tl(I), but not of Tl(III), towards temperature and metabolic inhibitors. Using whole plants (maize), the differences in uptake could not be confirmed, but the authors suggested that, prior to the uptake, Tl(III) may be reduced in the soil to Tl(I) (Logan *et al.*, 1984).

6.4 Distribution in plants

Thallium distribution at the cellular level has been investigated with rape grown both on uncontaminated soil and on soil spiked with non-toxic amounts of Tl (Günther & Umland, 1989). At each test concentration about 70% of the Tl was concentrated in the cytosol (comparable to human data). In the exposed plants nearly all the Tl was in the form of free Tl(I) ions; no Tl(III) ions or dimethylthallium compounds were detected. However, in all the rape grown on uncontaminated soil, the cytosolic Tl was bound, probably to a peptide. This native Tl-complexing agent lacked sulfur-containing amino acids and could not be induced in rape by the application of Tl (Günther & Umland, 1989).

In addition to its varied distribution at the subcellular level, Tl distribution in green plants depends on the developmental stage and the part of the plant. Only in mushrooms was no specific distribution pattern found to exist (Seeger & Gross, 1981). Rape seedlings grown on soil contaminated by a cement plant (1 to 3 mg Tl/kg dry soil) contained 3 to 5 times higher concentrations of Tl than full-grown plants. The concentrations in different parts of full-grown rape (leaf, 47 mg/kg dry weight; shoot, 5.5 mg/kg; seed, 2.1 mg/kg) (Lehn & Bopp, 1987) indicate that Tl concentrations are higher in the chlorophyll-containing regions, a fact also known from plants grown on uncontaminated soils (Weinig & Zink, 1967). In rape grown on artificially contaminated soil (1 mg Tl nitrate/plant), yellowing leaves showed higher concentrations (up to 200 mg/kg dry weight) than green leaves, while the seeds contained only about 1 to 2% of the concentration found in the yellow leaves. However, in rape grown in the field near a cement plant, the leaves contained up to 85 mg Tl/kg dry weight and the seeds about 20 mg/kg (Arndt *et al.*, 1987).

Experimentally, Tl concentrations of 0.0001 to 2.5 mg/litre substrate increased the concentration in the shoots of the grass *Lolium perenne* from < 0.075 mg/kg dry weight to 144.05 mg/kg and in the roots from 0.42 to 576 mg/kg (Al-Attar *et al.*, 1988).

The distribution of Tl also varies in different vegetables. For instance, in gardens around Lengerich, leaves of kohlrabi contained a 350-fold higher concentration than the tubes, while in other vegetables the differences in concentrations between leaves and other parts ranged from 3 to 45 times (Hoffmann *et al.*, 1982). In studies with bush beans and green rape, differences in Tl accumulation in the plants were evident (Makridis & Amberger, 1989): after incubation in a liquid culture medium (1 mg Tl(III) trichloride/litre) for 10 days, roots and shoots of beans contained 742 and 62 mg/kg and those of rape 57 and 244 mg/kg, respectively. At higher concentrations the difference between roots and leaves disappeared in both species, the concentration in the roots of rape increasing more strongly than in the shoots, which, in part, was an effect of reduced growth. Kaplan *et al.* (1990), using Tl(I) sulfate (0.55 and 1 mg/litre), observed at least 4-fold higher concentrations of Tl in the roots of soya beans than in the pods or the lower or higher leaves.

These data indicate that plants which are more resistant to Tl do not have a reduced uptake, but a reduced transport of Tl to the leaves.

7 RELEASES TO THE ENVIRONMENT

7.1 Air

Thallium is released to the atmosphere mainly from coal-burning power plants, cement factories and ferrous and nonferrous smelting operations (EPA 1988; Ewers 1988). Thallium emissions in the United States of America were estimated at 140 tons/year each from coal-burning power plants and from iron and steel production (Ewers 1988). Total air releases reported from industrial sources were about 27 tons in 1987.

Davison *et al.* (1974) reported concentrations of Tl on airborne fly ash emitted from a coal-burning power plant ranging from 29 to 76 µg/g, the Tl concentration increasing with decreasing particle size. The highest concentrations (greater than 60 µg/g) were on particles less than 7.3 µm in diameter. The authors reported that these concentrations were representative of eight other United States power plants burning various types of coal. The highest Tl concentrations were also found on the smaller diameter (0.2 – 0.8 µm) particles of fly dust emitted from a West German cement plant (Ewers 1988).

No quantitative estimates of Tl emissions from other domestic sources were located. However, additional sources of airborne Tl may include manufacturers of alloys, artificial gems, electronic equipments, optical glass, and domestic heating plants (ATSDR, 1999).

Metallic Tl oxidizes slowly in air (Lee 1971), and thallos chloride is photosensitive (Cotton and Wilkinson 1980). However, there are no evidences that Tl is transformed significantly by photochemical reactions in the atmosphere (Schoer, 1984).

7.2 Water

The major sources of Tl releases to water include nonferrous metals, iron and steel manufacturers and various mining, inorganic chemicals, refining, and ore-processing industries (Ewers 1988). Thallium concentrations in raw or treated waste waters from these industries ranged up to 2 g/l (EPA 1983). Thallium has been detected in urban waste waters, apparently from commercial and industrial sources. Thallium has been detected in both surface and groundwater samples

at hazardous waste sites (TRI, 1989). Data from the Contract Laboratory Program Statistical Database (CLPSD, 1989) indicate that Tl occurred in surface water at a mean concentration of 23 ppb in and in groundwater at a mean concentration of 11 ppb.

7.3 Soil

Thallium releases to soil are mainly solid wastes from coal combustion and smelting operations (Ewers 1988). In the United States Tl was detected at a mean concentration of 1.7 ppm in positive soil samples from an unspecified number of hazardous waste sites (CLPSD 1989). Atmospheric Tl pollution contributes to soil contamination in the vicinity of Tl emission sources (Brockhaus *et al.* 1981). It should be noted that land disposal restrictions were implemented by EPA in 1987. Prior to this time disposal of pesticides had been to municipal and industrial landfills. Since Tl is relatively stable in the environment, it is assumed that landfills contain Tl or Tl-containing products.

7.4 Plants

The Tl content in the plants is a function of Tl concentrations in the soils (Weigert, 1991; Kabata-Pendias & Pendias, 2001). Herbage and woody plants apparently contain higher amounts of Tl than do other plant species (Kabata-Pendias & Pendias, 2001). There is an assumption that some plant, especially of the *Cruciferae* and *Gramineae* families, can serve as hyperaccumulators for phytoremediation of contaminated soils. Some species of *Cruciferae* family can accumulate Tl above 2000 mg/Kg from soils with about 40 mg/Kg of this metal. Plants grown around coal power plants and cement factories are most likely to have elevated levels of Tl; for example, *Cruciferae* species accumulated up to approximately 450 mg/kg Tl near a cement plant in Germany (McGrath, 1998).

In fact Tl is not necessarily fixed in the weathered sediments, but may be recycled via biological and chemical agents (Förstner & Salomons, 1991).

Uptake of Tl by vegetation from the rhizosphere is determined by the solubility of the compound, and it increases with increasing soil acidity.

Thallium may be bioconcentrated by organisms from water. A bioconcentration factor (BCF) relates the concentration of a chemical in the tissues of aquatic animals or plants to the concentration of the chemical in the water in which they live. Experimentally-measured BCF values have been reported: 18.2 for clams and 11.7 for mussels (Zitko & Carson, 1975).

Bioconcentration factors for the muscle tissue of juvenile Atlantic salmon have ranged from 27 to 1,430 (Zitko *et al.*, 1975b). The maximum BCF for bluegill sunfish was 34 in the study of Barrows *et al.* (1978).

8 ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

Because of the limited industrial uses of Tl, emission on a global scale resulting from the production and use of Tl compounds is unlikely. However, Tl is present in relatively large amounts in the raw materials used in various industrial processes (*e.g.*, smelting of sulphide ores, power generation using coal, brick and cement manufacturing, Table 8), that, when released, can significantly increase environmental exposure to Tl on both a local and regional scale.

8.1 Air

Bowen (1979) reported mean values of 0.06 ng particulate Tl/m³ air for Europe and 0.22 ng/m³ for North America, and Arnold (1986) a range of 0.1 to 30 ng/m³. The air of six large American cities contained < 0.04 to 0.1 ng Tl/m³ (Ohnesorge, 1985). In a detailed study at Chadron, Nebraska, USA, Struempfer (1975) found yearly mean values for Tl of 0.22 ± 0.08 (range 0.07 to 0.48 ng/m³) and of 0.15 ± 0.04 ng/m³ during the summers of 1973 and 1974, respectively.

In industrial and urban areas of Genoa, Italy, the geometric mean concentrations of Tl have been found to be 15 and 14 ng/m³ air, respectively, with maximal values of 58 ng/m³, but often values were below 1 ng/m³ (Valerio *et al.*, 1988, 1989). In London, levels of 0.07 to 6 mg Tl/kg dust were measured (Bowen, 1979).

Air emission of Tl is mainly caused by mineral smelters, power-generating plants and cement plants (ATSDR, 1992). Thallium compounds are volatile at high temperatures and are not efficiently retained by most emission control facilities. In consequence, large amounts of Tl are released into the atmosphere if the raw material (coal or ores) is not selected for a low Tl content.

8.2 Water

In the majority of reports, the authors did not specify whether they determined dissolved and/or particulate Tl in samples of water. This information was included if possible, according to the methodology used in the study.

8.2.1 Areas not contaminated by thallium

Seawater contains < 0.01 to 0.02 µg/litre, and river water < 0.01 to 1 µg/litre (Mason, 1966; Smith & Carson, 1977; Bowen, 1979; Kemper & Bertram, 1984; Wachs, 1988).

In volcanic springs, low concentrations have been found (0.25 µg/l, Arnold, 1986) and in three samples of hydrothermal water it was below the detection limit of 0.6 µg/l (Korkisch & Steffan, 1979). Although, in these and the wastewater investigation, dissolved and particulate Tl were not determined separately, Henshaw *et al.* (1989) found concentrations of up to 0.41 µg Tl/l in filtered water from freshwater lakes. In three wastewater treatment facilities in Massachusetts, USA, that had no major industrial waste inputs, the Tl concentration in the influent was below the detection limit of 5 µg/l (Aulenbach *et al.*, 1987).

However, wastewater from oilfields (oil-well brines) in the USA contained 12.9 to 672 µg Tl/l, 5 out of 13 samples containing > 400 µg Tl/l (Korkisch & Steffan, 1979).

8.2.2 Areas contaminated by thallium from industrial sources

Data on Tl emission in water are available for areas with oilfields, mineral industry and cement plants (Table 11). Increased concentrations of Tl in well water and in water from an irrigation canal in China resulted from old waste materials from the mining of mercury and coal (Zhou & Liu, 1985). Effluents from tailing ponds of base-metal mining operations in New Brunswick, Canada contained 27 and 1620 µg dissolved Tl/l and up to 88 µg/l was found in connecting rivers (Zitko *et al.*, 1975b; Zitko, 1975).

Raw wastewater from a pyrite ore mine at Lennestadt, Germany (which was the source of the pyrite roasting residues used by the cement plant in Lengerich, Germany) showed a Tl concentration of 160 µg/litre (LIS, 1980). Treatment in sedimentation ponds and with lime and chlorine, reduced the concentration to 2-35 µg/litre. In a stream, used as main drainage channel, the Tl

concentration rose from $< 1 \mu\text{g/litre}$ (detection limit) to $1 \mu\text{g/litre}$ after the inlet. This level is similar to that found in the River Rhine, Germany (0.5 and $2.5 \mu\text{g/litre}$, LIS, 1980).

Groundwater directly below a deposit for pyrite roasting residues in Duisburg, Germany contained $17 \mu\text{g Tl/l}$, and, at a distance of some 100 m , up to $6 \mu\text{g/litre}$ (LIS, 1980).

In the vicinity of the cement plant in Lengerich, Germany Tl levels were monitored in wells, rivers and wastewater (LIS, 1980). In rivers, levels of $7.3 \mu\text{g/litre}$ 1 km from the plant decreased to $1.8 \mu\text{g/litre}$ at a distance of 5 km and to $1.0 \mu\text{g/l}$ at a distance of 10 km (Mathys, 1981). In all private wells and water works, Tl concentrations were below the detection limit of $1 \mu\text{g/l}$. Around other cement plants, Tl concentrations in private wells, water works and surface water were below the detection limit (< 5 and $< 50 \mu\text{g/l}$). Pond water from the vicinity contained $130 \mu\text{g/l}$. In drip-water from the storage of flue dust, a concentration of $800 \mu\text{g/l}$ was determined (LIS, 1980).

The elimination of Tl from wastewater varies. Only 28% of the Tl could be removed by conventional wastewater treatment (liming) (Zitko *et al.*, 1975a) whereas 80 to 98% was removed in Lennestadt (LIS, 1980).

Table 11. Concentrations of thallium in water from contaminated areas ^{a)}. ^{a)} Further literature summarized by Schoer (1984). From: ¹⁾ BGA (1979), ²⁾ EPA (1980), ³⁾ Korkisch & Steffan (1979), ⁴⁾ LIS (1980), ⁵⁾ Mathys (1981), ⁶⁾ MISA (1989), ⁷⁾ MISA (1991a), ⁸⁾ MISA (1991b), ⁹⁾ Smith & Carson (1977), ¹⁰⁾ Zhou & Liu (1985), ¹¹⁾ Zitko *et al.* (1975).

Locality	Source	Thallium concentration ($\mu\text{g/litre}$)
Underground water, Düsseldorf, Germany	zinc smelter	$13\text{-}820$ ¹⁾
Wastewater, different locations, USA	smelters	$< 0.1\text{-}2400$ ⁹⁾
Tailing ponds, New Brunswick, Canada	mining	$27; 1620$ ¹¹⁾
Rivers, different locations, USA	mining	$21\text{-}30$ ²⁾
Rivers, New Brunswick, Canada	mining	$1\text{-}88$ ¹¹⁾
River, Lennestadt, Germany	mining	$< 1\text{-}1$ ⁴⁾
Wastewater, Lennestadt, Germany	mining	$2\text{-}160$ ⁴⁾
Well, China	mining	$17\text{-}40$ ¹⁰⁾
Irrigation canal, China	mining	$6\text{-}96$ ¹⁰⁾
Wells, Lengerich Germany	cement plant	< 1 ⁴⁾
Surface water, Lengerich, Germany	cement plant	$< 1\text{-}1$ ⁴⁾
Water, Lengerich, Germany	cement plant (distance 1 km)	7.3 ⁵⁾
Wastewater, Lengerich, Germany	cement plant	$< 1\text{-}37$ ⁴⁾
Wells, Erwitte etc., Germany	cement plant	$< 5\text{-}50$ ⁴⁾
Surface water, Erwitte etc., Germany	cement plant	$< 50\text{-}130$ ⁴⁾
Wastewater, Erwitte etc., Germany	cement plant (flue dust)	800 ⁴⁾
Wastewater, USA	oil drilling (natural brines)	$12.9\text{-}672$ ³⁾
Wastewater, Canada	iron and steel plants	mean = 60 ⁷⁾
	pulp and paper mills	$230;$ mean = 52 ⁸⁾
	petroleum refineries	$310;$ mean = 19 ⁶⁾

8.3 Rocks, soil and sediment

8.3.1 Areas not contaminated by thallium

Thallium concentration in rocks, soils and sediments has already been discussed, and tables 2, 3, 4, 5, 6 and 9 show Tl natural contents in the different environmental media. Other data are given in Table 12.

8.3.2 Areas contaminated by thallium from industrial sources

Cases of contamination of sediment and soil by Tl are mainly caused by mineral mining and smelters and by dust fall-out from emissions of power-generating plants, brickworks and cement plants (ATSDR, 1992, Table 13).

Emissions from the cement plant in Lengerich, Germany caused a remarkable increase in Tl concentrations in sediments of rivers and brooks (Mathys, 1981). Sediment levels of 18 mg Tl/kg dry weight found in a brook 1 km from the plant decreased to 8.7 mg/kg within 4 km and then to 7.5 mg/kg in the River Glane into which the brook flowed. Sediments of the following River Ems contained 5.0, 2.7 and 0.8 mg/kg at distances of 30, 70 and 100 km, respectively. In comparison, river sediments from industrialized areas contained 0.05 to 1.8 mg/kg dry weight. Very high Tl levels were detected in sediments from areas with zinc mining or iron ore industry, *e.g.*, 40.0 mg/kg in the River Lenne. After transport to the River Ruhr, sediment Tl levels were 3 mg/kg dry weight (Mathys, 1981).

Large amounts of contaminated waste materials from the mining of mercuric ore and coal containing 25 to 106 mg Tl per kg resulted in chronic Tl poisoning in China. As a result of dispersal of the waste materials, the garden soil of poisoned owners showed levels from 28 to 61 mg/kg (mean: 43 mg/kg), whereas the soil levels in gardens of unaffected families contained 6 to 11 mg/kg (mean, 8 mg/kg); this was still much higher than in other villages (mean 0.011 mg/kg). In the affected village, the concentration of soluble Tl salts decreased with increasing pH, with 8.0, 2.0 and < 0.15 mg/kg at soil pH values of 1-2, 3-4 and 6-7, respectively.

The lower soil pH in the dry season (3.5-4.5 compared to pH 6-7 in the rainy season) correlated with an increase in the number of intoxications during these months, presumably due to an increase in the Tl concentration in cabbage. After the experimental addition of lime to contaminated soil, the Tl concentration in cabbage was reduced (Zhou & Liu, 1985).

Sabbioni *et al.* (1984b) calculated the emissions from a hypothetical coal-fired power-generating plant for a period of 40 years. They deduced an air-borne deposition of Tl around the power-generating plants of 0.005 mg/kg, and the factor of increase over the background level was estimated to be 0.001.

Around four small brickworks, samples of soil were digested by strong acids and analysed for total concentration of Tl (Brumsack, 1977). Compared to a soil background level of 0.2 mg/kg, the contaminated samples of soil showed a maximum accumulation factor of 3, while for samples taken directly around the factory the factor was about 5.

Clear effects were found when the weather side of a hill was just opposite the smoke stack. Interestingly, shale from uncontaminated areas showed a similarly high content (0.99 mg/kg).

Thallium emission by the cement plant in Lengerich, Germany caused an increase of Tl concentrations in the soil over an area of 1 to 2 km radius from the plant, with a maximal level of 6.9

mg/kg dry soil (LIS, 1980). Up to 4 mg/kg soil was determined in agricultural soil and up to 6 mg/kg in the soil of house gardens (Crössmann, 1984). Samples of soil taken at different depths always showed highest Tl contaminations in the upper layers, decreasing with increasing depth (LIS, 1980). The soil around the two plants that had produced the residues from pyrite roasting was also highly contaminated, with maximal levels of up to 10.5 and 2.3 mg/kg, respectively (LIS, 1980).

Soil from the vicinity of two other cement plants in Germany contained only slightly elevated concentrations of Tl, up to 0.5 mg/kg soil, in the upper layers (Table 13) (Arndt *et al.*, 1987).

Table 12. Concentrations of thallium in uncontaminated geological samples. Detailed data summarized in Smith & Carson (1977); Bowen (1966, 1979); Schoer (1984).

Source	Thallium concentration (mg/kg)	
	Mean	Range
Basalt		< 0.2 - 0.7
Basalt	0.08	
Basalt		0.02 - 0.06
Clay	0.3	
Clay		440 - 470
Clay	0.9	
Coal	0.38	< 0.2 - 1.4
Coal	0.2	0.01 - 2
Coal	0.6	0.12 - 1.3
Brown coal (18% ash)	0.027	
Hard coal (8.7% ash)	0.51	
Hard coal (13.9% ash)	0.72	
Dunite	0.0005	
Granite	3.1	0.3 - 6.4
Granite	1.1	
Limestone	1.7	
Limestone	0.14	
Limestone		0.1 - 0.9
Sandstone	0.8	
Sandstone	0.36	
Sandstone		0.05 - 0.4
Shale (low in organic carbon)	0.68	
Shale	1.2	
Shale	3.1	
Black shale (rich in organic carbon)	25	

8.4 Plants

Thallium occurs in low amounts in almost all living organisms, including humans. It seems to be a non-essential cation in animals and plants (Yopp *et al.*, 1974). Some species accumulate this element.

Table 13. Concentrations of thallium in soil from the vicinity of factories in Germany. ^{a)} The investigation was performed 6 years after a ban on the use of iron pyrite residues with high thallium contaminations. Owing to the method used (acid digestion with concentrated nitric acid for 2 h at 90-95°C and addition of 10% sulphuric acid), the concentrations measured correspond to the extractable soluble emitted thallium and not the total thallium in the soil. From: ¹⁾Arndt *et al.*, 1987; ²⁾Brumsak, 1977; ³⁾Hoffmann *et al.*, 1982; ⁴⁾Lis, 1980.

Locality	Source	Distance (m)	Thallium concentration (mg/kg)
Göttingen	lead-zinc smelter ²⁾		1.07
Duisburg	copper smelter ⁴⁾	500-1400	< 0.2-2.1
Leimen, Wiesloch	mining and cement plant ³⁾		5.5-21
Lengerich	cement plant ⁴⁾	500-5000	< 0.1-6.9
Erwitte	cement plant ⁴⁾	350-1800	0.1-10.5
Schelklingen ^{a)}	cement plant ¹⁾	< 3200	0.1-0.5
Mergelstetten ^{a)}	cement plant ¹⁾	< 800	0.1-0.5
Duisburg	sulfuric acid plant ⁴⁾	0-1000	< 0.2-10.5
Duisburg	sulfuric acid plant ⁴⁾	350-1100	< 0.2-2.3
Göttingen	brickwork ²⁾		0.6

8.4.1 Areas not contaminated by thallium

Usually Tl concentrations in plants are much less than 0.1 mg/kg dry weight (Geilmann *et al.*, 1960) or 1 mg/kg ash (Dvornikov *et al.*, 1973, 1976), and levels exceeding 2 mg/kg ash are unusual (Smith & Carson, 1977, Table 14). However, such high Tl concentrations have been found in plants from areas with a geogenic very high Tl concentration, *e.g.*, the Alsar in Macedonia, Yugoslavia (Zyka, 1972, Table 15).

Wild plants normally contain only traces of Tl, whereas the levels in garden plants can be increased by repeated use of sewage sludge or potash fertilizers, which can contain 100 to 210 µg/kg sludge or 15 to 310 µg/kg fertilizer (Geilmann *et al.*, 1960; Heinrichs, 1982). Also phosphate and copper fertilizers may contain up to 400 µg Tl/kg (Boysen, 1992).

8.4.2 Areas contaminated by thallium from industrial sources

Soils contaminated through mineral smelters, power-generating plants, brickworks or cement plants can greatly increase the concentrations of Tl found in food of plant origin (Tables 16 and 17), which are the major route of entry of Tl into the food chain. Data on bioconcentration factors are listed in Table 10. In the contaminated area of Lengerich, Germany, consumption of home-grown food was correlated with high levels of Tl in urine and hair, and possibly with Tl-

related health disorders among local people (Brockhaus *et al.*, 1981b; Dolgner *et al.*, 1983). The importance of these findings is underlined by the similarly elevated levels of Tl found in the urine of family members consuming the home-grown vegetables (Ewers, 1988).

Table 14. Concentrations of thallium in plants from uncontaminated areas (L = leaves, needles; S = stems). From: ¹⁾Bowen, 1979; ²⁾Dvornikov *et al.*, 1973; ³⁾Dvornikov *et al.*, 1976; ⁴⁾Geilmann *et al.*, 1960; ⁵⁾Seeger & Gross, 1981; ⁶⁾Shacklette *et al.*, 1978; ⁷⁾Weinigin & Zink, 1967.

Plant	Concentration of thallium	
	($\mu\text{g}/\text{kg}$ dry weight)	(mg/kg ash)
<i>Achillea millefolium</i>		0.01-0.04 ²⁾
<i>Achillea setacea</i>		0.04-0.9 ³⁾
Alpine fir		2-100 (L); 2-70 (S) ⁶⁾
<i>Anthemis tinctoria</i>		< 0.1-0.5 ³⁾
<i>Artemisia absinthum</i>		0.02-0.6 ³⁾
<i>Artemisia campestris</i>		0.057 ³⁾
<i>Asperula humifusa</i>		0.1-1.0 ³⁾
Clover	8-10 ⁴⁾	
<i>Echium vulgare</i>		0.1-0.3 ³⁾
Endive	80 ⁴⁾	
Engelmann's spruce		2-10 (L); 15 (S) ⁶⁾
<i>Euphorbia virgata</i>		0.03-0.3 ³⁾
<i>Festuca sulcata</i>		0.2-0.6 ³⁾
Green cabbage	125 ⁴⁾	
Hay	20-25 ⁴⁾	
Head-lettuce	21 ⁴⁾	
Herbaceous vegetables	30-300 ¹⁾	
Kale	150 ¹⁾	
Leek	75 ⁴⁾	
Limber pine		2-5 (L); 3-5 (S) ⁶⁾
Lodgepole pine		2-5 (L); 3-7 (S) ⁶⁾
Mushrooms	< 0.25-5.5n ⁵⁾	
Myrtle blueberry		2-7 (L, S) ⁶⁾
Ponderosa pine		15 (S) ⁶⁾
Potato	25-30 (L, S) ⁴⁾	
Rape	25-30 (L) ⁴⁾	
Red cabbage	40 ⁴⁾	
<i>Salvia nemorosa</i>		0.04-0.8 ³⁾
Stinging nettle	28.8 (L) ⁷⁾	
<i>Tanacetum vulgare</i>		0.06-0.2 ³⁾
Tobacco	24-100 (L) ⁴⁾	
<i>Verbascum ovalifolium</i>		0.01-0.7 ³⁾
Woody gymnosperms	50 ¹⁾	

Table 15. Concentrations of thallium in plants from the Alsar region in Yugoslavia possessing a high natural concentration of thallium in the soil (F = flowers; L = leaves, needles; P = pods and seeds; S = stems). According to Zyka (1972).

Plant	Concentration of thallium (mg/kg ash weight)
<i>Campanula sp. (L, S, F)</i>	5990
<i>Centaurea sp. (P)</i>	75
<i>Centaurea sp. (L, S)</i>	105
<i>Dianthus sp. (F)</i>	5200
<i>Echinops sp. (L)</i>	15
<i>Eryngium sp. (L)</i>	3
<i>Eryngium sp. (F)</i>	10
<i>Galium sp. (F)</i>	17 000
<i>Lavatera sp. (L, S)</i>	125
<i>Lavatera sp. (F)</i>	45
<i>Linaria triphylla</i>	3000
<i>Linaria triphylla</i>	3800

Table 16. Concentrations in plants from thallium-contaminated areas; all the localities are in Germany, except for New Brunswick (Canada). From: ¹⁾ Arndt *et al.* (1987), ²⁾ Kemper & Bertram (1984), ³⁾ LIS (1980), ⁴⁾ Mathys (1981), ⁵⁾ Zitko *et al.* (1975).

Organism	Source of emission	Locality	Concentration of thallium (mg/kg)	
			(dry weight)	(fresh weight)
Algae	mining	New Brunswick	9.5 - 43.4 ⁵⁾	
Algae	cement plant	Lengerich		0.665 ³⁾
<i>Betula</i>	cement plant	Lengerich	100.3 ⁴⁾	0.585; 0.654 ³⁾
<i>Caltha</i>	cement plant	Lengerich	187.3 ⁴⁾	
<i>Elodea</i>	cement plant	Lengerich	87.4 ⁴⁾	0.29; 6.5 ³⁾
Grass	sulphuric acid plant	Duisburg	52.0 ³⁾	
Moss	mining	New Brunswick	125; 162 ⁵⁾	
Rape	cement plant	Lengerich	1095 ³⁾	29.2 ³⁾ ; 23.7 ²⁾
Rape	cement plant	Mergelstetten	679.6 ¹⁾	
Rape	cement plant	Schelklingen	19.1 ¹⁾	
<i>Sparganium</i>	cement plant	Lengerich		0.265 ³⁾

Waste materials from the mining of mercuric ore and coal in China increased the concentration of Tl in cabbage and grain. Cabbage from gardens of affected families contained 42 mg/kg fresh weight (range 39 to 49), whereas cabbage eaten by healthy families contained 5.6 mg/kg (range 3 to 11). Other vegetables from the gardens of affected families usually contained less than 10 mg/kg (Zhou & Liu, 1985).

An accumulation in vegetables of the genus *Brassica* was also observed in Lengerich. In the area with the highest contamination, the majority of plants and fruits contained <0.1 to 0.4 mg/kg fresh weight. Higher Tl levels were sometimes found in strawberries, potatoes, beans, tomatoes, carrots and leeks, while in parsley, celery, red currants, and all *Brassicaceae* high levels were

Table 17. Concentrations in vegetables and fruits from thallium-contaminated areas; individual values (^a) mean values). From: ¹) Hoffmann *et al.* (1982), ²) Kemper & Bertram (1984), ³) LIS (1980), ⁴) Scholl & Metzger (1982).

Plant	Part	Source emission	Thallium concentration (mg/kg)	
			(dry weight)	(fresh weight)
Apple	fruit	cement plant		0.2 ³⁾
Bean	fruit	cement plant		0.7 ³⁾
Blackberry	fruit	cement plant		0.5 ³⁾
Black-currant	fruit	cement plant		0.527 ²⁾
Brussels sprout	leaf	cement plant		0.5 ³⁾
Carrot	root	cement plant		1.0 ³⁾
Carrot	leaf root	mining and cement plant	0.30 ¹⁾ 0.10 ¹⁾	
Celeriac	stem	cement plant		0.8 ³⁾
Cucumber	leaf fruit	mining and cement plant	0.70 ¹⁾ 0.10 ¹⁾	
Green cabbage	leaf	cement plant		14.9 ²⁾ ; 45.2 ³⁾
Green cabbage ^{a)}	leaf	cement plant		22.6 ⁴⁾
Kohlrabi	leaf stem	mining and cement plant	35.00 ¹⁾ 0.10 ¹⁾	
Kohlrabi ^{a)}	stem	cement plant		3.1 ⁴⁾
Kohlrabi	stem	cement plant		4.9 ³⁾
Onion	stalk bulb	mining a nd cement plant	0.10 ¹⁾ 0.01 ¹⁾	
Onion	stalk	cement plant		0.4 ³⁾
Parsley	leaf	cement plant		1.2 ³⁾
Pear	fruit	cement plant		0.5 ³⁾
Potato	tuber	cement plant		0.8 ³⁾
Radish	leaf root	mining and cement plant	5.90 ¹⁾ 0.40 ¹⁾	
Red beet	leaf root	mining and cement plant	2.40 ¹⁾ 0.60 ¹⁾	
Red beet	root	cement plant		0.7 ³⁾
Red-currant	fruit	cement plant		1.1 ³⁾
Savoy cabbage ^{a)}	leaf	cement plant		8.5 ⁴⁾
Strawberry	fruit	cement plant		0.9 ³⁾
Tomato	fruit	cement plant		0.6 ³⁾
White cabbage ^{a)}	leaf	cement plant		3.1 ⁴⁾
Zucchini	leaf stem	mining and cement plant	0.90 ¹⁾ 0.02 ¹⁾	

usual (LIS, 1980). Within this genus uptake of Tl varied: the bioconcentration factor of white and red cabbage was relatively low; it was 5 to 10-fold higher in the stems of kohlrabi. Savoy cabbage and green kale were found to contain the highest Tl concentrations, exceeding those of the soil (Crössmann, 1984). The maximal value of 45.2 mg/kg fresh weight was found in green kale (LIS, 1980). Most forage plants, *e.g.*, turnips, hay, grass and fodder corn,

contained <5 mg/kg dry weight, but 46% of rape plants contained >100 mg/kg (up to 1095 mg/kg dry weight) and 22% of the maize 10 to 50 mg/kg (LIS, 1980).

The accumulating capacity of rape also became evident in an investigation at cement factories in Schelklingen and Mergelstetten, Germany, 6 years after the use of the same pyrite residues that had been used in Lengerich was banned. The soil contained only slightly elevated concentrations of Tl, and in the majority of the plants, four of them Brassicaceae, no Tl was detectable (Arndt *et al.*, 1987). However, rape contained increased levels of 2.4 to 679.6 mg Tl/kg dry weight at Mergelstetten and 1.8 to 19.1 mg/kg dry weight at Schelklingen (Table 16). The highest levels detected in single rape plants were found within an area extending 150-400 m downwind from the cement plant. The majority of the rape grown in that area contained more than 5 mg Tl/kg dry weight and could not be used as animal feed.

8.5 Animals

8.5.1 Areas not contaminated by thallium

Investigations of three species of freshwater fish, the omnivorous white sucker (*Catostomus commersoni*) and the more carnivorous yellow perch (*Perca flavescens*) and brook trout (*Salvelinus fontinalis*), show them to have similar average concentrations of Tl in their axial muscle (< 0.07 to 3.0 mg/kg dry weight), which were independent of water pH (Heit, 1985, Table 18). Extensive studies of different marine shellfish and fish revealed average concentrations of 0.14 mg/kg; only in three species (occasionally *Clupanodon punctatus* and *Trachurus japonicus* and often *Penaeus japonicus*) were concentrations above 1 mg/kg found (Hamaguchi, 1960). In marine invertebrates concentrations were even lower.

Thallium concentrations in marine mammals have rarely been investigated. In the blubber, liver, kidney, spleen and muscle of bowhead whales, concentrations are nearly always below 0.01 mg/kg fresh weight (Byrne *et al.*, 1985).

Meat from farm animals contains very low levels of Tl (Table 18).

8.5.2 Areas contaminated by thallium from industrial sources

Different animals as well as different organs vary with respect to their accumulation capacity for Tl. Data of Tl concentration in fishes, birds and mammals are summarized in Table 19.

In a case of fish poisoning, three species were found to contain 77 to 96 mg/kg muscle (Palermo *et al.*, 1983). The liver and kidneys of fish from a pond contaminated by a cement plant contained 1.6 and 1.3 mg/kg fresh weight, respectively (LIS, 1980). In the same area, fish from other ponds and waters usually contained < 0.1 mg/kg muscle.

In farm animals intake of Tl mainly occurs through contaminated feed. Thallium poisoning in cattle was caused by silage (41 mg Tl/kg fresh weight) bought from a farm in a contaminated

Table 18. Concentrations of thallium in animals from uncontaminated areas. In parenthesis the number of measurements. From: ¹⁾Bowen, 1979; ²⁾Clausen & Carlog, 1984; ³⁾Geilmann *et al.*, 1960; ⁴⁾Hamaguchi, 1960; ⁵⁾Hapke *et al.*, 1980; ⁶⁾Heit, 1985; ⁷⁾Holm *et al.*, 1987; ⁸⁾Kemper & Bertram, 1984; ⁹⁾Konermann *et al.*, 1982; ¹⁰⁾Lis, 1980; ¹¹⁾Munch *et al.*, 1974; ¹²⁾Noddack & Noddack, 1939.

Animal	Organ	Thallium concentration	
		µg/kg wet weight	mg/kg dry weight
Invertebrates			
Colorado beetle	whole (1)		18 ³⁾
Different marine invertebrates			0.001-0.03 ¹²⁾
Echinoderms	hard parts	110 ¹⁾	
Molluscs	soft parts	340 ¹⁾	
Shellfish and fish			
Brook trout	muscle (5)		< 3.0 ⁶⁾
White sucker (<i>Catostomus commersoni</i>)	muscle (28)		< 2.0 ⁶⁾
Yellow perch (<i>Perca flavescens</i>)	muscle (27)		< 3.0 ⁶⁾
Birds			
Duck	kidney (10)	0.129 ⁷⁾	
Duck	liver (10)	0.207 ⁷⁾	
Hen	liver (2)	< 50 ¹⁰⁾	
Hen	muscle (2)	< 50 ¹⁰⁾	
Mammals			
Cattle	hair (1)		20 ³⁾
Cattle	hoof (1)		16 ³⁾
Cattle	horn (1)		10 ³⁾
Fox	intestine (25)	< 2.7 ¹¹⁾	
Fox	kidney (27)	0.01-1.5 ¹¹⁾	
Fox	liver (27)	0.01-1.6 ¹¹⁾	
Goat	hair (1)		7 ³⁾
Goat	hoof (1)		9 ³⁾
Hare	hair (1)		17 ³⁾
Horse	hair (1)		7 ³⁾
Horse	hoof (1)		4 ³⁾
Marten	brain (7)	< 0.1-0.7 ²⁾	
Marten	intestine (13)	< 0.01-0.57 ²⁾	
Marten	kidney (17)	< 0.01-3.5 ²⁾	
Marten	liver (36)	< 0.01-1.4 ²⁾	
Pig	hair (1)		9 ³⁾
Pig	hoof (1)		11 ³⁾
Pig	muscle (1)		0.028 ⁸⁾
Pig	muscle (43)	< 70 ⁹⁾	
Pig	kidney (43)	< 70 ⁹⁾	
Pig	kidney (6)	< 50 ¹⁰⁾	
Pig	liver (43)	< 70 ⁹⁾	
Pig	liver (6)	< 50 ¹⁰⁾	
Rabbit	hair (1)		60 ³⁾
Rabbit	hair (1)		< 1.5 ¹⁰⁾
Roe deer	liver (19)	30 ⁷⁾	
Roe deer	kidney (19)	30 ⁷⁾	
Sheep	hair (1)		9 ³⁾
Sheep	hoof (1)		12 ³⁾
Sheep	kidney (3)	50-60 ⁵⁾	
Sheep	liver (3)	< 50 ⁵⁾	
Sheep	muscle (3)	50-60 ⁵⁾	

area (Frerking *et al.*, 1990). Thallium mainly accumulates in the kidneys, liver and bones. Since 0.5 mg/kg fresh weight is the limit set by the federal state of North Rhine-Westphalia for Tl concentrations in human food, a critical level for pigs seems to be a daily intake corresponding to 1.9 mg Tl/kg dry matter of food (Koneremann *et al.*, 1982).

Exposure of farm animals to Tl in the vicinity of the cement plant in Lengerich, Germany, resulted increased Tl levels in the liver and kidneys of various animals (LIS, 1980): 0.8% of the samples of internal organs contained > 10 mg/kg fresh weight, 1.3% contained 5 to 10 mg/kg, 12.6% contained 1 to 5 mg/kg and 14.5% contained 0.5 to 1 mg/kg. In 0.2%, 3% and 4.4% of meat from various farm animals, 5-10, 1-5 and 0.5-1 mg/kg were found, respectively.

Concentrations above 0.5 mg/kg fresh weight were sometimes also found in eggs and chicken meat (up to 0.8 mg/kg), rabbit meat (up to 5.8 mg/kg) and roe deer (1.6 mg/kg) (Table 19) (LIS, 1980). In whole eggs with a concentration of 1.26 mg/kg fresh weight, the concentration in albumin and yolk was 0.394 mg/kg, while in the shell it was 4.94 mg/kg (Kemper & Bertram, 1984).

9 DISTRIBUTION IN HUMANS

Background Tl concentrations found in human body fluids and tissues are given in Table 20. After poisoning, Tl concentrations ranging up to nearly 36 mg/litre in blood, 25 mg/litre in urine and 8 mg/kg in hair have been found (Table 21).

9.1 Increased concentrations after lethal poisoning

In reports of postmortem examinations after suicide or homicide, data on the distribution of Tl in different organs are rarely included with data on dose and application routes (Table 21). The distribution pattern shows no consistent trend. In a single individual, concentrations in bones, fat and muscles from different parts of the body may vary, *e.g.*, in vertebrae (12.7 mg/kg), *sternum* (7.0 mg/kg), *femur* (16.4 mg/kg) and *tibia* (9.0 mg/kg) (Arnold, 1986). With respect to the total amount per organ, liver or lung were found to contain 2 to 6 times and the brain about 1.5 to 2 times more Tl than the kidneys (Curry *et al.*, 1969; Arnold, 1986).

A comparison between the white and grey matter of the brain revealed that in the latter the concentration was three times higher (Cavanagh *et al.*, 1974). Detailed data of Tl concentrations in different regions of the nervous system were given by Davis *et al.* (1981).

9.2 Increased concentrations after long-term sublethal poisoning

Thallium levels in urine (Table 22), blood or saliva of chronically exposed people offer better indications of the actual burden than those derived from hair samples, since elevated levels in hair can be caused by exogenous dust (Bertram *et al.*, 1985).

People consuming food grown in private gardens and living at a distance of more than 3 km from the cement plant at Lengerich, Germany showed significantly higher concentrations of Tl in their urine, decreasing with increasing distance from the plant, than people who did not consume food from their gardens. Peak values were 76.5 µg/litre in urine and 565 µg/kg in hair (Ewers & Brockhaus, 1982). In this area, a medical survey was carried out immediately after the occurrence of Tl emissions had been recognized; urine Tl levels in about 80% of the population were found to exceed the upper normal limit of 1 µg/litre (Brockhaus *et al.*, 1980; Dolgner *et al.*, 1983). Only a few cases resulting from industrial exposure have been reported and seem to be mainly a result of skin contact or inhalation (Kazantzis, 1986; Ewers, 1988).

Table 20. Background concentrations of thallium in humans. ^{a)} 1.5 months after death; ^{b)} silicosis patient; ^{c)} saw setters suffering pneumoconiosis; ^{d)} welders suffering emphysema; ^{e)} 6 months after death. Data summarized by EHC 182 (1996) from several sources.

Material	Number of measurements	Thallium concentration		Concentration unit
		Mean \pm SD	Range	
Blood, whole	2		0.33 - 0.59	$\mu\text{g/litre}$
	13		< 20	
	320		0.47 - 9	
	418	0.39 \pm 0.05	< 5-80 0.1 - 1.1	
plasma			0.5-2	
	1		< 2.5	
	1		< 2.5	
Bone	2		0.84 - 2.51	$\mu\text{g/kg}$ fresh weight
	1		2	
	5		< 0.1 - 0.1	
Bone ^{a)}	1		0.7; 0.9	
Brain			< 0.5	mg/kg dry weight
Bronchoalveolar lavage fluids	1 ^{b)}		0.258	ng/1000 cells
	1 ^{c)}		0.011	
	1 ^{d)}		0.016	
	1 ^{d)}		0.050	
Faeces	5		< 0.02 - 3.0	$\mu\text{g/kg}$ fresh weight
Hair	7	18.6 \pm 14.9	7 - 51	$\mu\text{g/kg}$ fresh weight
	6	10.4 \pm 4.3	4.8 - 15.8	
	1		< 20	
Heart			< 0.4	mg/kg dry weight
Kidney			< 0.4	mg/kg dry weight
Kidney	6	2.7 \pm 1.1	1.44 - 4.1	$\mu\text{g/kg}$ fresh weight
	259		0.03 - 8.6	
Liver	11	0.47 \pm 0.13	< 0.4 - 0.9	mg/kg dry weight
Liver	6	1.1 \pm 0.9	0.55 - 2.85	$\mu\text{g/kg}$ fresh weight
	6		1-9	
Lung	4	1.1 \pm 0.7	0.36 - 1.8	$\mu\text{g/kg}$ fresh weight
Muscle			< 0.4	mg/kg dry weight
Muscle	6	2.1 \pm 2.1	0.52 - 7.05	$\mu\text{g/kg}$ fresh weight
	3		15 - 100	
Muscle ^{e)}	1		0.4	$\mu\text{g/kg}$ fresh weight
Nail	6	51.2 \pm 12.1	40 - 74	$\mu\text{g/kg}$ fresh weight
	6	2.6 \pm 1.4	0.72 - 4.93	
Skin			< 0.2	mg/kg dry weight
Urine	10		< 0.02 - 1.0	$\mu\text{g/kg}$ fresh weight
			0.05 - 0.1	$\mu\text{g/litre}$
Urine	14	0.7 \pm 0.5	0.07 - 1.69	
			0.05 - 20	
	31	0.4 \pm 0.2	< 0.1- 1.2	
	10	0.3 \pm 0.2	< 0.1- 0.9	
	149	0.3 \pm 0.14	0.02 - 0.7	
	72	0.22 \pm 0.14	0.06 - 0.61	
	496	0.42 \pm 0.09	0.06 - 0.82	
			0.05 - 1.5	
			< 0.3 - 1.1	mg/kg creatinine
		10	2.2 \pm 1.6	

Table 21. Concentrations of thallium in cases of poisoning. ^{a)} Concentrations indicative for poisoning; ^{b)} three years after death. Data summarized by EHC 182 (1996) from several sources.

Material	Number of cases	Range of thallium concentration	Concentration unit
Blood, whole		50-6000 ^{a)}	µg/litre
Blood	2	29; 7700	
Blood, whole	3	350-36000	
Blood, plasma	2	300; 1500	
Blood, erythrocyte	2	400; 2300	
Bone	1 ^{b)}	0.9-2.1	µg/kg fresh weight
Faeces	1	6500-38400	
Hair	1	650	
Hair	1 ^{b)}	6.8	
Hair	1	420-1800	
Hair	250-8000 ^{a)}		
Heart	1	3600	
Intestine	1	3600	
Intestine	1	0.8; 4.0	
Kidney	5	2700-11600	
Kidney	1	106000	
Liver	1	75 000	
Liver	2	3700; 5500	
Lung	2	3300; 7700	
Muscle	1 ^{b)}	< 0.02; 1.3	
Nails	1	2400	
Spleen	3	2900-6600	
Urine		50-25000 ^{a)}	µg/litre
Urine	15	500-20400	
Urine	1	3100	
Urine	3	10-13800	
Urine	2	2700-30000	µg/litre fresh weight
Urine		0.65	mg/kg creatinine

High concentrations of Tl were found in lung tissue from two coal miners (20.2 and 29.5 µg/kg wet weight). Concentrations in most other tissues were normal (Weinig & Zink, 1967).

In Italy, slight but significant increases in Tl levels were found in the urine of cement workers (0.4 µg/litre) and cast iron workers (0.3 µg/litre), compared with a non-exposed group (0.2 µg/litre). There was no correlation with age or the duration of exposure (Apostoli *et al.*, 1988).

Comparing a total of 128 men, no correlation was found between duration of employment at a cement plant (1 to 42 years) or age (16 to 62 years) and Tl concentrations in the urine (< 0.3 to 6.3 µg Tl/g creatinine) (Schaller *et al.*, 1980).

Therefore, it can be concluded that the uptake of low amounts of Tl does not cause accumulation in the body.

4 10 HAZARD EVALUATION AND LIMITING CONCENTRATIONS

Thallium is a non-essential metal present in low concentrations in human tissues. The minimum lethal dose of soluble Tl salts has been estimated to be 0.7 – 1.1 g or 10-15 mg/kg for a 70 kg adult (Moeschlin, 1980). Studies of Tl exposure to humans in a wide variety of geographic locations have indicated less than 2 µg as the average daily intake of Tl from the environmental sources, especially from vegetables (Kazantkiz, 2000; Sabbioni *et al.*, 1984a). Its similarity in ionic radius with potassium permits it to accumulate in cells at the expense of K. Lipid peroxidation is a marked effect, with an accumulation of lipid peroxides in the brain (Kazantzis, 2000).

Thallium intoxication with hair loss, visual disturbances have been observed. The lethal dose of 6-40 mg/kg body mass is very small, but the cause of death by Tl poisoning is very difficult to prove if there are no hints to suspect it. The most conspicuous feature of Tl poisoning is the loss of hair since all other symptoms such as severe stomach and neuralgiform pains, high blood pressure and *tachycardia* are unspecific and do not seem to be related to it (Sobott, 1992; Kazantzis, 2000). Correlation between Tl-content in the environment and cardiovascular disease also have been demonstrated (Wappelhorst *et al.*, 2000). Chronic Tl poisoning begins with tiredness, fatigue, headache and insomnia, nausea and vomiting, muscle and joint pains, paraesthesia, numbness of fingers and toes followed by motor weakness (Kazantzis, 1986, 2000). Cardiovascular and respiratory system diseases were correlated to Tl-content in mosses (Wappelhorst *et al.*, 2000).

Table 22. Concentrations of thallium following environmental or occupational exposure. In parenthesis median values. ^{a)} Children; ^{b)} data of people with high concentrations of thallium or possibly thallium-related disorders determined in the first survey and about 1 year later in the following line. Data summarized by EHC 182 (1996) from several sources.

Material	Number of people	Source	Thallium concentration		Concentration unit
			Mean ± SD	Range	
Hair	1163	cement plant	20.3 ± 42.7	0.6 - 565	µg/Kg fresh weight
Urine	50	cement plant	(0.6)	< 0.3 - 4.9	mg/kg creatinine
	47	cement plant	(1.65)	0.4 - 6.3	mg/kg creatinine
	21	cement plant	(0.34)	< 0.3 - 2.9	mg/kg creatinine
	10	zinc smelter	7.1 ± 6.0		mg/kg creatinine
	1265	cement plant	5.2 ± 8.3	< 0.1 - 76.5	µg/litre
	82	cement plant	2.4 ± 4.3	< 0.1 - 35.8	µg/litre
	117	cement plant	3.0 ± 5.6	0.2 - 37.7	µg/litre
	34 ^{a)}	cement plant	3.4 ± 3.5	0.4 - 14.8	µg/litre
	30	cement plant	0.38 ± 0.30	0.08 - 1.22	µg/litre
	20	cement plant	0.40 ± 0.34	0.08 - 1.22	µg/litre
	10	cement plant	0.33 ± 0.16	0.09 - 0.60	µg/litre
	9	iron smelter	0.38 ± 0.29	0.10 - 1.04	µg/litre
	74 ^{b)}		16.0 ± 16.9	0.2 - 76.5	µg/litre
	74	cement plant	7.9 ± 8.8	0.2 - 42.6	µg/litre
	21	iron smelter	0.33 ± 0.27	0.06 - 1.04	µg/litre
12	iron smelter	0.29 ± 0.21	0.06 - 0.70	µg/litre	

Men can adsorb it for inhalation of dust or fumes, through the skin and from gastrointestinal way, ingesting contaminated aliments (Fowler, 1982).

Chronic effects have followed population exposure living in the vicinity of coal fired power plants, mineral smelters, brickworks and cement plants.

An epidemiological study was carried out on a sample of 1200 people in the vicinity of a cement plant in Germany and a clear dose-response relationship was found between Tl concentration in urine and the prevalence of the symptoms over elencated (Brockhaus *et al.*, 1981).

Because of its potential to cause adverse health effects in exposed people, a number of legislations and guidelines have been established for Tl by various national and state agencies. Threshold limits are in fact important in the field of occupational medicine and environmental control to prevent health risks. Some of these values are summarized in Table 23.

Table 23. Summary table of statutory limits of Tl element in soil (mg/Kg), its phytotoxic levels and global soil mean value (Demetriades, 1999).

Finland	Italy		US Connecticut	Global soil mean	Phytoxic levels	
	Residential	Industrial	Residential		Min	Max
1	1	10	5.4	0.5	-	1

The admissible concentrations for Tl drinking water content is 0.002 mg/l; for Tl air content is 10 $\mu\text{g}/\text{m}^3$. These values are suggested from several organizations as World Health Organization (WHO), Environmental Protection Agency (EPA), Health European Committee (EC). The cancellation of all pesticide products containing Tl sulphate has been imposed (EPA, 1985).

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