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## **Thallium in soils**

Bakalářská práce

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Podpis

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## **SUMMARY:**

Thallium is a nonessential element, more toxic than mercury, lead, cadmium, zinc or copper. It exists in the two oxidation states  $Tl^+$  and  $Tl^{3+}$ . Thallium is toxic to all organisms in both monovalent and trivalent form. In biological processes it can substitute  $K^+$  due to their similar ionic radii. In the past it was extensively used for medicinal purposes and as a rodenticide. In the present there are over 150 uses and potential applications for thallium and its compounds. Thallium is generally present in very low concentrations (less than  $1 \text{ mg.kg}^{-1}$ ), however, in artificially polluted areas (in the vicinity of power plants, cement factories, smelting works, sulphide ore wastes from mining activity and others) it may exceed much higher levels. The amount of thallium of natural origin strongly depends on the lithology of the parent rock on which soil was derived. Detection of thallium in soils is usually performed by ICP-MS. The total intake of thallium should be less than  $5 \mu\text{g}$  per day, but no recommended maximum values are available in the present time in most countries. Different soil properties can influence the behavior of thallium. Through uptake by plants thallium is entering the food chain. Plant varieties and plant parts differ in the degree of uptake and accumulation of thallium, thus, in Tl-rich areas suitable crops should be planted accordingly.

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## 1. INTRODUCTION

Thallium (Tl) is a rare but widely dispersed element. All forms of Tl are toxic to living organisms. It is more toxic to humans than mercury, cadmium, lead, copper or zinc and has been responsible for many cases of poisoning and even deaths since its discovery in 1861. Mostly monovalent thallium occurs predominantly in soils. It can pose a threat to humans, because through plants uptake it is entering food chain and it can substitute for potassium in biological processes. Tl from both pedogeochemical and anthropogenic origin contributes to concentration of this non-essential metal in soils.

## 2. THALLIUM CHARACTERISTICS

### 2.1 Physical and chemical properties

Thallium was discovered in 1861. The name derived from the green spectral line, which initially identified the element. Pure thallium is soft, malleable, bluish-white metal that is found in trace amounts in the earth's crust. In its pure form, thallium is odourless and tasteless. It can also be found combined with other substances such as bromine, chlorine, fluorine, and iodine. When it combined, it appears colourless to white or yellow. Thallium remains in the environment since it cannot be broken down to simpler substances. Thallium with an atomic number of 81 and a relative atomic mass of 204.37 is a ubiquitous trace element. On account of its density ( $11.83 \text{ g.cm}^{-3}$ ), it is classified as a heavy metal. Some of the physical and chemical properties of thallium are shown in Table 1 (John Peter, Viraraghavan, 2005).

**Table 1.** Physical and chemical properties of thallium (John Peter, Viraraghavan, 2005).

Property	Value
Atomic number	81
Ground state electron configuration	[Xe] $4f^{14}5d^{10}6s^26p^1$
Melting point (K)	577
Boiling point (K)	1746
Density ( $\text{g/cm}^3$ )	11.83
Thermal conductivity at 300 K (W/mK)	46.1
Atomic radius (Å)	1.704

Thallium is a member of group IIIA and is set between Pb and Hg in the periodic table of elements. It shares some properties with its chemical neighbours. First, thallium is a trace element, i.e. its concentration is less than  $100 \text{ mg.kg}^{-1}$  on a dry matter basis (DM) in living organisms and less than  $1000 \text{ mg.kg}^{-1}$  DM in the lithosphere (Tremel et al., 2007).

Thallium exists in two oxidation states,  $\text{Tl}^+$  and  $\text{Tl}^{3+}$ , but  $\text{Tl}^+$  generally forms most stable compounds.  $\text{Tl}^+$  is stable and has properties similar to potassium;  $\text{Tl}^{3+}$  resembles aluminium, has strong oxidation properties and is slowly converted to a monovalent state.  $\text{Tl}^+$  ions are dominant species in most natural

environments in terms of pH and Eh indicating that thallium is theoretically very mobile (John Peter, Viraraghavan, 2005).

Thallium displays chalcogenic behaviour and can be found in some sulphide minerals and in sulphur containing ores (Pavličková et al., 2006a).

While being a highly toxic element, thallium has been studied to a much lesser degree than other toxic elements such as lead, cadmium or mercury. This is mainly because Tl is often undetected by classical analytical methods which tend to have poor sensitivity for Tl than for other elements. Economically, thallium is not as important as other trace metals such as Pb, Hg, Cr, Ni or Zn. It is seldom recovered from metal-based mining, ore processing, or smelting operations and is therefore discarded as part of the tailing into the environment. Ecotoxicological importance of thallium is derived from its high acute toxicity on living organisms, comparable to that of lead and mercury. There is an increasing demand for thallium in the high technology and future technology fields. Since the discovery of high temperature superconduction components in the system (Tl-Ca-Ba-Cu-O), Tl has attracted greater attention as a potential pollution source on a large scale in future. Thallium toxicity may not be of great global importance as of now. Nevertheless, it may be grave enough in certain mining areas and hence it is necessary to minimize the thallium levels in the environment because of its toxicity to the public health (John Peter, Viraraghavan, 2005).

## **2.2 Thallium in the environment**

Thallium (Tl) is a nonessential trace metal. There is relatively little literature available regarding the fate of this potentially hazardous element in terrestrial environments, even though thallium is more toxic to mammals than cadmium, lead, and even mercury. Tl is included in the US EPA list of priority toxic pollutants (Jacobson et al., 2005).

As a natural constituent of earth crust, thallium is present in nearly all environmental media. Thallium is a rare but widely spread element with average concentrations of 0.49 ppm in the continental crust and of 0.013 ppm in the oceanic crust. But this wide distribution does not represent its availability, for the major amount of the metal is found in potash minerals, which have no commercial significance at the present time (John Peter, Viraraghavan, 2005).

Mean concentrations of thallium in the earth's crust are of the order of 0.1-1.7 mg.kg<sup>-1</sup>, mainly present in the sulphide ores of zinc, copper, lead and also in coal. Higher values have been found in granite and shale, with intermediate values for limestone, sandstone and coal. Much higher values have been found in organic rich shales and coals of the Jurassic period with values up to 1000 mg.kg<sup>-1</sup>. Lorandite and crooksite are minerals with thallium levels up to 60%. There are a few areas world-wide which have been identified as having naturally very high thallium concentrations (Kazantzis, 2000).

Although not more than about 15 tons of thallium are produced worldwide annually, it is estimated that 2000-5000 tons per year are mobilized by industrial processes (John Peter, Viraraghavan, 2005).

## **2.3 Uses of thallium**

There are over 150 uses and potential applications for thallium and its compounds.

### **2.3.1 Historical usage**

In the past, thallium was extensively used for medicinal purposes. It was widely used in the treatment of venereal diseases, tuberculosis and malaria. It was used also as a rodenticide against rats and squirrels (Kazantzis, 2000).

Thallium salts have been utilized as a depilatory, being marketed to treat scalp ringworm as they rapidly caused alopecia (baldness) enabling ointments to control the fungal infection to be applied more effectively (John Peter, Viraraghavan, 2005).

Until the early years of the 20th century, thallium salts were used extensively to treat syphilis (since 1883), to reduce night sweats in tuberculosis patients (since 1898). The use of thallium salts as poisons for rodents and later as insecticides began in 1920 and for the next 45 years remained the principal use for this element (John Peter, Viraraghavan, 2005).

Tl rodenticides were first used in Germany from about 1920 and by the late 1920`s,  $TlSO_4$  in sugar syrups was used as insecticide, especially for ants. However, in the 1960s and 1970s Tl-based pesticides were banned in many countries, e.g. in France by 1966 and in 1972 in the USA. The reasons given were dermal absorption, accidental or criminal ingestion, accumulation in the body and persistence in the environment (Tremel et al., 2007).

### 2.3.2 Present usage

Other uses of thallium and its salts are in the manufacture of imitation jewellery, low-temperature thermometers, ceramic semiconductor material, scintillation counters for radioactivity quantitation and in optical lenses to which it confers a high refractive index. Thallium is used for oxidation of hydrocarbons and olefins, for polymerization and for epoxidation. Thallium compounds are used in infrared spectrometers, in crystals, in other optical systems, and for colouring glass. Thallium is mainly used in alloys, electronic devices, and special glass. The greatest use of thallium is in specialized electronic research equipment. Among the growing uses of thallium are in the semiconductor and laser industry, in fiber (optical) glass, in scintillographic imaging, in superconductivity, and as a molecular probe to emulate the biological function of alkali-metal ions. Other uses of thallium compounds include fireworks (thallium nitrate), pigments (thallium chromate) and dyes, impregnation of wood and leather against fungi and bacteria, and in mineralogical separation. Thallium ions show excellent nuclear magnetic resonance properties and have been used as a probe to emulate the biological functions of alkali metal ions, especially  $K^+$  and  $Na^+$  (John Peter, Viraraghavan, 2005).

## 2.4 Thallium toxicity

The acute and chronic toxicity of thallium is similar to the toxicity of cadmium, mercury and lead. Thallium is toxic to all organisms in both monovalent and trivalent form. Human exposure to this element can result in harmful effects, including death. Intoxication is associated with disorders of the nervous and digestive system and Na/K metabolism. Symptoms include polyneuropathy and loss of hair. In spite of the potential toxicity to animals and humans thallium has received little attention (Pavličková et al., 2006a).

Nondiscriminatory uptake of  $Tl^+$  over  $K^+$  has been suggested as a mechanism for its toxicity to biota (Jacobson et al., 2005).

The well-known mechanism of thallium toxicity is related to the interference with the vital potassium-dependent processes, substitution of potassium in the ( $Na^+/K^+$ ). Since  $Tl^+$  and  $K^+$  are both univalent ions with similar ionic radii, thallium is able to interfere with potassium-dependent processes, and then mimics potassium in its movement and intercellular accumulation in mammals. The capability of thallos ( $Tl^+$ ) ions to mimic the biological action of potassium ions has been attributed to the remarkable inability of cell membranes to distinguish between thallium and potassium, possibly due to their similar ionic charges and radii. Thus, thallium is expected to interfere competitively with some



potassium-dependant biological reactions, as the chemical properties of thallium and potassium are sufficiently alike. Thallium has been shown to replace the physiological ion potassium in the activation of several monovalent cation activated enzymes. Thallium has also been found to replace potassium in the stabilization of ribosomes, as well as in physiological functions such as muscle contraction (John Peter, Viraraghavan, 2005).

The minimum lethal dose ( $LD_{LO}$ ) of soluble thallium salts has been estimated to be 0.7-1.1 g or 10-15  $mg.kg^{-1}$  for a 70-kg adult. The oral reference dose (RfD) for Tl is 0.056 mg/day or 0.0008  $mg.kg^{-1}/day$  for a 70-kg adult. The RfD represents an estimate of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime (Xiao et al., 2004).

The average dietary intake of thallium in the natural uncontaminated environment is usually less than  $5\mu g.day^{-1}$ . Thus, thallium, although a non-essential metal, is universally present in our environment, but in low concentrations (Kazantzis, 2000).

Studies of Tl exposure to humans in a wide variety of geographic locations have indicated less than 2  $\mu g$  as the average daily intake of Tl from environmental sources. Tl in the contaminated soils is being readily transferred to the human body through the food chain. The other two pathways for toxic metals to enter the local food chain may come from the drinking water and consumption of domestically raised animals (Xiao et al., 2004; Pavlíčková et al., 2006b).

#### 2.4.1 Thallium exposure

It has been said that Tl compounds are non-essential and toxic to all organisms; it ranks alongside Pb, Hg and Cd in terms of ecotoxicology. The  $LD_{50}$  (median lethal dose, the point where 50% of test subjects exposed would die) is 8-12  $mg Tl kg^{-1}$  for a man and 30  $mg Tl kg^{-1}$  for a rat (Tremel et al., 2007).

Thallium exposure can be through air, water, and food. However, the levels of thallium in air and water are very low. The greatest exposure occurs by eating food, mostly home grown fruits and green vegetables contaminated by thallium. Small amounts of thallium are released into the air from coal-burning power plants, cement factories and smelting operations. This thallium falls out of the air onto nearby fruit and vegetable gardens and enters food because it is easily taken up by plants through the roots. A repeated surveillance of exposure to thallium in a population living the vicinity of a cement plant emitting dust containing thallium showed that majority of the population in the area has significantly elevated urinary thallium levels. The major route of the population's increased intake of thallium was found to be the consumption of vegetables and fruit grown in private gardens in the vicinity of the cement plant. Polyneuritic symptoms, sleep disorders, headache, fatigue and other signs of psychasthenia were found to be the major health effects associated with increased thallium levels in urine and hair (John Peter, Viraraghavan, 2005).

More information about Tl toxicity will be given in chapter 2.4.3.

#### 2.4.2 Toxicity to animals

The widespread use of thallium as a rodenticide has led to the death of large numbers of dogs, cats, badgers, wild martens and red foxes, and vegetation with high thallium content has led to widespread poisoning in farm animals. Due to its toxicity, the use of thallium as a rodenticide has been banned in many countries, but is still used in some developing countries, giving rise to concern. Sheep died without any outward signs of disorder of disease, and rabbits and horses were reported to loose fur and hair because of heavy Tl contamination (John Peter, Viraraghavan, 2005).

Thallium poisoning deleteriously affects sexual behaviour and reproductive organs of the mammals. In animal experiments with chronic ingestion of small amounts of thallium, damage and changes in the mitochondrial system of nervous cells have also been observed. Little is known about the chronic intoxication with small amounts of thallium. Tl is teratogenic in chick embryos, deformity, microcephaly and decreased fetal size (John Peter, Viraraghavan, 2005).

#### 2.4.3 Toxicity to humans

Thallium is highly toxic which has given rise to a number of outbreaks of poisoning, with a high mortality. Following low level environmental exposure, non-specific symptoms including tiredness, sleep disorders, headaches and muscle pains have been reported. Such symptoms were found to be correlated with urinary thallium levels in a population based study, living in a contaminated area in the vicinity of a cement plant in Germany (Kazantzis, 2000).

Thallium is absorbed through skin and mucous membranes, is widely distributed throughout the body and accumulates in bones, renal medulla and, eventually, in the central nervous system. The biological half-life of thallium is 3-8 days. Thallium is excreted mainly in the urine. The diagnosis of thallium poisoning is not very easy and requires chemical analysis to confirm it (John Peter, Viraraghavan, 2005).

##### 2.4.3.1 Acute toxicity

Studies in people who ingested large amounts of thallium over a short time have reported vomiting, diarrhea, temporary hair loss, and effects on the nervous system, lungs, heart, liver and kidneys. It has caused death. It is not known that the effects are from ingesting low levels of thallium over a long time (John Peter, Viraraghavan, 2005).

The principal features of acute thallium poisoning in humans are gastro-enteritis, polyneuropathy and alopecia, or hair fall. An extreme sensitivity of the legs characterized by the “burning feet syndrome” followed by hair fall should alert to the likelihood of acute thallium poisoning. In less severe cases and in chronic poisoning, similar but milder symptoms are seen (Kazantzis, 2000).

Dermic signs may include palmar erythema, acne, anhidrosis and dry scaly skin which is caused by the toxic effect of thallium on sweat and sebaceous glands. With acute intoxication, the exposure to a large single dose, there is usually an initial hypotension and bradycardia owing to direct effects of the sinus node on cardiac muscle, followed by hypertension and tachycardia thought to be due to vagal nerve degeneration. The central and peripheral nervous system is the main critical organ in thallium intoxication. Symptoms of acute toxicity depend on age, route of administration and dose (John Peter, Viraraghavan, 2005).

##### 2.4.3.2 Chronic toxicity

Chronic effects of thallium poisoning have been seen following occupational exposure. Such exposure has followed inhalation of dust and fumes, ingestion of food contaminated with thallium, and hand or skin contact. Chronic thallium 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. Hair loss may follow after a period of few weeks (Kazantzis, 2000).

Other symptoms of chronic thallium poisoning include anorexia, pains in abdomen, upper arms and thighs and even in all over the body. In extreme cases, alopecia, blindness and even death may be caused. Some studies indicated that there is no thallium mutagenicity or teratogenicity. White streaks

(Mee's lines) may be seen on fingernails and toenails if the intake of thallium has occurred over a long period. Limited data are available on the effects of thallium on human reproduction. Menstrual cycle, libido and male potency may be adversely affected. Sperm are known to be affected following chronic intoxication (John Peter, Viraraghavan, 2005).

Chronic effects have followed population exposure living in the vicinity of coal fired power plants, mineral smelters, brickworks and cement plants (Kazantzis, 2000).

An epidemiological study of population exposed to emissions from a cement plant in Germany showed a clear relationship between thallium concentration in urine and the prevalence of tiredness, weakness, sleep disorder, headache, nervousness, paraesthesia, muscle and joint pain. A similar dose response relationship was also reported for thallium in hair used as an indicator of exposure. However, there was no evidence of hair fall in the population sampled, and the observed effects were all subjective. It has been concluded that the relationship found between thallium concentrations in urine and hair and the symptoms reported in the population sampled, possibly indicate early adverse health effects of thallium (Kazantzis, 2000; Heim et al., 2002).

### **3. THALLIUM IN SOILS**

Thallium high potential for toxicity was well demonstrated. Thallium is more toxic to mammals than cadmium, lead, copper or zinc, and it is known to cause many accidental, occupational and therapeutic poisonings since its discovery in 1861. Although widely distributed in the natural environment, Tl is generally present in very low concentrations in soils. Concentrations of Tl in uncontaminated soils generally range from 0.01 to 3 mg.kg<sup>-1</sup>, but most soils contain Tl at concentration of less than 1 mg.kg<sup>-1</sup>. Thallium minerals and mineralization are rare in nature, thus Tl is often excluded from the list of metals to be analysed despite its high toxicity. Thallium environmental impact related to the natural occurrence of Tl has received relatively little attention. A full understanding of the behaviour of Tl in a local ecosystem is vitally important and critical for the identification, remediation and management of Tl-related health problems (Xiao et al., 2004).

Environmental impact of soils with naturally high Tl contents has received little attention. This fact could be due to the relatively high stability of Tl-bearing phases (predominantly formed by silicates and crystalline oxides) with low potential for Tl release and availability under common soil conditions. On the other hand it was found that soils with increased lithogenic Tl present an important source of this metal through preferential biotransfer (hyperaccumulation) to some plant species. From these findings it can be concluded that soils developed on Tl-rich geological substrates can pose an environmental hazard with respect to the potential entry of Tl in the food chains (Vaněk et al., 2009).

Manganese (III, IV) oxides were evaluated as the dominant phases responsible for the retention of Tl bound to the reducible fraction. On the contrary, Tl retention by more abundant Fe (III) oxides is considered to be negligible. The presence of CaCO<sub>3</sub> in soils may significantly decrease Tl release (Vaněk et al., 2010a).

Thallium is pollutant with affinities for lithophilic, chalcophilic and organic materials (Jacobson et al., 2005).

Concentrations of Thallium in soils reported in studies from various countries are listed in Table 2. Polluted and non-polluted soils are not distinguished, but generally the concentrations in non-polluted soils are below 1.5 mg.kg<sup>-1</sup>.

**Table 2.** Concentrations of Thallium in soils reported in studies from various countries (John Peter, Viraraghavan, 2005; Sasmaz et al., 2007; Vaněk et al., 2009; Xiao et al., 2004; Pavlíčková et al., 2006).

Country	Concentration
Austria	0.08 – 0.91 mg.kg <sup>-1</sup>
Canada	0.17 – 0.22 mg.kg <sup>-1</sup>
China	1.5 – 124 mg.kg <sup>-1</sup>
Czech Republic	0.3 – 6.3 mg.kg <sup>-1</sup>
France	0.13 – 55 mg.kg <sup>-1</sup>
Turkey	0.01 – 27.6 mg.kg <sup>-1</sup>
USA	0.2 – 2.8 mg.kg <sup>-1</sup>

### 3.1 The origin of thallium in soils

Most frequent Tl concentrations are between 0.13-1.53 mg.kg<sup>-1</sup>. In other studies we can see range 0.01-3 mg.kg<sup>-1</sup>. Tl from both pedogeochemical (parent material weathering, pedogenesis) and anthropogenic (atmosphere fallout, agricultural practices) origin contribute to this range of Tl values (Tremel et al., 2007).

Generally the natural process involves the Tl-Hg-As rich-weathering products migrating downslope to be deposited in the arable soils and thus producing a toxic metal-rich environment. The human disturbance involves the addition of mine wastes and the coal ash, enhancing the concentrations of toxic metals in soils. These two processes explain the high enrichment of Tl and other metals in arable soils (Xiao et al., 2004).

It is often difficult to determine whether Tl originates from pedogeochemical or anthropogenic sources. Industrial (e.g. atmosphere fallout) and agricultural activities (e.g. organic matter, fertilizers and pesticides) are considered to be anthropogenic. Two field methods can be used to assess the origin of Tl. The first is the “vertical comparison”. When the Tl concentration in the upper soil layer was much higher than that in the lower soil layers, Tl could be considered to be an anthropogenic contaminant. This is valid only where different soil layers have similar properties. The second is the “horizontal comparison”. When soils next to a potential Tl source contained more Tl than more distant soils, located in the same direction, as similar sites (same soil texture and parent material, no plant cover, etc.), the anthropogenic activity is considered to be the Tl source. Both methods suppose that there have been no movement of topsoil near the site, e.g. by landscaping or building (Tremel et al., 2007).

#### 3.1.1 Thallium natural origins

The natural processes of chemical and physical weathering of the highly altered outcrops or near surface bedrock can lead to a transfer of large amounts of Tl to the soils, producing high concentrations of this toxic trace element (Xiao et al., 2004).

Thallium is normally associated with sulphide minerals and is often found in mineralized areas interspersed with sulphide deposits. Thallium bearing sulphide minerals exist but in low

concentrations, e.g. the following sulphide minerals have been identified: carlinite, lorandite, christite, ellisite, weissbergite, galkhaite, crookesite, vrbaitite, and hutchinsonite (John Peter, Viraraghavan, 2005).

In hydrothermal systems, thallium is bound to sulphides such as pyrite, sphalerite or marcasite. Weathering of these sulphides leads to thallium dispersion in sedimentary rocks, as well as in iron and manganese hydroxides and organic matter, including coals (Jakubowska et al., 2007).

### 3.1.2 Thallium anthropogenic origins

Thallium is found in sulphide ores of heavy metals, in particular lead, zinc and copper and in coal. The combustion of fossil fuels, oil refining, metal smelting and other industrial processes, in particular cement production, has led to soil and water deposition, raised levels and uptake by plants and farm animals (Kazantzis, 2000).

Emission levels being dependent on the thallium content of the raw materials. Large amounts of thallium may also be present in waste materials from non-ferrous metal, in particular copper, iron and steel production (Kazantzis, 2000).

An inspection of the production process proved pyrite roasting is the main Tl source (Tremel et al., 2007).

Although not more than about 15 tons of thallium are produced world-wide annually, it is estimated that about 2000-5000 tons year<sup>-1</sup> are mobilized by industrial processes. In the USA, it has been estimated that about 1000 tons of thallium are released annually into the environment, of which 350 tons are emitted in vapours and dusts, 60 tons bound to non-ferrous metals and more than 500 tons in fluid and solid wastes. Power generating plants, in particular those using brown coal or coal from the Jurassic period provide the major sources of thallium emission into the atmosphere. Thallium volatilizes during the burning of coal and then recondenses on the surface of ash particles. Fly ash thallium contents is negatively correlated with particle size, with concentration in the smallest particles which pass through conventional power generating plant filters, remain in the atmosphere, are respirable and are deposited in the lower respiratory tract (Kazantzis, 2000).

Since thallium compounds are volatile at high temperatures, they are not efficiently retained by electrostatic precipitators or other emission control facilities. Thus, a large fraction of thallium, which enters these processes, is released into the atmosphere (John Peter, Viraraghavan, 2005).

Large portion of Tl may be released into the atmosphere and enter the surrounding ecosystems. Information about Tl retention in soils is generally attributed to simple exchange reactions on organic matter, oxides, or specific silicates. The minerals responsible for Tl immobilization in soils include predominantly illite clays and Mn oxides. The general role of soil organic matter (SOM) on Tl sorption seems to be low (Vaněk et al., 2010a).

Higher thallium concentrations were exhibited by soils in the area of old ore mines (73 µg.g<sup>-1</sup>), from thallium rich sulphide ores of mercury, arsenic and gold (40-124 µg.g<sup>-1</sup>), from pyrite processing areas (5-15 µg.g<sup>-1</sup>) and from lead-zinc exploitation zone (8.8-27.8 µg.g<sup>-1</sup>) (Jakubowska et al., 2007).

It is possible that a geoenvironment favourable to the dispersion of naturally occurring Tl may create environmental health hazards, unless proper planning is undertaken to manage land use for mining, agriculture and human settlement. However, individual mines often do not want their thallium concentrations published (John Peter, Viraraghavan, 2005).

Xiao et al. (2004) say that human activity is important factor contributing to the concentrated toxic metals in the arable soils. The high concentrations of Tl and other toxic metals in the arable soils

downslope and downstream from the mining area and along the stream are generally in excess of baseline values, implying more input of these metals to the soils than the contribution from natural processes. The higher concentration of Tl in the arable soils along the stream and its branches is probably caused by the mining operations, which over the year released Tl-bearing mine wastes to the farm lands downstream.

Inputs by agricultural practices are especially difficult to detect because they are diffuse and the Tl concentration of agricultural additives is not well known. The major agricultural input of Tl may be manure because 98% of Tl ingested by cattle is excreted through urine and faeces. However, inputs of Tl may be of importance only when cattle food contains high quantities of Tl (Tremel et al., 2007).

Another possible source of Tl contamination in soils in this study is from the domestic utilization of coal at the location. For example in some areas in China local coals are enriched in Tl, with levels up to 12-46 mg.kg<sup>-1</sup>, and are often crushed and mixed with mud from the mine wastes to make small coal balls for easy storage and combustion. The ash of such fuel is often used to pave village roads (Xiao et al., 2004).

### **3.2 Thallium sampling and detection**

Xiao et al. (2004) in their study describes the method of sampling soils rich in Tl. The soil samples were collected using a stainless steel shovel from natural sites and mining localities around the mineralized area so as to represent the natural soils and also the arable soils on which the locally consumed crops and wild plants are grown. At each sampling site, 3 sub-samples (0-20 cm depth) were taken over an area of 5 m<sup>2</sup> to form a final composite sample.

Heim et al. (2002) in the sampling procedure followed the pan-European moss monitoring project, which requires that most samples be taken from the soil in open areas – preferably forest clearings. The sampling sites should be at least 300 m from the nearest major road, town/village or industrial facility and at least 100 m from smaller country roads and individual houses.

All the soil samples were kept in polyethylene bags and air-dried in the laboratory pending final processing. The soils were processed for geochemical analysis by disaggregation to pass through a 2-mm sieve. The sieved fraction were then ground in ceramic dish grinder followed by reduction to 80-mesh (<180 µm) powder in a ceramic ball mill (Xiao et al., 2004).

Xiao et al. (2004) also sampled crops and plants typical for the studied area in order to determine concentration of Thallium and its availability in the food chain. Crops and wild plant samples were also collected in the study area, including crop samples from the background area.

The edible parts of the crops (vegetables and cereals) were the focus of the investigation for toxic metals. The vegetables include Chinese cabbage, green cabbage, chilli and carrot root, mainly collected during the harvest season. Some wild plants (fern leaf and edible wild herbs for livestock or human consumption) were also collected in the study area.

The determination of trace metals in soils employed a microwave digestion method using concentrated nitric acid (HNO<sub>3</sub>). Samples were spiked with internal standards and analysed by ICP-MS for Tl (Xiao et al., 2004).

A crucial factor for the potential toxic effect of thallium in the investigated soils is thallium mobility. This can be determined by a sequential extraction of soil. In accordance with the BCR protocol, acid soluble and exchangeable fraction, reducible fraction and oxidable fraction can be selected by the use of suitable extractants (Jakubowska et al., 2007).

In the study of Tremel et al. (2007) the Tl content of the extracts was determined by graphite furnace atomic absorption spectrometry (GFAAS).

AAS is recommended method for thallium determination in a wide range of environmental and biological samples (Tsakovski et al., 1994).

Vaněk et al. (2009) uses an inductively coupled plasma mass spectrometer ICP-MS under standard conditions in order to determine Tl in all soil samples.

In other studies, Tl concentrations were also determined by ICP-MS in top-soil samples, the roots and shoots of the plant (Sasmaz et al., 2007; Heim et al., 2002).

### 3.3 Thallium content in soils

Thallium concentrations in soil are of the order of 0.1 to about 1.0 mg.kg<sup>-1</sup> (or 0.1-3 mg.kg<sup>-1</sup> according to some other studies) with higher values in the vicinity of some metallic ore deposits (Kazantzis, 2000).

Concentrations exceeding 1 mg.kg<sup>-1</sup> in soil (basis on dry weight) are usually indicative of an anthropogenic source (Sasmaz et al., 2007).

Worldwide, the Tl content of soils seems to depend largely on the geological origin of the parent material. In general, most reported concentrations are <1 mg.kg<sup>-1</sup>. There are exceptions, however, such as the clayey soils in France with natural Tl contents as high as 55 mg.kg<sup>-1</sup>. Examples of soil contaminated with Tl include soils near cement plants in Germany with concentration as high as 15 mg.kg<sup>-1</sup>, soils near old mines in Germany with concentration up to 73 mg.kg<sup>-1</sup>, and mine tailings-impacted soils in China with Tl concentrations up to 61 mg.kg<sup>-1</sup> (Jacobson et al., 2005).

Common thallium contents in mafic rocks range from 0.05-0.4 mg.kg<sup>-1</sup> and in acid rocks from 0.5-2.3 mg.kg<sup>-1</sup>. Calcareous sedimentary rocks contain as little as 0.01-0.14 mg.kg<sup>-1</sup> Tl. The median content of thallium 0.29 mg.kg<sup>-1</sup> and a maximum of more than 50 mg.kg<sup>-1</sup> were found in French soils. Content of thallium in soils ranging from 1.5-6.9 mg.kg<sup>-1</sup> was reported in China in the area of natural Tl-rich sulphide mineralization. It was found that pedogeochemical concentration of thallium in some areas of the Czech Republic is more than ten times higher than the median of the values (maximum 3.7 mg.kg<sup>-1</sup>; median 0.25 mg.kg<sup>-1</sup>). In Czech Republic, according to this study, no anthropogenic contamination was proved and higher thallium contents were only of pedogeochemical origin. The highest contents of this element were found in soils derived from granite (2-4 mg.kg<sup>-1</sup>) or paragneiss (0.5-1 mg.kg<sup>-1</sup>) (Pavličková et al., 2006a).

A concentration range of 0.17-0.22 µg.g<sup>-1</sup> in garden soils in Canada and a range of 0.2-2.8 µg.g<sup>-1</sup> on various soils in the USA were reported (John Peter, Viraraghavan, 2005).

Information about Tl sorption by soils or soil minerals is limited and generally attributed to simple exchange mechanisms on organic matter or oxides with some speculation that micaceous clay minerals may selectively sorb Tl (Jacobson et al., 2005).

Xiao et al. (2004) report that in contaminated area thallium occurs at high concentrations in soils derived from mineral wastes, ranging from 40-124 mg.kg<sup>-1</sup>. In slope wash materials, concentrations of Tl range from 20-28 mg.kg<sup>-1</sup>. In alluvial deposits Tl content ranges from 14-62 mg.kg<sup>-1</sup>, with a median 31 mg.kg<sup>-1</sup>. Comparatively, the undisturbed natural soils within and around the mining area show lower concentrations of Tl, ranging from 1.5-6.9 mg.kg<sup>-1</sup>. Soils from the background area have very low Tl contents ranging from <0.2 to 0.5 mg.kg<sup>-1</sup>.

In uncontaminated soils, thallium concentration profiles were gradually increasing downwards in both contrasting soils with the concentration maxima in the bottom horizons C (1.7 and 2.1 mg.kg<sup>-1</sup>

respectively). Lower Tl contents in upper parts of the studied soils can be explained by the long-term alteration/dissolution of Tl-bearing phases as a result of acid soil solution effect. Low pH conditions are generally responsible for heavy metal mobilization and consequent migration downwards the soil profiles (Vaněk et al., 2009).

However, thallium concentration in soil strongly depends on the lithology of the parent rock on which soil was derived and is distinctly higher in the top soil (0-0.2 m) than in the bottom soil (0.8-1.0 m). The bottom soil represents the background thallium soil concentration free of the recent anthropogenic activity. The highest concentration in the bottom soil was found in soil derived from dolomites, ore-bearing dolomites, limestones and marls (median from seven samples, equal to  $1.33 \mu\text{g}\cdot\text{g}^{-1}$ ). The lowest concentration was found in soil derived on glaciofluvial sands and gravel (median from 29 samples equal to  $0.1 \mu\text{g}\cdot\text{g}^{-1}$ ). The soils derived from loesses, slope wash sands and loams, as well as flood-plain sands gravel and silt have medians of thallium concentration between 0.33 and  $0.38 \mu\text{g}\cdot\text{g}^{-1}$  (Jakubowska et al., 2007).

The bottom soil contained only 0-8.8% of the labile thallium and above 90% of the residual thallium entrapped in the parent matter. Non-contaminated soil contained 98% thallium in the residual fraction (Jakubowska et al., 2007).

The major part of the labile thallium i.e. thallium in four fractions is located in the reducible fraction. Second in terms of significance is the fraction of oxidizable thallium. The fraction of oxidizable element is considered as entrapped in sulphides and in the organic matter of the soil (Jakubowska et al., 2007).

In order to build a more general picture of thallium behaviour in the investigated soil, the following should be taken into account:

- 1) anthropogenically dispersed thallium should be mostly entrapped in the sulphide fraction.
- 2) Lead-zinc ores can break the ground surface and therefore participate in soil formation (Jakubowska et al., 2007).

### **3.4 Environmental standards for Thallium**

The International Program on Chemical Safety (IPCS) of the World Health Organization (1996) has produced a detailed Environmental Health Criteria Monograph on thallium. The monograph concludes that in the general population, the total intake of thallium has been estimated to be less than  $5 \mu\text{g}$  per day, mostly from foodstuffs, and that this does not constitute a threat to health (John Peter, Viraraghavan, 2005).

There is a threshold limit value (TLV) of  $0.1 \text{ mg}/\text{m}^3$  for thallium in work place air. This value is based on analogy to other toxic metals. This standard has been adopted by the Occupational Safety and Health Administration, and is the same as that for Germany. The Russian standard is  $0.01 \text{ mg}/\text{m}^3$ . According to Swiss clean air ordinance (1985), the thallium fall out is limited to  $2 \mu\text{g}\cdot\text{m}^{-3}$  per day. According to Swiss ordinance on soil contaminants (1986), the maximum admissible level of thallium in agricultural soil is  $1 \text{ mg}\cdot\text{kg}^{-1}$  dry weight. The Canadian guideline for thallium levels in soils (agricultural uses, residential/park land uses, commercial land uses and industrial uses) is  $1 \text{ mg}\cdot\text{kg}^{-1}$  and for fresh water aquatic life is  $0.8 \mu\text{g}\cdot\text{L}^{-1}$  (John Peter, Viraraghavan, 2005).

In Germany  $0.46\text{-}2.24 \text{ mg}\cdot\text{kg}^{-1}$  DM was established for feed (Pavličková et al., 2006a).

No recommended maximum values are available at the present time in most countries.



### 3.5 Thallium behaviour in different soils

Once deposited, thallium tends to persist in soils containing large amounts of clay, organic matter, iron and manganese oxides. Thallium is retained in the upper soil layers, retention is less effective in acidic soils (Kazantzis, 2000).

The relationship between Tl concentration and other physic-chemical properties of the soils was studied on a representative sub-population of 79 soils for Tl distribution, i.e. the same median and 90<sup>th</sup> percentile values. The aim was to find the major parameters that could be indicative of high Tl soil concentrations (Tremel et al., 2007).

#### *Effects of parent material on Tl concentrations in soils*

Soils derived from calcareous and marl parent materials showed the highest Tl concentrations among soils derived from sedimentary parent materials. It can be explained by the fact that 1m<sup>3</sup> of soil derives from 627m<sup>3</sup> of limestone. During the weathering K, Na, Ca, Mg are leached out, while Tl is concentrated (Tremel et al., 2007).

In the same study, the number of samples derived from magmatic or metamorphic parent materials was very small, so no correlation could be made. High Tl concentration in micas and feldspars is not surprising because they are known to be major hosts of Tl in minerals along with clay. Tl<sup>+</sup> replaces K<sup>+</sup> in these minerals.

#### *Effects of texture on Tl soil concentrations*

Silty and silty-clay soils showed the highest Tl concentrations. Tl concentrations of <0.1 mg Tl kg<sup>-1</sup> soil are found when clay contents are <11%. Primary and secondary silicates (feldspars, micas and clay minerals) and oxides may be the major hosts of Tl in soils. Generally, these minerals belong to the granulometric clay and silt fraction, the sand fraction having a much lower content (Tremel et al., 2007).

#### *Correlation between Tl concentrations and other physic-chemical soil properties*

Significant positive correlations of Tl concentrations with some chemical and physical properties could be detected: Ba, V, Pb, Fe, Ni, Cd, Zn, Co, As and especially Mn.

A negative correlation between Tl and pH for all soils was noticed.

Very high Mn concentrations were noticed in 90% of soils whose Tl concentrations was greater than the 90<sup>th</sup> percentile value. This relationship may be explained by the binding of Tl with Mn-oxide in oxidizing conditions. Two hypotheses are available. First, the oxidizing conditions, Tl (III) could enter the Mn oxides by sorption; second, Tl (I) could replace K (I) in the oxide (Tremel et al., 2007).

Jacobson et al. (2005) investigated the dual lithophilic/chalcophilic tendencies of Tl by characterizing the sorptive behaviour of environmentally significant trace levels of this metal to soil. Therefore 3 kinds of soils were used to examine the effect of soil texture, mineral content, and organic matter content on Tl sorption. It also studied the effect K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> on Tl sorption. The studies were conducted using acid rain and both short-term (24 h) and long-term (6 month to 1 year) to give a more complete picture of their long-term retention in soils.

The organic matter-rich soil's retention of Tl was similar to that of the sandy soil. Amounts of Tl sorbed to the mineral soils increased after a 1-year incubation period. Tl sorption to the peaty-muck

soil was unaffected with time. Mn oxides may play a role in Tl retention by soils; whereas, *contrary to other reports*, iron oxides do not effectively sorb Tl. Acid rain and addition of potassium ( $K^+$ ) and ammonium ( $NH_4^+$ ) as competing ions had no long-term effect on Tl sorption. Thallium remaining in the all the batch sorption solutions, as determined by flame atomic adsorption spectroscopy (FAAS) was completely labile, which may have important environmental consequences (Jacobson et al., 2005).

Vaněk et al. (2009) studied the differences in Tl distribution and speciation in forest and grassland soils, developed on an identical geological substrate and investigated the effect of contrasting land use on geochemistry of lithogenic Tl in soil and evaluated the influence of different land cover on lithogenic Tl uptake. The study proved the preferential association of Tl with primary silicates (mainly orthoclase and muscovite) and probably secondary illite in all studied horizons. This suggests that stable silicates are the dominant phases controlling the solubility of lithogenic Tl in both the forest and grassland soils.

Fig. 2 shows the chemical fractionation of Tl in individual horizons of the studied soils. There were no statistically significant differences between the non-residual fractions of both the forest and grassland soils separately tested. Thallium was primarily bound, as mentioned before, in the residual fraction (up to 95% of the total content) suggesting thus its low mobility. A high portion of residuum associated Tl indicates its lithogenic origin. A small part (approximately 1%) of Tl was generally present in the exchangeable/acid-extractable (easily mobilisable) fraction in the studied soil horizons (Vaněk et al., 2009).

Soil forming processes like bioturbation and probably dust deposition may lead to a significant input of lithogenic Tl into the forest floor layer. Moreover, the largest portion (approximately 5 %) of „labile“ Tl was found here indicating a distinct role of forest SOM on Tl mobilization and bioavailability. The combination of chemical fractionation data and XRD proved the preferential association of Tl with primary silicates (mainly orthoclase and muscovite) and probably secondary illite in all studied horizons. This finding suggests that stable silicates are the dominant phases controlling the solubility of lithogenic Tl in both the forest and grassland soils. Thallium adsorption was dominated by an identified non-crystalline Mn (III, IV) oxide and this phase may be thus defined as a Tl „scavenger“ in the studied mineral soils. In contrast, the role of common Fe(III) oxides like goethite and ferrihydrite on Tl adsorption seems to be negligible. Organically bound Tl in the forest floor was found to be associated with primary SOM corresponding to the raw and partially decomposed litter. Moreover, a relatively high Tl content was recorded on the fresh fallen needles of Norway spruce indicating that these species and possibly other coniferous trees can accumulate Tl. In contrast, lithogenic Tl uptake by common grasses like red clover or timothy grass seems to be very low. The present study showed that complex soil-plant investigation supplemented with combined mineralogical methods is essential for understanding the behaviour of lithogenic Tl in soils (Vaněk et al., 2009).

### 3.6 Thallium uptake by plants

Uptake of thallium by vegetation is determined by the solubility of the compound, and uptake increasing soil acidity. The source of the thallium contaminant has also been found to influence plant uptake, thus thallium contamination from cement factory dust has been found to be more available than thallium content of soil. Thallium uptake in contaminated land is also determined by plant species (Kazantzis, 2000).

Neutral soils high in CEC and organic matter are able to bind thallium more effectively than poor acid soils and the transfer of Tl into plants from these soils substantially lower. Thus, it can be concluded that Tl is more plant-available from acid soils with low content of organic matter than from neutral soils with higher content of organic matter (Pavličková et al., 2006b).

Thallium concentration in plants is usually below  $0.1 \text{ mg.kg}^{-1}$  dry weight. The brassicaceous plants have been termed a thallopilic species, with thallium concentrations of the order of  $1.5 \text{ mg.kg}^{-1}$  fresh weight. Thallium levels have been found to increase in garden plants treated repeatedly with sewage sludge or potash fertilizers (Kazantzis, 2000).

Thallium is readily taken up by the root system of the plants. The uptake of Tl into the plants is likely due to the close geochemical affinity between thallium and potassium. These two elements have similar ionic radii of  $\text{Tl}^+$  (0.133 nm) and  $\text{K}^+$  (0.147 nm). Because of the very similar ionic radii, Tl can readily substitute for K in plants during biochemical processes. Isomorphous substitution can be also between  $\text{Tl}^+$  and  $\text{NH}_4^+$ , as a result of their close ionic radii:  $\text{Tl}^+$  0.133 nm and  $\text{NH}_4^+$  0.148 nm. The substitution of Tl for K in plants has been described by many researchers (Xiao et al., 2004; Tsakovski et al., 1994).

In biochemical processes, Tl occurs as a singly-charged, weakly-hydrated cation ( $\text{Tl}^+$ ) with ionic radius similar to  $\text{K}^+$ , and is expected to interfere competitively with K-dependent biological reactions (Xiao et al., 2004; Pavlíčková et al., 2006b).

The enrichment of Tl in crops and other plants is closely related to the concentration of Tl in soils. High concentrations of Tl in the plants growing in the Tl-rich soils in the study area support the idea that toxic metals are being transferred from soil to crops through the roots of the plants. In contrast, crops growing in uncontaminated soils in the background area show low concentration of Tl. Therefore, the high concentrations of Tl in plants directly reflect its immediate source in the contaminated soils (Xiao et al., 2004).

Vaněk et al. (2010b) studied the uptake by white mustard on two types of moderately contaminated soils. Generally higher Tl levels were found in mustard grown on soil with a large portion of labile Tl.

The total content of thallium in soil, physicochemical form and form of binding to soil particles seem to be the main factors influencing the uptake by a plant (Pavlíčková et al., 2006a).

Xiao et al. (2004) in their study also show that the amounts of major elements Ca and Mg in plants seem to be one of the factors contributing to the different degree of uptake of Tl. The higher accumulation of Tl in crops generally corresponds to elevated concentrations of Ca and Mg. However, the mechanism whereby the high concentrations of Ca and Mg trigger uptake of Tl by plants is still not clear. There may be other factors that favour the high uptake of Tl by certain crops and this warrants further study.

It was also observed that high concentrations of metals such as Mo, Cu, Pb, Zn, Ag and As inhibit the Tl uptake by plant roots and shoots. It can, therefore, be said that these antagonistic effects can benefit in controlling the Tl uptake abilities of plants (Sasmaz et al., 2007).

The maximum concentrations of Tl were detected in stems of young mustard shoots, followed by leaves and roots. Approximately 3-fold lower concentrations of Tl were observed in roots and stems of the mature plants. These findings indicate that the rate of Tl uptake is decreasing with the age of the plant (Vaněk et al., 2010b).

Uptake of thallium by plants is species-dependent. Plant varieties and plant parts differ in the degree of uptake and accumulation of Tl. Some brassicaceous plants commonly grown as vegetables behave as hyperaccumulators of Tl (Pavlíčková et al., 2006a).

Uptake of thallium by different plants was studied mainly on anthropogenically contaminated soils or in the field and pot experiments after addition of thallium. It was found that plants exhibit species dependent preferences and particularly brassicaceous plants can reach very high concentration of thallium in their tissues without any symptoms of phytotoxicity. Selection of suitable cultivars with low thallium uptake can contribute to reduce the food chain contamination (Pavlíčková et al., 2006a).

Xiao et al. (2004) in their study present the results of an investigation into the natural occurrence of Tl in soils and its uptake by crops and other plants in Tl-Hg-As mineralized area, and outline the impact of Tl dispersion on the local ecosystem. The studied area has been widely developed for agricultural and residential purposes.

Xiao et al. (2004) investigated the concentrations of Thallium in some crops and plants. The enrichment of Tl in crops is also characterized as species-dependant. Thallium is more enriched in green cabbage than in other crops, generally 2 orders of magnitude higher. Thallium generally shows higher concentrations in green cabbage, Chinese cabbage, and carrot than in chili, corn and rice. Thallium concentrations also differ depending on the period of growth for the same species of crops.

Thallium shows the highest concentrations in green cabbage, ranging from 120 to 495 mg.kg<sup>-1</sup> with an average of 338 mg.kg<sup>-1</sup>, whereas only 0.4 mg.kg<sup>-1</sup> has been detected in cabbage from the background area. However, Tl shows lower concentrations (15-32 mg.kg<sup>-1</sup>) in the early growing stage of the green cabbage. This implies that Tl accumulation in vegetation increases with time throughout the growth process. The widely-planted Chinese cabbage contains 0.87-5.4 mg.kg<sup>-1</sup>Tl with an average of 2.5 mg.kg<sup>-1</sup>, whereas Tl concentration in samples from the background area was 0.31 mg.kg<sup>-1</sup>. Thallium concentration in chili ranged from 0.8 to 5.3 mg.kg<sup>-1</sup>, and 0.27 mg.kg<sup>-1</sup> Tl from the background area. Shelled rice contained 1 – 5.2 mg.kg<sup>-1</sup> Tl, with an average of 2.4 mg.kg<sup>-1</sup>, and 0.27 mg.kg<sup>-1</sup> Tl from the background area. Thallium in granular corns showed lower concentrations, ranging from 0.78 to 3.1 mg.kg<sup>-1</sup> and averaging 1.4 mg.kg<sup>-1</sup>, are only 0.07 mg.kg<sup>-1</sup> Tl on average from the background area. One sample of carrot root contained 22 mg.kg<sup>-1</sup> of Tl. Some wild herbs (for livestock forage or human consumption) also showed high concentrations for Tl, with an average of 36 mg.kg<sup>-1</sup>. The highest concentration was observed mainly in the green parts of the particular plants (Xiao et al., 2004).

Average Tl concentration in grass biomass (shoots/roots) specific for the grassland sampling site were as follows: 0,005/0,02 mg.kg<sup>-1</sup> for red clover and 0,002/0,01 mg.kg<sup>-1</sup> for timothy grass. Such Tl concentrations in the grass shoots can be regarded as low. Therefore, only a long-term cultivation including grass cutting can be responsible for Tl removing from the upper parts of the grassland soil (Vaněk et al., 2009).

In the fresh fallen needles of Norway spruce representing the biomass sampled at the forest sampling site, there was reported an average Tl concentration of 0,12 mg.kg<sup>-1</sup>. Such Tl concentrations present in needles can be regarded as much higher compared to the grass species. Norway spruce can accumulate Tl to some extent in areas with high Tl background content (Vaněk et al., 2009).

### **3.7 Thallium in food chain**

Tl<sup>+</sup> is believed to be a major chemical form of Tl in soils. As a result Tl is rapidly taken up from soil by plants and is transmitted through the food chain (Tremel et al., 2007).

Due to the high uptake of Tl by crops, Tl is the main metal triggering chronic poisoning of human health. The pathway of Tl entering the food chain is mainly through the consumption of the local harvested vegetables and other crops grown in the Tl-rich contaminated soils (Xiao et al., 2004).

Xiao et al. (2004) in their study document the reality of Tl poisoning engendered by soil contamination and Tl uptake by crops in a Tl-bearing sulfide-mineralized area. It is important to note that Tl contamination may occur in the absence of mining activity, although mining may speed up the transfer of toxic elements from bedrock to the food chain. The results also contribute to our knowledge base of environmental hazards related to naturally occurring Tl and its dispersion. This information is vital for planning and monitoring land use as well as for safeguarding the health of the population.

The concentration of thallium in vegetables in many cases can substantially exceed the concentration of thallium in soils. Thus, thallium content should be monitored and the plant with high thallium accumulation power should be excluded from growing for human or animal nutrition in contaminated areas. The above-mentioned facts are often neglected because legal measures are usually taken only for the areas anthropogenically contaminated as a result of human activity. Uptake of thallium from soils with a naturally high content of thallium can be high enough to seriously endanger food chains (directly by consumption of plants grown on contaminated soils, or indirectly by consumption of meat from animals fed by rape cattle cakes, a by-product of rapeseed oil production) (Pavličková et al., 2006a).

The main goal should be to find suitable crops that can be planted in Tl-rich areas without contamination of the food chain by thallium and also to find plants that should be avoided in the areas of their ability to accumulate thallium in their tissues (Pavličková et al., 2006a, Pavličková et al., 2006b).

#### **4. CONCLUSIONS**

The daily total intake of Tl should be less than 5 µg per day. However, in places with increased concentration of Tl in soils this intake can be much higher and cases of acute or chronic poisoning can appear. Industrial activities using Tl-rich ores (such as metal mining and smelting, cement plants and others) should be monitored and appropriate protective measures should be taken. There is a need to develop treatment technologies to reduce thallium levels. The limited use of thallium will not lead to a global contamination of the environment, but localized problems may exist or develop in the future. Its use in high temperature superconduction components may also increase. For uptake of Tl by plants is species-dependent, suitable crops should be planted in contaminated areas.

## **5. REFERENCES:**

- Heim M., Wappelhorst O., Markert B., 2002: Thallium in terrestrial environment – occurrence and effects, *Ecotoxicology*, 11: 369-377.
- Jacobson A. R., McBride M. B., Baveye P., Steenhuis T. S., 2005: Environmental factors determining the trace-level sorption of silver and thallium to soils. *Science of the Total Environment*, 345: 191-205.
- Jakubowska M., Pasieczna A., Zembrzusi W., Świt Y., Lukaszewski Z., 2007: Thallium in fractions of soil formed on floodplain terraces. *Chemosphere*, 66: 611–618.
- John Peter A. L., Viraraghavan T., 2005: Thallium: a review of public health and environmental concerns. *Environment International*, 31: 493-501.
- Kazantzis G., 2000: Thallium in the environment and health effects. *Environmental Geochemistry and Health*, 22: 275-280.
- Pavličková J., Zbiral J., Smatanová M., Habarta P., Houserová P., Kubáň V., 2006a: Uptake of thallium from naturally-contaminated soils into vegetables. *Food Additives and Contaminants*, 23(5): 484-491.
- Pavličková J., Zbiral J., Smatanová M., Habarta P., Houserová P., Kubáň V., 2006b: Uptake of thallium from artificially contaminated soils by kale (*Brassica oleracea* L. var. *acephala*). *Plant, Soil and Environment*, 52 (12): 544-549.
- Sasmaza A., Sena O., Kayab G., Yamanb M., Sagioglua A., 2007: Distribution of Thallium in Soil and Plants Growing in the Keban Mining District of Turkey and Determined by ICP-MS. *Atomic Spectroscopy*, 28: 157-163.
- Tremel A., Masson P., Sterckeman T., Baize D., Mench M., 1997: Thallium in French agrosystems I. – Thallium contents in arable soils. *Environmental Pollution*, 95: 293-302.
- Tremel A., Masson P., Garraud H., Donard O. F. X., Baize D., Mench M., 1997: Thallium in French agrosystems II. – Concentration of Thallium on field-grown rape and some other plant species. *Environmental Pollution*, 97: 161-168.
- Tsakovski S., Ivanova E., Hawzzov I., 1994: Flame AAS determination of Thallium in soils. *Talanta*, 41: 721-724.
- Vaněk A., Chrastný V., Mihaljevič M., Drahot a P., Grygar T., Komárek M., 2009: Lithogenic thallium behavior in soils with different land use. *Journal of Geochemical Exploration*, 102.: 7-12.
- Xiao T., Guha J., Boyle D., Liu C., Chen J., 2004: Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China. *The Science of the Total Environment*, 318: 223–244.
- Vaněk A., Chrastný V., Komárek M., Galušková I., Drahot a P., Grzgar T., Tejnecký V., Drábek O., 2010a: Thallium dynamics in contrasting light sandy soils – soil vulnerability assessment to anthropogenic contamination. *Journal of Hazardous Materials*, 173: 717-723.

Vaněk A., Komárek M., Chrastný V., Bečka D., Mihaljevič M., Šebek O., Panušková G., Schusterová Z., 2010b: Thallium uptake by white mustard (*Sinapis alba* L.) grown on moderately contaminated soils - agro-environmental implications, *Journal of Hazardous Materials*, 182: 303-308.