Chemical Constituents in Coal Combustion Product Leachate: Thallium

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1016801

Final Report, December 2008

Cosponsors

Southern Company Services, Inc.
Project Manager
J. Pugh

American Electric Power Service Corp.
Project Manager
T. Webb

South Carolina Electric & Gas
Project Manager
W. Caughman

EPRI Project Manager
K. Ladwig

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Southern Company Generation

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REPORT SUMMARY

This report provides comprehensive information on the environmental behavior of thallium. Included are discussions of thallium's occurrence in soil and water, occurrence in coal and coal combustion products (CCPs), CCP leaching characteristics, effects on human health and ecology, geochemistry, and treatment/remediation options.

Background

Thallium occurs naturally in a wide range of environmental media, including soil, water, air, and coal. The United States Environmental Protection Agency (U.S. EPA) has established a relatively low maximum contaminant limit in drinking water of 2 µg/L for thallium. Its occurrence in natural groundwater and its mobility in the groundwater environment have not been extensively studied. Knowledge about thallium's geochemistry, health effects, and treatment is important to the electric power industry due to its occurrence in coal and CCPs and its relatively low regulatory limits.

Objectives

To assemble and synthesize available information regarding the occurrence and geochemical behavior of thallium and present a comprehensive overview of environmental and treatment data for thallium.

Approach

The project team performed a literature search to identify and review relevant sources of information on thallium. These sources included EPRI resources and databases, as well as other resources. The team organized and summarized their findings so that key data and information can be quickly and easily accessed.

Results

Thallium concentrations in U.S. coal vary widely, with the median concentration measuring less than 1 mg/kg. Concentrations in coal fly ash are higher, ranging up to about 85 mg/kg, with a median of 7.5 mg/kg for bituminous coal fly ash. The thallium in fly ash most likely resides as an oxide or in the nonvolatilized sulfide fraction. Thallium leaching from CCPs may be a result of mineral solubility or cation exchange with ammonium, an issue that calls for further research. Concentrations in field leachates have ranged from below detection to a maximum of 17.6 µg/L, with a median of less than 1 µg/L. Leachate concentrations were generally higher at bituminous coal ash sites compared to subbituminous coal ash sites and at impoundments compared to landfills.

There is no evidence that thallium is carcinogenic. The majority of information on thallium toxicity comes from case reports on accidental or intentional thallium poisoning incidents. Sublethal doses of thallium are associated with gastrointestinal problems, such as abdominal pain, vomiting, diarrhea, and nausea. One of the most characteristic signs of thallium toxicity is hair loss. Symptoms of oral chronic thallium toxicity are similar to acute effects, although symptoms are delayed. The U.S. EPA issued a draft revision of the thallium risk assessment in January 2008, suggesting a four-fold lowering of the risk level based on new interpretation of existing data on alopecia (hair loss) in female rats. Further research is warranted due to uncertainties surrounding the derivation and revision of the U.S. EPA oral reference dose.

Thallium principally occurs as the thallium ion Tl(+1) in aqueous solutions. Information on thallium mobility in groundwater is limited, but what is known suggests that thallium is relatively immobile under typical pH conditions and increases in mobility under acidic conditions. At present, the U.S. EPA's best demonstrated available technology for thallium remediation is chemical oxidation, followed by chemical precipitation with hydroxide compounds, settling, and filtration. Research on additional treatment and remediation methods is in progress, but those methods are not well developed at this time.

EPRI Perspective

This report is part of a series addressing key constituents at utility CCP management sites and coal storage areas. Previous reports dealt with boron, beryllium, and arsenic. Over the last 25 years, EPRI has developed a wealth of data on the leaching and groundwater transport characteristics for a wide range of inorganic constituents. This series of reports synthesizes that data along with other pertinent research results from the literature to provide a unique compendium for assessing the behavior of constituents in the environment. The reports will be updated as new information is developed by EPRI or becomes available in the published literature.

Keywords
Coal combustion products
Thallium
Geochemistry
Treatment
Leachate

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1
INTRODUCTION

Coal combustion products (CCPs) are produced from the burning of coal to generate electricity, and include fly ash, bottom ash, boiler slag, and flue gas desulfurization solids. CCP production in the United States in 2006 was 124.8 million tons, and the utilization rate was 43.43% (ACAA, 2007). Production in 2006 increased from a 2005 total of 123.1 million tons, and the utilization rate increased by 3.1%. CCPs that are not utilized are typically managed in landfills or impoundments.

The regulatory status of metals and trace constituents in CCPs is continually evolving as new data on health and ecological effects are developed. This is particularly true for thallium. The current Maximum Contaminant Level (MCL) for thallium is 2 µg/L. Recent EPA review of the oral reference dose (RfD) for thallium compounds may lower the oral RfD by 4 to 4.5 times, increasing its apparent risk. As a result, regulatory criteria for thallium concentrations in soil and groundwater may decrease, which may potentially affect decisions regarding beneficial reuse of CCPs and management in landfills or impoundments. Furthermore, knowledge of thallium's natural occurrence and geochemistry may be of value if this constituent is monitored at CCP management facilities.

This report describes the current understanding of thallium occurrence and behavior in natural systems and at CCP disposal facilities. Thallium concentrations in coal and CCPs are summarized, as well as the potential for thallium to enter the environment through CCP storage and disposal. Environmental fate and transport and the known human health and ecological effects of thallium are discussed, and needs for further research are highlighted.

2
OCCURRENCE, USES, AND SOURCES

Occurrence

Thallium occurs naturally in trace amounts in the environment (Table 2-1). Thallium is found in two valence states. Thallous compounds, which exist in the monovalent state, are more stable in the environment than thallic (trivalent) compounds (Galvan-Arzate and Santamaria, 1998).

Table 2-1
Thallium Concentrations in Environmental Media

Environmental media		Concentrations	Reference
Atmosphere		0.02 to 0.1 ng/m^3	U.S. EPA (1980)
U.S. Soil		0.01 to 3 mg/kg	ATSDR (1992)
Water	U.S. Tap Water Survey	Mean detected: 0.89 μg/L (99.32% non-detect)	U.S. EPA (1980)
	Ocean	Estimated mean: 0.013 μg/L	Smith and Carson (1977)
Rocks and minerals	Igneous	0.7 to 1.3 mg/kg	Shaw (1952); Smith and Carson (1977)
	Metamorphic	0.2 to 1.9 mg/kg	
	Clay and shale	0.69 mg/kg	
	Sandstone	0.82 mg/kg	
	Carbonaceous shales	1.23 mg/kg	
	Limestone	0.5 mg/kg	
U.S. coals		Average: 0.78 mg/kg Median: 0.50 mg/kg Range: 0.02 to 32.00 mg/kg	Braggs et al. (1998)

Soil

Thallium's crustal abundance ranges from 0.3 to 3 mg/kg, averaging less than 1 mg/kg (Smith and Carson, 1977). Most thallium in the crust is contained in potassium-bearing minerals like feldspars or micas, or in sulfides such as pyrite. In the U.S., a survey of Illinois soils found that thallium ranged from 0.02 to 2.8 mg/kg with a mean of 0.57 mg/kg. Michigan reported higher levels, with means ranging from 1.4 to 2.3 mg/kg depending on soil type and location. New Jersey reported mean levels of 0.01 mg/kg and less (Shacklette and Boerngen, 1984). A wider range of soil thallium concentrations—0.05 to 24 mg/kg—was found in European topsoil, with a 90th percentile value of 1.38 mg/kg (Salminen et al., 2005).

Water

A survey of tap water from 3,834 homes in the United States (U.S. EPA, 1980) detected thallium in only 0.68% of the samples, with an average concentration of 0.89 µg/L. However, Smith and Carson (1977) estimated average thallium concentrations in groundwater and stream water as 7.25 µg/L and 0.02 µg/L, respectively. Based on tap water data reported in U.S. EPA (1980), an average thallium concentration of 7.25 µg/L in groundwater is likely an overestimate. To date, no comprehensive surveys of thallium concentrations in United States groundwater or non-polluted stream water have been published.

Air

Thallium enters the air via multiple sources. Human activities that may potentially release relatively high amounts of thallium include nonferrous metal smelting, coal combustion, cement production, and mining (ATSDR, 1992). In areas distant from active releases, thallium can enter air via the resuspension of soil. Information on the amount of thallium in air is limited, but in six U.S. cities, U.S. EPA found that levels typically ranged from 0.02 to 0.1 ng/m^3 (U.S. EPA, 1980).

Uses

Starting in the early 1920s, thallium (thallium (I) sulfate) was widely used as a rodenticide and insecticide. Thallium (I) sulfate was also used as an antibacterial agent in the treatment of diseases such as tuberculosis, syphilis, and malaria (Peter and Viraraghavan, 2005; ATSDR, 1992). It has also has been used as a depilatory (hair removal) agent. In the U.S. and most other industrialized countries, the use of thallium for these purposes has been banned because of its toxicity; however, some developing countries may still use thallium as a pesticide (IPCS, 1996; Galvan-Arzate and Santamaria, 1998). Present day uses for thallium are varied and limited to specialized industries. The semiconductor industry uses thallium alloyed with other metals in the manufacturing of switches and closures. Thallium is also used as a component in special glasses to confer a high refractive index and high melting point (Peter and Viraraghavan, 2005). Thallium is used as an additive in electroplating of gold, chromium, nickel, lead, and zinc to improve adherence and coating uniformity (Kaplan and Mattigod, 1998). Interestingly, a radioactive isotope of thallium (thallium-201) is commonly used as an imaging aid to help

doctors identify problems in the heart, liver, thyroid, and testes (IPCS, 1996). There are a variety of other industrial uses for thallium (*e.g.*, as a pigment and as a component in thermometers and imitation jewelry), but, overall, the total amount of thallium used by industry is relatively small (Peter and Viraraghavan, 2005).

Sources

Most anthropogenic sources of thallium to the environment are related to coal combustion and heavy-metal smelting and refining (Sager, 1994). Other sources include the production and waste of electroplating, and battery manufacturing (Kaplan and Mattigod, 1998). Studies conducted in Germany in the vicinity of mining, smelting, and cement manufacturing operations found that soil levels ranged from undetectable to 73 mg/kg, although most concentrations were 10 mg/kg or less (IPCS, 1996; Lin and Nriagu, 1998). Soils in the vicinity of cement plants typically had the highest concentrations. Sabbioni et al. (1984) modeled thallium emissions from a hypothetical coal burning plant and determined that, over a 40-year period, thallium emissions within the vicinity would be negligible, adding only 0.005 mg/kg to background levels.

The major source of thallium releases to water include nonferrous metals, iron and steel manufacturers, and various mining, inorganic chemicals, refining and ore-processing industries (ATSDR, 1992). A U.S. study found that runoff from smelting and mining operations had thallium concentrations as high as 30 µg/L (U.S. EPA, 1980).

3
HUMAN HEALTH EFFECTS AND RISK ASSESSMENT

Thallium Uptake, Metabolism, and Excretion in the Human Body

The limited data available on thallium absorption suggest that it is well absorbed through various routes of exposure in humans and experimental animals (ATSDR, 1992; IPCS, 1996; OEHHA, 1999). A radioactive tracer solution of thallium nitrate administered to rats by six routes of exposure (oral, intravenous, intramuscular, subcutaneous, intratracheal, or intraperitoneal) was rapidly and almost completely absorbed by all routes tested (Lie et al., 1960, as cited in OEHHA, 1999). Several human intoxication cases (*e.g.*, following both oral and topical applications of thallium compounds during depilatory treatment) and cases of human poisonings indicate that thallium can be absorbed through both the gastrointestinal tract and skin (OEHHA, 1999).

Once absorbed, thallium is rapidly taken into the circulatory system and distributed to all organs with an apparent blood half-life of less than 5 minutes (Talas and Wellhoener, 1983 and Talas et al., 1983, as cited in ORNL, 1994). Thallium crosses the blood-brain and placental barriers to some extent (ORNL, 1994; OEHHA, 1999), although in mammals, maternal concentrations of thallium are greater than fetal concentrations, likely because the placenta limits the passage of thallium (Leonard and Gerber, 1997).

Based on animal studies, the distribution pattern of thallium does not appear to be affected by the route or duration of administration (IPCS, 1996). Initially, high concentrations of thallium appear in the kidney, with lower concentrations in fat tissue and the brain and intermediate concentrations in the other organs; later, the thallium concentration in the brain increases (IPCS, 1996).

Little information is available on thallium metabolism (OEHHA, 1999; IPCS, 1996; ATSDR, 1992). Sabbioni et al. (1980, as cited in ORNL, 1994 and IPCS, 1996) reported that the two oxidation states of thallium ions (I and III) showed a similar intracellular distribution, suggesting that the different oxidation states of thallium were transformed *in vivo* to a single valence. However, the *in vivo* valence of thallium is unknown.

Elimination of thallium may occur through the gastrointestinal tract, kidneys, hair, skin, sweat, saliva, and breast milk (IPCS, 1996). The primary routes of thallium excretion for animals and humans are the urine and feces, but differences exist between species. Limited studies in humans suggest that thallium is excreted in the urine with little fecal excretion (Barclay et al., 1953, as cited in ORNL, 1994), while in rats and rabbits fecal excretion exceeds urinary excretion (Lie et al., 1960, Rauws, 1974, and Talas and Wellhoener, 1983, as cited in ORNL, 1994). Also, the rate of excretion is generally much lower in humans than in laboratory animals. The biological half-life of thallium in laboratory animals generally ranges from 3 to 8 days; in

humans it is about 10 days but values up to 30 days have been reported (IPCS, 1996). Aoyama et al. (1989, as cited in Galvan-Arzate and Santamaria, 1998) showed that, although thallous compounds may be eliminated more rapidly than thallic compounds, they both exhibit similar toxicity.

Thallium Measurement in Humans

The total amount of thallium in the body has been estimated to be 100 µg per 75 kg body weight in an unexposed population (Weinig and Zink, 1967, as cited in IPCS, 1996). Urinary thallium levels are considered the most reliable biological indicator of thallium exposure, particularly under steady-state conditions (ATSDR, 1992; IPCS, 1996). Thallium has a relatively short biological half-life; about 50% of total urinary elimination occurs within 9 to 11 days (Weinig and Schmidt, 1966, as cited in IPCS, 1996). In general, the mean urinary thallium concentration in unexposed populations is about 0.3 to 0.4 µg/L, accounting for approximately 70% of the total daily excretion of thallium (IPCS, 1996). Some other surveys in unexposed populations found somewhat higher levels, with background urinary concentrations ranging as high as 2.0 µg/L (Smith and Carson, 1977, as cited in IPCS, 1996).

Thallium Health Effects

The majority of information on thallium toxicity comes from case reports on accidental or intentional thallium poisoning incidents. Poisonings have informed on the characteristics of both acute (short-term) and intermediate-term toxicity. Occupational exposure has provided the most information on chronic (long-term) exposure. There are only a few isolated cases where exposure to thallium in the environment has been associated with toxicity. More detailed information on thallium toxicity is presented below.

Acute Health Effects

Numerous health effects have been documented to occur following acute oral thallium exposure, mainly from incidents involving intentional or accidental poisonings. There is little to no data available on potential effects involving acute exposures via other exposure routes (*e.g.*, inhalation, dermal). Because thallium was historically used medicinally, data are also available on the side effects of patients who received thallium treatment. Individual doses associated with fatality have ranged considerably, but they generally average 10-15 mg/kg (OEHHA, 1999), although death at lower levels has been documented (ATSDR, 1992). In general, higher doses are associated with immediate death (within a few hours), while relatively lower doses may cause a more protracted death. Death is often associated with cardiac or respiratory failure (ATSDR, 1992).

Sub-lethal doses of thallium are associated with gastrointestinal problems, such as abdominal pain, vomiting, diarrhea, and nausea (Chander and Scott, 1986, as cited in Repetto et al., 1998). One of the most characteristic signs of thallium toxicity is hair loss (Galvan-Arzate and Santamaria, 1998). Hair loss can occur as early as 8 days post-exposure (ATSDR, 1992). Neurological deficits can also develop, including parenthesis, limb weakness, and abnormal mental function (Repetto et al., 1998; Galvan-Arzate and Santamaria, 1998). Used as a

therapeutic agent in the 1930s, thallium dosed at about 8 mg/kg caused peripheral neuropathy in about 10% of patients (Cavanagh, 1979, as cited in IPCS, 1996).

Chronic Noncancer Health Effects

Limited data are available on chronic thallium exposure via inhalation. The only available studies are occupational and usually involve exposure to multiple chemicals. Overall, reported symptoms include gastrointestinal effects, leg pains, fatigue, alopecia, and psychological deficits (Ohnesorge, 1985, as cited in IPCS, 1996; Saha, 2005; and Galvan-Arzate and Santamaria, 1998). For example, workers employed at a cement plant (employment ranging from 5 to 44 years) exhibited several neurological deficits, including paresthesia, numbness of toes and fingers, and muscle cramps (Ludolph et al., 1986 as cited in ATSDR, 1992). The results of this study, however, are unreliable because exposure levels were not quantified, there was no control group, and workers suffered from other illnesses that may have contributed to neuropathy. Symptoms consistent with thallium toxicity such as alopecia, skin changes, abdominal pain, mild neuropathy, and microcirculation disorders have been observed in individuals exposed to thallium through glass production (Bachanek et al., 2000; Hirata et al., 1998). Workers at a salt magnesium battery plant (thallium levels reported to be about 0.14 and 0.22 mg/m^3) had no increase in cardiovascular or gastrointestinal effects compared to non-exposed controls (Marcus, 1985, as cited in ATSDR, 1992).

Symptoms of oral chronic thallium toxicity are similar to acute effects, although symptoms are delayed. Information on oral chronic thallium toxicity is mainly from a few isolated studies on populations living in the vicinity of industries commonly associated with thallium releases. For example, Zhou and Ling (1985) reported 189 cases of chronic thallium poisoning in a Chinese population living in the vicinity of a mining area. The most common symptoms were alopecia, peripheral neuropathy, visual deficits, and gastrointestinal problems. Treatment with a chelating agent led to a full recovery in all individuals, except in five people, who suffered irreversible visual impairment. Biomonitoring of this population revealed higher levels of thallium in hair and urine compared to a control group. In the exposed group, urinary levels of thallium were 0.6 to 2.25 mg/L compared to 0.14 to 0.31 mg/L in the unexposed group.[1] An environmental investigation of the area revealed that waste slag from the nearby mining industry had contaminated the soil in family gardens. Garden soils in the most affected areas averaged 43.2 mg/kg thallium. The investigation further revealed that the consumption of cabbage grown in the contaminated soil (containing average thallium levels of 41.7 mg/kg) was the major source of the widespread thallium toxicity.

Brockhuas et al. (1981, as cited in Repetto et al., 1998) reported thallium toxicity in a population living in the vicinity of a cement plant in Germany. This population was not as highly exposed as the Chinese population described above; the mean urinary thallium concentration in exposed individuals was 2.6 µg/L, with a maximum level of 75.6 µg/L. While some symptoms consistent with thallium toxicity were observed, such as sleep and psychological disorders, some of the symptoms most characteristic of thallium toxicity (*e.g.*, hair loss and gastrointestinal disorders) were not increased in the more highly exposed individuals. Again, the population was presumed

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[1] Note that compared to the general population, the control group in this study had relatively high urinary thallium concentrations, most likely due to the widespread contamination in the area. However, despite the relatively high urinary levels in the control group, this group did not experience any significant adverse health effects.

to have received the most exposure from vegetables and fruit grown in nearby contaminated soil. Neither the incidental ingestion of soil (even for young children) nor the inhalation of dust was considered to be a significant pathway of thallium exposure.

One study on the potential developmental effects of long-term, environmental exposure to thallium in humans is available. In this retrospective study, Dolgner et al. (1983) examined the incidence of birth defects of 297 children born to mothers living in the vicinity of a cement manufacturing facility in Germany. Of the 297 births, 11 children had confirmed developmental abnormalities; however, there was no pattern of defects, and it was uncertain if rates in the study area were higher than nationwide rates. Also, the study did not control for other possible confounders. Maternal urine samples taken at the time of the study (and not during pregnancy) indicated that mothers giving birth to children with developmental abnormalities had lower than average thallium exposure compared to the rest of the exposed population. Due to these issues, the authors concluded that a causal relationship between thallium and human birth defects was unlikely. This conclusion is consistent with information on women intentionally or accidentally poisoned during pregnancy. In a review of 25 cases of thallium poisoning in pregnant women from 1903 to 2000, Hoffman (2000) reported significant fetal effects only at doses that were maternally toxic. In fact, in many cases even though the mother experienced severe thallium toxicity, children had no symptoms.

Reproductive and developmental toxicity has also been studied in animal models. Experiments have shown chicks to be more sensitive than mammals. Mammals (mice, rabbits, and rats) showed only slight teratogenic effects, even when mothers experienced significant toxicity (Gibson et al., 1967, as cited in Gregotti and Faustman, 1998). Some scientists have attributed the lower teratogenic potential in mammals (including humans) compared to chicks to a limited ability for thallium to cross the placenta (Leonard and Gerber, 1997).

While all of the human studies above describe thallium exposure and potential adverse heath outcomes, it should be noted that in most cases exposure was not limited to thallium. Co-exposure to other toxic compounds could have played a role in observed health effects.

Cancer Health Effects

No human or animal studies demonstrate that thallium causes cancer (Leonard and Gerber, 1997). Moreover, there is convincing evidence that thallium is not mutagenic (*i.e.*, causing direct DNA damage). Some genotoxicity reports exist for thallium, but many of the experiments involved co-exposure to other compounds (Gregotti and Faustman, 1998). In a review of the evidence for potential carcinogenicity of thallium compounds, Leonard and Gerber (1997) concluded that "[i]nformation on mutagenic, carcinogenic risks of thallium and its compounds are extremely scanty, but what is available does not indicate that thallium could be mutagenic or carcinogenic." They further noted that, from a public health perspective, noncancer toxicity is more important than any carcinogenic risk from thallium (if it exists).

Thallium Human Health Risk Assessment

Noncancer and cancer toxicity information is used to develop chemical-specific toxicity factors, which are used to quantitatively evaluate human health risks. Reference doses (RfDs) are used to assess noncancer risks, and cancer slope factors (CSFs) are usually used to evaluate cancer risks. All U.S. EPA-derived toxicity factors are published on the Integrated Risk Information System (IRIS). The IRIS database serves as an important resource because it allows scientists to standardize the risk assessment process by using a common set of toxicity criteria.

Evaluation of Noncancer Risks

As defined by the U.S. EPA, an RfD is intended to represent a level of daily human exposure experienced over the course of a lifetime that is likely to be without an appreciable risk of deleterious effects, even for susceptible members of the population (U.S. EPA, 1993). For noncancer risks, a threshold for chemical toxicity is typically assumed (*i.e.,* there is a dose below which adverse health effects are not observed). To derive an RfD, the chemical-specific threshold dose must be defined. This is accomplished by identification of a Lowest-Observed-Adverse-Effect-Level (LOAEL) and/or a No-Observed-Adverse-Effect-Level (NOAEL), from either human epidemiology or laboratory animal toxicology studies. After determining the NOAEL or LOAEL, this dose is divided by uncertainty factors (UFs) to account for potential uncertainties (including inter- and intra-species differences in sensitivity, insufficient study durations, use of a LOAEL instead of a NOAEL, and data deficiencies) to arrive at a final RfD. The application of UFs in the derivation of the RfD helps ensure that the RfD is health-protective. It should be noted, however, that, according to the U.S. EPA, "it should not be categorically concluded that all doses below the RfD are 'acceptable' (or will be risk-free) and that all doses in excess of the RfD are 'unacceptable' (or will result in adverse effects)" (U.S. EPA, 1993).

Derivation of the U.S. EPA Oral RfD for Thallium Compounds

U.S. EPA (2007a-e) derived oral RfDs for thallium compounds based on the results of a 90-day subchronic study in which rats were treated orally with solutions of thallium (I) sulfate (U.S. EPA, 1986a). Data generated from this study included information on body and organ weights, food consumption, hematology and clinical chemistry parameters, neurotoxicologic examinations, ophthalmologic examinations, histopathology, and neuropathology. The authors reported apparent dose-related increases in the incidence of alopecia, lacrimation, and abnormal eye protrusion (*i.e.*, exophthalmos) throughout the study, as well as subtle dose-related changes in some blood chemistry parameters. The only significant clinical observation at necropsy thought to be treatment-related was alopecia, particularly in female rats. However, the alopecia occurred without a consistent anatomical pattern and microscopic evaluation did not reveal any histopathologic alterations (U.S. EPA, 1986a, 2007a). Based on the results of this study, U.S. EPA (2007a) identified the highest dose, 0.25 mg/kg/day thallium sulfate, as a NOAEL.

The NOAEL for thallium sulfate was converted to corresponding NOAELs for each of the other thallium compounds based on molecular weights (U.S. EPA, 2007b-e). U.S. EPA then divided each NOAEL by an uncertainty factor of 3,000 (includes factors of 10 to extrapolate from

subchronic to chronic data, 10 for intraspecies extrapolation, 10 to account for interspecies variability, and 3 to account for lack of sufficient reproductive and chronic toxicity data) to arrive at a chronic oral RfD. The resulting RfDs (and corresponding NOAELs) for each of the thallium compounds evaluated by U.S. EPA are shown in Table 3-1. For example, the resulting RfD was 0.00008 mg/kg/day for thallium sulfate (U.S. EPA, 2007a). Both U.S. EPA Region III and Region IX have also adjusted the oral RfD for thallium sulfate, based on the molecular weight of thallium relative to thallium sulfate, to derive an oral RfD of 0.00007 mg/kg-day (rounded) for elemental thallium (U.S. EPA, 2004a). It should be noted that given the large amount of uncertainty incorporated into the RfD, thallium risks estimated in a risk assessment are conservative, and likely overestimate human health risks to a significant degree.

Table 3-1
NOAELs and RfDs for Thallium Compounds Evaluated by U.S. EPA

Compound	Molecular Weight	NOAEL (mg/kg/day)	RfD (mg/kg/day)
Thallium sulfate	504.8	0.25	0.00008
Thallium nitrate	266.4	0.26	0.00009
Thallium chloride	239.8	0.23	0.00008
Thallium carbonate	468.8	0.23	0.00008
Thallium acetate	263.4	0.26	0.00009
Thallium (elemental)	204.4	--	0.00007

Potential Revision to the U.S. EPA Oral RfD for Thallium Compounds

In January 2008, U.S. EPA issued a draft revision to the oral RfD for thallium, resulting in an oral RfD of 0.00002 mg/kg/day. This value is approximately 4 to 4.5 times lower than the current value, and results from a lowered NOAEL level from 0.25 mg/kg/day to 0.05 mg/kg/day for thallium sulfate. A lowered NOAEL results from a difference in interpretation of the same principal study – the interpretation that alopecia and atrophy of the hair follicles in female rats at 0.05 mg/kg/day was an adverse effect attributable to thallium. The previous interpretation of the rat study considered alopecia to be attributable to the cyclic pattern of hair growth in rodents, not of biological significance. However, the uncertainty in this derivation is considered high (confidence is low). Currently, no changes have been made to the IRIS database.

Derivation of the ATSDR MRL for Thallium

The Agency for Toxic Substances and Disease Registry (ATSDR) independently develops chemical-specific toxicity criteria based on noncancer health effects. The ATSDR values are termed Minimal Risk Levels (MRLs), and are defined as "an estimate of daily human exposure to a substance that is likely without an appreciable risk of adverse effects (noncarcinogenic) over a specified duration of exposure." For thallium, ATSDR did not find the data to be sufficient to derive any MRLs (ATSDR, 1992).

Evaluation by the International Programme on Chemical Safety

The International Programme on Chemical Safety (IPSC) is a joint committee of the United Nations, the International Labour Organization, and the World Health Organization. The IPSC (1996) evaluation of potential thallium risk determined that, while there was uncertainty, thallium exposure producing urinary thallium levels of 5 µg/L or less (at steady state) was unlikely to be associated with any adverse health effects. This urinary level corresponds to a thallium intake of about 10 µg/day. They further determined that thallium exposure resulting in urinary levels of thallium between 5 and 500 µg/L was associated with uncertain toxicological outcomes that vary greatly among individuals, while exposure producing over 500 µg/L was clearly linked to adverse clinical outcomes.

Evaluation of Cancer Risks

Thallium carcinogenicity has not been adequately evaluated in humans or animals (OEHHA, 1999; IPCS, 1996). However, as discussed in the cancer health effects section, thallium is not mutagenic and there has been no evidence of cancer in individuals with elevated thallium exposures. U.S. EPA classifies the evidence for human carcinogenicity of thallium compounds as Classification D – not classifiable as to human carcinogenicity (U.S. EPA, 2007a-e). Therefore, no cancer slope factor (CSF) has been derived for thallium.

Regulations and Screening Criteria for Thallium in Soils, Tap Water, and Ambient Air

Regulatory standards and criteria for environmental media are derived using toxicity criteria (RfDs and CSFs), human exposure assumptions, and other information. For drinking water, the U.S. EPA establishes Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs). An MCLG is a non-enforceable regulatory standard that, according to U.S. EPA, reflects "the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety" (U.S. EPA, 2006a). Establishing a non-enforceable (and non-achievable) MCLG is consistent with U.S. EPA's general regulatory approach for drinking water contaminants. For most water contaminants, U.S. EPA also establishes an enforceable standard called an MCL. An MCL is set as close to the MCLG as possible while considering factors such as feasibility and cost-benefit. U.S. EPA has established an MCLG of 0.0005 mg/L (0.5 µg/L) and an MCL of 0.002 mg/L (2 µg/L) for thallium (U.S. EPA, 2006a; U.S. EPA, 1992a). The MCL has been set at 2 µg/L because U.S. EPA believes that, given present technology and resources, this is the lowest level to which water systems can reasonably be required to remove this contaminant should it occur in drinking water (U.S. EPA, 2006b).

In contrast to enforceable standards, Ambient Water Quality Criteria (AWQC) and cleanup criteria, such as Soil Screening Levels (SSLs), serve as non-enforceable recommendations. AWQCs are developed by U.S. EPA based on human health risk assessments, without consideration of technological feasibility or economic impact (U.S. EPA, 2000).

The U.S. EPA has developed an AWQC of 0.24 µg/L for thallium to protect human health (U.S. EPA, 2006c). U.S. EPA assumes that surface water is potable, and that organisms living in water systems will be consumed in the diet. It also considers water use for agriculture and recreational purposes. Additionally, the AWQC establishes thallium levels to protect plants and animals in the environment. These criteria are discussed in more depth in the section "Ecological Regulatory Criteria and Guidelines."

Soil Screening Levels (SSLs) are generic, risk-based values developed by U.S. EPA's Office of Solid Waste and Emergency Response (OSWER). They are used to screen sites to determine if additional investigation is needed. SSLs are based on reasonable maximum exposure (RME) scenarios for residential settings, and are derived to reflect exposure concentrations that will not exceed a hazard quotient of 1 for noncarcinogens or a cancer risk of $1x10^{-6}$ for carcinogens (U.S. EPA, 1996). SSLs have been developed by the U.S. EPA using default exposure values and are acknowledged to be conservative and thus health-protective for the majority of sites (U.S. EPA, 1996). As noted by U.S. EPA (1996), exceedance of an SSL does not automatically trigger remediation activities, but rather indicates that further evaluation of the site is warranted to determine if remediation is necessary. In 2002, OSWER published supplemental guidance for developing SSLs as a companion to the 1996 guidance (U.S. EPA, 2002). It builds upon the soil screening framework for residential land use scenarios established in the original guidance, adding new scenarios for soil screening evaluations. It also updates the residential scenario in the 1996 guidance, adding exposure pathways and incorporating new modeling data. SSLs for thallium, as presented in U.S. EPA guidance (2002), are presented in Table 3-2.

U.S. EPA Region III (2003, 2008) and Region IX (U.S. EPA Region IX, 2004a,b) have independently developed screening levels for soil (residential and industrial), as well as screening criteria for tap water and ambient air, for several hundred chemicals, including thallium. These screening criteria are called risk-based concentrations (RBCs) and preliminary remediation goals (PRGs), by Region III and Region IX, respectively. A comparison of the RBC and PRG values for thallium shows slight differences (see Table 3-2 below). For example, in calculating the residential and industrial soil RBC for thallium (5.2 mg/kg; 67 mg/kg), Region IX assumed that the resident or worker would be exposed to thallium through incidental ingestion, dermal contact, and inhalation of soil particulates, whereas Region III (5.5 mg/kg; 72 mg/kg) considered exposure only through the incidental ingestion pathway (U.S. EPA Region IX, 2004a,b; U.S. EPA Region III 2003, 2008).

In addition to the direct contact scenarios, the U.S. EPA has also developed SSLs to protect groundwater from chemicals that may leach (Table 3-2). OSWER has developed SSLs for two dilution attenuation factors (DAFs): 1 and 20. A DAF of 1 means that no dilution or attenuation is assumed, and that the concentration at the receptor point is equivalent to the leachate concentration. A DAF of 20 assumes that dilution and attenuation cause concentration at the receptor to be 1/20th of the leachate concentration. Although the attenuation varies widely from chemical to chemical and is dependent on numerous variables such as soil characteristics and depth to groundwater, U.S. EPA has assumed that all chemicals have a DAF of 1 or 20. OSWER and Region III U.S. EPA have developed soil screening levels for thallium based on migration to groundwater assuming DAFs of 1 and 20.

Table 3-2
Regulatory Screening Criteria for Thallium in Soil, Water, and Air

Source	Residential Soil (mg/kg)	Industrial Soil (mg/kg)	Drinking Water (µg/L)	Air (µg/m^3)	Soil-Migration to Groundwater (mg/kg)	
					DAF 20 (mg/kg)	DAF 1 (mg/kg)
U.S. EPA MCL	NA	NA	2	NA	NA	NA
U.S. EPA AWQC	NA	NA	0.24	NA	NA	NA
U.S. EPA SSL	6	91/160[a]	NA	NA	0.7	0.04
U.S. EPA Region IX PRG	5.2	67	2.4	NA	NA	NA
U.S. EPA Region III RBC	5.5	72	2.6	0.26	3.6	0.18

[a] Both values are for the commercial/industrial scenario; the first value is for the outdoor worker receptor; the second value is for the indoor worker receptor.

PRG – Preliminary Remediation Goal

RBC – Risk-Based Concentration

SSL – Soil Screening Levels from Soil Screening Guidelines

MCL – Maximum Contaminant Level

AWQC – Ambient Water Quality Criteria (assuming human consumption of water and aquatic organisms)

NA – Not applicable or Not Available

Thallium is not a common environmental contaminant. ATSDR (1992) noted that, of the 1,177 National Priority List sites identified by U.S. EPA at that time, thallium (in excess of screening criteria) had been found at only 18 of them (though the number of sites evaluated for this chemical is unknown). A review of U.S. EPA decisions regarding hazardous waste site cleanups (U.S. EPA, 2006d) revealed that thallium, when identified, is not often found at levels exceeding screening criteria. It is important to note, however, that when exceedances of screening criteria do occur, they do not necessarily warrant regulatory action (*e.g.*, cleanup). A regulatory screening criterion is not a bright-line that separates acceptable risk from unacceptable risk; what constitutes an acceptable risk is determined on a case-by-case basis.

Human Health Risk Assessment Toolbox

Government websites and reports provide useful information on risk assessment. The list below presents some of the key human health risk assessment resources. Some resources are specific to thallium, while others present information on a wide range of environmental contaminants.

Thallium-Specific Resources

U.S. EPA's IRIS file for Thallium sulfate (CASRN 7446-18-6) (U.S. EPA, 2007 a-e)
Website: http://www.epa.gov/iris/subst/0116.htm

ATSDR's Toxicological Profile for Thallium (ATSDR, 1992)
Website: http://www.atsdr.cdc.gov/toxprofiles/tp54.pdf

U.S. EPA's Ground Water and Drinking Water Consumer Fact Sheet on Thallium (U.S. EPA, 2006b)
Website: http://www.epa.gov/safewater/contaminants/dw_contamfs/thallium.html

General Resources

U.S. EPA's Soil Screening Guidance: Technical Background Document (U.S. EPA, 1996)
Website: http://www.epa.gov/superfund/health/conmedia/soil/toc.htm

U.S. EPA's Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites (U.S. EPA, 2002)
Website: http://www.epa.gov/superfund/health/conmedia/soil/pdfs/ssg_main.pdf

Current National Recommended Water Quality Criteria (U.S. EPA, 2006c)
Website: http://www.epa.gov/waterscience/criteria/wqcriteria.html

U.S. EPA Region IX Preliminary Remediation Goal (PRG) Table and User's Guide (U.S. EPA, Region IX, 2004a,b)
PRG Table Website: http://www.epa.gov/region09/waste/ sfund/prg/files/04prgtable.pdf
User's Guide Website http://www.epa.gov/region09/waste/ sfund/prg/files/04usersguide.pdf

U.S. EPA Region III RBC Table and User's Guide (U.S. EPA, Region III, 2003, 2008)
RBC table website: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/index.htm
User's guide website: http://www.epa.gov/reg3hwmd/risk/human/info/tech.htm

4

ECOLOGICAL EFFECTS AND RISK ASSESSMENT

Ecological effects of thallium in wildlife occur mostly via exposure to water, sediment, soil, and food (*e.g.,* plant material). Since most anthropogenic sources of thallium in the environment are emissions and solid wastes from smelting, mining, cement production, and coal combustion, thallium is either deposited on the earth's surface via atmospheric deposition or released to surface water via industrial wastewater. The toxicity of thallium to aquatic species is the major focus of this section, but discussions on terrestrial toxicity, plant uptake and accumulation, and regulatory SSLs for the protection of plants and wildlife are also presented. The final part of this section discusses the wider implications of thallium toxicity values and regulatory guidelines for the protection of wildlife.

Thallium Toxicity to Aquatic Species

This section presents information on thallium toxicity to a wide range of aquatic species for several different endpoints.

Procurement and Selection of Ecotoxicity Data

Ecotoxicity data are collected for species considered to be representative of, or that can serve as indicator species for, each trophic level that comprises the ecosystem. The trophic level of an organism indicates its position in the food chain. For aquatic ecosystems, plants such as alga (*e.g., Pseudokirchneriella subcapitata*) represent the primary producers, and daphnids (*e.g.,* *Daphnia magna*) and fish [*e.g.*, fathead minnow (*Pimephales promelas*)] represent primary and secondary consumers, respectively. In general, these three species (alga, daphnids, and fish) are representative of plants, invertebrates, and vertebrates, respectively, in aquatic environments.

A robust review of the pre-1980 data is available in the thallium AWQC document (U.S. EPA, 1980). The AWQC for the protection of aquatic life are regulatory criteria used to evaluate compliance with the Clean Water Act. However, due to insufficient data, numerical thallium AWQC for the protection of ecological receptors were not developed; instead, the Lowest Observed Effects Level (LOEL) values were presented (U.S. EPA, 1980; 1986b). The range and geometric mean of acute and chronic values (in terms of total thallium concentration) by species based on the review of pre-1980 data on thallium are presented in Table 4-1.

Table 4-1
Summary of Pre-1980 Aquatic Toxicity Data for Thallium[a]

Species	Species Mean Acute Value[b] (µg/L)	Range of Acute Values[c] (µg/L)	Species Mean Chronic Value[d] (µg/L)	Range of Chronic Values[e] (µg/L)
Freshwater Species				
Invertebrates				
Water Flea (*Daphnia magna*)	1,400	910-2,180	130	100-181
Vertebrates				
Fathead Minnow (*Pimephales promelas*)	1,800		57	40-81
Bluegill (*Lepomis macrochirus*)	126,000	121,000-132,000		
Plants				
Alga (*Pseudokirchneriella subcapitata*)		100-110[f]		
Alga (*Chlamydomonas reinhardi*)	40,800			
Saltwater Species				
Invertebrates				
Mysid (*Americamysis bahia*)	2,130			
Vertebrates				
Sheepshead Minnow (*Cyprinodon variegatus*)	20,900		6,000	4,300-8,400
Tidewater Silverside (*Menidia beryllina*)	24,000			
Plants				
Alga (*Dunaliella tortolecta*)	4,080			
Alga (*Phaeodactylum tricornutum*)	51,200			

Notes:

[a] All data are from the thallium AWQC Document (U.S. EPA, 1980).

[b] Represents the geometric mean of the available acute values.

[c] Represents the range of reported LC50 (lethal concentration for 50% of test organisms) or EC50 (effective concentration for 50% test organisms) values.

[d] Represents the geometric mean of the available chronic values.

[e] Represents the range of chronic toxicity values involving embryo-larval, life cycle, or partial life cycle tests.

[f] Represents range of benchmark values for different endpoints such as chlorophyll inhibition and cell number.

The post-1980 thallium data represented in this section were obtained by searching the most relevant journals and the ECOTOX database (U.S. EPA, 2007f), a freely available online database of ecotoxicological data compiled from primary literature. Benchmarks developed from toxicity studies are presented for comparison across species and, where available, under different exposure conditions. Example benchmarks include lethal concentrations for half of the test organisms (LC50s), inhibition concentrations for 25% of the test organisms (IC25s), and no observed effect concentrations (NOECs). Thallium screening criteria described later in this section were derived by considering a large body of toxicity data, such as those shown in Tables 4-2 to 4-4. To determine the potential for ecological risk from thallium, the criteria values are compared to thallium concentrations in site soil or surface water. Toxicity to individual species is relevant only if a specific species is targeted, *e.g.*, for threatened or endangered species or commercially important species.

Sensitivity of Aquatic Animals to Thallium

Aquatic species differ widely in their sensitivity to thallium. Tables 4-2 and 4-3 summarize thallium ecotoxicity data for freshwater and saltwater organisms, respectively; listed values include LC50, NOEC, EC50 (concentration at which effects are observed in 50% of the organisms tested), etc. The experimental designs are also listed in Tables 4-2 and 4-3. In a static test (S), the test solution is not refreshed, so thallium concentration may decrease during the test. In contrast, the solutions are refreshed either continuously in a flow-through test (F) or intermittently in a renewal test (R) to ensure that the test organisms are exposed to a constant thallium concentration during the test.

Acute toxicity of thallium to freshwater invertebrates varies widely (Table 4-2); the acute benchmark values range from 100 μg/L [for a scud (*Gammarus minus*)] to 1,460,000 μg/L [for a stonefly (*Tallaperla maria*)]. A lower variance, but still representing a wide sensitivity, is also observed for acute thallium toxicity to freshwater fish (Table 4-2); the 96-hour LC50 value for fathead minnow (*Pimephales promelas*) is about 140 times lower than that for bluegill (*Lepomis machrochirus*). Although daphnids appear to be less sensitive than *P. Promelas*, daphnids are generally more sensitive than fish to acute toxicity due to thallium (Table 4-2). Higher sensitivity of daphnids than fish to acute thallium toxicity is also reflected in species mean acute values based on pre-1980 data—1,400 μg/L for *D. magna* and 126,000 μg/L for *L. macrochirus* (Table 4-1).

Table 4-2
Summary of Post-1980 Freshwater Aquatic Toxicity Data for Thallium

Species Common Name (Scientific Name)	Endpoint[a]	Effect Measurement	Test Duration	Exposure Type[b]	Concentration (µg/L)	Reference
Invertebrates						
Fairy shrimp (*Streptocephalus proboscideus*)	LC50	Mortality	24 hours	NA	163.5	Calleja et al. (1994)
Midge (*Chironomus riparius*)	LC50	Mortality	96 hours	S	229,000	Horne et al. (1983)
Nematode (*Caenorhabditis elegans*)	LC50	Mortality	96 hours	S	123,000	Williams and Dusenbery (1990)
Pond snail (*Physa heterostropha*)	LC50	Mortality	96 hours	S	2,700	Horne et al. (1983)
Rotifer (*Brachionus calyciflorus*)	LC50	Mortality	24 hours	NA	3,843	Calleja et al. (1994)
Scud (*Hyalella azteca*)	EC25	Reproduction	10 weeks	S	4.50	Borgmann et al. (1998)
	EC25	Growth	6 weeks	S	7.12	Borgmann et al. (1998)
	LC25	Mortality	4 weeks	S	9.81	Borgmann et al. (1998)
Scud (*Gammarus minus*)	LC50	Mortality	96 hours	S	100.0	Horne et al. (1983)
Stonefly (*Tallaperla maria*)	LC50	Mortality	96 hours	S	1,460,000	Horne et al. (1983)
Water flea (*Ceriodaphnia dubia*)	LC50	Mortality	7 days	S	370	Pickard et al. (2001)
	IC25	Reproduction	7 days	S	100	Pickard et al. (2001)
Water flea (*Daphnia magna*)	EC50	Immobility	24 hours	NA	1,697	Calleja et al. (1994)
	LC50	Mortality	48 hours	S	2,010	Pickard et al. (2001)
Water flea (*Daphnia pulex*)	EC50	Immobility	24 hours	S	1,876	Lilius et al. (1995)

Table 4-2
Summary of Post-1980 Freshwater Aquatic Toxicity Data for Thallium (continued)

Species Common Name (Scientific Name)	Endpoint[a]	Effect Measurement	Test Duration	Exposure Type[b]	Concentration (µg/L)	Reference
Vertebrates						
Bluegill (*Lepomis macrochirus*)	LC50	Mortality	24 hours	S	> 600,000	Buccafusco et al. (1981)
	LC50	Mortality	96 hours	S	120,000	Buccafusco et al. (1981)
Fathead minnow (*Pimephales promelas*)	LC50	Mortality	96 hours	NA	860	LeBlanc and Dean (1984)
	MATC	Mortality	30 days	F	< 40	LeBlanc and Dean (1984)
Rainbow trout (*Oncorhynchus mykiss*)	LC50	Mortality	96 hours	S	2,300	Horne et al. (1983)
	LC50	Mortality	96 hours	S	4,270	Pickard et al. (2001)
Plants						
Duckweed (*Lemna minor*)	EC50	Growth	10 days	R	32.7-47.0	Kwan and Smith (1988)
Green algae (*Pseudokirchneriella subcapitata*)	IC25	Growth	72 hours	S	90	Pickard et al. (2001)

Notes:

[a]   LC50 = Lethal concentration to 50% of test organisms; ECX = Effective concentration for x% of tested organisms; IC25 = Inhibition concentration resulting in 25% with respect to control; MATC = Maximum Acceptable Toxicant Concentration [theoretical threshold geometric mean between the NOEC and LOEC (lowest observed effect concentration)].

[b]   R = Renewal; S = Static; F = Flow-through; NA = Not available.

Table 4-3
Summary of Post-1980 Saltwater Aquatic Toxicity Data for Thallium

Species Common Name (Scientific Name)	Endpoint[a]	Effect Measurement	Test Duration	Exposure Type[b]	Concentration (µg/L)	Reference
Invertebrates						
Bay shrimp (*Crangon septemspinosa*)	LC50	Mortality	48 hours	S	2,500	Horne et al. (1983)
Brine shrimp (*Artemia salina*)	LC50	Mortality	24 hours	NA	16,148	Calleja et al. (1994)
Calanoid copepod (*Acartia tonsa*)	LC50	Mortality	48 hours	S	2,400	Horne et al. (1983)
Daggerblade grass shrimp (*Palaemonetes pugio*)	LC50	Mortality	48 hours	S	5,600	Horne et al. (1983)
Scud (*Gammarus annulatus*)	LC50	Mortality	48 hours	S	4,200	Horne et al. (1983)
Polychaete worm (*Neanthes arenaceodentata*)	LC50	Mortality	48 hours	S	17,000	Horne et al. (1983)
Vertebrates						
Sheepshead minnow (*Cyprinodon variegatus*)	NOEC	Mortality	96 hours	S	14,000	Heitmuller et al. (1981)
	LC50	Mortality	96 hours	S	21,000	Heitmuller et al. (1981)
	LC50	Mortality	24 hours	S	> 45,000	Heitmuller et al. (1981)

Table 4-3
Summary of Post-1980 Saltwater Aquatic Toxicity Data for Thallium (continued)

Species Common Name (Scientific Name)	Endpoint[a]	Effect Measurement	Test Duration	Exposure Type[b]	Concentration (µg/L)	Reference
Plants						
Diatom (*Phaeodactylum tricornutum*)	NA	Growth	NA	S	143.1[c]	Puddu et al. (1988)
Diatom (*Ditylum brightwellii*)	EC50	Growth	5 days	S	330	Canterford and Canterford (1980)
	NA	Mortality	5 days	S	750	Canterford and Canterford (1980)
Green algae (*Dunaliella tertiolecta*)	NA	Growth	NA	S	81.8[c]	Puddu et al. (1988)

Notes:

NA Not available

[a]   EC50 = Effective concentration for 50% of test organisms; LC50 = Lethal concentration for 50% test organisms; NOEC = No observed effect concentration

[b]   S = Static

[c]   The endpoints and the test durations are not available

Thallium's chronic toxicity to aquatic species has not been investigated as extensively as its acute toxicity. Species' mean chronic values of 130 μg/L for *D. magna* and 57 μg/L for *P. promelas* are reported based on a review of pre-1980 data (U.S. EPA, 1980). These species' mean chronic values are comparable to the chronic benchmark values in Table 4-2; IC25 for a seven-day reproduction test with *C. dubia* is 100 μg/L (Pickard et al., 2001) and MATC (maximum acceptable toxicant concentration) for a 30-day mortality test for *P. promelas* is < 40 μg/L (LeBlanc and Dean, 1984). More recently, Borgmann et al. (1998) reported results from 4- to 10-week-long tests, in which LC25 and EC25 values ranged from 4.50 to 9.81 μg/L for thallium toxicity to scuds (*Hyella azteca*) (Table 4-2). These lower EC25 values indicate a potential for chronic effects of thallium on aquatic organisms. However, inhibitory effects of potassium ions (K^+) observed in the same study (Borgmann et al., 1998) and the overall bioavailability of thallium need further assessment. The absence of K^+ in artificial medium reduced the six-week EC25 to 1.76 μg/L from 7.15 μg/L (in tap water with K^+), but the effective body concentrations remained statistically the same: 41.9 mg/kg vs. 48.4 mg/kg. These results indicate that thallium can exert toxic effects on *H. azteca* only after it enters the body, and that thallium uptake may be inhibited by the presence of K^+ and other aquatic conditions. The effect of potassium is significant because it is typically present in CCP leachate (EPRI, 2006). Therefore, in assessing thallium toxicity to aquatic organisms, the modifying effects of site-specific conditions on bioavailability should be considered.

Saltwater animals appear to vary less widely than the freshwater animals in their sensitivities to thallium toxicity. The LC50 values for the saltwater animals range from 2,400 μg/L for calanoid copepod (*Acartia tonsa*) to 21,000 μg/L for sheepshead minnow (*C. variegates*). The thallium AWQC document reports a similar range for acute toxicity to saltwater species; benchmark values range from 2,130 μg/L for mysids (*Americamysis bahia*) to 24,000 μg/L for tidewater silverside (*Menidia beryllina*). These data also indicate that saltwater animals are likely to be less sensitive to acute thallium toxicity than the most sensitive freshwater animals, based on dissolved thallium concentrations.

Sensitivity of Aquatic Plants to Thallium

Plants are generally more sensitive to thallium toxicity than animals (Tables 4-2 and 4-3), with freshwater plants showing similar sensitivities. At concentrations ranging from 32.7 to 47.0 μg/L, thallium inhibited duckweed (*Lemna minor*) growth by 50% in 10 days (Kwan and Smith, 1988). A 25% inhibition in algae growth occurred at 90 μg/L (Pickard et al., 2001). Based on post-1980 data, lower plants (alga and diatoms) have similar sensitivities to thallium both in freshwater and saltwater, with benchmark values ranging from 81.8 to 330 μg/L (Tables 4-2 and 4-3).

Thallium Toxicity to Terrestrial Species

The effects of thallium on wildlife in the context of its use as a pesticide are not reviewed here. According to a study carried out between 1977 and 1981, no elevated levels of thallium were found in birds (Wiemeyer et al., 1986) following the 1972 ban on thallium use in pesticides in the U.S. (Smith and Carson, 1977). An extensive review of thallium toxicity to terrestrial animals and plants by the International Programme on Chemical Safety (IPCS, 1996) is

available; however, a majority of the reported benchmark values are based on either the body burden (*i.e.*, mg thallium/kg animal tissue) or the uptake (*i.e.*, mg thallium/kg plant dry weight). These benchmark values are not reviewed here because they do not represent thallium concentrations in the medium of concern (*e.g.*, soil or soil porewater) and cannot be compared directly to environmental thallium screening guidelines.

In a study by Heim et al. (2002), the hatching success for the snail (*Arianta arbustorum*) was the most sensitive endpoint—LOEC of 1 mg/kg—for thallium toxicity to soil invertebrates. In the same study, an LOEC of 10 mg/kg was reported for thallium toxicity toward plant growth [garden cress (*Lepidium sativum*)]. The LOEC values for terrestrial organisms from Heim et al. (2002) are presented in Table 4-4. Benchmark values based on solution concentrations may also be relevant when soil porewater concentration of thallium is available at a site. For plant seedlings [ryegrass (*Lolium perenne*)], an NOEC of 0.1 mg thallium/L in nutrient solution has been reported (Al-attar et al., 1988).

Table 4-4
Soil Thallium LOEC for Terrestrial Organisms

Species Common Name (Scientific Name)	Effect Measurement	Test Duration	Concentration (mg/kg)
Invertebrates:			
Earthworm (*Eisenia fetida*)	Mortality	4 weeks	500
	Growth	4 weeks	100
	Reproduction (No. Cocoons)	4 weeks	250
	Reproduction (No. Juveniles)	8 weeks	5
Snail (*Arianta arbustorum*)	Reproduction (Hatching)	4-7 weeks	1
	Growth	4 weeks	100
Plant:			
Garden Cress (*Lepidium sativum*)	Root Growth	7 days	100
	Shoot Growth	7 days	10

Note: Data are from Heim et al. (2002).

Ecotoxicity of Thallium (I) vs. Thallium (III)

Studies conducted before 1980 lack a general consensus regarding the relative toxicity of monovalent thallium (Tl(I)) and trivalent thallium (Tl(III)). For example, while Tl (III) was more toxic to a fungus (*Colletotrichum falcatum*) at low concentrations than Tl(I) (1 and 5 mg/L), Tl(I) was more toxic at higher concentrations than Tl(III) (Srivastava et al., 1973). In contrast, Tl(I) affected the growth of pea plants more than Tl(III) at concentrations of 0.2 to 3 mg/L (Logan et al., 1984).

A more recent study (Ralph and Twiss, 2002) has shown Tl(III) to be intrinsically more toxic than Tl(I) (*i.e.*, in terms of free ion concentration); however, at environmental conditions, Tl(I) is likely to be more toxic than Tl(III) due to differences in Tl(I) and Tl(III) chemistry. Whereas Tl(III) is strongly hydrolyzed to $Tl(OH)_3$ species, Tl(I) is not hydrolyzed readily. The first hydrolysis constant for Tl(III) (log $K_{TlOH^{2+}}$) equals 11.3, and that for Tl(I) is 2.3—nine orders of magnitude lower. Therefore, Tl(III) requires over eight orders of magnitude more dissolved concentration of thallium than Tl(I) to achieve the same free ion concentration (Ralph and Twiss, 2002). Consequently, even if Tl(III) is approximately 50,000 times more toxic than Tl(I) toward unicellular alga (*Chlorella* sp.) in terms of the respective free ion concentrations, Tl(I) is likely to control thallium toxicity at environmental conditions (Ralph and Twiss, 2002). Since Tl(I) is the most dominant thallium species in the environmental pH and Eh (Vink, 1993), and is effectively more toxic than Tl(III), this section focuses on the ecological effects of Tl(I).

Thallium Uptake and Accumulation by Plants

Potential for thallium accumulation in plants may be of concern in the context of food-web contamination. Although thallium (I) is not essential as a nutrient, it can be actively taken up by plants because thallium (I) and potassium (K^+)—a macro nutrient—have similar properties (Kwan and Smith, 1988).

In assessing thallium accumulation by plants, the nature of thallium uptake—active vs. passive transport—and environmental thallium concentrations need consideration. If thallium uptake is entirely a biologically mediated process (*i.e.*, active transport as in *L. minor*), the uptake and accumulation of thallium are expected to be controlled at low environmental thallium concentrations. At higher environmental concentrations, thallium's toxic effects on plants may be more important than its accumulation. While plants growing in uncontaminated soils are reported to normally contain 0.01 to 0.3 mg thallium/kg dry weight, those growing in contaminated areas may contain levels as high as 100 to 1,000 mg thallium/kg dry weight (IPCS, 1996). In soils with thallium concentrations ranging from 40 to 124 mg/kg, crops and vegetables accumulated between 0.78 and 495 mg thallium/kg plant dry weight (corn and green cabbage, respectively) (Xiao et al., 2004). Among studied vegetables, cabbages appear to be one of the most significant thallium accumulators (Sager, 1998; Xiao et al., 2004).

Although plants accumulate significant amounts of thallium, the potential risk of thallium enrichment may be mitigated by thallium transformation to less bioavailable forms and other environmental conditions. Sparingly soluble forms of thallium (*e.g.*, chloride salts and polyphosphates) present in soils may not be readily available for uptake. Soil pH also alters the

solubility of thallium in soil porewaters, and thus its availability for uptake by plants (Zhou and Ling, 1985). As soil pH increases (*i.e.*, becomes more alkaline), the amount of thallium available for plant uptake decreases because of increased sorption and hydrolysis of thallium. Additionally, the uptake of thallium by a plant species is inhibited by the presence of competitive cations such as K^+ and Ca^{2+} (Kwan and Smith, 1988). Therefore, in assessing the potential risk of thallium accumulation by plants, the specific plant species and the inhibitory effects of site-specific environmental conditions need to be considered.

Ecological Regulatory Criteria and Guidelines

Because of insufficient data, an AWQC for the protection of aquatic life for thallium has not been determined. Instead, a summary of LOELs are presented (U.S. EPA, 1980; 1986b). The values are presented in Table 4-5, along with other available thallium screening values for the protection of aquatic and terrestrial wildlife. Regulators compare these values to thallium concentrations in site soil or surface water to determine the potential risk of ecological effects. The lower screening values generally consider long-term exposure scenarios and chronic effects, and, therefore, provide a more conservative estimate of levels associated with ecological protection. For example, the Canadian Environmental Quality Guideline of 0.8 μg/L for freshwater aquatic life is intended for the protection of all life stages during an indefinite exposure to thallium in water, *i.e.*, protection of 100% of aquatic species in Canada 100% of the time (CCME, 2002). Screening criteria are typically based on the most sensitive benchmark value (*e.g.*, LOEL) and incorporate safety factors. For example, the Canadian water quality guideline values were derived by multiplying the available LOEL by a safety factor of 0.1, and the U.S. EPA Region IV surface water screening values (Table 4-5) were determined by dividing the LOEL values from the thallium AWQC document by 10. Therefore, these values are typically conservative and are only suitable for screening-level risk assessments.

It is apparent from Table 4-5 that different screening values are recommended for different conditions and risk targets, such as freshwater vs. saltwater environments and acute vs. chronic effects. Therefore, a proper application of a criterion requires adequate understanding of the underlying assumptions regarding the types of organisms, endpoints, and levels of protection desired.

Implications of Thallium Ecological Toxicity Data

Individual benchmark values provided in Tables 4-2 and 4-3 are typically not used to determine potential risk due to thallium at a site. Rather, extrapolations to populations, communities, and ecological functions are considered. The regulatory guidelines provided in Table 4-5 incorporate different trophic levels of an ecosystem as a whole, and target the protection of whole ecosystems. Single-species benchmark values are relevant only in cases where federal- or state-listed threatened or endangered species, or commercially important species, are targeted for protection.

Table 4-5
Water and Soil Quality Criteria and Guidelines for the Protection of Aquatic and Terrestrial Wildlife

Regulatory Agency	Criterion	Concentration	Reference
	For Water	**(µg/L)**	
U.S. EPA	Freshwater LOEL: Acute Chronic Saltwater LOEL: Acute	 1,400 40 2,136	U.S. EPA (1980; 1986b)
U.S. EPA, Region IV	Surface Water Screening Values for Hazardous Waste Sites: Acute Chronic	 140 4.0	U.S. EPA, Region IV (2001)
U.S. EPA, Region V	Ecological Screening Levels for Surface Water	10	U.S. EPA, Region V (2003)
U.S. EPA, Region VI	Surface Water Screening Benchmark: Freshwater Marine	 40 21	TNRCC (2001)
Canadian Environmental Quality Guideline	Freshwater Aquatic Life	0.8	CCME (2002)
U.S. Department Of Energy	Surface Water Screening Benchmarks: LCV Aquatic Plants LCV Daphnids LCV Fish Tier II Surface Water Screening Benchmarks: SAV (Secondary Acute Value) SCV (Secondary Chronic Value)	 100 130 57 110 12	Suter and Tsao (1996)

Table 4-5
Water and Soil Quality Criteria and Guidelines for the Protection of Aquatic and Terrestrial Wildlife (continued)

Regulatory Agency	Criterion	Concentration	Reference
	For Soil	**(mg/kg)**	
Oak Ridge National Laboratory (ORNL)	Soil Screening Benchmark for Plants	1.00	Efroymson et al. (1997)
U.S. EPA, Region IV	Soil Screening Value for Hazardous Waste Sites	1.00	Efroymson et al. (1997)
Canadian Environmental Quality Guideline	Soil Screening Value	1.00	CCME (2002)
U.S. EPA, Region V	Ecological Screening Levels	0.057[a]	U.S. EPA, Region V (2003)
U.S. EPA, Region VI	Surface Soil Screening Benchmark for Plants	1.00	TNRC (2001)
Dutch Ministry Standards	Soil Screening Levels: Intervention Value[b] Target Value[c]	14.0 1.00	Swartjes (1999)

Notes:

LCV = Lowest Acceptable Chronic Value

[a]　Based on exposure to a masked shrew (*Sorex cinerus*)

[b]　The Intervention Value is the concentration expected to be hazardous to 50% of the species in the ecosystem.

[c]　Target Values represent the environmental exposures associated with negligible risk for ecosystems. These values are assumed to be 1% of the Maximal Permissible Risk (MPR) level for ecosystems, where MPR is the concentration expected to be hazardous for 5% of the species in the ecosystem, or the 95% protection level.

The type and the extent of contamination also require consideration in determining potential ecological risks due to thallium. Background levels of thallium at a site may be high due to natural occurrence and diffuse anthropogenic sources. At these sites with high background levels of thallium, thallium-sensitive species may be absent, and the ecosystem may be healthy (*i.e.*, all trophic levels are present and functional). Ecological risks may be unnecessarily overestimated at sites with high background thallium levels by using regulatory criteria representing thallium-sensitive species. Wildlife surveys can be used at these sites with high background levels of thallium to demonstrate that a healthy ecosystem exists, instead of relying on comparisons with regulatory criteria that are not suitable given the site-specific conditions.

The soil screening values (Table 4-5) are within the range of soil background thallium concentrations. Hence, thallium may be perceived as a contaminant of concern even in areas with negligible anthropogenic sources of thallium. In such cases, the potential risks to soil organisms and species diversity may be determined using laboratory tests and soil surveys. Ecological effects may not be observed at specific sites even at concentrations exceeding the screening levels because existing forms of thallium may not be readily bioavailable. Mineralogy, interactions with soil (*e.g.*, sorption and precipitation), and presence of other cations (*e.g.*, K^+ and Ca^{2+}) may mitigate potential exposure of soil organisms to thallium.

Ecological concerns seldom drive thallium cleanup efforts, although thallium is potentially toxic to wildlife at relatively low environmental concentrations (*i.e.*, within the range of natural background). This is because the default thallium regulatory criteria and guidelines for the protection of human health are lower (*i.e.*, more stringent) than for the protection of wildlife. For example, the thallium AWQC of 0.24 µg/L for human health (for the consumption of water and aquatic organisms) is lower than all the surface water screening levels presented in Table 4-5. Ultimately, the cleanup goals for thallium at any given site take into account site-specific circumstances that reduce thallium exposure to both humans and wildlife, so cleanup goals may not necessarily reflect default regulatory screening values. Nevertheless, when both humans and wildlife are potentially exposed to thallium, remediation to achieve human health risk goals is typically more stringent than that required to achieve ecological risk goals. In the absence of human health concerns, ecological concerns can drive thallium remediation.

Ecological Benchmark Toolbox

Government and private websites and reports provide useful information on risk assessment. The list below presents some key ecological risk assessment resources.

Ecological Benchmark Tool (RAIS, 2007)
Website: http://rais.ornl.gov/tools/eco_search.php

This website provides a searchable database with a comprehensive set of ecotoxicological screening benchmarks for surface water, sediment, and surface soil applicable to a range of aquatic organisms, soil invertebrates, and terrestrial plants. Also provided are the links to supporting technical reports from which the benchmarks were obtained.

The ECOTOX Database (U.S. EPA, 2007f)
Website: http://cfpub.epa.gov/ecotox/quick_query.htm

This searchable database provides aquatic and terrestrial life toxicity data and the associated primary literature references, and can be searched by chemical name.

Ecological Risk Analysis: Guidance, Tools, and Applications (ORNL, 2003)
Website: http://www.esd.ornl.gov/programs/ecorisk/contaminated_sites.html

This page contains information that can be used to conduct screening and baseline ecological risk assessments at hazardous waste sites.

Cleanup Levels For Hazardous Waste Sites (Anon., 2001)
Website: http://cleanuplevels.com/cleanup.htm

This private website is a list of primary government sources and their Internet links for cleanup and screening levels at hazardous waste sites.

5
GEOCHEMISTRY, FATE, AND TRANSPORT

Basic Physical and Chemical Properties

Thallium is the heaviest among group IIIA elements, which include boron, aluminum, gallium, and indium. Most thallium compounds are similar to alkali metal compounds, and thallium's aqueous behavior often resembles that of potassium because its most stable valence state is +1 (Table 5-1). Two naturally occurring thallium isotopes are stable, with atomic masses of 202.97 (29.52% abundance) and 204.97 (70.48% abundance). Thallium easily volatilizes during coal combustion. It will readily form thallium (I) oxide (Tl_2O) when exposed to air and moisture, and, at higher temperatures, can form thallium (III) oxide (Tl_2O_3). The hydroxides TlOH and $Tl(OH)_3$ may also occur upon hydration. Generally, TlOH is considered too soluble to precipitate under normal environmental conditions, and $Tl(OH)_3$, although quite insoluble ($K_{sp} = -45.2$), will only exist in very oxidizing environments (Lin and Nriagu, 1997).

Table 5-1
Basic Chemical and Physical Properties of Thallium

Property	Value
Atomic No.	81
Atomic Wt.	204.37
Density, 20°C	11.85 g/cm^3
Melting Point	302°C
Boiling Point	1453°C
Valence	+1,+3
Ionic Radius	1.4 Å (+1) 0.95 Å (+3)
Data from Kaplan and Mattigod (1998) in Nriagu (1998)	

Solid Phase Geochemistry

Thallium Minerals

Thallium in natural settings is closely related to Au, As, Sb, Hg, Pb, and Zn mineralization and typically forms the following associations: Sb-As-Tl, Sb-Pb-Zn-Tl, and Sb-As-Hg (Peter and Viraraghavan, 2005). Accumulation is common in sulfide ores, and several thallium sulfide minerals have been identified (Table 5-2). Thallium occurrence in the world's single thallium-only mine in China is associated with pyrite, lorandite, and hutchinsonite.

Table 5-2
Thallium-bearing Minerals

Mineral Name	Mineral Formula	Mineral Name	Mineral Formula
Crookesite	$(Cu,Tl,Ag)_2Se$	Routhierite	$TlHgAsS_3$
Sabatierite	Cu_6TlSe_4	Hutchinsonite	$(Tl,Pb)_2As_5S_9$
Cuprostibite	$Cu_2(Sb,Tl)$	Wallisite	$(Cu,Ag)TlPbAs_2S_5$
Carlinite	Tl_2S	Bernardite	$Tl(As,Sb)_5S_8$
Picotpaulite	$TlFe_2S_3$	Vrabaite	$Tl_4Hg_3Sb_2As_8S_{20}$
Raguinite	$TlFeS_2$	Rebulite	$Tl_5Sb_5As_8S_{22}$
Thalcusite	$Tl_2Cu_3FeS_4$	Gillulyite	$Tl_3(As,Sb)_8S_{13}$
Bukovite	$Tl_2(Cu,Fe)_4Se_4$	Weissbergite	$TlSbS_2$
Rayite	$Pb_8(Ag,Tl)_2Sb_8S_{21}$	Rohaite	Cu_5TlSbS_2
Rathite	$(Pb,Tl)_3As_5S_{10}$	Vaughanite	$TlHgSb_4S_7$
Hatchite	$(Pb,Tl)_2AgAs_2S_5$	Chalcothallite	$Tl_2(Cu,Fe)_6SbS_4$
Thalfenisite	$Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$	Pierrotite	$Tl_2Sb_6As_4S_{16}$
Lorandite	$TlAsS_2$	Parapierrotite	$Tl(Sb,As)_5S_8$
Ellisite	Tl_3AsS_3	Criddleite	$TlAg_2Au_3Sb_{10}Sb_{10}$
Imhofite	$Tl_6CuAs_{16}S_{40}$	Chabourneite	$(Tl,Pb)_5(Sb,As)_{21}S_{34}$
Simonite	$TlHgAsS_6$	Avicennite	Tl_2O_3
Christite	$TlHgAsS_3$	Monsmedite	$K_2O:Tl_2O_3:8SO_3:15H_2O$

Thallium in Coal

Thallium concentrations in U.S. coals are typically within the range of average crustal abundance, but 2 out of 378 values were reported as >100 mg/kg (Table 5-3). Thallium occurrence in coal is most often attributed to the sulfide fraction (Finkelman, 2007; personal communication). Dai et al. (2005) found that the main carrier of Tl, As, Sb, and Hg in anthracite from southwest China was an epigenetic getchellite ($AsSbS_3$), resulting from hydrothermal fluid migration through the coal seam. Xiao et al. (2004) associated thallium enrichment in sulfides and coal in southwest China with high As and Hg, and with the mineral lorandite ($TlAsS_2$), the most common Tl-bearing mineral. Kolker et al. (2002) determined that thallium in Ohio bituminous coal is associated with pyrites (50% by weight), silicates (15% by weight), monosulfides (15%), and organics (10% by weight), but reported no measurable thallium leached from Powder River Basin subbituminous coals.

Table 5-3
Thallium Concentrations in Coal

Coal	Average (mg/kg)	Median (mg/kg)	Range (mg/kg)	No. Samples
Anthracite	0.79	0.66	0.17-2.10	40
Bituminous	0.76	0.48	0.02-32.00	4733
Lignite	1.09	0.86	0.13-15.00	148
Semi-anthracite	1.02	0.96	0.26-1.90	10
Subbituminous	2.29 (0.82)*	0.56 (0.56)*	0.07-420.00 (32.00)*	378 (376)*
All	1.1 (0.78)*	0.6 (0.5)*	0.02-420.00 (0.02-32.00)*	5,309 (5,307)*
Average crustal abundance	0.1 to 3 mg/kg			

Data from Braggs et al.(1998)
*Values in parentheses reflect data edited to exclude two outliers of 140 and 420 mg/kg

To summarize, thallium enrichment in coal is associated with either pyrite or thallium-bearing sulfides, such as lorandite. Some thallium may be associated with clay minerals due to thallium's tendency to substitute for potassium. However, the highest thallium concentrations in coal result from accumulation in sulfides.

Thallium in CCPs

Thallium total elemental concentrations in CCPs in the EPRI PISCES database exhibit a wide range, and are enriched compared to coal samples and typical crustal abundance (Table 5-4). No study has directly identified thallium's mode of occurrence in CCPs. Thallium is believed to volatilize during coal combustion and recondense on fly ash particles at cooler temperatures as an oxide (ATSDR, 1992). This is supported by the study of Natush et al. (1974), who associated thallium enrichment with fly ash particle size. They reported thallium concentrations in fly ash emitted from a coal-burning power plant of between 29 and 76 mg/kg, with concentrations increasing with decreasing particle size and the greatest concentration occurring on particles less than 7.3 μm in diameter (Figure 5-1).

Table 5-4
Total Elemental Thallium Concentrations in CCPs

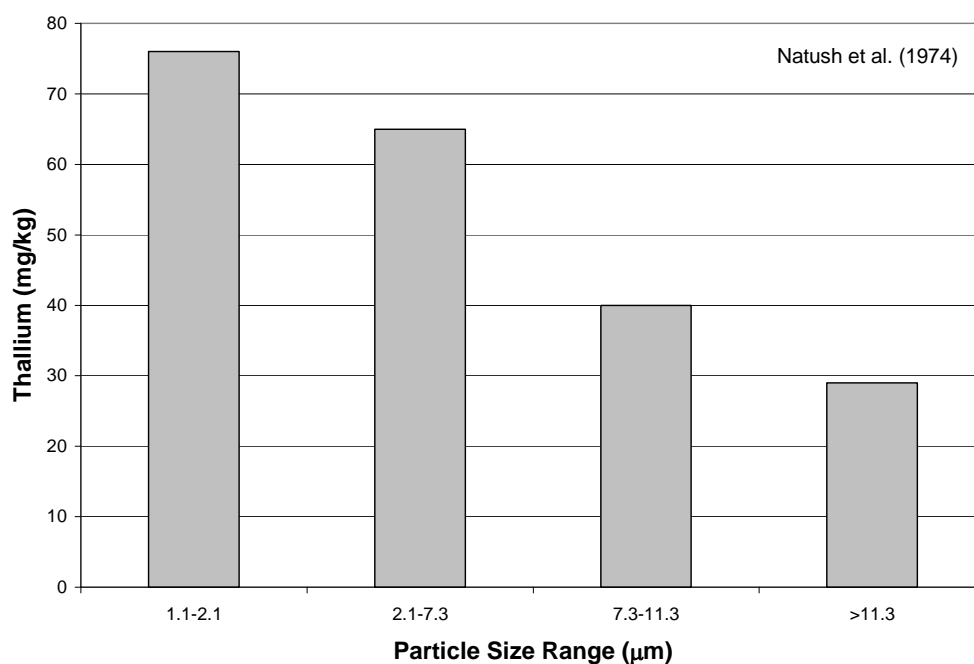| CCP Type	Number of Samples	Number of Non-Detects	Median (mg/kg)	Maximum (mg/kg)
Fly ash (bituminous coal)	108	52	7.5	85
Fly ash (subbituminous coal)	16	15	BDL	BDL
Fly ash (lignite coal)	8	7	BDL	69

BDL – Below Detection Limit
All data from EPRI PISCES database – 2003

Figure 5-1
Example of Variation of Thallium Concentration in Coal Fly Ash With Particle Size

Aqueous-Phase Geochemistry

Redox Properties and Speciation

Dissolved thallium exists primarily as Tl^+ under most conditions (Figure 5-2). The Tl^{3+} redox state should only exist in highly oxidizing solutions, such as highly acidic environments containing strong oxidizing agents. Electrochemical properties of thallium are listed in Table 5-5.
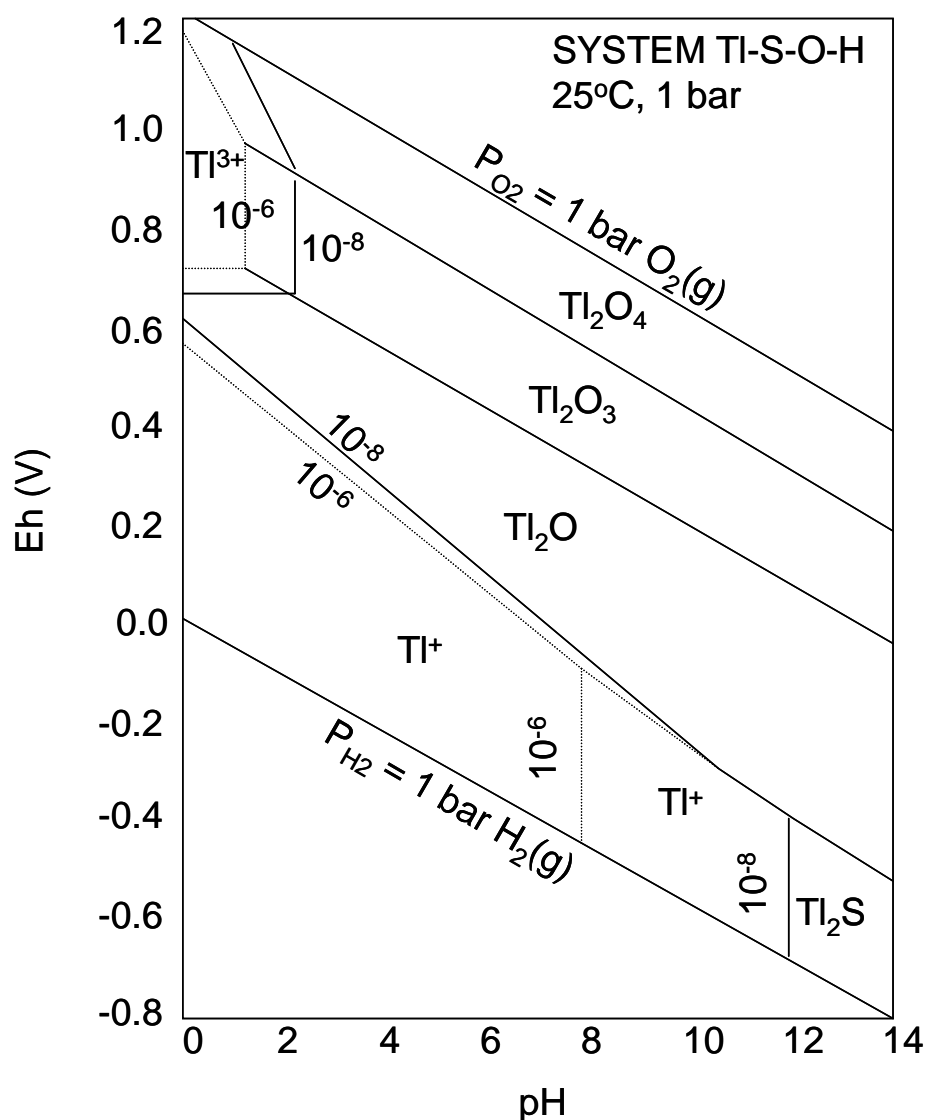

Figure 5-2
Eh-pH diagram for the system $Tl-O_2-S-H_2O$, assuming $\sum Tl = 10^{-8}$ and 10^{-6} mol/kg and $\sum S = 10^{-3}$ mol/kg (modified after U.S. EPA, 2004a; originally from Brookins, 1988)

Table 5-5
Electrochemical Properties of Thallium

Reaction	Standard Electrode Potential (V)
$\frac{1}{2}O_2 + 2e^- + 2H^+ = H_2O$	2.45
$H^+ + e^- = \frac{1}{2}H_2$	0.00
$Tl^+ + e^- = Tl$	-0.336
$Tl^{3+} + 2e^- = Tl^+$	1.25
$Tl(OH)_3 + 2e^- = TlOH + 2OH^-$	-0.05

Appreciable oxidation of Tl^+ to Tl^{3+} may occur at mineral surfaces, a proposed mechanism of thallium immobilization. In particular, studies have shown amorphous manganese oxides to be capable of oxidizing Tl^+ to Tl^{3+} at low pH. Under reducing conditions, Tl^+ can be reduced to the metallic state by the reaction: $Tl^+ + e^- = Tl(metal)$ at a standard potential of -0.336 V. This process may allow for thallium immobilization under reducing conditions, in addition to formation of sulfides.

Aqueous Complexes and Solid-Phase Solubility

Thallium behavior in aqueous media is commonly compared to that of potassium, due to the fact that both exhibit a +1 valence state under most conditions. If oxidized to the +3 valence state, its behavior tends to reflect that of aluminum. Hydrolysis of Tl^+ is considered negligible, but hydrolysis of Tl^{3+} is notable in the pH range of natural waters (Figure 5-3). Above pH ~9, thallium (III) will carry a negative charge. Thallium (I) and thallium (III) will form many aqueous inorganic and organic complexes (Table 5-6), most commonly with Cl^-, OH^-, and SO_4^{-2}. Solid phases and solubility data are listed in Table 5-7.
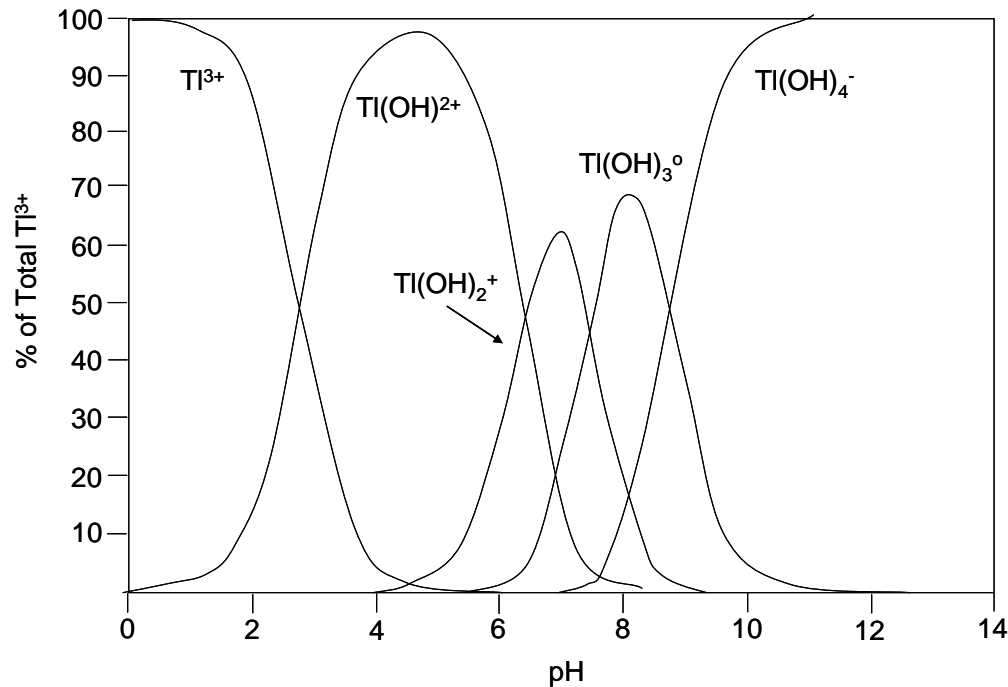
Figure 5-3
Distribution of Thallium (III) Species as a Function of pH in Pure Water

Adsorption

Jacobson et al. (2005) reviewed the adsorption characteristics of thallium on a wide range of soils and minerals. The following results were notable:

- Thallium sorbed more strongly to birnessite (amorphous Mn-oxide) than ferrihydrite (amorphous Fe-oxide) in batch experiments;

- Thallium (I) may be oxidized at MnO_2 surfaces, precipitating thallium (III) oxides;

- NH_4^+ was found to compete with thallium (I), but K^+ had little effect;

- Thallium showed very little affinity for soil organic matter, and sorption was not influenced by the soil's overall cation exchange capacity;

- Thallium (I) may bind to clay particles by specific adsorption at illitic clay interlayer sites.

Table 5-6
Equilibrium Stability Constants for Various Thallium Reactions at 25°C and 1 atm

Reaction	Log K	Reaction	Log K
$Tl^+ + H_2O = TlOH + H^+$	-13.207	$Tl^+ + I^- = TlI$	1.4279
$Tl(OH)_3 + 2H^+ = TlOH^{+2} + 2H_2O$	2.694	$Tl^+ + 2I^- = TlI_2^-$	1.8588
$Tl(OH)_3 + H^+ = Tl(OH)_2^+ + H_2O$	1.897	$Tl(OH)_3 + 4I^- + 3H^+ = TlI_4^- + 3H_2O$	34.7596
$Tl(OH)_3 + H_2O = Tl(OH)_4^- + H^+$	-11.697	$Tl^+ + HS^- = TlHS$	2.474
$Tl^+ + F- = TlF$	0.1	$2Tl^+ + HS^- = Tl_2HS^+$	5.974
$Tl^+ + Cl^- = TlCl$	0.51	$2Tl^+ + 3HS^- + H_2O = Tl_2OH(HS)_3^{-2} + H^+$	1.0044
$Tl^+ + 2Cl^- = TlCl_2^-$	0.28	$2Tl^+ + 2HS^- + 2H_2O = Tl_2(OH)_2(HS)_2^{-2} + 2H^+$	-11.0681
$Tl(OH)_3 + 3H^+ + Cl^- = TlCl^{+2} + 3H_2O$	11.011	$Tl^+ + SO_4^{-2} = TlSO_4^-$	1.37
$Tl(OH)_3 + 3H^+ + 2Cl^- = TlCl_2^+ + 3H_2O$	16.771	$Tl^+ + NO_2^- = TlNO_2$	0.83
$Tl(OH)_3 + 3H^+ + 3Cl^- = TlCl_3 + 3H_2O$	19.791	$Tl^+ + NO_3^- = TlNO_3$	0.33
$Tl(OH)_3 + 3H^+ + 4Cl^- = TlCl_4^- + 3H_2O$	21.591	$Tl(OH)_3 + NO_3^- + 3H^+ = TlNO_3^{+2} + 3H_2O$	7.0073
$Tl(OH)_3 + Cl^- + 2H^+ = TlOHCl^+ + 2H_2O$	10.629	$Tl^+ + Fe^{+2} + 6Cyanide^- = TlFe(Cyanide)_6^{-3}$	38.4
$Tl^+ + Br^- = TlBr$	0.91	$Tl^+ + Citrate^{-3} = Tl(Citrate)^{-2}$	1.48
$Tl^+ + 2Br^- = TlBr_2^-$	-0.384	$Tl^+ + Nta^{-3} = Tl(Nta)^{-2}$	5.39
$Tl^+ + Br^- + Cl^- = TlBrCl^-$	0.8165	$Tl^+ + Edta^{-4} = Tl(Edta)^{-3}$	-43.5136
$Tl^+ + I^- + Br^- = TlIBr^-$	2.185	$Tl^+ + Edta^{-4} + H^+ = TlH(Edta)^{-2}$	13.68
$Tl(OH)_3 + 3H^+ + Br^- = TlBr^{+2} + 3H_2O$	12.803	$Tl^+ + Acetate^- = Tl(Acetate)$	-0.11
$Tl(OH)_3 + 3H^+ + 2Br^- = TlBr_2^+ + 3H_2O$	20.711	$Tl^+ + Tartarate^{-2} = Tl(Tartarate)^-$	1.4
$Tl(OH)_3 + 3Br^- + 3H^+ = TlBr_3 + 3H_2O$	27.0244	$Tl^+ + Tartarate^{-2} + H^+ = TlH(Tartarate)$	4.8
$Tl(OH)_3 + 4Br^- + 3H^+ = TlBr_4^- + 3H_2O$	31.1533	$Tl^+ + Glycine^- = Tl(Glycine)$	1.72

All data from minteqV4.dat thermodynamic database (distributed with PHREEQC Interactive)

Table 5-7
**Solubility of Thallium Phases With Existing Thermodynamic Data**

Solid Phase	Reaction	Log K	Solid Phase	Reaction	Log K
Tl_{metal}	$Tl = Tl^+ + e^-$	5.6762	TlBr	$TlBr = Tl^+ + Br^-$	-5.44
Tl_2S	$Tl_2S + H^+ = 2Tl^+ + HS^-$	-7.19	TlI	$TlI = Tl^+ + I^-$	-7.23
Tl_2Se	$Tl_2Se + H^+ = 2Tl^+ + HSe^-$	-18.1	Tl_2CO_3	$Tl_2CO_3 = 2Tl^+ + CO_3^{-2}$	-3.8367
Tl_2O	$Tl_2O + 2H^+ = 2Tl^+ + H_2O$	27.0915	$TlNO_3$	$TlNO_3 = Tl^+ + NO_3^-$	-1.6127
TlOH	$TlOH + H^+ = Tl^+ + H_2O$	12.9186	Tl_2SO_4	$Tl_2SO_4 = 2Tl^+ + SO_4^{-2}$	-3.7868
Avicennite	$Tl_2O_3 + 3H_2O = 2Tl(OH)_3$	-13	Tl_2CrO_4	$Tl_2CrO_4 = 2Tl^+ + CrO_4^{-2}$	-12.01
$Tl(OH)_3$	$Tl(OH)_3 = Tl^{3+} + 3OH^-$	-45.2*	Tl_2SeO_4	$Tl_2SeO_4 = 2Tl^+ + SeO_4^{-2}$	-4.1
TlCl	$TlCl = Tl^+ + Cl^-$	-3.74	Tl_2MoO_4	$Tl_2MoO_4 = MoO_4^{-2} + 2Tl^+$	-7.9887

Data from minteqV4.data thermodynamic database
*Data for $Tl(OH)_3$ from Lin and Nriagu (1998)

Jacobson et al. (2005) concluded that iron oxides and organic matter play a very small role in thallium adsorption as compared to manganese oxides. This is not surprising, because studies as early as Shaw (1952) have illustrated an enrichment of thallium in manganese deposits, and a general lack of thallium in iron oxide minerals. Thallium's affinity for manganese oxides has been observed by other researchers. Bidoglio et al. (1993) reported precipitation of Tl_2O_3 onto δ-MnO_2 surfaces. Koschinsky and Hein (2003) found Tl^+ associated with ferromanganese crusts in seawater primarily sorbed to MnO_2 surfaces; Tl^{3+} in the crusts was associated with FeOOH.

Studies have shown that thallium can be easily released from solids that were anthropogenically enriched in thallium (Lehn and Schoer, 1987; Sager, 1992). This most likely occurs when thallium is held weakly to cation exchange surfaces, as opposed to incorporation into a mineral lattice or precipitation onto a mineral surface. A cation exchange reaction involving K^+ and Tl^+ would be represented as:

$$KX(s) + Tl^+(aq) = TlX(s) + K^+(aq)$$
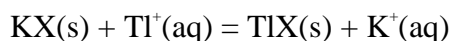
where X is the exchange surface site. NH_4^+ may also participate in this reaction. Sager (1992) reported that more than 95% of adsorbed thallium on river sediments was easily exchangeable by addition of 1M ammonium acetate.

As described by Jacobson et al. (2005), thallium likely adsorbs to micaceous minerals by a cation fixation mechanism (Nriagu, 1998). This occurs when a cation is the correct size to fit between layers comprising the mica mineral. This was hypothesized by Jacobson et al. (2005) to account for thallium adsorption to a wide range of soils. Thallium (I) will readily displace K^+ in clays and secondary silicate minerals as a result of its greater electronegativity (Nriagu, 1998).

In summary, studies have suggested that thallium will adsorb to solid surfaces by:

- Cation exchange (easily exchangeable),

- Surface precipitation of oxide or hydroxide (relatively immobile), or

- Specific adsorption of Tl$^+$ at interlayer sites in micaceous minerals (tightly bound).

Environmental Fate and Transport

Transport Coefficients

One approach toward quantifying the various processes that contribute to the retardation of mobility of a particular contaminant relative to water is referred to as the retardation factor, R_f.

$$R_f = {V_p}\big/{V_c}$$

where R_f = retardation factor, V_p = velocity of water through a control volume, and V_c = velocity of contaminant through a control volume (U.S. EPA, 2004b).

The partitioning of thallium between solid and water phases is characterized by its distribution coefficient, K_d^{Tl}. $K_d^{Tl} = C_S/C_L$, where C_S is the concentration of thallium on solids (measured in mg/kg) and C_L is the concentration of thallium in water (measured in mg/L).

The retardation factor is related to the distribution coefficient by the equation (U.S. EPA, 2004b):

$$R_f = 1 + (\rho_b/\eta_e)K_d$$

where ρ_b = porous media bulk density and η_e = effective porosity at saturation.

For 1-dimensional advection-dispersion flow with chemical retardation, the transport equation incorporates the retardation factor as follows:

$$\frac{\partial C_i}{\partial t} = \frac{\left[D_x \frac{\partial^2 C_i}{\partial x^2}_i - v_x \frac{\partial C_i}{\partial x} \right]}{R_f(i)}$$

Distribution Coefficient (K_d)

The distribution coefficient (K_d) describing thallium retardation relative to groundwater flow is not well understood. To date, only Jacobson et al. (2005) have targeted thallium sorption behavior in controlled experiments. Based on visual interpretation of isotherms published in their study, estimated K_d values range from 125 to 250 L/kg, with values increasing with increasing experimental equilibration times (Table 5-8). Karlsson (2006) reported K_d values for thallium in lake sediment porewater on the order of 10^4 to 10^5 L/kg, much larger than previously reported.

Table 5-8
Thallium K_d Values Approximated From Experiments of Jacobson et al. (2005)

Soil	Approximated K_d (L/kg)*	Experimental Conditions
Arkport	125	24-hr equilibration; $Ca(NO_3)$ and synthetic acid rain solutions
Genesee	250	24-hr equilibration; $Ca(NO_3)$ and synthetic acid rain solutions
Hudson (surface)	125	24-hr equilibration; $Ca(NO_3)$ and synthetic acid rain solutions
Hudson (subsurface)	250	24-hr equilibration; $Ca(NO_3)$ and synthetic acid rain solutions
Orange County muck	125	24-hr equilibration; $Ca(NO_3)$ and synthetic acid rain solutions

*Approximated K_d based on visual inspection of Jacobson et al. (2005) published isotherms

U.S. EPA (1996) presented empirically-derived K_d values for thallium as a function of pH (Figure 5-4). A different U.S.EPA calculation for thallium K_d, based on Mintaq modeling suggested a range from 20 to 247 L/kg at pH 6.8, with a median of 71 L/kg (U.S.EPA, 1992b). The predicted range and median was slightly lower at pH 4.9 (median = 44 L/kg) and slightly higher at high pH (median = 124 L/kg).

Both the calculated and experimental K_d values suggest that thallium has low mobility in groundwater. However, data are limited and thallium distribution coefficients and sorption mechanisms need to be evaluated further under a variety of experimental conditions.
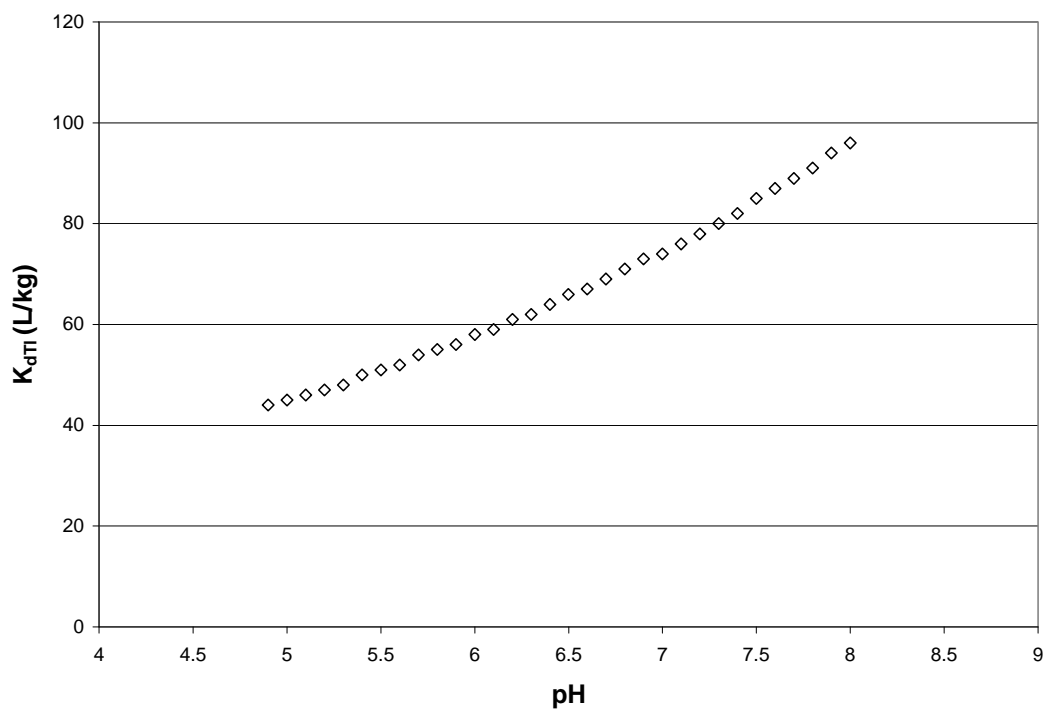
Figure 5-4
K_d for Thallium as a Function of pH Calculated by U.S. EPA (1996)

6
LEACHING AT CCP SITES

This section summarizes data on thallium occurrence in CCP leachate based upon the EPRI (2006) field leachate study. EPRI (2006) is a compilation of field leachate samples collected by a single contractor and analyzed by a single laboratory. The consistency in sample collection and laboratory analysis yields a highly comparable dataset containing 81 samples from 29 CCP sites. This database contains analytical results for dissolved thallium in CCP leachate.

Thallium Concentrations in CCP Leachate

Concentrations

The EPRI (2006) database contains 81 field leachate samples collected from leachate wells, leachate collection systems, sluice lines, and pond water. Forty-three (43) of 81 field leachate samples contained thallium concentrations at less than the method detection limit of 0.1 µg/L. The maximum concentration was 17.58 µg/L, and the median concentration for all samples and subsets of samples was less than 1 µg/L. In terms of coal type and management criteria, the following relationships exist for thallium:

- Fly ash samples had a higher range than FGD samples, but there was little difference in the median concentrations (Figure 6-1);

- Thallium concentrations in fly ash leachate are highest when the source coal is bituminous and when the fly ash is managed in impoundments (as opposed to landfills) (Figure 6-2); and

- Thallium concentrations in FGD leachate are similar for bituminous and subbituminous source coal, but concentrations are higher in impoundments than in landfills (Figure 6-3).

In terms of geochemical factors, elevated thallium occurs when: 1) field-measured Eh values are above +200 mV (Figure 6-4), and 2) pH values are less than about 9 (Figure 6-5). This relationship to Eh and pH is shown qualitatively in Figure 6-6 as bubbles that are sized relative to the thallium concentration in leachate samples. A cluster of elevated samples occurs from pH 7-8 at Eh values from +200 to +350 mV.
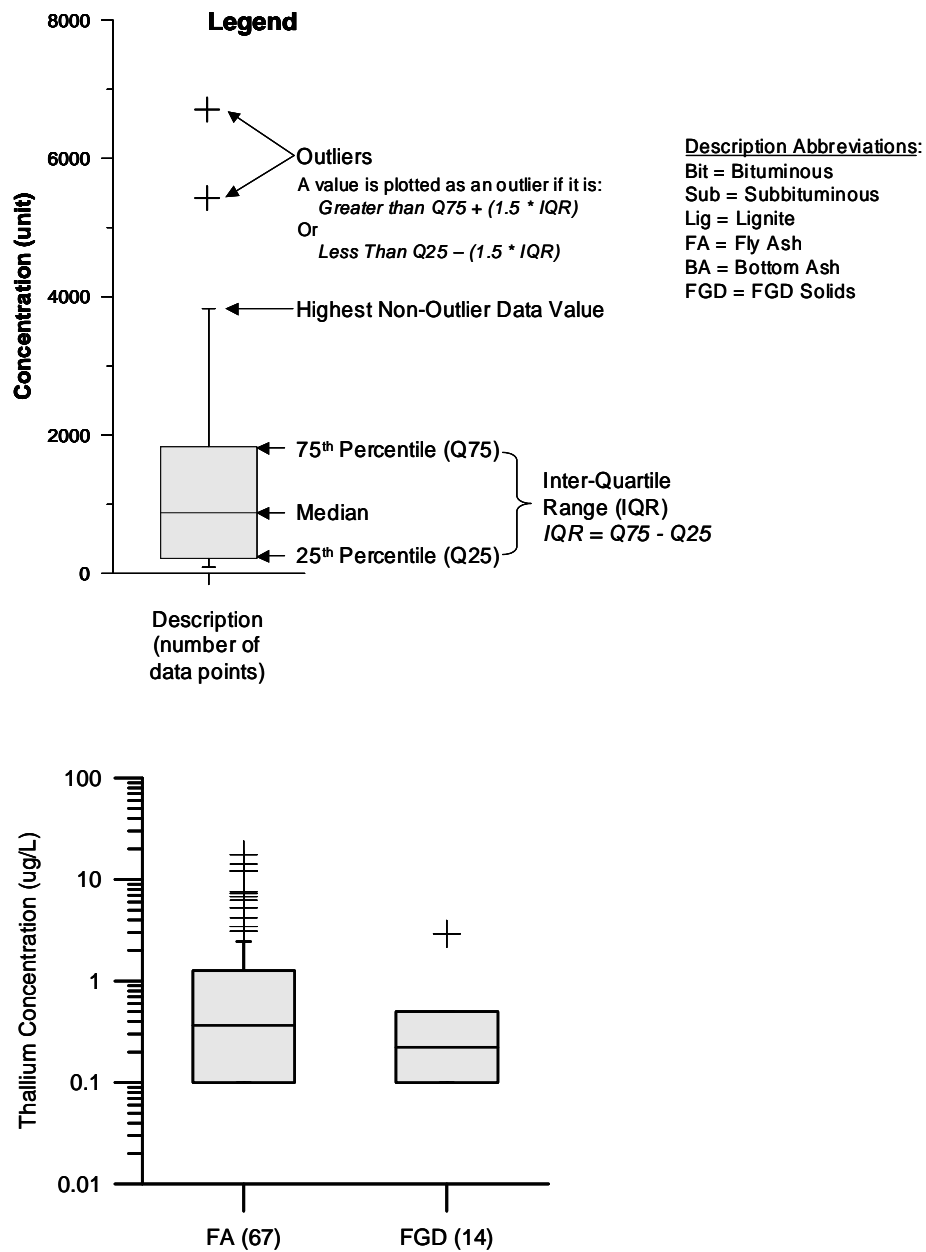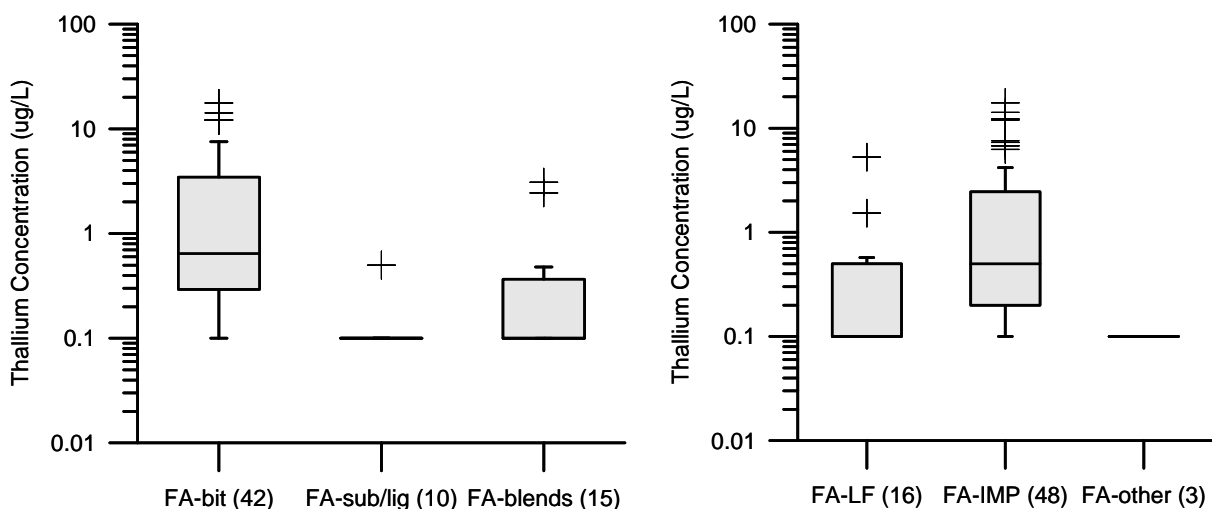
Figure 6-1
Thallium Concentrations in Fly Ash (FA) and FGD Leachate

Figure 6-2
Thallium concentrations in fly ash (FA) leachate categorized by source coal and management method (Landfill – LF; Impoundment – IMP)

Note: Single lines indicate all or majority of samples were less than method detection limit of 0.1 ug/L; lack of median line indicates median and 25th percentile are the same
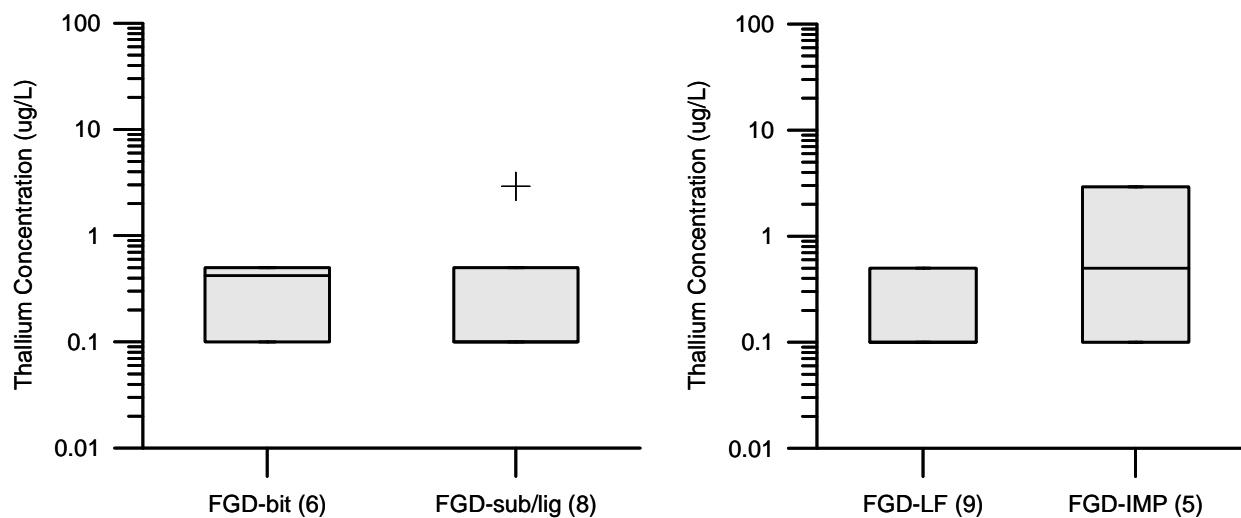
Figure 6-3
Thallium concentrations in FGD leachate categorized by source coal and management method (Landfill – LF; Impoundment – IMP)

Note: (lack of median line indicates median and 25th percentile are the same)

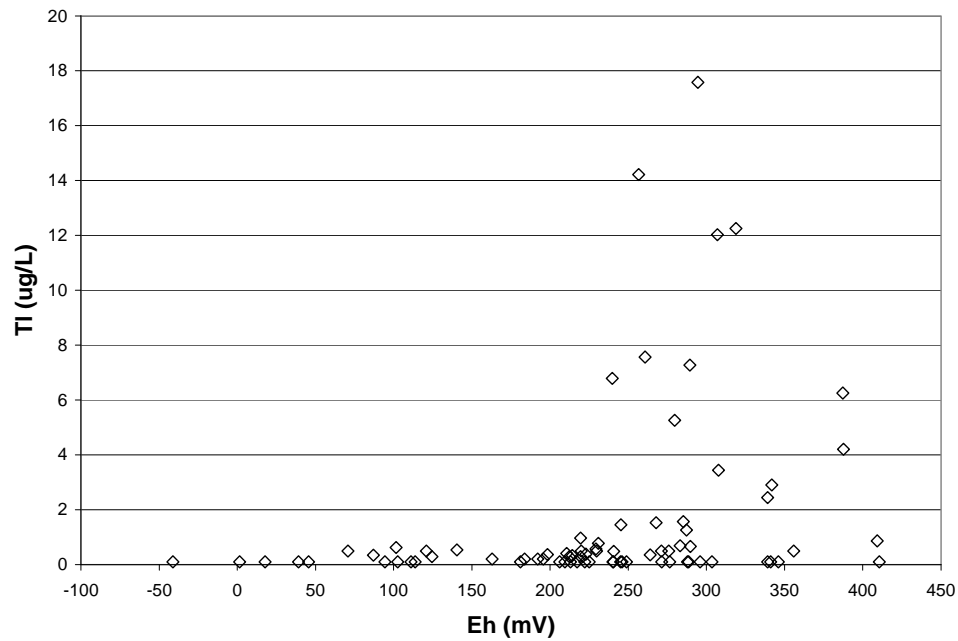**Figure 6-4**
Thallium concentrations in CCP leachate as a function of Eh, showing elevated thallium at Eh values greater than +200 mV and less than +350 mV (non-detects plotted as 0 μg/L)
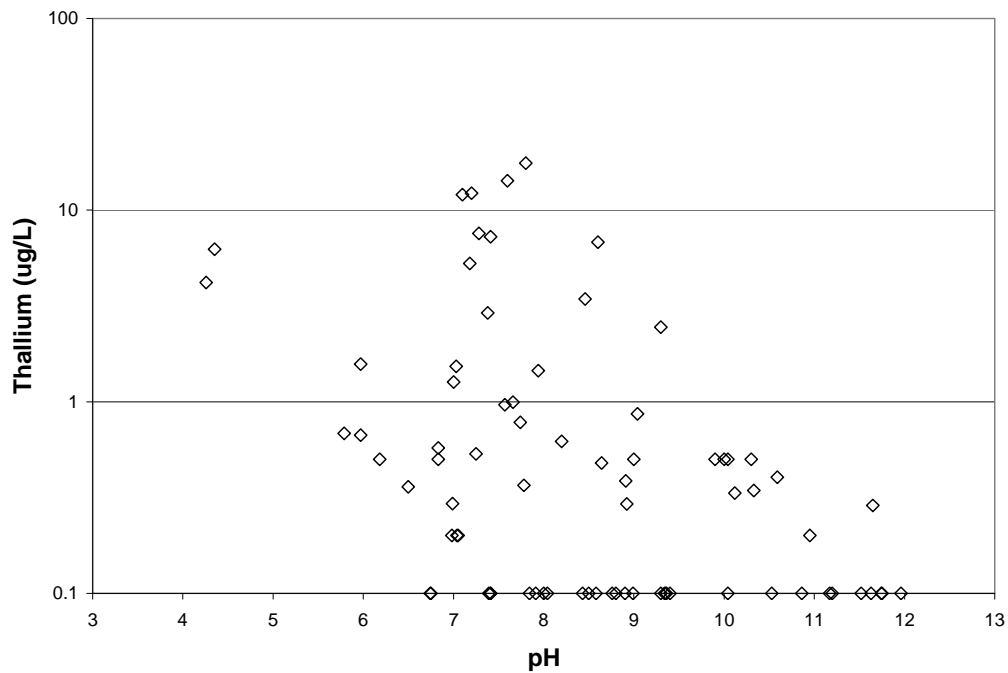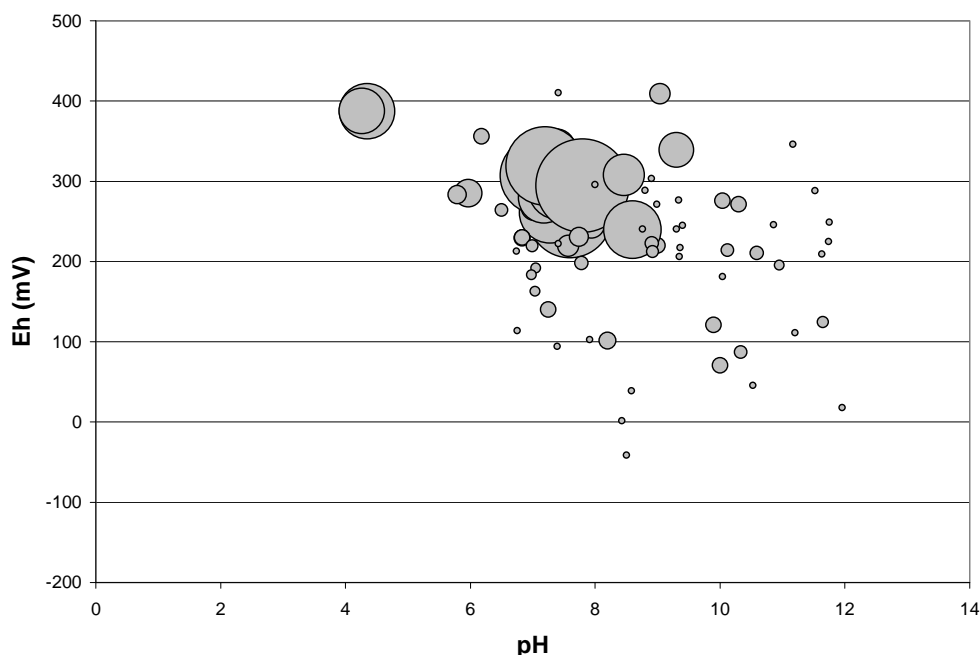

Figure 6-5
Thallium Concentrations in CCP Leachate as a Function of pH (non-detects plotted as 0.1 μg/L)

Figure 6-6
Thallium concentrations shown qualitatively as a function of pH and Eh, illustrating most elevated thallium occurring at neutral pH and oxidizing conditions

Speciation and Mineral Saturation Indices

Thallium speciation in the CCP leachate data was not measured, but calculated using PHREEQC, incorporating the minteq.V4.dat thermodynamic database. The majority (>90%) of dissolved thallium in CCP leachate is present as Tl^+ or $TlSO_4^-$, with the exception of samples with pH > 11 (Figure 6-7). At high pH, other species contributing to total dissolved thallium include $TlCl^0$, $TlOH^0$, $Tl(OH)_3^0$, and $Tl(OH)_4^-$ (Figure 6-8). Data indicate that the occurrence of Tl^{+3} species is restricted to pH 10-12. Thallium speciation in CCP leachate is similar to its speciation in groundwater (Table 6-1).

Geochemical modeling of CCP leachate data can be used to evaluate what mineral phases, if any, might control thallium concentrations by calculating the saturation index (SI) of a variety of minerals. SI values greater than zero indicate a tendency of a mineral to precipitate, values of zero indicate an equilibrium condition with that mineral, and values less than zero indicate a tendency of a mineral to dissolve. SI values for thallium-bearing minerals with thermodynamic data were evaluated as a function of pH (Figure 6-9). Data show that only Tl_2Se approaches an equilibrium condition (SI near zero), and that all other mineral phases exhibit a strong tendency to dissolve. The conclusion from modeling is that, from available thermodynamic data, only Tl_2Se is predicted to exist as a solid, thallium-bearing phase.
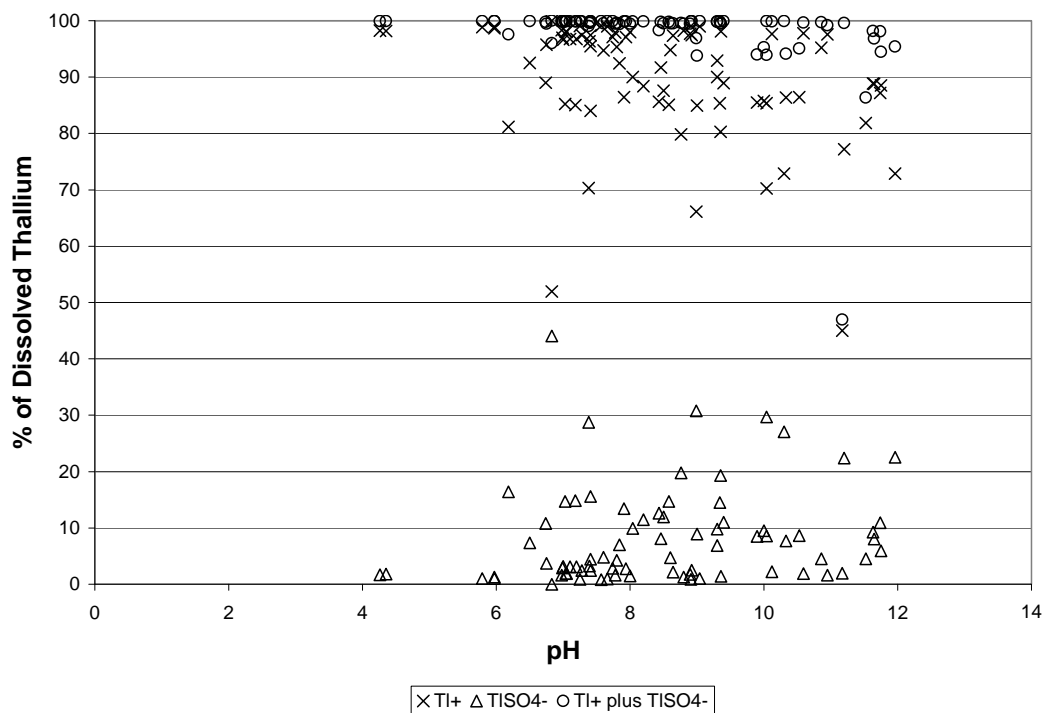
Figure 6-7
Major Thallium Species in CCP Leachate
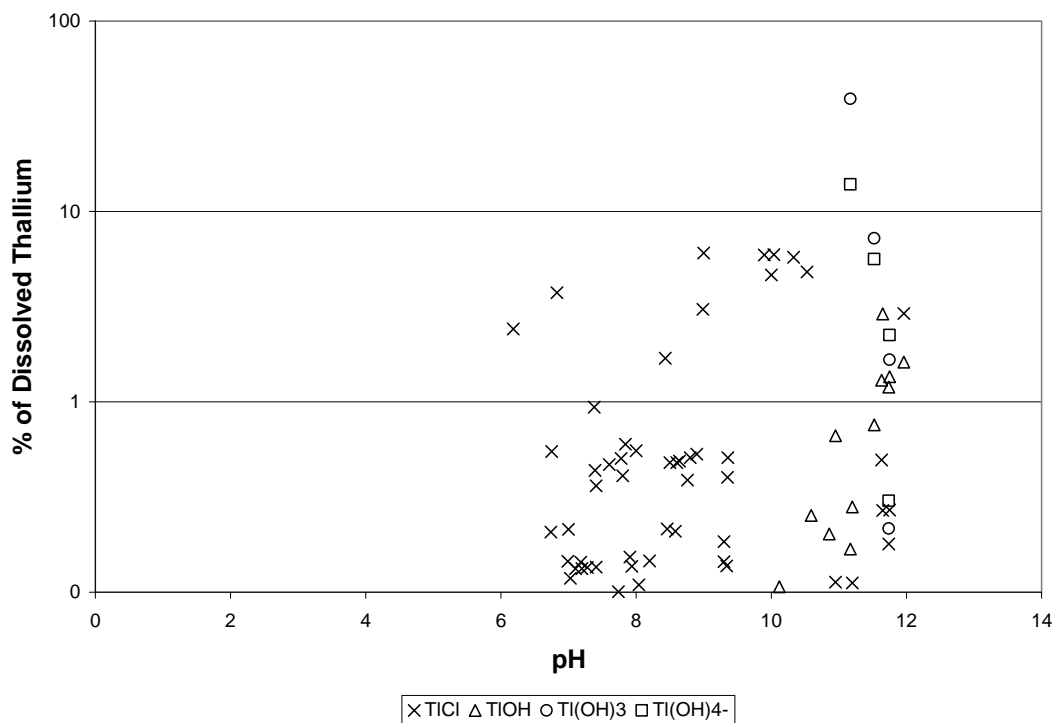
Figure 6-8
Minor Thallium Species in CCP Leachate

Table 6-1
Thallium (I) Aqueous Speciation in Various Water Types and CCP Leachate

Aqueous Species*	Groundwater**	River Water*	Eutrophic lake Water*	Bog Water*	Seawater*	CCP Leachate***
Tl^+	90.4	82.7	76.8	32.4	51.9	90.02
$TlHCO_3^0$	4.4	1.2	2.0	-	0.5	-
$TlCO_3^-$	-	-	-	-	0.1	-
$TlSO_4^-$	3.6	0.4	0.8	-	11.2	8.14
$TlCl^0$	0.1	0.1	0.1	-	30.7	0.78
$Tl(Cl)_2^-$	-	-	-	-	5.4	0.01
$Tl\text{-fulvate}^0$	1.4	15.6	20.3	67.6	0.2	-

*Data presented as a percentage of the total dissolved thallium in a particular water type.
**Speciation data other than CCP leachate from Nriagu (1998)
***Tl-fulvate^0 species not considered in CCP leachate

Figure 6-9
Saturation Indices of Thallium-Bearing Minerals in CCP Leachate as a Function of pH

If sulfur speciation were evaluated, then this conclusion could be revised. For example, leachate data show a strong correlation with a Tl_2S mineral solubility curve at low pH, and with Tl_2Se at mid-range pH (Figure 6-10). The adherence to Tl_2Se solub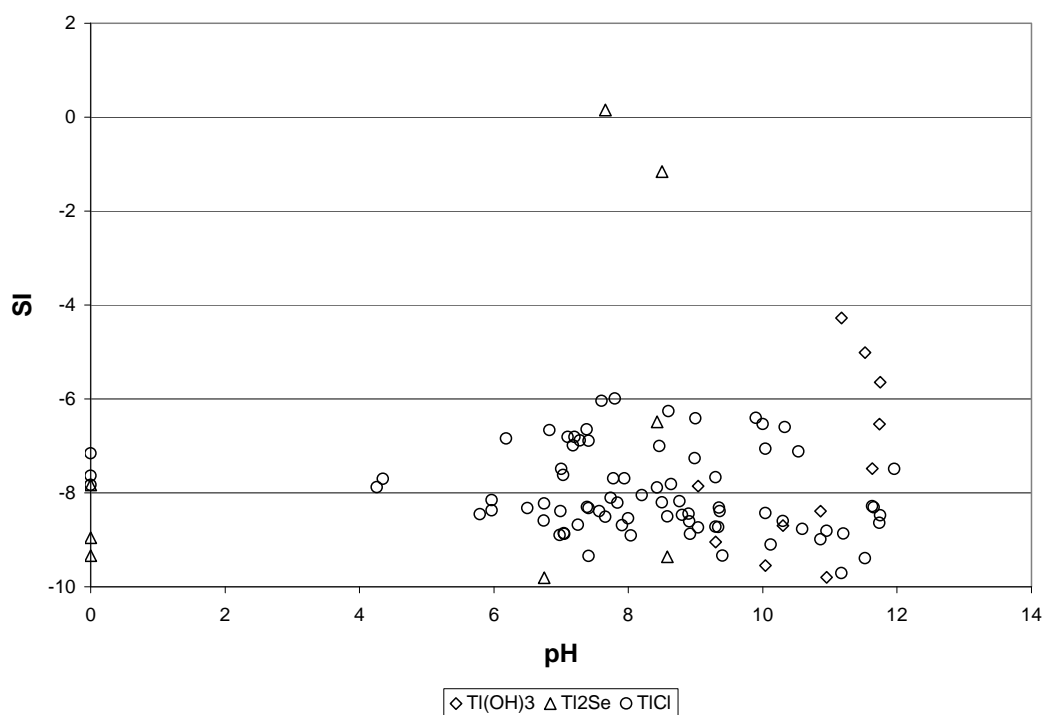ility trend with pH is predicted by the near-zero saturation index at pH ~8. The plot in Figure 6-10 suggests the existence of Tl_2S at low pH in the absence of sulfur speciation data. Although informative, the data still do not account for thallium sulfide phases that are known to be common in coal, but lack reliable thermodynamic data, such as lorandite.
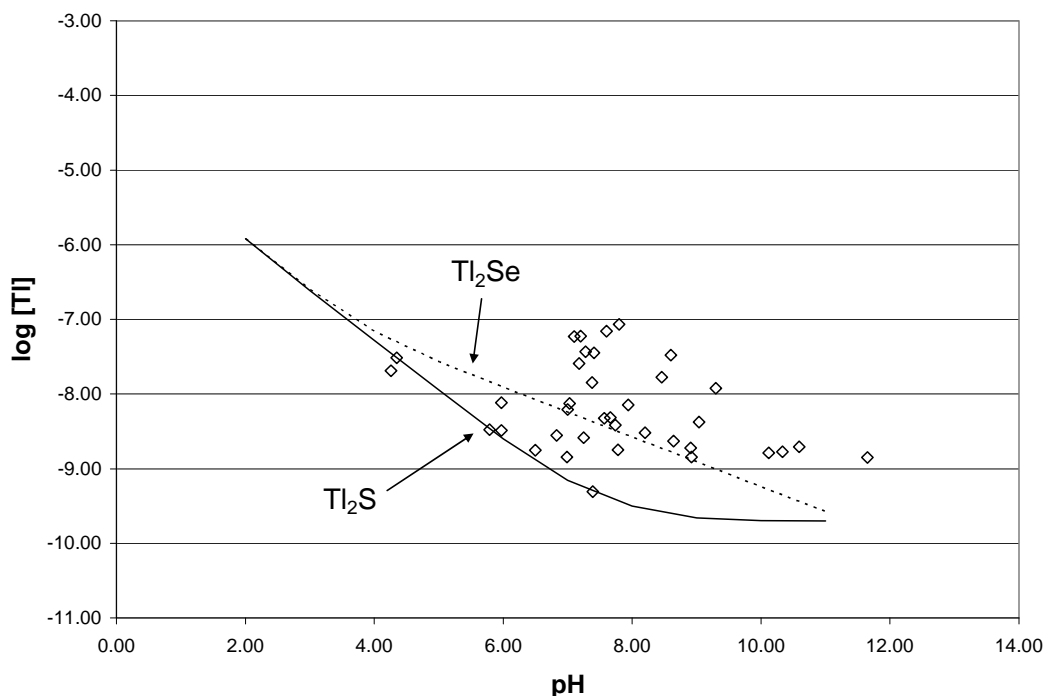
Figure 6-10
Thallium Concentrations in CCP Leachate Plotted With Tl₂S and Tl₂Se Solubility Curves

Common Association Evaluation: Pb, Zn, Sb, As, and Hg

Since there is evidence to link thallium leaching to sulfide mineral solubility, it is worthwhile to investigate the occurrence of thallium with elements commonly associated with thallium in sulfide complexes: Pb, Zn, Sb, As, and Hg (Figures 6-11 to 6-13). Thallium shows no direct correlation with any of these elements. Thallium is generally present in low concentrations where the others are elevated. A notable correlation is observed if a principal thallium-bearing sulfide (lorandite – $TlAsS_2$) is assumed to exist. Thallium is most elevated when the As:Tl molar ratio is approximately equal to one (Figure 6-14). This relationship with trivalent arsenic, in combination with a close fit of thallium concentrations to the Tl_2S solubility curve, may support the existence of lorandite and Tl_2S at low pH in the absence of thermodynamic data. Elevated thallium at high ORP may indicate thallium release by sulfide oxidation.

Figure 6-11
Relationship of Tl With Pb and Zn in CCP Leachate

Figure 6-12
Relationship of Tl With Sb and As in CCP Leachate

Figure 6-13
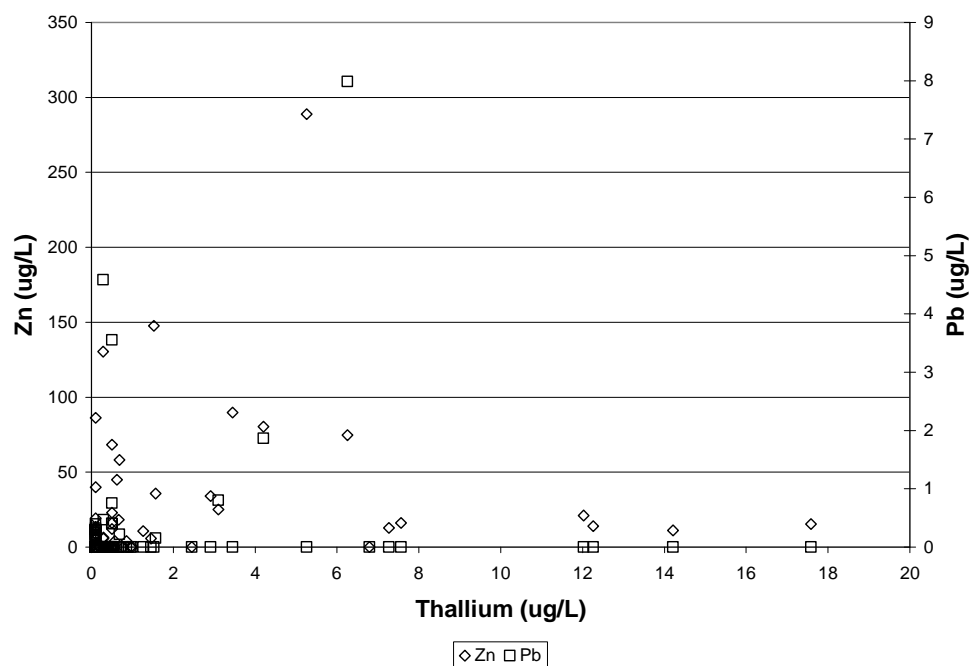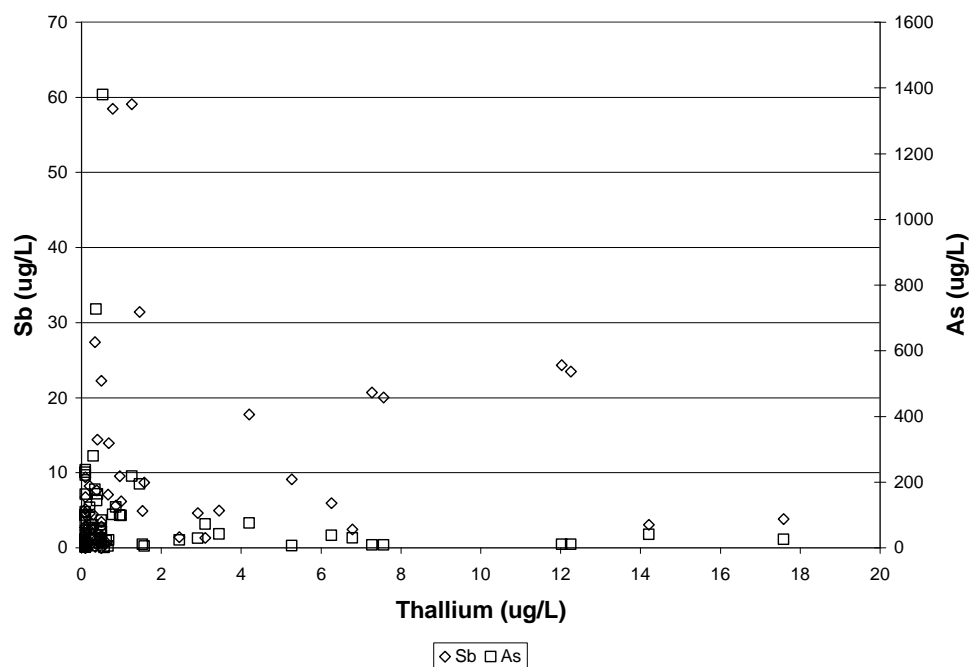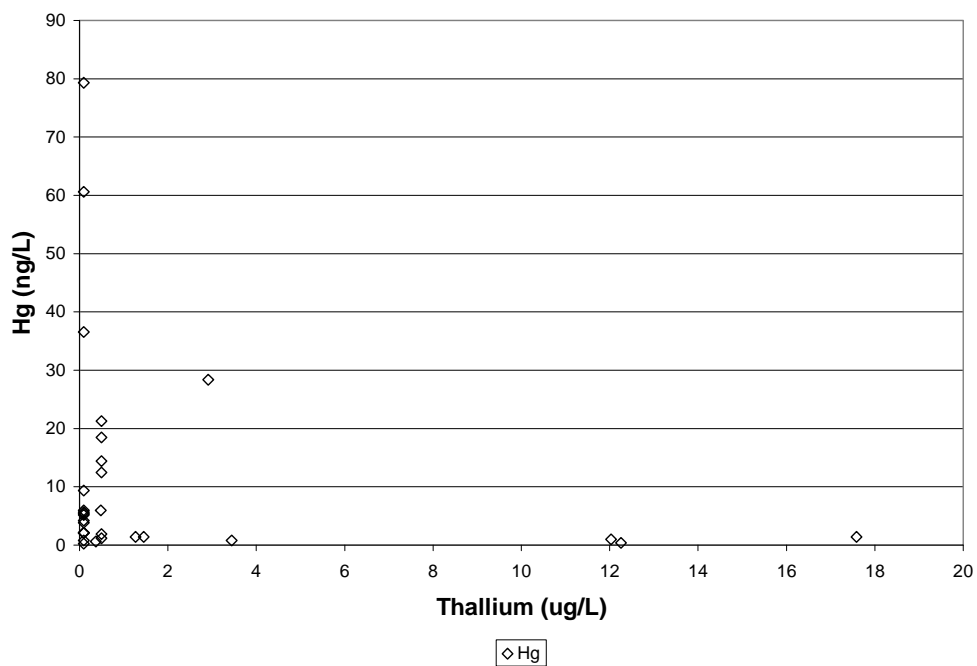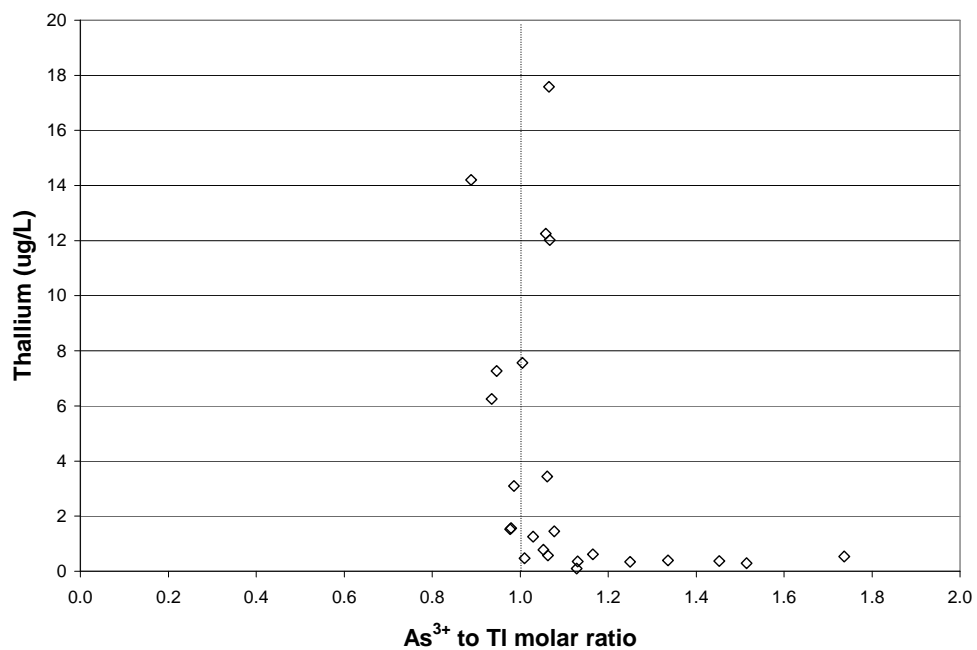**Relationship of Tl With Hg in CCP Leachate**

Figure 6-14
Thallium Concentration as a Function of the As³⁺ to Tl Ratio in CCP Leachate

Case Study Example

In the measured Eh ranges indicative of elevated thallium (+200 to +350 mV), denitrification and nitrate reduction reactions may be occurring, in addition to oxidation reactions involving sulfide and ferrous iron. The fact that thallium is most elevated under conditions that are conducive to these reactions suggests that thallium may be associated with the sulfide or ferrous iron sources in these environments (*e.g.*, pyrites or thallium-sulfides). Introduction of high concentrations of nitrogen species such as NH_3 or NO_3 may initiate biologically mediated reduction reactions that also involve sulfide oxidation.

This potential thallium release mechanism is supported with data collected from a power plant site with seasonal elevations in thallium in ash pond water, primarily in the summer months. The seasonality appears linked to elevated concentrations of NH_3 (Figure 6-15), along with Cu and Mn. Iron concentrations were lower during periods of elevated Tl, NH_3, Cu, and Mn, potentially due to formation of ferric hydroxide. Interestingly, oxyanion concentrations such as Se and As are also lower, potentially due to adsorption onto precipitating ferric hydroxide (Figure 6-16).

Even with evidence of potential oxidation reactions releasing thallium, cation exchange of thallium with NH_4^+ cannot be excluded as a release mechanism, especially given the concurrent elevations of both NH_3 and Tl over time at the site. If thallium is held to easily exchangeable adsorption sites, then temporary increases in NH_4^+ may result in short-term thallium release, followed by re-equilibration to low concentrations over time as observed in laboratory studies by Jacobson et al. (2005).

The important point to consider after evaluating data trends observed at the above power plant site and field leachate data collected by EPRI (2006) is that the same trends of increased thallium at mid-range pH are observed in both data sets (Figure 6-17). This indicates a thallium release mechanism that is not necessarily site-specific, but is widespread, is potentially predictable, and needs further research.
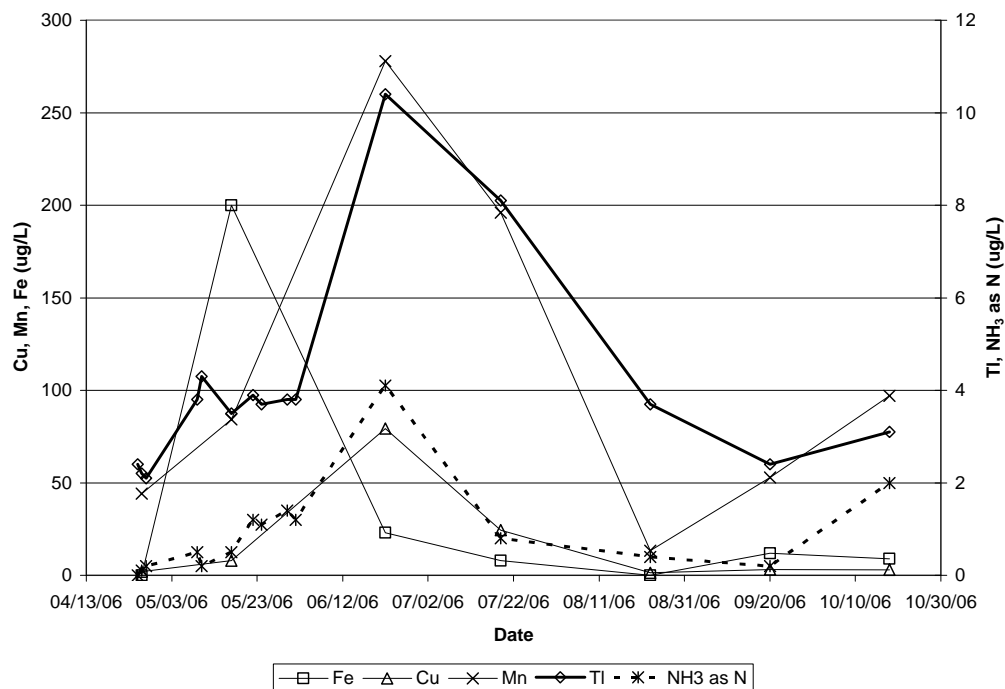
Figure 6-15
Seasonal Trend of Thallium and NH$_3$ in an Ash Pond
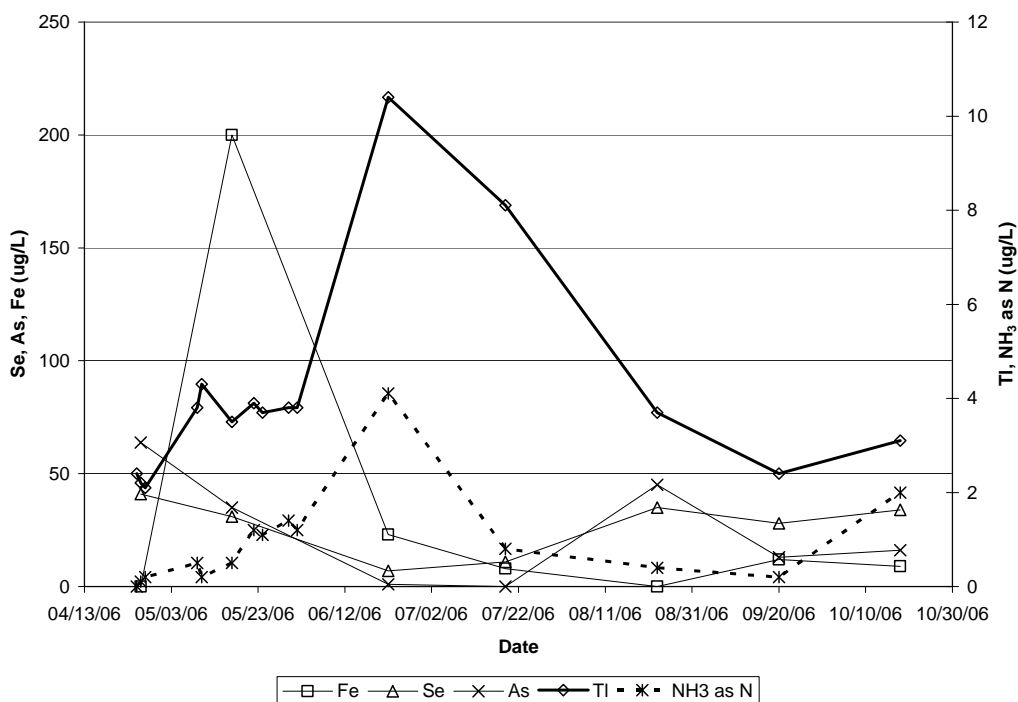
Figure 6-16
Seasonal Trends of Se, As, Fe, Tl, and NH$_3$ in an Ash Pond
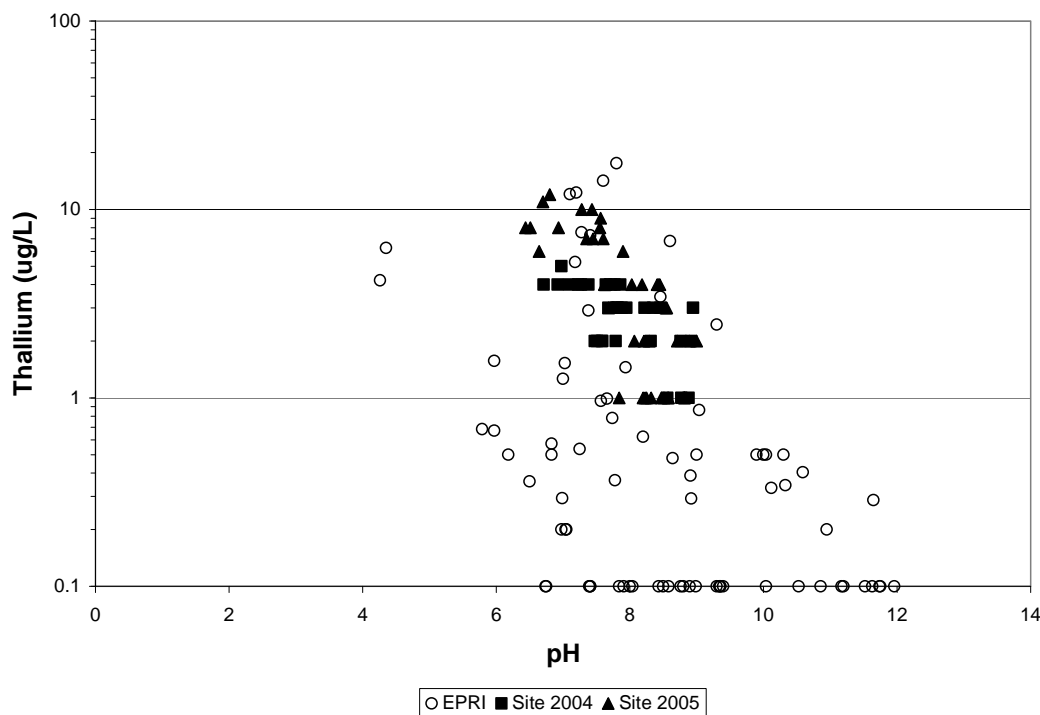
Figure 6-17
Comparison of EPRI field leachate thallium concentrations with the case study, showing common pH conditions of elevated thallium

Thallium Field Leachate Summary

The primary mechanisms controlling thallium mobility include mineral solubility and cation exchange. Highest thallium concentrations in CCP leachate occur under oxidizing conditions (as indicated with measured ORP), and at either low pH or near-neutral pH. Saturation indices support the existence of Tl_2Se. Thallium sulfide minerals are also suggested as present, but SIs were not evaluated due to lack of sulfur speciation data. Highest thallium concentrations in field leachate data also occur when the molar ratio of trivalent arsenic to thallium is approximately equal to one. This suggests possible oxidation of a Tl- and As-bearing mineral, such as lorandite ($TlAsS_2$).

Data from an ash pond with seasonally elevated thallium indicate highest concentrations of thallium concurrent with elevated NH_3, indicating the possibility that thallium release by sulfide oxidation may be coupled to NH_3 reduction. However, the potential for cation exchange with NH_4^+ cannot be excluded. Weakly adsorbed thallium may be temporarily released to the water column by competition with increased NH_4^+. Both sulfide oxidation and cation exchange appear to be viable release mechanisms for thallium.

7
ENVIRONMENTAL SAMPLING AND ANALYSIS

Analytical methods for determining thallium concentrations in environmental samples are listed in Tables 7-1 and 7-2. In most cases, ICP-AES should be avoided due to its lack of sensitivity toward thallium. Using ICP-AES to achieve detection limits less than 2 µg/L is largely experimental. Both AAS and ICP-MS techniques can measure thallium at concentrations less than its maximum contaminant level of 2 µg/L. Analysis by ICP-MS is more efficient than AAS, and is likely the method of choice for routine analysis of aqueous samples.

Table 7-1
Methods for Determining Thallium Concentrations in Aqueous Samples

Matrix	Analytical Method	Detection Limit
Water	AAS	1 µg/L
Natural water	Electrothermal AAS	0.0033 µg/L
	GFAAS	0.01 µg/L
	LIF-GF	0.001 µg/L
	LEAFS	0.0003 µg/L
	ICP-MS	0.002 µg/L
	ICP-AES	1.3 µg/L
Seawater	GFAAS and DPASV	1 µg/L
	Potentiometric stripping voltammetry	10 µg/L
Wastewater	ICP/AES	40 µg/L
	GFAAS	1 µg/L

AAS=Atomic absorption spectroscopy; ICP/AES=Inductively coupled plasma atomic emission spectroscopy; GFAAS=Graphite furnace atomic absorption spectroscopy; LIF-GF=Laser induced fluorescence in graphite furnace; LEAFS=Laser excited atomic fluorescence spectrometry; DPASV=Differential pulse anodic stripping voltammetry; ICP-MS=Inductively coupled plasma mass spectrometer
Table modified from ATSDR (1992) and Nriagu (1998)

Table 7-2
Methods for Determining Thallium Concentrations in Solid Samples

Matrix	Analytical Method	Detection Limit
Soil	FAAS	0.01 µg/g
Sediments, coal, coal fly ash	GFAAS	0.1 µg/g
Stream sediments	FAAS	0.2 µg/g
Coal fly ash	GFAAS	0.1 µg/g
Sediments	LEAFS	0.001 µg/g
Solid waste	AAS	100 µg/L*
Solid waste	AAS	1 µg/L*
Solid waste	ICP/AES	40 µg/L*

*Detection limit of liquid digestate, not corrected for solid
AAS=Atomic absorption spectroscopy; ICP/AES=Inductively coupled plasma atomic emission spectroscopy; GFAAS=Graphite furnace atomic absorption spectroscopy; LEAFS=Laser excited atomic fluorescence spectrometry; FAAS=Flame atomic absorption spectroscopy
Table modified from ATSDR (1992) and Nriagu (1998)

8
TREATMENT AND REMEDIATION

The U.S. Environmental Protection Agency's Best Demonstrated Available Technology (BDAT) is chemical oxidation of thallium followed by chemical precipitation with hydroxide compounds, settling, and filtration (U.S. EPA, 2004a). However, other remedies have been investigated, as summarized below:

- Kyo (1995) (U.S. Patent 5419882) utilized manganese dioxide sludge produced from the electrolysis of zinc to remove thallium from wastewater.

- Nriagu (1998) proposed that TlCl may provide a substantial sink for thallium in contaminated waters. If thallium concentrations are high enough, relatively low amounts of Cl may be required to precipitate thallium from solution. No achievable concentrations are included in this summary, as the proposition was strictly theoretical.

- Mueller (2001) reported thallium removal from contaminated water by microbially mediated thallium sulfide precipitation. Straw and manure were mixed with a gravel matrix, in combination with sulfate-reducing bacteria to precipitate the sulfide. Influent thallium concentrations between 450 µg/L and 790 µg/L were reduced to less than 2.5 µg/L.

- U.S. EPA (2004a) reported successful thallium removal from 300 µg/L to <1 µg/L in mine waste waters by sulfide precipitation. The experiments used metallic iron to reduce the electric potential to levels favorable for thallium sulfide precipitation. Sodium sulfide was used as a source of sulfide. In general, pH greater than 6 s.u. and Eh <-100 mV were necessary to remove thallium as a sulfide.

- EPRI (2008) performed batch tests using CCP leachate samples and several reactive media to determine their effectiveness in reducing concentration of several constituents in CCP leachate, including thallium. Three leachate samples were used in the study but none had sufficient thallium for testing, so one was spiked to achieve a thallium concentration of ~900 µg/L. The initial pH of the sample was alkaline, and since pH was not controlled during the test, the final pH values were media-specific, ranging from more-alkaline than the original leachate sample to neutral. Five media (Humasorb®, activated alumina, compost and wood chips, zero-valent iron, and clinoptilolite) reduced thallium concentration by more than 99% after 30 days, and one (ArsenX[np]) reduced thallium concentration by more than 90% after 30 days. Most of the concentration reduction occurred within the first 1 to 7 days of the test. These tests demonstrate potential for treating water with elevated thallium concentrations by passing it through in situ or ex situ reactive media.

- Dutrizac (1997) found that Tl(I) substitutes for the alkali ion in the jarosite structure, providing an effective means of thallium removal from zinc processing circuits. The author reported nearly ideal jarosite solid solutions with thallium and potassium, and preferential incorporation of thallium relative to ammonium or sodium. In solutions with 0 to 3,000 mg/L thallium, approximately 80% of dissolved thallium can be removed by ammonium jarosite.

- Lacoste et al. (2001) grew green bean, beetroot, green cabbage, lettuce, onion, pea, radish, spinach, tomato, turnip, watercress, and the hyperaccumulator *I. intermedia* on thallium-contaminated soils. It was concluded that phytoremediation of thallium-contaminated soils containing greater than 1 mg/kg thallium will never be feasible by use of common vegetables. For soils containing 1 mg/kg thallium or less, use would have to be made *of I. intermedia* or *Brassica napus* (canola, rapeseed) rather than common vegetables.

- Wierzbicka et al. (2003) examined four plant species (*Plantago lanceolata* (English plantain), *Biscutella laevigata*, *Dianthus carthusianorum* (Carthusian pink), and *Silene vulgaris* (bladder campion)) that were found growing on a 100-year old calamine waste heap for thallium uptake potential. The study was conducted due to findings of elevated thallium in small mammals and bird feathers in the area. Results showed that *P. lanceolata* accumulated extremely large amounts of thallium (average, 65 mg Tl/kg dry wt; maximum 321 mg Tl/kg dry wt in roots). *S. vulgaris* and *D. carthusianorum* accumulated much less (averages, 10 and 6.5 mg Tl/kg dry wt, respectively); and *B. laevigata* accumulated negligible amounts of thallium. The concentration of thallium in plants (shoots, roots) from the calamine waste heap was 100–1000 times the level normally found in plants (0.05 mg Tl/kg dry wt).

- Al Najar et al. (2005) studied the thallium accumulating potential of *Brassica oleracea acephala* L. cv. Winterbor F1 (kale), and candytuft, *I. intermedia* Guers. Thallium was most easily taken up by plant roots in soils where the source of thallium was anthropogenic, rather than geogenic. They found no relationship between the amount of thallium taken up by plant roots and the total thallium concentration in the soil. Instead, thallium availability to the plant is thought to depend most upon the mode of occurrence of thallium in the soil matrix.

- Twiss et al. (2004) found bioactive uptake of inorganic and organic thallium by chlorophytes and diatoms in Lake Erie and Lake Superior. Results showed that the presence of elevated potassium in Lake Erie suppressed inorganic thallium uptake, but not organic thallium uptake. Volume-based bioconcentration factors for Tl(I) after 72 h of exposure were 5×10^4 and 1.1×10^4 for *Chlorella sp*. and *S. hantzschii*; for dimethyl-thallium they were 7.8×10^2 and 8.3×10^3. Both Tl(I) and Tl(III) were concentrated similarly by *Chlorella sp*. These results suggest that chlorophytes, but not diatoms, accumulate Tl(I) to a greater extent than dimethyl-thallium. Greater bioaccumulation factors of inorganic Tl are possible in waters containing low amounts of K^+.

The ability of various media to precipitate and sorb thallium is consistent with the relatively high K_d values reported for this constituent. Data are lacking on the effect of pH on treatment effectiveness, particularly for acidic environments; however, acidic environments are not typical at CCP management facilities.

9
SUMMARY

The objective of this report was to assemble and synthesize available information regarding thallium occurrence at CCP management facilities, and to present an overview of environmental data for thallium. As discussed in the report, thallium occurs naturally in soil, water, and air, as well as in the coal burned to generate electricity. As a result of this process, thallium is also present in coal combustion products (CCPs) such as fly ash, bottom ash, and flue gas desulfurization gypsum.

Included in the report is a wide range of information on the occurrence, health effects, groundwater transport, and treatment of thallium. Data presented can be used to estimate leachate concentrations, to predict migration in soil and groundwater using transport models, to assess effects on potential receptors, to narrow the field of potential treatment options, and to identify data gaps requiring further research. Major findings are summarized as follows.

Occurrence

- Thallium occurs naturally in a wide range of environmental media, including soil, water, and air. Concentrations of thallium in both surface water and groundwater are generally low, and its mobility is limited.

- Thallium is naturally present in coal. Concentrations in U.S. coal vary widely, with the median concentration measuring less than 1 mg/kg. However, concentrations in CCPs are significantly higher, with thallium most likely residing as an oxide or in the non-volatilized sulfide fraction.

- Most anthropogenic sources of thallium to the environment are related to coal combustion, cement manufacturing, and heavy-metal smelting and refining. Major sources of thallium releases to water include nonferrous metal, iron, and steel manufacturers, and various mining, inorganic chemicals, refining, and ore-processing industries.

Health and Ecological Effects

The thallium RfD of 0.00007 mg/kg/d is based on a rat study, and includes an uncertainty factor of 3,000. However, a recent U.S. EPA review of the oral RfD for thallium may result in a lowering of the RfD by 4 to 4.5 times. The revision would result from the new interpretation that hair loss experienced by female rats in the principal study was, in fact, an adverse health effect attributable to thallium rather than a normal cycle of hair growth in rodents. The ATSDR, which independently develops chemical-specific toxicity criteria based on non-cancer health effects called Minimal Risk Levels (MRLs), did not find the data to be sufficient to derive any MRLs

for thallium. The U.S. EPA has indicated that thallium is not mutagenic and that there has been no evidence of cancer in individuals with elevated thallium exposures.

The limited data that are available regarding thallium's health effects indicate the following:

- Thallium is well absorbed through various routes of exposure (e.g., the gastrointestinal tract and skin) in both humans and experimental animals. Little to no data is available regarding other routes of exposure (e.g., inhalation).

- Health effects resulting from acute oral thallium exposure include gastrointestinal problems, hair loss, and neurological deficits. Symptoms of oral chronic thallium toxicity are similar to acute effects, though their development is delayed.

- Human exposure to thallium in the environment has been documented only in a few isolated cases. From these exposures, it was determined that a causal relationship between thallium and human birth defects was unlikely.

- Aquatic species differ widely in their sensitivity to thallium. In assessing thallium's toxicity to aquatic organisms, the modifying effects of site-specific conditions on bioavailability should be considered.

- Thallium accumulation in plants may be of concern in the context of food-web contamination, given that plants are generally more sensitive to thallium toxicity than animals. However, although plants accumulate significant amounts of thallium, the potential risk of thallium enrichment may be mitigated by thallium transformation to less bioavailable forms and other environmental conditions.

Leaching from CCPs and Groundwater Transport

- Thallium concentrations in CCP leachate are typically low. Slightly more than half of the samples had non-detectable concentrations, and the median concentration was less than 1 µg/L. The maximum thallium concentration observed in 81 field-collected leachate samples was 17.58 µg/L.

- Thallium concentrations in CCP leachate were slightly higher in impoundments than in landfills. Thallium concentrations higher than 1 µg/L were noted in CCP leachate when: 1) field-measured Eh values were above +200 mV, and 2) pH values were less than about 9.

- Thallium release from CCPs may be caused by sulfide oxidation, oxide dissolution, or cation exchange. Thallium is readily displaced by NH_4^+, a potentially widespread mechanism releasing thallium from CCPs that deserves more focused research.

- Thallium mobility in aquatic systems is limited by its strong tendency to partition to the solid phase by oxide precipitation or surface adsorption.

- Partitioning coefficients (K_d values) describing thallium's tendency to partition between water and soil are not well constrained. However, even the lowest K_d values found in the literature suggested that thallium has low mobility in groundwater.

- Thallium adsorbs preferentially to manganese oxides when compared to other adsorbents.

Treatment of Thallium

Thallium treatment methods are not well established. At present, the U.S. EPA's best demonstrated available technology for thallium remediation is chemical oxidation, followed by chemical precipitation with hydroxide compounds, settling, and filtration. Recent EPRI research has suggested that several reactive media are potentially effective in removing thallium from water. Other remedies continue to be investigated, including removal from water by:

- Sorption to manganese oxides

- Sulfide precipitation

- Substitution into mineral structures (jarosite)

- Uptake by diatoms and chlorophytes

Additional research has focused on thallium uptake from contaminated soils and found that:

- Uptake of anthropogenic (human source) thallium is more efficient than uptake of geogenic (original rock source) thallium,

- Uptake levels depend more heavily on thallium's mode of occurrence than on total thallium concentration in the soil, and

- *Iberis Intermedia* (candytuft) is a well-known thallium hyperaccumulator that can accumulate >10,000 mg/kg when grown in soils containing as little as 16 mg/kg.

Future Research Needs

Further research focusing on thallium mobility in the environment is warranted because of its low MCL of 0.002 µg/L. The low MCL also highlights a need for further research regarding thallium treatment methods. Furthermore, if the mechanisms responsible for releasing thallium from CCPs are directly identified from focused research, then preventative measures may be taken to limit release of thallium from CCPs.

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