Thallium: Occurrence in the Environment and Toxicity to Fish

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Small amounts of thallium are present in base-metal sulfide ores such as galena, chalcopyrite and sphalerite [ROBINSON 1973]. The market for thallium is limited so that in most cases thallium is not recovered. It is not known how much thallium is discharged in effluents from ore processing. The conventional waste water treatment in the base-metal mining industry, liming and sedimentation, is not likely to remove thallium. Thallium (I) hydroxide is highly soluble in water [REMY 1956].

Little is known about the toxicity of thallium to aquatic fauna. It is lethal to fish in 72 h at concentrations of 10-60 mg/ℓ, and to aquatic insects and invertebrates at 2-4 mg/ℓ [NEHRING 1962]. Tadpoles are killed at a thallium concentration of 0.4 mg/ℓ [DILLING and HEALEY 1926].

This paper reports the concentration of thallium in water and flora of three rivers, draining a base-metal mining area in New Brunswick, Canada, and reports the acute toxicity of thallium to juvenile Atlantic salmon (*Salmo salar*).

EXPERIMENTAL

Study area and sampling. Tailings pond effluents from base-metal mining operations are discharged into South Tomogonops and South Little River in northeastern New Brunswick. Samples of water were taken from the South Tomogonops, the Little and from the South Little River, a tributary of the Little River. Water samples from the South Tomogonops River were taken monthly in April and May, 1973, and weekly throughout the remainder of the year. Water samples from the other rivers were collected in July, September, and November. The samples from the South Tomogonops River were analyzed within one month, those from the other rivers within 2-3 days after collection. Algae and moss samples were collected in September and freeze-dried within one week.

Determination of thallium in water was carried out by

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anodic stripping voltammetry (see for example SINKO and GOMISCEK 1973), using a Metrohm Polarecord E-261 with a hanging mercury drop electrode and a saturated silver-silver chloride reference electrode. Sodium acetate (2M, 2 mℓ), EDTA (0.2M, 2 mℓ), and distilled water (x mℓ) were added to the sample ((20-x)mℓ), and the solution was de-aerated by nitrogen (15 min). The plating potential was -0.89V (SCE) and the plating time was 1-15 min, depending on the concentration of thallium. Thallium was quantitated by the method of standard additions, and the samples were analyzed in 2-5 replicates.

Determinations of copper, zinc, and hardness were carried out by standard procedures.

Determination of thallium in biological samples. Freeze-dried algae and moss were dried to constant weight at 105°C, oxidized by hydrogen peroxide (50%, 0.5 mℓ/0.1 g) and extracted with distilled water. Samples of fish from the toxicity tests were digested with concentrated sulfuric acid and hydrogen peroxide (0.4-0.5 g tissue, 1.0 mℓ sulfuric acid, and after 30 min 1 mℓ 50% hydrogen peroxide) at room temperature until clear, then at 40-50°C until colorless. In both types of digests thallium was determined spectrofluorimetrically by a modified method of KIRKBRIGHT *et al.* (1965). The digest was cooled in ice, diluted with distilled water (1-2 mℓ), sodium hydroxide (10M, 2 mℓ) was added, and the solution was transferred to a 125 mℓ-separatory funnel. Ferric chloride (1%, 0.5 mℓ) and hydrogen peroxide (50%, 0.1 mℓ) were added, the volume was adjusted to 20 mℓ with distilled water and thallium was extracted with diethyl ether (25 mℓ). The ether phase was washed with hydrochloric acid (1.5M, 10 mℓ) and evaporated to dryness in a 50 mℓ beaker. The residue was dissolved in diluted hydrochloric acid (12M hydrochloric acid, 0.5 mℓ, 25 mℓ distilled water). Sulfur dioxide was passed through the solution for 5 sec, the solution was evaporated to 5-10 mℓ on a hot plate and transferred to a 50 mℓ volumetric flask, containing a saturated potassium chloride solution (10 mℓ). The contents were diluted to 30 mℓ with distilled water, hydrochloric acid (12M, 15 mℓ) was added slowly, the volume was adjusted with distilled water to 50 mℓ, and the solution was set aside for 15-60 min in subdued light. The fluorescence was measured on a Perkin-Elmer MPF-2A spectrofluorimeter (excitation 250, emission maximum 430 nm, emission spectrum recorded from 360 to 460 nm). Thallium standards were treated in the same way, and several thallium-spiked samples of fish were also analyzed. Fish exposed to thallium in the toxicity tests were dissected and the muscle, liver and gills were analyzed. Three to four fish were analyzed at each thallium concentration.

Confirmation of thallium was carried out in the July sample of the South Little River water by the spectrofluorimetric method and by paper chromatography. The spectrofluorimetric determination was performed as described above. For paper chromatography, an aliquot was concentrated on a rotatory evaporator at 36°C (1 liter to 100 mℓ), the precipitate was filtered off and an aliquot of the filtrate was chromatographed on a Whatman No. 1 paper, using a mixture of methanol-25% sulfuric acid-water 7:1:4 as the developing solvent (BLOCK et al. 1958]. The location of the thallium zone was determined using thallium standards, detected by spraying the chromatogram with 10% potassium iodide, the thallium zone was eluted with water and thallium was determined in the eluate by anodic stripping voltammetry.

Toxicity tests were carried out as described previously by ZITKO et al. (1973) using juvenile Atlantic salmon of 7.6-13.8 cm. In long-term tests the fish were fed after the first 15 days. Water samples were analyzed for thallium at least once a week, for copper and zinc daily. Water temperature ranged from 7 to 17.5°C and hardness was 14 mg/ℓ as calcium carbonate.

RESULTS AND DISCUSSION

Determination of thallium in water. The reproducibility of the determination of thallium by anodic stripping voltammetry, expressed as relative standard deviation, was 17% at 2 and 18 μg/ℓ, 12 and 8% at 45 and 70 μg/ℓ, respectively. The loss of thallium during the storage of samples in polyethylene bottles, determined on a spiked South Tomogonops water sample, was 30, 40, 44, and 46% after 1, 2, 3, and 4 weeks, respectively. The data in Table 1 are corrected accordingly.

The concentration of thallium in the South Tomogonops River was quite low for most of the year except for the period of the spring runoff in April and May. Thallium concentration in the South Little and Little River was much higher. It is possible that the contribution of thallium to the pollution of this river system is now relatively minor in comparison to the pollution by copper, zinc, and sulfuric acid [ZITKO and CARSON 1969]. Thallium may, however, become the major contaminant once these other pollutants are removed by the conventional wastewater treatment. In our experiment only 28% of thallium was removed from South Little River water by the precipitation of heavy metal hydroxides at pH = 9.6 and centrifugation.

TABLE 1

Results of water analyses

Date	Location*	Concentration (μg/ℓ) Tl	Cu	Zn	Hardness mg/ℓ	Flow m^3/min
April	ST	20.0	6.0	33.3	270	85.3
May	ST	5.8	2.7	31.0	255	108.0
June-Jan.	ST					
mean		2.5	7.4	182	538	15.6
range		0.7-8.0	1-21	10-2500	250-890	4.2-32.4
July	SL	88.3	41	32000		19.6**
September	SL	51.0	190	4150	1050	
	L	42.4	160	2350	915	13.4**
November	SL	9.0	93	6320	400	374**

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*ST, SL, L = South Tomogonops, South Little, and Little River, respectively.

**flow in the Little River.

The concentration of thallium in two grab samples of the tailings pond effluents, discharging into the South Tomogonops and South Little River in September, was 26.6 and 1620 μg/ℓ, respectively.

The thallium concentration determined by spectrofluorimetry in the July sample from the South Little River was 60.0 μg/ℓ. Thallium in this sample was also confirmed by paper chromatography.

Thallium in algae and moss. Thallium was detected in all samples. The concentration found in three algae samples was 9.5, 10.6, 19.6, and 19.8, 35.3, 43.4 μg/g dry weight in the South Tomogonops and the South Little River sample, respectively. Two moss samples from the South Tomogonops River contained thallium at 125 and 162 μg/g dry weight. The significance of these levels of thallium is not known, since the concentration of thallium in plant material is seldom reported [BOWEN 1966]. The accumulation coefficient of thallium by *Ulva lactuca* is relatively low [POLIKARPOV 1970].

Toxicity of thallium to juvenile Atlantic salmon. Salmon die relatively slowly in thallium solutions (Fig. 1). No incipient lethal level is visible as a sharp break-off point on the lethality (LT50 vs concentration) curve. In contrast, an incipient lethal level is clearly visible on the lethality curve of copper [ZITKO *et al.* 1973] and zinc [SPRAGUE 1964]. At the lowest thallium concentration, indicated in Fig. 1, the mortality was the same as for the control fish and it is

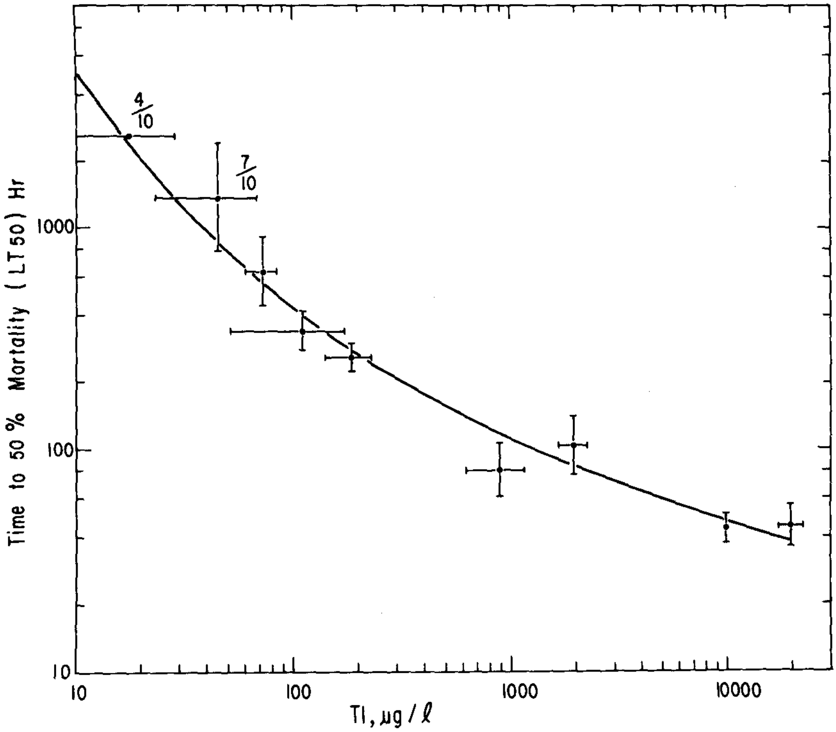

Figure 1. Toxicity of thallium to juvenile Atlantic salmon. Empirical equation of the curve is $\log(LT50) = 1/(0.161 + 0.109 \log c)$. Confidence intervals (95%) are indicated in the Figure. Mortality was 100% except for the two low concentrations, where the mortality was 70 and 40% at the termination of the test (2600 h).

possible that an incipient lethal level may exist at approximately 30 µg/ℓ. Thallium then would be as acutely toxic as copper on weight basis, and 3-4 times more acutely toxic on molar basis, to juvenile Atlantic salmon. In any case, thallium is much more acutely toxic to this species than to those tested by NEHRING (1962).

Humic acid decreases the toxicity of copper to juvenile Atlantic salmon as a result of complex formation [ZITKO et al. 1973]. Thallium is not complexed by humic acid [O'SHEA 1972] and thallium toxicity is probably not affected by its presence. The general lack of complex formation by thallium [LEE 1972] may make the thallium toxicity also independent of water hardness.

The toxicity of copper-thallium and zinc-thallium mixtures is not additive (Table 2). Fish are killed either by copper (zinc) or by thallium and the LT50 values are similar to those obtained with each metal alone.

TABLE 2

Toxicity of copper-thallium and zinc-thallium mixtures.

Concentration, µg/ℓ			
Tl	Cu	Zn	LT50, h
-	37		25
100	33		37
-	30		10% mortality in 743 h
100	29		460
-		1290	52
100		1273	50
-		885	No mortality in 839 h
100		859	570

TABLE 3

Mean accumulation coefficients of thallium in laboratory exposed juvenile Atlantic salmon (Exposures over 300 h)

Thallium concentration in water, µg/ℓ	Accumulation coefficient*		
	Muscle	Liver	Gills
17.9	130	216	1430
45.0	114	150	27
100	146	235	300
200	135	80	161

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*tissue concentration, µg/g wet weight, divided by water concentration, µg/mℓ.

Mean recovery of thallium from spiked fish tissues was 90%. The accumulation coefficients of thallium in juvenile Atlantic salmon are presented in Table 3. The values are somewhat higher than those reported for copper [KARIYA *et al.* 1967; BRUNGS *et al.* 1973], zinc [MOUNT 1964; HOSS 1964; LEBEDEVA and KUZNETSOVA 1969], and cadmium [MOUNT and STEPHAN 1967]. At exposure times below 200 h (thallium concentration 1000-10,000 μg/ℓ) the fish died before an equilibrium was reached in the thallium uptake. In these cases, the levels of thallium at death were 3.6-34, 5.7-46, and 7-89 μg/g wet weight in the muscle, liver, and gills. respectively. There is practically no information in the literature on the natural levels of thallium in aquatic fauna [BOWEN 1966].

CONCLUSIONS

Thallium is present in the effluents of the base-metal mining industry, and its acute toxicity to juvenile Atlantic salmon is approximately equal to that of copper. The usual treatment of waste water with alkali to remove heavy metals by precipitation has little effect on thallium. The limited use of thallium will not lead to a global contamination of the environment, but localized problems may exist or develop in the future, mainly as a result of mineral processing.

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