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Local Impacts of Coal Mines and Power Plants across Canada. I. Thallium in Waters and Sediments

V. Cheam,* G. Garbai, J. Lechner and J. Rajkumar

National Water Research Institute, Environment Canada, P.O. Box 5050, Burlington, Ontario L7R 4A6

A Canada-wide survey was undertaken of sites associated with coal mines and coal-fired electrical generating stations. Several water samples were found to contain very high concentrations of thallium, iron and manganese. High thallium concentrations were found in several sites in Eastern Canada, in spite of the greater coal consumption and production in the western and central regions. The data suggest that coal type (rather than quantity) and/or regional geological contributions are responsible for the high Tl concentrations observed. Our findings, coupled with others around the world, strongly indicate that Tl is an environmental pollutant. In sediments, the observed high ratios of Tl/Hg suggest there is an enrichment of Tl by at least 25% when compared to crustal concentration ratios.

Key words: **coal mine, power plant, thallium, thallium enrichment, mercury, waters and sediments**

Introduction

Coal is Canada's most abundant fossil fuel. Its annual production and consumption exceed 78 and 55 million tonnes, respectively (Table 1, The Coal Association of Canada 1997). Across Canada there are 35 active coal mines and 25 coal-fired generating stations (Tables 2 and 3). Coal is also important to the Canadian economy and its exports are worth $2 billion (Natural Resources Canada 1994).

However, the effects of coal production and consumption may be detrimental to the environment. For example, Smith and Carson (1977) reported that the air emissions from the 415 American coal-burning power plants in highly populated regions form the largest collective source of thallium (Tl) discharged atmospherically. Four states around the Great Lakes (including Ohio), along with Texas, have the highest coal-fired generating capacity in excess of 15,000 megawatts of electrical power. Indeed, we recently found that the concentration of dissolved Tl in the Great Lakes waters, particularly Lake Erie, is higher than that of cadmium (Cd). These two facts led us to suspect that high concentrations of Tl and other metals, as well as organics, may be found surrounding coal

* Corresponding author; *ven.cheam@cciw.ca*

Table 1. Production, consumption, import and export of coal in Canada (in tonnes)

Province	Production	Consumption	Import	Export
British Columbia	27,892,747	200,817	—	27,278,581
Alberta	36,343,416	26,264,343	—	9,181,069
Saskatchewan	11,652,553	10,018,189	—	—
Manitoba	—	263,829	185,572	—
Ontario	—	13,877,042	11,393,496	—
Quebec	—	732,265	750,265	—
New Brunswick	170,958	1,326,676	1,150,622	—
Nova Scotia	2,632,994	3,051,199	—	49,924
Total	78,692,668	55,734,360	13,479,955	36,509,574

mines and coal-based power plants, with consequent environmental effects. This part of the study describes a Canada-wide survey of local impacts of coal mines and power plants in terms of thallium and other metals in waters, as well as thallium and mercury in sediments (part 2 will deal with metals, organics and toxicity in sediments).

Materials and Methods

Mines and Power Plants in Canada

The study was designed to include all Canadian active coal mines and coal-burning electrical power plants (generating stations), the locations of the principal ones being shown in Fig. 1 and 2. These mines have a saleable production of coal ranging from 0.27 million tonnes by NB Coal Limited to 12.7 million tonnes by Highvale (The Coal Association of Canada 1998). Alberta and other western provinces have more plants and mines than the eastern and central provinces combined. Most of the sites were accessible and therefore sampled, and the remaining sites were either closed or inaccessible, as access permission was not provided (by two companies).

The following companies provided permission to collect water and sediment samples from their sites: Alberta Power Limited, Cape Breton Development Corporation, Edmonton Power, Luscar Ltd., Manalta Coal Ltd./Prairie Coal Ltd. Mines, Manitoba Hydro, NB Coal Limited, New Brunswick Power Corporation, Nova Scotia Power, Ontario Hydro, Quinsam Coal Corporation, SaskPower, Smoky River Coal Limited, and TransAlta.

Sampling Protocols

At each sampling location (a mine or a generating station), there are at least three sampling sites: water intake such as upstream of a river,

Table 2. List of all active coal mines in Canada and their owners

Principal mines and their owners
(1997 data from the The Coal Association of Canada)

British Columbia
- Quinsam, Quinsam Coal Corporation
- Bullmoose, Teck Corporation
- Quintette, Teck Corporation
- Fording River, Fording Coal Ltd.
- Greenhills, Fording Coal Ltd.
- Line Creek, Line Creek Resources Ltd.
- Elkview, Teck Corporation
- Coal Mountain, Fording Coal Ltd.

Alberta
- Smokey River, Smokey River Coal Ltd.
- Obed, Luscar Ltd.
- Highvale, TransAlta Utilities Corporation
- Whitewood, TransAlta Utilities Corporation
- Luscar, Luscar Ltd.
- Gregg River, Manalta Coal Ltd.
- Coal Valley, Luscar Ltd.
- Genesee, Edmonton Power & Fording Coal Ltd.
- Vesta, Alberta Power Ltd.
- Paintearth, Luscar Ltd.
- Montgomery, Manalta Coal Ltd.
- Sheerness, Luscar Ltd.

Saskatchewan
- Poplar River, Manalta Coal Ltd.
- Utility, SaskPower
- Boundary Dam, Luscar Ltd.
- Costello, Manalta Coal Ltd.
- Shand, Luscar Ltd.
- Bienfait, Luscar Ltd.

New Brunswick
- NB Coal (Minto), NB Coal Ltd.

Nova Scotia
- Prince, Cape Breton Development Corporation
- Phalen, Cape Breton Development Corporation

Minor mines
(Natural Resources Canada 1998)

Alberta
- Dodds
- Egg Lake

Nova Scotia
- Stellarton
- Thomas Brogan
- Evans
- Thorbourn

Table 3. List of coal-based electrical generating stations and their owners

Alberta
Sundance, TransAlta Utilities Corporation
Wabamun, TransAlta Utilities Corporation
Keephills, TransAlta Utilities Corporatioin
Battle River, Alberta Power Ltd.
H.R. Milner, Alberta Power Ltd.
Sheerness, Alberta Power Ltd. and TransAlta Utilities Corporation
Genesee, Edmonton Power
Saskatchewan
Boundary Dam, Saskpower
Poplar River, Saskpower
Shand, Saskpower
Manitoba
Brandon, Manitoba Hydro
Selkirk, Manitoba Hydro
Ontario
Nanticoke, Ontario Hydro
Lakeview, Ontario Hydro
Lambton, Ontario Hydro
Thunder Bay, Ontario Hydro
Atikokan, Ontario Hydro
New Brunswick
Belledune, New Brunswick Power
Dalhousie, New Brunswick Power
Grand Lake, New Brunswick Power
Nova Scotia
Lingan, Nova Scotia Power
Glace Bay, Nova Scotia Power
Point Alconi, Nova Scotia Power
Trenton, Nova Scotia Power
Point Tupper, Nova Scotia Power

water discharge after the intake has gone through all necessary processes, and water at the tailing/disposal site such as downstream or pond. Additional samples such as those from settling lagoons, nearby lakes and rivers are also included if available.

Bottle washing

All containers were washed as follows: rinsed with hot tap water and emptied well, soaked with 30% nitric acid for at least 1 week, rinsed with Milli-Q water six times, and soaked with 0.2% nitric acid (high purity) for a minimum of 1 week before use. Sub-boiled Seastar acid was used to preserve samples.

Water sampling

Van Dorn bottles were used whenever possible. If the Van Dorn bottle was inappropriate, a "scoop" technique was used, where a "sampling bottle" (250-mL bottle) was scooped to an arm-length depth under the

Fig. 1. Coal-fired electrical generating stations in Canada.

Fig. 2. Principal coal mines in Canada.

water surface. A sample bottle was rinsed three times with the actua sample first before it was filled up to top. Standard precautions were fol lowed, such as avoiding touching the bottle rim throughout sample col lection and handling, tightening bottle caps to avoid cross contaminatioı due to possible leakage during transportation, bagging blanks separatel from samples, storing samples in ice chest immediately, collecting sedi ments last and bagging them completely separated from water samples A total of 279 different samples were collected.

Sediment sampling

Several sites for initial examination were selected in this study. Thirty- two sediment samples were collected, 17 from power plant sites and 15 from mine sites. A mini-ponar sampler (1 to 2 L) or an Eckman sampler was used to collect sediment samples. All containers, bags, spoons and other utensils used were plastic. All sediment samples were collected after water collection.

Collection of blanks and duplicate samples

The collection of blanks using a Van Dorn bottle was done as follows. On site and just before collecting the first upstream water sample, the Van Dorn bottle was well rinsed with 1 L of ultrapure water. The last part of the rinsing water was collected into a small bottle marked "blank before". The upstream water sample was then collected in duplicate by rinsing and then filling two separate small bottles to the rim. The "blank after" was obtained by rinsing the Van Dorn bottle with 1 L of ultrapure water, the last part of which was saved as blank.

The collection of blanks using a "scooping" technique was similarly processed as above. On site and just before collecting the first upstream water sample, a 250-mL sampling bottle was rinsed three times with 20 to 30 mL of ultrapure water and the fourth rinse was saved as "blank before". The upstream water sample was then collected in duplicate by scooping the 250-mL bottle into an arm-length depth and by rinsing then filling two separate small bottles to the rim. The "blank after" was obtained as above by collecting the fourth rinse. In total, about 7% of the samples were blank samples . More than 40% of the samples were measured for pH before acidification to give an idea of the sample acidity. Most samples had a pH between 7 and 8. Duplicate samples for discharge and downstream sites were collected as above.

Separate bagging

Samples for blanks, upstream, discharge, downstream and sediment were bagged separately to avoid cross-contamination.

Sample Collection, Handling and Preservation

Water samples were refrigerated immediately after collection and maintained at 4°C. When in our laboratory, the samples were allowed to settle in a 4°C room overnight or over the weekend. The clear samples, i.e., those without visible particulates, were preserved by acidifying the whole bottle content to 0.2 % HNO_3. From the samples with visible particulates settled at the bottom of the bottle, 20 mL of the clear upper layer was pipetted (called decantate) into a clean container and preserved at 0.2% HNO_3. The samples with suspended materials were centrifuged and the decantate acidified. Those samples, which were cloudy due to suspension or naturally colored due to humic substances, were centrifuged and acidified as above. Samples with high-salt content, as evidenced by severe peak height suppression during analysis for thallium, were diluted 10 times or more until the suppressive effect was manageable.

Sediment samples were refrigerated at 4°C until use. Plastic bottles of 250 mL in size were used for the wet sediments, which were freeze-dried, crushed, sieved and subsampled for the determination of Tl and Hg.

Analytical Methods and Analytes

Trace metals in waters were determined using the inductively coupled plasma–atomic emission spectrometry (ICP-AES). The detection limits (in mg/L) were 0.034 for Cd, 0.009 for Co, 0.009 for Cr, 0.01 for Cu, 0.012 for Fe, 0.002 for Mn, 0.02 for Ni, 0.025 for Pb, 0.126 for Tl and 0.009 for Zn. Thallium, undetected in both substrates by ICP-AES, was determined by the LEAFS (laser-excited atomic fluorescence spectrometric) methods recently developed by Cheam et al. (1996; 1998). The method for water analysis had a detection limit of 0.03 ng/L for thallium and that for sediment 0.5 ng/g of Tl. Mercury in sediments was determined by the cold vapor atomic absorption spectrometry, and the detection limit was 2 ng/L of mercury for aqueous solutions.

The sediment extraction procedures for metals were as follows. For thallium, a weight of 0.1 g of sediment was used and dissolved via the simple cold dissolution procedure; it used 2.5 mL of concentrated nitric acid and 2.5 mL of concentrated hydrofluoric acid, followed by a dilution (Cheam et al. 1998). For mercury, 0.2 g of sediment was weighed into a microwave Teflon bottle followed by the addition of 5 mL of HNO_3. The mixture was left to stand over the weekend and was microwaved. Three-and-a-half mL of the digested solution was pipetted into a volumetric flask, diluted to 100 mL, preserved by BrCl, and analyzed by a cold vapor atomic absorption method.

Results and Discussion

Thallium and Other Metals in Water

Metals determined by ICP included Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl and Zn. Seventy-nine percent of the total data showed "less than" values, and of the 21% reportable positive results, more than half were Fe and Mn results. For the Highvale Mine, the "pit 2 drain" site contained up to 70 mg/L of Fe and positive results for other metals, except Pb and Tl. The "pit 3 settling pond" inflow had 40 mg/L of Fe compared to only 0.01 mg/L for the outflow. For other metals, the inflow concentration was also greater than the outflow, indicating an effective removal mechanism of metals in the settling pond. It was interesting to note that the Fe concentration of the local groundwater (well water) contained a high Fe concentration of 20 mg/L. The three sites had positive, but relatively low results — < less than 1 mg/L, for Mn and most other metals.

The impoundment #5 discharge of the Paintearth Mine contained a very high Fe concentration of 122 mg/L. This mine is located by the Paintearth Creek, whose upstream Fe concentration was fairly high at 1.5 mg/L, and downstream concentration at 7 mg/L. Also the mine's runoff discharge contained 10 mg/L of Fe. The coal pile runoff of the Lingan generating station had a high Fe content of 72 mg/L and 4 mg/L of Mn, but the wastewater discharge to lagoon and ash lagoon return contained less than 1 mg/L of Fe and 2 mg/L of Mn, respectively. Other sites containing more than 1 mg/L of Fe included the spoil pond 5-5 of the Boundary Dam generating station, the ash lagoon slurry of the Keephills generating station and the settling pond discharge MSA of the Line Creek Mine. The sites at the Belldune generating station had high Mn concentrations, the treated discharge containing 73 mg/L, the equalization pit 55 mg/L and the coal pile runoff 14 mg/L of Mn. On the other hand, Fe concentrations in these sites were less than 1 mg/L. These sites also contained positive results of Ni and Co.

Besides Fe and Mn, nickel had only 24% of its data as reportable positive results and cobalt had 22%. Other metals had lower percentages: Cr 18%, Zn 16%, Cu 11%, Pb 6%, Cd 1% and Tl 0%. Since Tl is a very toxic element and of particular importance, according to the statement by Smith and Carson (1977) that the air emissions from coal power plants form the largest collective source of Tl discharge into the environment, Tl was also measured by the LEAFS method and is discussed below. For all the metals measured, the upstream metal concentrations were found to be smaller than the downstream, discharge or pond concentrations 95% of the time.

Table 4 shows Tl results in western coal mine waters. Samples with brown-black deposits and brown decantate such as those from the Highvale and Paintearth mines tended to have higher Tl concentrations than other samples. For three such samples from the Highvale mine, centrifugation did not help bring down Tl concentration of the decantates. It appears that decantation (careful pipetting of 20 mL of the solution above the deposit) was representative of the water samples. Also, samples from settling pond, pit water, downstream and discharge usually had concentrations (1100 to 1300 ng/L) higher than those from upstream or water intakes (low ng/L). The eastern mines, including the abandoned ones, showed high Tl concentrations of about 700 ng/L (Table 5). Although these concentrations were not as high as those observed in the eastern power plant sites (discussed below), they might have come from the same Tl sources.

Table 4. Thallium concentrations in ng/L in waters from western coal mines

Western mines	Site/sample description	Tl concentration
Whitewood Mine (TransAlta Utility Corp.)	Pit water discharge (some black deposit, clear decantate), decanted[a]	6.64
Highvale Mine (Manalta Coal)	Pit 2 drain (brown deposit, ~ clear dark brown decantate), decanted	463.6
	Duplicate, centrifuged[b]	518.5
	Pit 3 (some brown deposit, ~ clear dark brown decantate), decanted	106.9
	Duplicate, centrifuged	109.3
	Beaver Creek (clear)	2.92
	Pit 3 settling pond — outflow (clear)	0.32
	Pit 3 settling pond — inflow (black deposit, clear dark brown decantate) decanted	846.1
	Duplicate, centrifuged	1326.2
	Well water (local groundwater) (visible particulates[c], clear decantate), decanted	5.47
Genesee Mine	Mine drainage (some brown deposit, clear decantate), decanted	7.52
Coal Valley Mine	Tailings discharge (visible particulates, clear decantate), decanted	7.20
Luscar — Sterco (Luscar Ltd.)	Lovett River intake (clear)	2.82
	Duplicate, centrifuged	2.43
	Coal Creek impoundment (clear)	2.70
	Lovett River downstream (clear)	8.64
	Duplicate	4.21
	25 ? east mine drain (visible particulates, clear decantate), decanted	16.4
	Centre Creek — treated water (clear)	16.6
	Reservoir — well water (clear)	1.74

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Gregg River Mine (Manalta Coal)	HI pit — plant makeup (clear)	16.3
	Plant site water reservoir (clear)	63.9
	Refuse = tailings (black coal-like deposit, clear decantate), decanted	9.49
	Well water — tap (clear)	3.67
Cardinal River Mine (Luscar Ltd.)	West Jarvis Creek intake (clear)	4.13
	Luscar Creek downstream plant (visible particulates, clear decantate)	6.54
	Duplicate, decanted	5.92
Cardinal River Mine (Luscar Ltd.)	Tailings (black coal-like deposit, clear decantate), decanted	17.1
	Well water (clear)	1.46
	Luscar Creek, downstream Cardinal and Gregg mines (clear)	3.56
Whitehorse Creek	At Mountain Park (clear)	1.78
	Downstream Mountain Park (clear)	1.33
	Downstream Cadomin — abandoned, but active quarry (clear)	2.39
Gregg River	Downstream Gregg River Mine, at Hwy 40 (clear)	2.59
Obed Mountain Coal (Luscar Ltd.)	E. conveyor settling pond (visible particulates, clear decantate), decanted	3.61
	Main tailings pond (lower) (visible particulates, clear decantate), decanted	0.91
	Reservoir (treated water) (visible particulates, clear decantate), decanted	7.97
	Main tailings pond (upper) (dark brown deposit, clear decantate), decanted	2.24
	Duplicate, decanted	2.95
	LSP2 — coal storage drain (for rail shipment) (clear)	19.1
Smoky River Coal (Smoky River Coal)	Sheep Creek upstream Smoky River (clear)	2.42

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Line Creek Mine (Manalta Coal)	Settling pond discharge — MSA north ponds (clear)	5.26
	Line Creek upstream — 0200335 (clear)	0.66
	Duplicate	0.20
	South pit water (dark brown deposit, clear decantate), decanted	217.4
	Line Creek downstream (clear)	6.92
	Duplicate	5.37
	Wash water after thickener (visible particulates, clear decantate), decanted	38.5
	Tap water not treated (clear)	9.07
Elk River	At Sparwood downstream from four mines (clear)	2.51
Crowsnest Creek	Crowsnest Pass (downstream coal mountain mine) (clear)	9.09
Sheerness Mine (Luscar Ltd.)	Pit water (visible particulates, light decantate), decanted	10.6
Montgomery Mine (Manalta Coal)	Pit water (visible particulates, light decantate), decanted	1.84
	Settling pond discharge (visible particulates, light decantate), decanted	4.55
Carolside reservoir	Downstream mines and GS (visible particulates, light decantate), decanted	4.19
Paintearth Mine (Luscar Ltd.)	Surface runoff discharge (very brown, brown decantate), decanted	811.2
	Section 7 Lake (pit and surface runoff) (dk brown, lt brown decantate),decanted decanted	63.0
	Impoundment #5 discharge (black deposit, visible brown decantate), decanted	1119.1
	Paintearth Creek downstream (very brown deposit, light brown decantate), decanted	257.3
	Paintearth Creek upstream (brown deposit, very light brown decantate), decanted	35.7
	Blank before	0.73
	Blank after	0.93

(continued)

Table 4. *(continued)*

Western mines	Site/sample description	Tl concentration
Vesta Mine	North drainage (brown deposit, very light brown decantate), decanted	53.5
(Manalta Coal)	Vesta east — Pond 3 (brown deposit, clear decantate), decanted	51.7
Crowsnest River	Upstream Chinook coal plant, Coleman, Alberta (clear)	4.29
(Chinook Coal)	Decommissioned in 1978 (clear)	4.72
(Manalta Coal)	Blank before (clear)	0.14
	Blank after (clear)	0.72
	Downstream Chinook coal plant (clear)	3.96
	Duplicate	4.72
	Downstream Coleman and Frank slide (clear)	5.07
	Downstream Leitch Colliery (clear)	2.95
Hell's Gate	Groundwater (clear)	2.58
Athabasca River	Hwy. 93 south of Jasper (clear)	1.03
Poplar River North Mine	Settling pond NSP1 (clear)	2.81
(Prairie Coal Ltd.)	Upstream East Poplar River (clear)	0.92
	Duplicate	1.19
	East Poplar River — upstream blank (clear)	0
	Duplicate	0
	East Poplar River — downstream (clear)	3.79
Utility Mine (Prairie Coal Ltd.)	Settling pond E-4	34.9
	Pond near coal storage pile	6.86
	Dewatering discharge into BD reservoir	8.05

(continued)

Table 4. *(concluded)*

Western mines	Site/sample description	Tl concentration
Boundary Dam mine (Estervan Coal Corp.)	Settling pond/holding pond	17.7
Bienfait Mine	Dewatering discharge from west side of mine	50.7
(Estervan Coal Corp.)	Discharge from mine areas of section 4-2-6-W2M (V-notch weir)	12.8
Costello Mine expansion (Prairie Coal Ltd.)	Dewatering discharge from proposed mine	1.26
Old Mac Mine — abandoned	Old coal spoil pond (Old Mac Mine)	0.31
Quinsam Mine	Blank before (clear)	1.13
(Quinsam Coal Corporation)	Blank after (clear) on Quinsam River flowing towards mine (clear)	0.19
	Duplicate	0.68
	Settling pond (clear)	5.69
	Duplicate	6.27
	Downstream from the mine on Quinsam River before going into the small lake (clear)	0.35
	Duplicate	0.53
	Downstream outlet of the small lake (clear)	1.47
	Duplicate	1.07

[a] Decanted refers to 20 mL pipetted from the top of bottle, which was left to settle in the cold room overnight or longer.
[b] Centrifuged refers to sample being centrifuged as compared to decanted.
[c] Visible particulates are particulates at bottom of bottle.

Table 5. Thallium concentrations in ng/L in waters from eastern coal mines

Eastern mines	Site/sample description	Tl concentration
8200 Salmon Harbour Mine (New Brunswick Coal)	Pit water (visible particulates, clear decantate), decanted[a]	53.3
	Duplicate, decanted	35.2
	Lagoon discharge (visible particulates, [b]clear decantate), decanted	9.33
	Duplicate, decanted	6.55
	Lake water (visible particulates, clear decantate), decanted	7.72
	Duplicate, decanted	7.43
Phalen Colliery, Nova Scotia (Cape Breton Development)	Mine water discharge (high Na) (brown clear decantate), decanted	424.0
	Town water (from tap at security) (clear)	4.13
	Surface runoff brook (visible particulates, clear decantate), decanted	169.2
Victoria Junction coal Preparation plant, Nova Scotia (Cape Breton Development)	V.J. tailings basin — old final discharge KL1 (clear)	18.9
	V.J. tailings basin KL3 (clear)	1.47
	V.J. final discharge WWT3 — treated water (clear)	121.1
	North and south process wells — for wash and town water (clear)	0.64
	Surface water pond WWT1 (brown, clear brown decantate), decanted	404.3
Prince Colliery, Nova Scotia (Cape Breton Development)	Process water — reservoir and well combined (clear)	1.95
	Mine discharge and coal pile runoff (light clear decantate), decanted	698.3
	Treated lagoon discharge (clear)	565.0
	Downstream discharge (clear)	552.5
	Duplicate	514.0

(continued)

Table 5. *(concluded)*

Eastern mines	Site/sample description	Tl concentration
Abandoned coal mines[c]		
Gardiner Mine	Mine discharge (clear brown decantate)	0.15
Pioneer Coal	At Sydney Airport	100.9
	Duplicate	107.2
Brogan Brothers	At Point Aconi 5th seep	83.8
Brogan Brothers	At Point. Aconi 11th seep	76.5
Prince	At Edwards Pond	660.6
Prince	Duplicate	718.5

[a] Decanted refers to 20 mL pipetted from the top of bottle, which was left to settle in the cold room overnight or longer.

[b] Visible particulates are particulates at bottom of bottle; .particulates in decantate may give high results if decantate is not diluted — filtration or digestion may be needed for more accurate results if dilution is not done.

[c] Samples were subsampled by Henry Wong, NWRI, Environment Canada.

The majority of results for the generating stations in western provinces were low (Table 6). The blank values ranging from 0 to 6 ng/L were considered acceptable as the clean-room practices (clean hood, special clean clothes or gloves) were not followed since it was deemed unnecessary to use them in this study. The results for discharge water, ash lagoon, ash slurry or downstream were higher than for other locations, but even the highest results — 97 ng/L for Long Creek below Boundary Dam reservoir, or 140 to150 ng/L for Keephills ash lagoon slurry — were low when compared to the high results of some sites to be discussed below.

Samples collected from the eastern power plants sites in New Brunswick and Nova Scotia generally contained higher Tl content than their western or central counterparts (Table 7). For example, the ash lagoon discharges of Grand Lake and Trenton power plants contained some 12,000 ng/L and 24,000 ng/L of Tl, respectively. The other generating stations, such as Belledune, Lingan, Point Aconi and Point Tupper, also had elevated Tl concentrations of up to 5000 ng/L. These levels could be the result of the local geological contribution in the eastern provinces, or the type of coal used. The Belledune generating station, for example, reportedly had been using 75% Columbian coal and 25% Salmon Harbour coal. The Tl concentrations in the central (Ontario) sites were relatively low, the highest being only 175 ng/L (Table 7) and the mean value 38 ng/L. The western sites had a mean value of 47 ng/L (range between 0 and 1326 ng/L), whereas the eastern sites' mean value was 1376 ng/L (range between 0 and 23,605 ng/L). Even if we include the Tl concentrations in lakes around the Inco smelters in Sudbury, Ontario, which we recently measured, the mean value for the central region would still be small. Also, several water samples collected from the province of Quebec were found to contain small Tl concentrations.

Even though the Great Lakes are surrounded by the biggest consumers of coal used in coal-fired generating stations in both the U.S. (Fig. 3) and Canada (Table 8), the concentrations of Tl in the Great Lakes waters (Cheam et al. 1995) were much lower than those found in waters from the eastern generating stations (Table 7). The numerous power plants and mine sites in Western and Central Canada also contained smaller Tl concentrations than their eastern counterparts. These two facts tend to indicate that it is not the amount but the type of coal used and/or the local geochemical contributions that caused some of the higher Tl concentrations observed in the eastern provinces. Chou and Uthe in 1995 had observed high Tl content in Belledune Harbour and although the source of Tl was obscure, they suspected that the nearby fertilizer plant and the lead smelter, as well as the power plant, were the sources of thallium. Zitko et al. (1975) reported very high Tl concentrations (up to 88,300 ng/L) in the South Tomogonops River, Little River and South Little River in northeastern New Brunswick. South Tomogonops and South Little rivers received discharges from base-metal mining operations. Wong (personal communication) had found very high Tl content in some local sediment samples, such as those from Upsalquitch Lake.

Table 6. Thallium concentrations in ng/L in waters from western generating stations (GS)[a]

Western GS	Site/sample description	Tl concentration
Wabamun GS (TransAlta Utility)	Intake water (clear)	0.15
	Duplicate	0.61
	Blank before (clear)	0.90
	Blank after (clear)	0.05
	Ash lagoon effluent (clear)	5.87
	Duplicate	4.57
	Ash slurry (some black deposit, clear decantate), decanted[b]	8.44
	Duplicate, centrifuged[c]	11.4
	Discharge water (clear)	2.53
Wabamun Lake	At Wabamun downstream Wabamun GS (clear)	1.78
Sundance GS (TransAlta Utility)	North Saskatchewan River intake (clear)	2.27
	Duplicate	2.01
	Blank before (clear)	1.02
	Blank after (clear)	0.27
	Pond discharge (clear)	5.83
Keephills GS (TransAlta Utility)	River makeup (clear)	1.40
	Duplicate	3.29
	Blank (clear)	0.04
	Cooling pond discharge (clear)	4.32
	Duplicate	4.36
	Ash recirculation water (clear)	8.46
	Ash lagoon slurry (some black deposit, clear decantate), decanted	140.2
	Duplicate	150.6

(continued)

Table 6. *(continued)*

Western GS	Site/sample description	Tl concentration
Genesee GS	Intake water (clear)	7.27
(Edmonton Power)	Duplicate	7.06
	Blank before (clear)	3.97
	Blank after (clear)	1.32
	Discharge water (clear)	15.1
	Duplicate	12.4
North Saskatchewan River	Downstream Keephills and Sundance GS. (clear)	15.1
H.R. Milner GS	Wastewater — discharge (visible particulates,[d] clear decantate), decanted	9.25
(Alberta Power Ltd.)	Smoky River intake (clear)	1.15
	Final discharge (visible particulates, clear lt brown decantate), decanted	4.09
	Duplicate	6.90
	Duplicate, centrifuged	2.26
H.R. Milner GS	Smoky River downstream discharge (clear)	2.69
Smoky River	Upstream Sheep Creek (clear)	3.17
	Duplicate	2.89
	Upstream H.R. Milner GS at Hwy. 40 (clear)	1.89
	Duplicate	3.40
	Blank before (clear)	0.03
	Blank after (clear)	0.01

(continued)

Table 6. *(continued)*

Western GS	Site/sample description	Tl concentration
Sheerness GS (Alberta Power Ltd.)	Intake water (visible particulates, clear decantate), decanted	5.13
	Discharge water (visible particulates, clear decantate), decanted	8.30
	Duplicate, decanted	8.65
	Duplicate, centrifuged	17.5
	Duplicate, centrifuged	8.41
	Cooling water lagoon (clear)	9.47
	Duplicate	6.43
Battle River GS (Alberta Power Ltd.)	Battle River upstream (visible particulates, clear decantate), decanted	7.87
	Duplicate, decantated	7.11
	Intake water (visible particulates, clear decantate), decanted	1.81
	Ash lagoon — input (some black deposit, clear decantate), decanted	37.9
	Ash lagoon — discharge (some dark deposit, clear decantate), decanted	18.6
	Discharge water (visible particulates, clear decantate), decanted	6.64
	Duplicate, decanted	2.62
	Spillway downstream (visible particulates, clear decantate), decanted	14.1
	Battle River downstream (clear)	3.53
	Duplicate	6.68
	Blank before (clear)	2.46
	Blank after (clear)	5.78

(continued)

Table 6. *(concluded)*

Western GS	Site/sample description	Tl concentration
Boundary Dam GS	Spoil pond 5-5 (SERM Station No. 72579) (clear)	36.2
(Saskpower)	Spoil pond 32-5 (SERM Station No. 72524) (clear)	30.5
	Long Creek inlet (BDC1-SERM208) — upstream Boundary Dam Reservoir (clear)	3.12
	Cooling water inlet (BDC2-SERM72506) (clear)	21.5
	Cooling water discharge canal: return to reservoir (BDC1-SERM44886) (clear)	24.7
	Long Creek below Boundary Dam reservoir (BDC3-SERM235) (clear)	97.5
	Upstream Souris River near Boundary Dam GS (clear)	4.48
	Duplicate (clear)	2.98
	Blank before (clear)	0.04
	Blank after (clear)	0.11
	Downstream Souris River at Nopney's Crossing	1.54
Poplar River GS	Auxiliary cooling water (ACW) canal discharging to Cookson reservoir	0.19
(Saskpower)	Downstream East Poplar River (SERM 541)	5.21
Shand GS zero discharge plant) (Saskpower)	Raw water sample	35.7
Estevan GS (inactive)	Discharge into drainage ditch No. 7	65.0
(Saskpower)	Ash lagoon No. 5 (SE corner)	6.32
Selkirk GS	Red River intake	16.5
(Manitoba Hydro)	Well intake	15.7
	Selkirk discharge	63.9

[a] GS, coal-fired electrical generating station.
[b] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight or longer.
[c] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight or longer.
[d] Visible particulates are particulates at bottom of bottle.

Table 7. Thallium concentrations in ng/L in waters from Eastern and Central Ontario generation stations (GS)[a]

	Site/sample description	Tl concentration
Belldune GS[b]	Coal pile runoff (brown-black deposit, clear decantate), decanted[c]	744.1
(New Brunswick Power)	Equalization pit (plant waters) (dark deposit, clear decantate), decanted	2376.6
	Treated discharge (visible particulates, clear decantate), decanted	4000.5
	Ash leachate pond discharge (clear)	5087.1
Grand Lake GS	Ash lagoon discharge (clear)	11989.0
(New Brunswick Power)	Duplicate	11453.0
	Lake (visible particulates, clear decantate), decanted	159.1
	Intake water (visible particulates, clear decantate), decanted	25.4
	Duplicate, decanted	23.3
Lingan GS	Ash lagoon return (visible particulates, clear decantate), decanted	4426.1
(Nova Scotia Power)	Wastewater discharge to lagoon (black deposit, clear decantate), decanted	885.4
	Pretreatment wastewater (visible black deposit, clear decantate), decanted	2660.0
	Coal pile runoff (visible particulates, clear yellowish decantate), decanted	417.5
Point Aconi GS	Ash leachate pond discharge (pH 12) (clear)	398.1
(Nova Scotia Power)	Coal pile runoff (visible particulates, clear brownish decantate), decanted	569.2
	Wastewater discharge (Lingan sample #96-150) (clear)	558.0
	Well water — intake water (clear)	0.53
Point Tupper GS	Wastewater — pretreatment (visible particulates, clear decantate), decanted	33.7
(Nova Scotia Power)	Coal berm runoff pond (brown-yellow clear, clear decantate), decanted	212.1
	Final wastewater discharge — treated (clear)	373.6
	Landrie Lake water (visible particulates, clear decantate), decanted	1.94
	Ash leachate pond discharge (clear)	1034.6
Trenton GS	Coal leachate pond (visible particulates, clear decantate), decanted	1076.0
(Nova Scotia Power)	Ash lagoon discharge (clear)	23605.0

(continued)

Table 7. *(concluded)*

	Site/sample description	Tl concentration
	Intake water — treated town water (clear)	0.86
	Pit B discharge — previously collected by Trenton — (clear)	982.0
Lambton Hydro GS	Coal pile runoff creek at Sarnia	55.6
(Ontario Hydro)	Duplicate	70.3
	Water intake channel at Sarnia	3.18
	Duplicate	3.18
Lakewiew GS	Intake channel at Toronto	6.06
(Ontario Hydro)	North coal runoff pond	112.1
	Blank at Toronto	0.00
	Ash lagoon filtration effluent at Toronto	175.3
Nanticoke GS	Outfall channel	18.2
(Ontario Hydro)	Intake channel	11.8
	Ash lagoon	41.5
	Coal pile runoff pond	50.1
Antikokan GS	Intake line	1.25
(Ontario Hydro)	Discharge/Sn. Lake	28.1
Thunder Bay GS	Intake canal	7.16
(Ontario Hydro)	Discharge canal	14.0
	Downstream Mission River	9.39

[a] GS, coal-fired electrical generating station.
[b] Belledune GS uses 75% Columbian coal and 25% Salmon Harbour mine coal.
[c] Decanted refers to 20 mL pipetted from the top of bottle, which has been left to settle in the cold room overnight of longer.
[d] Visible particulates are particulates at bottom of bottle. Particulates in decantate may show very high results if decantate is not diluted; filtration or digestion may be needed for more accurate results if dilution is not done.

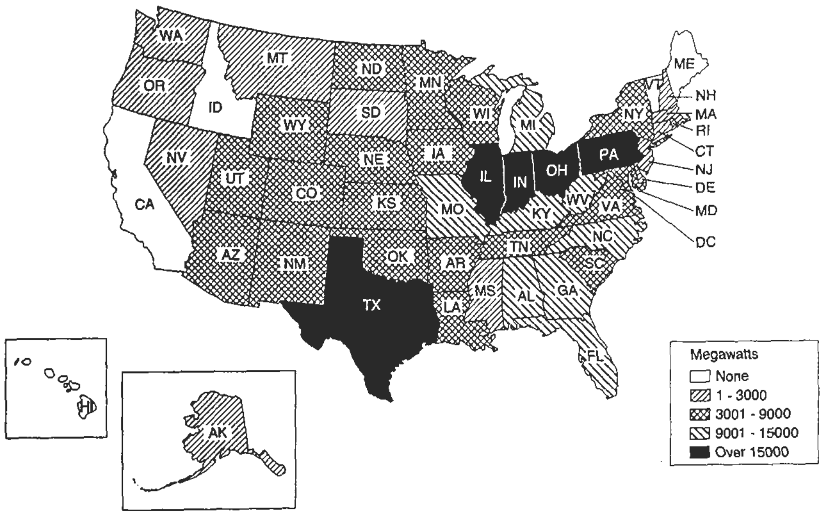

Fig. 3. Coal-fired generating capacity by state in USA (as of December 31, 1993).

These high Tl concentrations found in Canada (24,000 ng/L near a power plant and 88,300 ng/L in a river draining a base-metal mining) are by no means alone as there are numerous other high concentrations found around the world, which include the hot springs of New Zealand (7000 ng/L of Tl), a table mineral water in Germany (3500 ng/L), a cement plant wastewater in Germany (20,000 ng/L), an oil drill wastewater in the U.S. (672,000 ng/L), a smelter waste in Germany (800,000 ng/L), a mining waste in Germany (23,000 ng/L), an irrigation canal in China (96,000 ng/L), petroleum refineries in Canada (310,000 ng/L), wastewater in the U.S. (2,400,000 ng/L), and a tailings pond effluent in Canada (1,620,000 ng/L) (Schoer 1984; IPCS 1996). It is obvious that Tl, being a highly toxic element, is a global environmental concern.

Thallium and Mercury in Sediments

Table 9 gives the concentrations of Tl and Hg as determined respectively by LEAFS and CVAAS. The concentrations of thallium were in general similar to other Tl concentrations reported around the globe for sediments (Cheam 1999; Cheam et al. 1998), except one very high concentration found in the Obed Mountain Coal main tailings pond sample, which had a concentration of 3.39 µg/g. As a comparison, the highest concentration of Tl reported in the world's sediment reference materials was 2.9 µg/g, which was a certified value for a Chinese stream sediment (Govindaraju 1994). Of interest also, the highest concentration found in the Great Lakes reference materials was 2.6 µg/g; this sediment was from Hamilton Harbour (Cheam et al. 1998). Other fairly high concentrations, ~1 µg/g of Tl, were found in the Sundance generating station ash slurry

Table 8. Canadian coal-based electrical generation capacity in megawatts

Generating station	Owner	Total capacity (MW)
Sundance	TransAlta Utilities Corp.	1987
Wabamun	TransAlta Utilities Corp.	569
Keephills	TransAlta Utilities Corp.	754
Battle River	Alberta Power Ltd.	735
H. R. Milner	Alberta Power Ltd.	140
Sheerness	Alberta Power Ltd. and TransAlta Utilities Corp.	766
Genesee	Edmonton Power	400
Boundary Dam	SaskPower	875
Poplar River	SaskPower	592
Shand	SaskPower	272
Brandon	Manitoba Hydro	237
Selkirk	Manitoba Hydro	132
Thunder Bay	Ontario Hydro	423
Nanticoke	Ontario Hydro	4096
Lakeview	Ontario Hydro	2400
Lambton	Ontario Hydro	2040
Atikokan	Ontario Hydro	230
Belledune	New Brunswick Power	440
Dalhousie	New Brunswick Power	286
Grand Lake	New Brunswick Power	82
Lingan	Nova Scotia Power	602
Glace Bay	Nova Scotia Power	116
Trenton	Nova Scotia Power	350
Point Aconi	Nova Scotia Power	165
Point Tupper	Nova Scotia Power	150

sample, in the Keephills generating station ash lagoon cenospheres sample, in the Genesee Mine drainage sample, the Line Creek Mine settling pond, and Phalen Colliery surface runoff brook. Most of the Tl concentrations were, however, below 1 µg/g.

Mercury is likely the most studied element among the toxic metals because of the well-known bioaccumulation of the highly toxic compound methyl mercury, not because of its high concentration. In fact, mercury concentration in the environment is usually quite low compared to other toxic metals, and this study confirms it. Table 9 shows the concentrations of Hg were lower than Tl. The concentration differential between Tl and Hg is similar to the one found by Lentz in 1993 for the concentrations found in a massive sulfide deposit at Bathurst, New Brunswick. Also this differential occurs in most of the world's sediment reference materials (Cheam 1999). Similarly, the Earth's crust content is between 450 to 600 ppb of Tl, compared to only 200 ppb for Cd and 80 ppb for Hg (CRC

Table 9. Concentrations of thallium and mercury in sediments

Sample site	Site/sample description	Tl[a] µg/g	Hg[b] µg/gg
Wabamun GS, Alberta	Intake water	0.52	
Wabamum GS, Alberta	Ash lagoon effluent	0.43	
Sundance GS, Alberta	Ash slurry	0.99	
Keephills GS, Alberta	Cooling pond screen waste	0.69	
Keephills GS, Alberta	Ash lagoon slurry	0.35	
Keephills GS, Alberta	Ash lagoon venospheres	1.20	
Genesee GS, Alberta	Discharge	0.52	
Smoky River, Alberta	Upstream Sheep Creek, 5 km d/s HR Milner	0.39	
Smoky River, Alberta	Upstream H.R. Milner GS at Hwy 40	0.34	
Battle River GS, Alberta	Battle River upstream	0.36	0.04
Battle River GS, Alberta	Battle River downstream	0.47	0.04
Grand Lake GS, N.B.	Lake	0.78	0.02
Trenton GS, N.S.	Ash lagoon cenospheres	0.89	
Souris River, Saskatchewan	Upstream Estevan, mines and GS	0.68	0.11
Souris River, Saskatchewan	Upstream Estevan, mines and GS	0.68	0.10
Souris River, Saskatchewan	Downstream Estevan, mines and GS	0.49	0.06
Souris River, Saskatchewan	Downstream Estevan, mines and GS	0.45	0.07
Bienfait Mine, Saskatchewan	Pit water discharge	0.54	
Whitewood Mine, Alberta	Pit water discharge	0.47	
Highvale Mine, Alberta	Pit 2 drain	0.87	
Highvale Mine, Alberta	Pit 3 settling pond — Outflow	0.62	
Genesee Mine, Alberta	Mine drainage	1.04	
Coal Valley Mine, Alberta	Tailings discharge	0.47	
Coal Valley Mine, Alberta	Lovett River downstream	0.59	
Gregg River Mine, Alberta	Plant site water reservoir	0.52	
Obed Mountain Coal, Alberta	East conveyor settling pond	0.25	
Obed Mountain Coal, Alberta	Main tailings pond (upper)	3.39	
Obed Mountain Coal, Alberta	LSP2 — coal storage drain	0.42	
Line Creek Mine, B.C.	Settling pond	1.11	
#8200 Salmon Harbour Mine, N.B.	Lake water	0.74	0.05
Phalen Colliery, N.S.	Surface runoff brook	1.25	0.06
Prince Colliery, N.S.	Downstream discharge	0.61	0.06

[a] Tl was determined by LEAFS.
[b] Hg was determined by CVAAS. Other metals were determined by ICPAES.

handbook 1992–93; Korenman 1963). The crustal rock concentrations of Tl are also higher than those of Hg and Cd — 530 ppb of Tl versus 150 ppb for Cd, and 67 ppb for Hg (Winter 1998). These crustal concentrations give the Tl/Hg ratios of 5.6 to 7.9, whereas the ratios for the 10 samples investigated range from 6 to 39, with a mean value of 13 and a median value of 10. The ratio values seem to suggest there is an enrichment of Tl by at least 25%, or even as high as 117%, which indicates Tl input from other sources.

Conclusions

For metals in water samples, 95% of the upstream concentrations were smaller than the downstream, discharge or pond concentrations.

Some very high thallium concentrations were found in the eastern region near power plants. Since the western and central regions produced and consumed more coal than the eastern region, it was concluded that the coal type, not its amount and/or the regional geological contributions, were responsible for the observed high levels.

In addition to Canada, other countries also saw some very high thallium levels reported, which implies that thallium is a global environmental pollutant.

The high ratios of Tl/Hg observed in sediments, compared to crustal concentration ratios, seem to suggest a Tl enrichment by at least 25%.

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