Gaseous mercury emissions from natural sources in Canadian landscapes

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[1] Field measurements of mercury air-surface exchange from natural settings were made in various Canadian landscapes. Soil and water samples were analyzed for mercury concentrations, and air-surface exchange fluxes from these substrates were determined using dynamic chamber, micrometeorological, or modeling methods. Environmental variables, including air and soil/water temperature, solar radiation, humidity, and wind speed, were monitored concurrently with the air-surface exchange to better understand the processes affecting the environmental cycling of mercury. Average mercury fluxes from aquatic landscapes ranged from 0.0 to 5.0 ng m^{-2} h^{-1} with total mercury concentration in water ranging from 0.3 to 6.5 ng L^{-1}. A significant correlation ($R^2 = 0.47$) was found between gaseous Hg fluxes and total Hg concentration in water. Mean gaseous Hg fluxes from forest soils varied from -0.4 to 2.2 ng m^{-2} h^{-1}, while those from agricultural fields ranged from 1.1 to 2.9 ng m^{-2} h^{-1}. Non-mineralized bedrock, sand, and till sites yielded fluxes ranging from -0.03 to 5.9 ng m^{-2} h^{-1}. Mean fluxes from mercuriferous geological substrates at various locations were large compared to non-mercuriferous sites, ranging from 9.1 to 1760 ng m^{-2} h^{-1}, and represent natural emissions. The corresponding total mercury substrate concentrations ranged from 0.360 to 180 ppm. A significant correlation ($R^2 = 0.66$) was found between Hg fluxes and total Hg concentrations in mineralized and non-mineralized substrates. These gaseous Hg flux measurements represent a significant contribution to understanding natural mercury cycling, but there are still insufficient data and knowledge of processes to properly scale up fluxes from natural sources in Canada.

1. Background and Objectives

[2] It is known that volatile and semi-volatile species of mercury can be released, deposited and re-emitted into the atmosphere from soil, water, and vegetated surfaces [*Schroeder et al.*, 1989; *Poissant and Casimir*, 1998]. However, there is considerable uncertainty with respect to the biogeochemical cycling of mercury in the environment and the relative contribution of various sources of mercury [*Porcella et al.*, 1996; *Pai et al.*, 1998; *Lamborg et al.*, 2002; *Schroeder et al.*, 2002]. Although atmospheric deposition of mercury is often implicated as a major contributor to ecosystem mercury levels, mercury is ubiquitous in the environment and can be derived from a variety of natural and anthropogenic sources. During the last 25 years, extensive efforts have been made in many countries to identify and quantify the contribution of gaseous mercury from anthropogenic sources to the global atmospheric mercury budget, but natural and human-influenced mercury emissions from regionally representative landscape surfaces have only recently been quantified [*Rasmussen*, 1994; *Carpi and Lindberg*, 1998; *Rasmussen et al.*, 1998a, 1998b; *Gustin et al.*, 1999b; *Edwards et al.*, 2001; *Poissant*, 2002].

[3] To understand the biogeochemical cycle of Hg in the natural environment, it is important to determine spatial and temporal variability in deposition and evasion of gaseous mercury as it relates to environmental factors (e.g., soil moisture, soil porosity, substrate temperature, solar radiation), chemical factors (e.g., Hg species and content in soils and water such as, soil organic matter or dissolved organic matter and, substrate type), and surface characteristics (e.g., bare or vegetated surface, surface roughness). The interactions between all these factors lead to highly variable

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Figure 1. Geographical extent of sites monitored for mercury flux measurements in Canada. 1, MacMillan Pass, YT; 2, Pinchi, BC; 3, Thunder Bay, ON; 4, Elora, ON; 5, Clyde Forks, ON; 6, Hopetown, ON; 7 Rouyn Noranda, QC; 8, Kuujjuarapik, QC; 9, Lake Ontario, ON; 10, St. Lawrence River (Kingston to Brockville), ON; 11, Saint-Anicet, QC; 12, Lake Saint-Pierre, QC; 13, Lake Saint-François, QC; 14, Big Dam West Lake, Puzzle Lake, Cranberry Lake Kejimikujik, Pebbleloggitch Lake, Beaver-skin Lake, Meadow Brook, Halifax Harbour, NS. AB, Alberta; BC, British Columbia; MB, Manitoba; NB, New Brunswick; NF, Newfoundland; NT, Northwest Territories; NS, Nova Scotia; NU, Nunavut; ON, Ontario; PE, Prince Edward Island; QC, Québec; SK, Saskatchewan; YT, Yukon Territory.

mercury emissions, making it imperative to study emissions in a variety of landscapes over a sufficiently long time scale to understand biogeochemical mechanisms regulating air-surface mercury exchange processes.

[4] Although data on air-surface exchange of Hg have begun to emerge for certain parts of the world (e.g., Sweden and the United States), a data set is needed that reflects the diverse climates and environments in Canada. Canada's total area of 997 million ha is made up of approximately 44% forest, 8.2% wetlands, 7.9% fresh water, 6.7% grassland and cropland, 30.9% tundra and exposed rock, and 2.3% glaciers, with large amounts of these areas being frozen for at least half of the year (http://www.pfc.cfs. nrcan.gc.ca).

[5] A natural emissions inventory for mercury, determined for Canada in 1981 [*Environmental Protection Service (EPS)*, 1981], was mostly based on indirect estimates, rather than reliable data. Prior to the studies discussed in this paper, there were almost no direct measurements of mercury air-surface exchange for Canada. The scarcity of reliable data on mercury fluxes from natural settings, and the complexity of the cycling of mercury, required a multi-disciplinary, intensive effort aimed at better quantifying fluxes and understanding the processes driving mercury

exchange between the atmosphere and the chemically, physically and biologically diverse surfaces in Canada. The major goals of this project were as follows: (1) to better constrain the degree of uncertainty in previous estimates of natural Hg emissions from natural substrates such as soils, water surfaces, vegetation and bedrock in a variety of Canadian landscapes, climatic regions, and geological settings; (2) to understand the processes controlling the fluxes; and (3) to develop and apply methodologies for "scaling up" results generated from field sites to a larger region. This project has resulted in a major contribution to direct measurements of air-surface Hg exchange from natural sources and processes, but there is still much research needed in understanding processes controlling fluxes and in the development of methodologies for scaling up fluxes. This paper highlights achievements of goals 1 and 2 above, citing the improved estimates of natural mercury flux emissions, as well as some of the processes governing the fluxes. To achieve goal 3 requires more thorough knowledge of the processes controlling Hg flux, therefore scaling up these fluxes is beyond the scope of our study.

[6] Some Hg flux data from these studies have already been reported [*Beauchamp et al.*, 2002; *Boudala et al.*, 2000; *Edwards et al.*, 2001; *O'Driscoll et al.*, 2003; *Poissant*, 2002; *Poissant and Casimir*, 1998; *Poissant et al.*, 2000; *Rasmussen et al.*, 1998a, 1998b]. This paper summarizes results of Canadian mercury exchange measurements and compares them to those obtained in similar landscapes elsewhere. Additionally, this paper identifies knowledge gaps related to research needed in a Canadian context both to better understand the biogeochemical cycling of mercury and to scale up emissions from such a diverse landscape. An improved natural emission inventory for Canada will lead to a better understanding of the role of the atmosphere and natural ecosystems in mercury cycling.

2. Methods
2.1. Sites

[7] Studies were conducted at various locations across Canada (Figure 1). Table 1 presents a summary of the sites, landscape types, and periods of mercury flux measurements. The field sites were selected to (1) be representative of the local landscape (terrestrial and aquatic) and to represent contrasting landscapes found across Canada; (2) contain a wide range of substrate mercury concentrations, including both naturally mercuriferous and non-mercuriferous ("background") sites; and (3) be suitable for making both chamber and micrometeorological measurements. Terrestrial locations were chosen to include sites with naturally elevated mercury concentrations in the substrate, and sites with background concentrations (less than 100 ppb) at locations that are remote from industrial point sources, where long-range atmospheric transport would be the only possible anthropogenic source of mercury. More detailed rationales for site selection are given by *Poissant and Casimir* [1998], *Rasmussen et al.* [1998b], *Poissant et al.* [2000], and *Beauchamp et al.* [2002]. Freshwater sites were selected based on dissolved organic carbon (DOC) content covering a range from low to high DOC, while the Halifax Harbour site was selected as a marine ecosystem

Table 1. Summary of Locations and Study Duration for Various Canadian Landscapes and Regions

Location	Landscape Type	Date of Measurements
Pinchi, BC	Mercury sulphides	Jul 1998
Big Dam West Lake, NS	Forest soil	Summer 1997, 1999
	Fresh water	Summer 1997, 2000
Puzzle Lake, NS	Forest soil	Summer 1999
	Fresh water	Summer 1999
North Cranberry Lake, NS	Forest soil	Summers 1997, 1999
	Fresh water	Summer 1997
Kejimikujik, NS	Glacial till	Summer 1997
Pebbleloggitch Lake, NS	Granite/till	Summer 2000
	Fresh water	Summer 2000
Beaverskin Lake, NS	Granite/till	Summer 2000
	Fresh water	Summer 2000
Meadow Brook (bog drainage), NS	Fresh water	Summer 2000
Halifax Harbour, NS	Salt water	Summer 1999
Clyde Forks, ON	Background and mineralized fault zone	Aug 1996
Thunder Bay, ON	Background granite and black shale	Jul 1997;
	Vegetated overburden on black shale	Jun 2000
Hopetown, ON	Background, pasture land	Sep 1999
Elora, ON	Snow studies	Winter 2000
MacMillan Pass, YT	Black shale and moss	Jul 2001
Lake Ontario, ON	Fresh water	Jul 1998
St. Lawrence River (Kingston to Brockville), ON	Water	Jul 1998
Lake Saint-François, QC	Water	Jul 1995
Upper St. Lawrence River, Saint-Anicet, QC	Pasture	Jul 1995
Lake Saint-Pierre, QC	Marsh	Jul−Aug 1999
		May 2000
Kuujjuarapik, QC	Rock, sand, moss, lake	Spring 2000
		Summer 2001
Rouyn Noranda, QC	Sand and gravel pit	Jul−Aug 2000

moderately impacted by urban sewage and industrial activity [*Beauchamp et al.*, 2002].

2.2. Measurement Methods

[8] The field work involved conducting geochemical surveys of the site and/or soil and water sampling, making total gaseous mercury (TGM) flux measurements using either dynamic flux chamber or micrometeorological techniques, or both, and collecting supporting meteorological data. This multidisciplinary, comprehensive approach to data collection, along with the study of air-surface volatile Hg exchange processes in aquatic and terrestrial systems over a spectrum of environments, was chosen to facilitate the modeling of Hg cycling in the environment and the scaling up of in situ fluxes to local, regional and ultimately, global scales. Details of sampling and calibration protocols, and methods are given in *Poissant et al.* [1995], *Edwards et al.* [2001], and *Beauchamp et al.* [2002]. An intercomparison of micrometeorological and chamber methods was conducted and the results are given in *Gustin et al.* [1999b]. Some of the Hg fluxes from water were modeled with the methods described by *Poissant et al.* [2000] and *O'Driscoll et al.* [2003].

[9] TGM concentration measurements from flux chamber and micrometeorological methods were made using an automatic analyser (Tekran® 2537A). Total mercury concentrations in the soil were determined as described by *Poissant et al.* [1995], *Edwards et al.* [2001], and *Beauchamp et al.* [2002]. Dissolved gaseous mercury (DGM) and total mercury in water were measured using techniques described by *Poissant et al.* [2000].

[10] Whenever possible, supporting physical and chemical data measurements including meteorology (e.g., wind speed, air temperature, radiation, relative humidity), soil/water

temperature, soil moisture potential, were conducted concurrently with air-surface mercury exchange measurements.

3. Results
3.1. Aquatic Sites

[11] Mercury flux measurements for the Canadian aquatic landscape, as well as those from other aquatic studies, are presented in Table 2. Mean TGM fluxes measured from lakes and rivers in this study ranged from 0 to 5.0 ng m^{-2} h^{-1}, showing net emissions from these sources. These fluxes were slightly lower than those found for lakes [*Xiao et al.*, 1991; *Lindberg et al.*, 1995] and a river [*Gårdfeldt et al.*, 2001] in Sweden. The average TGM flux at a salt water harbour in Atlantic Canada in the summer months (0.7 ng m^{-2} h^{-1}) was within the range measured at a sea surface in Sweden (−0.57 to 1.01 ng m^{-2} h^{-1}) in June and August 1997, but higher than the range reported for June and July 1998 [*Gårdfeldt et al.*, 2001, Table 2].

[12] In the studies conducted by *Gårdfeldt et al.* [2001], sea surface emissions were ten times smaller than river emissions. They suggested that higher DOC (dissolved organic content, which is the sum of organic matter in water originating from compounds that will pass through a 0.45 micron filter) at the river site contributed to higher emissions from this site. In general, fluxes from lakes in the Atlantic region also increased with increasing DOC (Table 2). *Vaidya et al.* [2000] found that there was a high correlation between total Hg in water and TOC (total organic carbon, bonded to dissolved or suspended matter), indicating that organic carbon is an important variable to consider when assessing Hg air-surface exchange from water bodies.

[13] Mean TGM fluxes for a freshwater marsh in Quebec were 0.88 and 0.95 ng m^{-2} h^{-1}, under dry (i.e., sediments

Table 2. Comparison of TGM Fluxes Obtained at Various Aquatic Environments[a]

Reference	Location	Method	Time of Year	Hg Flux, $ng\ m^{-2}\ h^{-1}$	Total Mercury in Water, $ng\ L^{-1}$	Substrate Temperature, °C	Air Temperature, °C
			Water Bodies				
Present study, Canada	St. Anicet Quay, QC	FC	Jul 95	(0 to 0.96)	0.3	24.8 (22.8 to 25.6)	(17 to 28)
	St. Lawrence River ON to QC	Model	Jul 98	3.07 (0.02 to 9.28)	0.031[b]	22.4 (22.3 to 22.8)	
	Lake Ontario, North shore, ON	Model	Jul 1998	0.82 (0 to 2.8)	(0.053 to 0.104[b])	19 (11.4 to 23.1)	
	Lake Ontario, South shore, ON			3.39 (0.9 to 9.07)		22.5 (18.79 to 23.5)	
	Freshwater lake, northern QC		Summer 1998	0.31 (0.59 to 4.5)	0.30		
	Various freshwater lakes, NS	FC	Summer 1997,1999, 2000 (Low DOC)	0.6 to 2.2	0.7 to 2.8	20.3 to 23.4	19.3 to 21.2
			Summers 1997 and 2000 (High DOC)	0.0 to 5.0	4.0 to 6.5	20.3 to 26.1	19.3 to 21.8
	Bog drainage stream, NS	FC	Summer 2000 (High DOC)	0.01	5.4	22.0	20.2
	Halifax Harbour, NS, (saltwater)	FC	Summer 1999	0.7	0.8	16.7 (15 to 18)	14.9 (9 to 25)
Xiao et al. [1991]	Lake Gardsjön, Sweden	FC	May and Jun 1988 to 1989	6.9 (2.5 to 10.4)		16.6 (15 to 19)	15.5 (3 to 19)
	Lake Låresbovatten, Sweden		May and Jun 1988	11.2 (6.6 to 19.5)		21.3 (19 to 23)	17.7 (11 to 24)
	Lake Skarsjön, Sweden		May and Jun 1988	4.2 (1.3 to 6.4)		14.3 (12 to 18)	11.5 (0.4 to 20)
	Lake Hållungen, Sweden		May, Jun 1988	4.5 (1.6 to 8.0)		16.5 (14 to 21)	13.5 (5 to 21)
Xu et al. [1999]	Atlantic Ocean, NE USA	Model	Jul 1995	3.17			
Lindberg et al. [1995]	Lake Gardsjön, Sweden	FC	Jun 1994	8.5	1.5 to 2.3		
Gårdfeldt et al. [2001]	River, Sweden	FC	Aug 1999	11.0 (−2.5 to 88.9)			
	Sea surface, Sweden	FC	Jun/Jul 1997	(−0.35 to 0.42)	0.04 to 0.1[b]		
			Aug 1997	(−0.36 to 1.00)			
			Jun 1998	(−0.57 to 1.01)			
			Wetlands				
Present study, Canada	Wetlands, QC, Canada	MM	Jul–Aug 1999 (Dry)	0.88 (−1.5 to 2.40)	0.011[c]		
			May 2000 (Wet)	0.95 (−0.46 to 7.13)	0.96		
Lee et al. [2000]	Marsh, CT, USA	MM	Summer 1997 to Fall 1998	4.5 (−3.3 to 13.2)			
Lindberg and Meyers [2001]	Everglades (*Typha spp.*), FL, USA	MM	Spring and Fall 1996, Summer 1997	17		(18 to 20)	(22 to 22.5)
Poissant et al. [2004b]	Wetlands, QC, Canada	MM	Late summer 2002	32.1 (−110 to 278)	0.06[c] 1		17

[a]Average values are given, with the exception of numbers in parentheses, which give the range of values for a variable. MM, micrometeorological method; FC, flux chamber method.
[b](ng L^{-1} of DGM-dissolved gaseous mercury.)
[c](μg g^{-1} in sediment.)

exposed to air) and wet conditions, respectively [*Poissant et al.*, 2004a]. These fluxes fall within the range found for a saltwater marsh in the northeast United States [*Lee et al.*, 2000, Table 2], but are much smaller than those measured in late summer 2002 (32.1 ng $m^{-2}\ h^{-1}$) over plant canopy by *Poissant et al.* [2004b, Table 2], and those measured over plant canopy at the Everglades in Florida (17 ng $m^{-2}\ h^{-1}$ [*Lindberg and Meyers*, 2001], Table 2).

[14] There is a positive relationship ($R^2 = 0.47$, $p < 0.01$) between mercury flux and total Hg concentrations in water for the aquatic systems in Quebec and Nova Scotia, for total Hg concentrations in water ranging from 0.3 to 6.5 ng L^{-1}, and for similar water temperatures (Figure 2. N.B. Modeled fluxes, shown in Table 2, are not included, since they are based on DGM, rather than TGM content). The applicability of this relationship to scale up aquatic emissions in Canada will depend on the effects of pH, DOC, DGM, and climatic regimes, and is discussed further below. The flux measured from a bog drainage stream was very low, and was not included in the regression, as it was an outlier. This type of landscape is common in Nova Scotia and New Brunswick, and it was believed that bog drainage may be a source of mercury to lakes due to high DOC. Although TGM content in the water was high, the air-surface exchange was low. This flux is not likely representative as measurements were made over a short period and at only one location. More
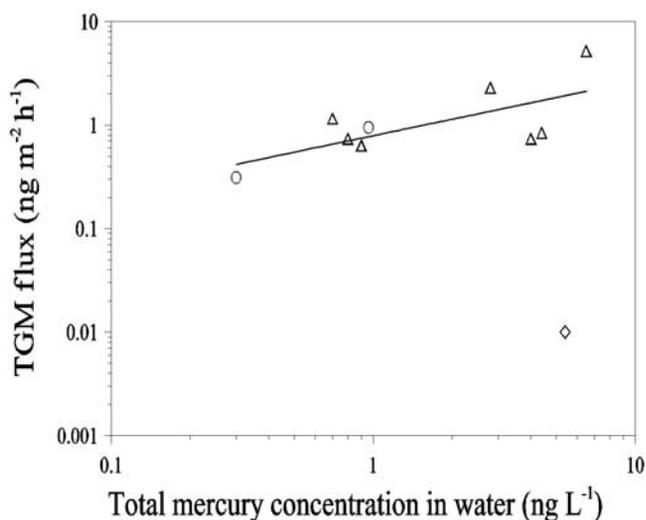
Figure 2. Total gaseous mercury fluxes from water versus total mercury concentration at various lakes and a marsh located in the provinces of Quebec (circles) and Nova Scotia (triangles), Canada. The equation of the line is as follows: log (Hg Flux) = 0.53 log (total mercury concentration) − 0.10 (R^2 = 0.47, p < 0.01). Flux from a bog drainage stream (diamond) was not used to calculate regression. See text for explanation.

flux measurements and a better understanding of the chemistry in bog drainage streams are needed to obtain better emission estimates from this landscape.

3.2. Forest Soils and Vegetated Sites

[15] Fluxes from forest soils in Nova Scotia varied from −0.4 to 2.2 ng m^{-2} h^{-1} (average equal to 1.1 ng m^{-2} h^{-1}, Table 3). These fluxes are similar to those reported by other researchers for forest soils in Sweden and in Michigan, United States [*Xiao et al.*, 1991; *Lindberg et al.*, 1998; *Zhang et al.*, 2001], but are lower than those reported by *Kim et al.* [1995], *Ferrara et al.* [1997], and *Carpi and Lindberg* [1998] (Table 3). TGM flux measurements in Nova Scotia were conducted at lower soil temperatures than in the latter studies and were measured under a closed canopy. *Carpi and Lindberg* [1998] observed changes in fluxes from forest floor, with larger fluxes in April (6.98 ng m^{-2} h^{-1}), under an open canopy, and smaller fluxes (2.00 ng m^{-2} h^{-1}) in June under a closed canopy, even though temperatures were comparable. They attributed this to changing radiation regimes at the forest floor surface as the canopy filled in.

[16] TGM flux measurements were conducted at two agricultural sites in Ontario that were located on overburden on mercuriferous bedrock, and at one pasture site in Quebec. The mean fluxes measured from pasture and fallow fields in Ontario and Quebec were similar to one another (1.1 to 3.0 ng m^{-2} h^{-1}, Table 3) but lower than those reported by *Carpi and Lindberg* [1998] and *Zhang et al.* [2001]. Higher temperatures were reported at the Nelson and Barn Field sites [*Carpi and Lindberg*, 1998, Table 3]. Since substrate concentrations were similar for the Nelson and Barn Fields and the fields in Ontario, the higher fluxes may be partially explained by the higher temperatures.

[17] Although substrate mercury concentrations were orders of magnitude different at the fallow and pasture sites in Ontario, the measured fluxes were similar. The study in Ontario was conducted in persistent rainy and cloudy conditions. Since the field remained wet throughout the study, this might inhibit Hg evasion. Thus, the effects of rain and overburden over Hg-enriched geology on TGM flux processes require more research.

[18] Mercury fluxes from moss-covered substrates were measured both in northern Quebec and in the Yukon. Fluxes ranged from −0.58 to 1.3 ng m^{-2} h^{-1} (average equal to 0.08 ng m^{-2} h^{-1}) at the Quebec site, and from −0.60 to 10.63 ng m^{-2} h^{-1} (average equal to 1.5 ng m^{-2} h^{-1}) at the Yukon site (Table 3). At the Yukon site, the fluxes were measured from moss on mercuriferous shale and were 5 times smaller than those measured from the same bare shale. Mosses are excellent Hg accumulators and are widely used as biomonitors for atmospheric loading of metals, thus more flux measurements from mosses might contribute to a better understanding of mercury cycling.

3.3. Fluxes From Contrasting Geological Sites Across Canada

[19] Mercury fluxes from sandy substrates at a northern remote and a rural site in Quebec averaged 0.44 and 5.9 ng m^{-2} h^{-1}, respectively (Table 4). Both sites were monitored during the month of August, but the Hg concentration in the substrate at the remote site was not measured, therefore it is not known whether the differences are due to Hg substrate concentration differences, or other factors. In contrast, average mercury fluxes from non-mineralized bedrock (granite/glacial till) at various sites in Quebec and Nova Scotia ranged from −0.03 to 1.7 ng m^{-2} h^{-1} (Table 4), suggesting that bedrock in these locations is not a significant emitter of volatile mercury (substrate concentration ranged from 0.005 to 0.250 ppm). These fluxes are slightly lower than the range reported for unaltered or undisturbed geological units with similar substrate concentrations in Nevada [*Engle and Gustin*, 2002; *Zehner and Gustin*, 2002; *Gustin et al.*, 2003; *Nacht and Gustin*, 2004] (Table 4).

[20] Fluxes from naturally mercuriferous zones in Canada were much larger than those from background sites, which are more representative of Canada's landmass. Fluxes for all Hg enriched sites in Canada ranged from 91.8 to 1760 ng m^{-2} h^{-1} for substrates containing elevated Hg concentrations (124.6 ppm (Cinnabar, British Columbia) to 179.5 ppm (mineralized soil, Ontario); Table 4). Fluxes from exposed mercuriferous shale units in the Yukon Territory (Selwyn Basin) and in Ontario (Rove Formation) were 9.1 to 213.5 ng m^{-2} h^{-1} for Hg substrate concentrations of 0.358 to 1.6 ppm. These observations are consistent with mercury fluxes reported from shale in Nevada (25.7 to 31.9 ng m^{-2} h^{-1} for substrate concentrations ranging from 0.05 to 0.76 ppm [*Nacht and Gustin*, 2004], Table 4).

[21] Average mercury fluxes from a cinnabar-enriched site in Central British Columbia (Pinchi Fault Zone) were 91.8 ng m^{-2} h^{-1} (substrate equal to 180 ppm), which are low compared to values reported by *Gustin et al.* [2002] for crushed ore (2583 to 5066 ng m^{-2} h^{-1} for substrate Hg concentrations of 267 ppm). The difference may be explained by the greater surface area of the crushed rock in the *Gustin et al.* [2002] study, compared to the solid in

Table 3. Comparison of TGM Fluxes Measured From Various Soils and Vegetated Sites[a]

Reference	Location	Method	Time of Year	Average Flux, ng m^{-2} h^{-1}	Substrate, ppm	Substrate Temperature, °C	Air Temperature, °C
			Forest Soils				
Present study, Canada	Various forest soils, NS, Canada	FC	Summer 1997 and 1999	−0.4 to 2.2	0.15 to 0.33	14.0 to 17.5	15.6 to 19.6
Zhang et al. [2001]	Shaded forest, MI, USA		Jun	1.4 (−0.2 to 2.4)	(0.006 to 0.098)	(13.8 to 19.4)	
Lindberg et al. [1998]	Forest soils, Sweden	MM	Jun 1994	−0.017 (−5.4 to 4.2)			(11.3 to 16.6)
Xiao et al. [1991]	Forest soil, Sweden	FC	Dec to Jan 1988	−0.4 (−1.3 to 1.4)		(−5 to 3)	(−10 to 2)
			May to Jun	0.25 (−0.8 to 2.5)		(10 to 13)	(10 to 20)
Kim et al. [1995]	Forest soil, TN, USA	MM	May to Aug 1993	−2.7 to 7.6 (−7.5 to 28.8)		(13.7 to 36.2)	(6.9 to 36.2)
Carpi and Lindberg [1998]	Various deciduous forest soils with litter, TN, USA	FC	Apr to Aug 1995	2.00 to 6.98 (1.11 to 13.94)		(12 to 24)	
			May to Jun 1995	2.70 (0.98 to 5.95)	0.469	(12 to 22)	
Ferrara et al. [1997]	Litter-covered forest soil, Italy	FC	Feb to Aug 1992	−0.5 to 6	0.5	4 to 20	5 to 23
			Agricultural Fields/Grass				
Present study, Canada	Pasture, QC	FC	Jul 95	3.0	0.006		12.29
	Pasture, ON	MM	Sep 99	1.1	0.047[b]		10.1 (0.7 to 23.1)
	Fallow field, ON	MM	Jun 2000	2.9	0.100[b]		12.7 (1.0 to 23.3)
Zhang et al. [2001]	Field, MI, USA		Jun	7.6	0.016	25.6	
Carpi and Lindberg [1998]	Open agricultural sites, TN, USA	FC	Apr to Aug 95	−0.66 to 1.21[c] 12.47[d]	0.061	(26 to 49)	
	Open agricultural site, TN, USA			16.8[c] 44.83[d]	0.111	(20 to 36)	
Ferrara et al. [1997]	Background rural unvegetated, Italy	FC	Feb 1991	1.5	0.6	3	3
			May 1991	8	0.6	11	13
			Jan 1991	3 to 30	1	0	1
			May 1991	30	1	20	20
			Mosses				
Present study, Canada	Moss, northern QC	FC	Aug 2001	0.08 (−0.58 to 1.3)			
	Moss over Hg-enriched shale, YT	FC	Jul 2001	1.5 (−0.60 to 10.63)			

[a]Average values are given, with the exception of numbers in parentheses, which give the range of values for a variable. MM, micrometeorological method; FC, flux chamber method.
[b]Overburden on Hg-enriched geology.
[c]Mean fluxes for shaded soil.
[d]Mean flux for soil exposed to sunlight.

situ bedrock monitored in the British Columbia study, as well as lower temperatures and reduced sunlight at the Canadian site. *Ferrara et al.* [1997] found much higher fluxes for cinnabar (Table 4) and attributed these higher fluxes to higher average ambient temperatures in the Mediterranean region which reached almost 40°C. According to *Ferrara et al.* [1997], higher temperatures, in addition to their effect on mercury evasion, might also increase any biological or photochemical processes which may be involved in forming volatile mercury species, both in water and in soil.

[22] Mercury fluxes from soil in a mineralized fault zone in Ontario were much higher than for the cinnabar (1760 ng m^{-2} h^{-1} for a substrate concentration of 125 ppm). These fluxes are comparable to those reported by others for mineralized soils/areas [*Ferrara et al.*, 1997; *Coolbaugh et al.*, 2002; *Engle and Gustin*, 2002; *Gustin et al.*, 2002] (Table 4).

[23] A relationship was found ($R^2 = 0.66$, $p < 0.01$) between TGM flux and substrate concentration for all background (less than 100 ppb) and mercuriferous sites

(Figure 3). A weaker relationship was found when using mineralized areas only ($R^2 = 0.49$, $p < 0.01$). When only background data were used, the relationship was lost ($R^2 = 0.06$, $p < 0.05$). *Nacht and Gustin* [2004] also reported a very weak and negative correlation for unaltered sites (i.e., background geology) and lower substrate Hg concentrations, and suggested that this was due to the smaller range of concentrations in the substrate for background (nonmercuriferous) geology. The slopes and constants for the relationship between substrate concentration and Hg flux are given in Table 5 for these and other studies. The slopes range from 0.20 to 0.68 and the constants range from 0.63 to 1.57, depending on the geological substrates used to determine the relationship. The implications for these findings are considered in the discussion below.

3.4. Fluxes From Weathered Versus Unweathered Geological Materials

[24] For scaling up purposes, it is important to differentiate between natural fluxes measured over weathered and unweathered surfaces (i.e., unweathered parent material).

Table 4. Comparison of Fluxes Measured Over Background and Mineralized Bedrock

Reference	Location	Method	Time of Year	Mean Flux Range, ng m^{-2} h^{-1}	Substrate Concentration Range, ppm	Air Temperature, °C
Present study, Canada	Shales, ON and YT	FC	Jul 1997 and 2001	9.1 to 213.5	0.358 to 1.6	11.9 to 20.1
	Cinnabar, BC	FC	Jul 1997	91.8	179.5	16.6
	Mineralized soil, ON	FC	Jun 1996	1760	124.6	17.1
	Sand and gravel pit, QC	FC	Aug 2000	5.9	0.010	18.6
	Sand, QC	FC	Aug 2001	0.44	N/A	14.8
	Background rock/till, ON, QC, and NS	FC	Summers 1997 to 2000	−0.03 to 1.7	0.005 to 0.25	17.3 to 19.7
Nacht and Gustin [2004]	Unaltered geological units, NV, USA	FC	Apr to Aug 2000	0.1 to 4.5 0.3 to 6.0 0.2 to 1.05 0.0 to 3.0	0.01 to 0.037[a] 0.013 to 0.027[b] 0.02 to 0.06[c] 0.015 to 0.064[d]	
	Altered geological units, NV, USA		Apr to Sep 2000	0.6 to 9.8 7.4 to 40.5 25.7 to 31.9	0.03 to 0.11[a] 0.16 to 8.60[b] 0.05 to 0.76[e]	
Coolbaugh et al. [2002]	Mining district peripheral soils, NV, USA	FC	Jul to Nov	2.6 to 47.7	0.3 to 2.5	
Zehner and Gustin [2002]	Background unenriched geologic units, NV, USA	FC	N/A	3.4 to 6.0	0.024 to 0.065	
Gustin et al. [2002]	Mineral soil, laboratory	FC	N/A	1215 to 6475[f] 589 to 4074[g]	130 to 131	
	Crushed ore, laboratory			3122 to 5066[f] 2583 to 2795[g]	267	
Gustin et al. [2003]	Undisturbed serpentinine soils NV, USA	FC	N/A	0 to 14.5	0.11 to 0.69	
Engle and Gustin [2002]	Hydrothermal and mineralized areas, NV, USA	FC	Sep 1999	−1.1 to 3240 (Flowery Peak)	0.012 to 99.7	2.8
			Sep 1999, Mar 2000	1.71 to 221 (Peavine Peak)	<0.010 to 1.33	15.8
			Apr 2001	−0.71 to 131.9 (Long Valley)	<0.010 to 0.351	7.5
Engle et al. [2001]	Mining district, NV, USA	FC	N/A	−0.1 to 51.7	0.019 to 0.114[a]	
Ferrara et al. [1997]	Roasted cinnabar banks, Spain	FC	Sep 1993	80000 to 110000	700	23 to 25
	Roasted cinnabar banks, Italy		Feb, May, Aug 1992	26 to 10000	180	6 to 38
	Mineralized soil, Spain		Sep 1993	5000	9	21
	Low mineralized soils, Spain			200	0.7	25

[a]Alluvium.
[b]Limestone.
[c]Rhyolite.
[d]Andesite.
[e]Shale.
[f]Fluxes measured in light conditions.
[g]Fluxes measured in the dark.

Weathering is caused by exposure to surface environmental variables, including temperature changes, solar radiation, wind, and precipitation, resulting in the physical breakdown of the parent material and chemical alterations including oxidation, dissolution, and precipitation. An unweathered surface is one that has not been exposed to surface environmental conditions and more closely resembles the original parent material.

[25] Mercury fluxes were measured over weathered (surface layer) and unweathered (parent material) black shale at Thunder Bay, Ontario. Substrate Hg concentrations were equivalent in both the weathered and unweathered shale. The chamber was placed over the weathered surface and TGM fluxes were measured (Table 6). The weathered surface layer (∼5 to 10 cm) was then excavated to expose the underlying parent material, and the chamber placed on the unweathered surface and sealed. Measured fluxes from the unweathered surface were an order of magnitude lower than those measured over the weathered substrate (Table 6). Soil temperature and net radiation indicate that the reduced fluxes were not a function of lower temperatures or net radiation. Thus, for similar Hg content,

weathered shale emits more TGM than non-weathered shale. The higher emissions from weathered surfaces is most likely related to the increase in surface area of the weathered constituents, caused by physical weathering processes, and oxidation of mercury compounds during chemical weathering. In weathered substrates, the smaller fractions will have a much greater surface area than that of a solid piece of substrate (black shale for example).

3.5. Mercury Flux Over Snow Covering Mercury Enriched Soil

[26] There are a limited number of measurements of mercury flux from snow-covered surfaces, therefore the dynamics of mercury air-snow exchange are not well understood. In particular, there are very few results of in situ mercury fluxes from snow-covered Hg-rich geological settings. *Jonasson* [1973] found that mercury could move from a mercuriferous soil in a mineralized area into snow cover, suggesting that mercury can evaporate through snow covers under the appropriate conditions. Since a significant portion of Canada is covered with snow for extended periods of time, it is important to understand how the
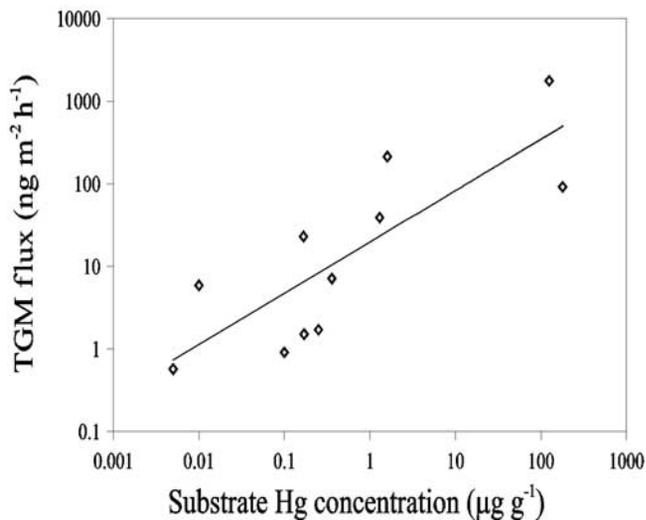
Figure 3. Total gaseous mercury fluxes from background and mineralized geology versus total mercury concentration in the substrate. Sites are located in the provinces of Quebec, Nova Scotia, Ontario, British Columbia, and Yukon Territory, Canada. The equation of the line is as follows: log (Hg Flux) = 0.62 log (total mercury substrate concentration) + 1.30 (R^2 = 0.66, p < 0.01).

presence of snow affects the flux of mercury from natural surfaces. In this project, field mercury fluxes were measured both from a background soil (less than 100 ppb Hg) naturally covered with fresh snow and a Hg-enriched soil, manually covered with snow. These measurements were conducted from February to March 2000 at Elora, Ontario.

[27] Mercury fluxes were measured over the Elora background soil with a fresh snow cover. Fluxes from February 16 to 21, 2000, are shown in Figure 4a, and averaged 0.09 ± 0.03 ng m^{-2} h^{-1} (Table 7). Mercury fluxes from a snow covered surface (December 1999 to March 2000) were very similar for southern Quebec (0.07 ng m^{-2} h^{-1}) [*Poissant*, 2002].

[28] Following this initial measurement period, the snow was removed from the soil surface and the top layer of background soil was mixed with soil from Clyde Forks, Ontario to dilute the mineralized soil, since the high Hg concentration in the soil overloads the Tekran® instrument. The mixed soil was spread over a 1.0 × 1.0 m plot to a depth of approximately 2 cm, and then the snow was piled back onto the soil.

[29] The initial mercury flux from the snow was highly variable (Figure 4b) and the first flush of mercury before midnight on February 21, may be an artifact of the experi-

Table 6. Chamber Measurements Over Weathered and Unweathered Black Shale Surfaces in Thunder Bay, Ontario[a]

Time	Location	Net Radiation, W m^{-2}	Soil Temperature, °C	TGM Flux, ng m^{-2} h^{-1}
10:30	weathered	299	19.5	19
11:00	weathered	360	31.5	27
11:30	weathered	414	39.1	36
13:30	unweathered	587	46.9	4.9
14:00	unweathered	388	46.7	3.3
14:30	unweathered	557	49.3	8.9

[a]Net radiation and temperature data were lower during study on weathered substrate, showing that these factors were not responsible for the higher fluxes during this study. Net radiation is the sum of direct and diffused radiation.

mental setup. It is expected that there would be a lag time for mercury gas in the soil to diffuse through the snow before being emitted. It is believed that the temperature of the spiked topsoil equilibrated with the subsoil and snow temperatures over this time period due to the thin layer applied. On February 22, the surface snow melted and the resulting water froze, forming a thin ice crust on the surface, resulting in the average flux decreasing from 8.3 ± 0.9 to 1.0 ± 0.2 ng m^{-2} h^{-1}. The flux was reinitiated at noon on February 23, when the frozen layer was removed, and for the next 24 hours, average fluxes increased again to 7.8 ± 0.5 ng m^{-2} h^{-1}.

[30] Following this period, the snow melted completely. The chamber was moved to a grassy surface (March 2 to 5), then back to the bare spiked soil (March 5 to 6), and back again to the grassy area (March 6 to 9; Figure 4c). Average mercury fluxes over grass were between 0 and 0.4 ng m^{-2} h^{-1}, in contrast to the fluxes from mercury rich soil, which averaged 295.0 ± 41.9 ng m^{-2} h^{-1} (Table 7).

[31] On March 13, snow was again placed on top of the Hg-rich soil (Figure 4d) and fluxes were monitored. The measured fluxes from March 13 to 16 were about 30 times smaller than those measured over bare spiked soil (Table 7, March 5 to 6). Although temperatures were similar for these periods, the higher net radiation and the moisture from the thawing snow, may have also enhanced fluxes for March 5 to 6. *Lee et al.* [2000] also observed an episodic release of Hg when the daily temperature increased above freezing point at a marsh site, and attributed this to ice melting during a warm event. More measurements from snow are needed to further understand the release of mercury from snow-covered surfaces and to scale up on a yearly basis.

4. Discussion

[32] A recent natural mercury emissions inventory, based on measurements of Hg fluxes in natural settings estimates

Table 5. Slopes and Constants for Log Flux Versus Log Substrate Concentration for Various Studies[a]

Reference	A	C	R^2	Substrate Concentration Range, ppm	Geology Types
Present studies, Canada	0.62	1.30	0.66	0.005 to 179.5	All geologic units
	0.50	1.57	0.49	0.167 to 179.5	Mineralized units only
	0.20	0.63	0.06	0.005 to 0.250	Background granite and till
Zehner and Gustin [2002] and *Gustin et al.* [2003]	0.55	1.43		0.012 to 4290	No geothermal sources Mining district
Nacht and Gustin [2004]	0.51	1.10		0 to 44.7	Altered material
Coolbaugh et al. [2002]	0.68	1.56		0.012 to 4290	Geothermal sources included

[a]The equation is of the form log (Flux) = A log (Hg concentration in substrate) + C.

Table 7. Chamber Measurements Over Hg-Enriched Soil With and Without Snow Cover at Elora, Ontario, February to March 2000[a]

Date	Conditions	Air Temperature, °C	TGM Flux, ng m^{-2} h^{-1}
Feb 16−21	Fresh snow over background soil	−7.0	0.09 (0.03)
Feb 21−22	Snow piled over Hg-rich soil	−2.5	8.26 (0.88)
Feb 22−23	Snow piled over Hg-rich soil, with ice crust	4.3	0.95 (0.15)
Feb 23−24	Snow piled over Hg-rich soil, ice crust removed	3.5	7.76 (0.54)
Mar 3−5	Grass, after snow melt	0.81	0.00 (0.01)
Mar 5−6	Hg-rich soil, after snow melt	2.11	295.0 (41.9)
Mar 6−9	Grass, after snow melt	9.8	0.38 (0.03)
Mar 13−16	Snow piled over Hg-rich soil	2.6	10.0 (1.0)

[a]Standard errors are given in parentheses.

the average natural Hg contribution in Canada to be 1.1×10^6 kg annually [*Richardson et al.*, 2003], which is about half of the total worldwide emissions of mercury from major anthropogenic source categories to the atmosphere (2.235×10^6 Kg yr^{-1} [*Pacyna and Pacyna*, 2001]). This inventory was based on calculations which did not account for the complexity of Hg evasion mechanisms and processes. For example, in the present studies, mean mercury flux values showed net emissions for the most part, but deposition events also occurred at these sites.

[33] Before a robust natural mercury emission inventory, which reflects the complexity of the biogeochemical cycling of mercury, can be constructed for Canada, many sources of variability must be considered. The present study provides data for a variety of Canadian landscapes and climates, but also highlights issues and limitations, which will determine the magnitude of the emissions, as well as the environments to which they can be applied. These sources of variability are related to climatic/environmental factors, spatial differences, soil and water organic content, soil mercury chemistry and the underlying geology, surface cover, vegetation cover, and water chemistry.

[34] Mercury fluxes from freshwater were highly variable (Table 2), and reflect season, geographical location, acidity, type of humic substances, DOC, and water Hg content [*Xiao et al.*, 1991]. The role of acidity has not been extensively studied, but it is known that lower pH tends
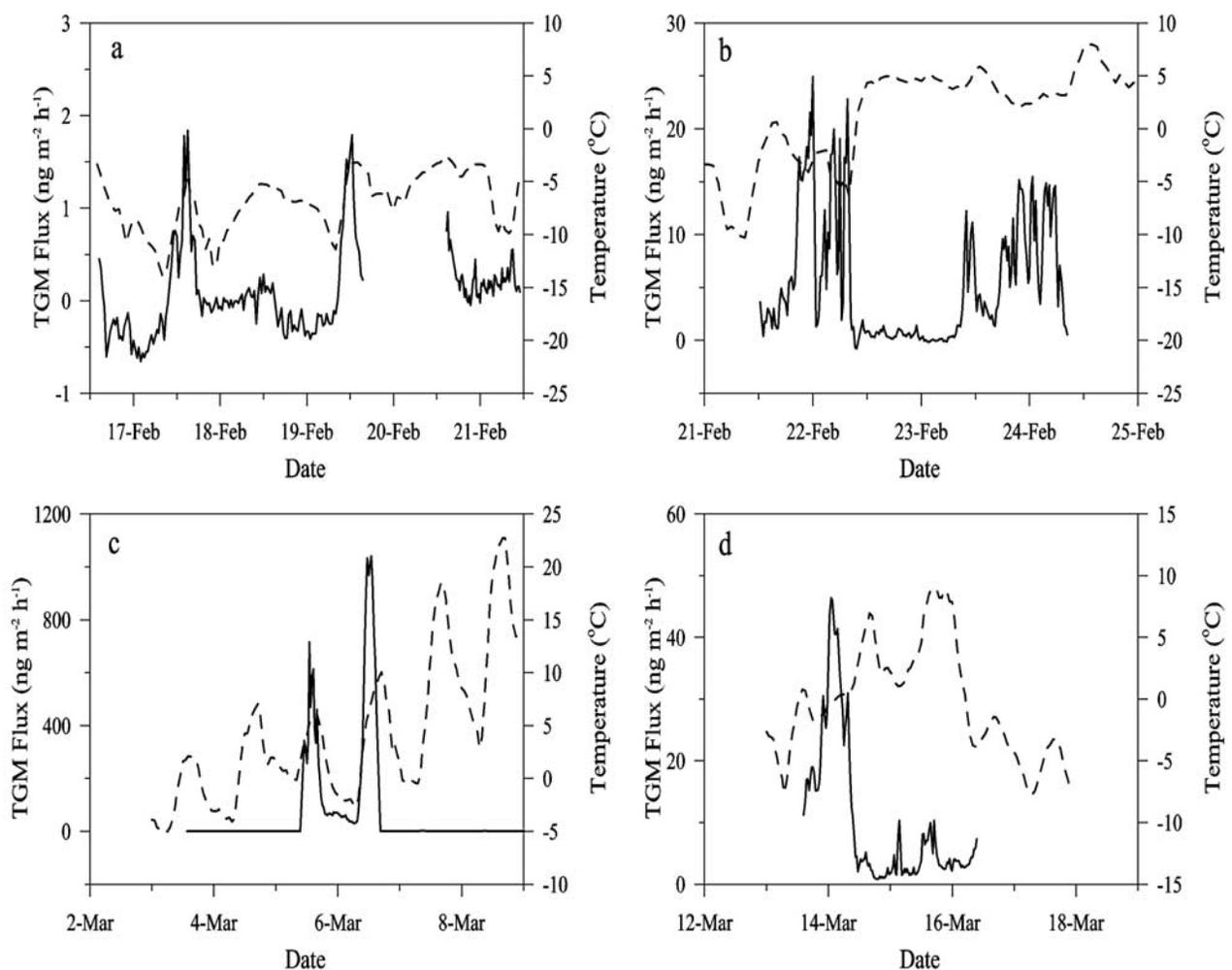

Figure 4. Mercury fluxes measured at Elora, Ontario, 2000, over (a) fresh snow on background soil; (b) snow piled over thin layer of Hg-rich soil; (c) grass and Hg-rich soil after snow melt; (d) snow piled on top of Hg-rich soil after thaw. Solid lines indicate fluxes, and dashed lines show temperature.

to stabilize and retain Hg, with higher Hg fluxes found for lakes with higher pH [*Xiao et al.*, 1991]. DGM production and volatilization may be affected by DOC, which may have several roles in the redox reactions of Hg, some of which are complicated by sunlight effects [*O'Driscoll et al.*, 2003]. The relationship between total-Hg content and organic content is related to the importance of humic substances in collecting, stabilizing, and transporting Hg in aquatic ecosystems [*Vaidya et al.*, 2000].

[35] For any type of substrate studied, including water, the amount of mercury present that can be transformed from the existing form to volatile forms must be considered. For example, total mercury in water, which represents both dissolved and particulate Hg, was used as a predictor of flux in Figure 2, but it is not known how much particulate Hg can be transformed into volatile forms. For these reasons, the relationship between flux and total Hg content in water should only be applied to scale up once all these factors are considered and the processes better understood.

[36] Canada has the world's longest coastline, making Hg emissions from oceans and seas important. The Halifax Harbour study represents one flux measurement period from the eastern part of Canada. More measurements of ocean and sea fluxes in Canada are needed to reflect the temporal and spatial variability. Temperature, ice formation, and other factors will affect the magnitude of emissions from this landscape.

[37] Scaling up wetland emissions presents particular challenges, as there was a large variability observed in fluxes depending on water levels [*Poissant et al.*, 2004a, Table 3] and season [*Lee et al.*, 2000]. *Lee et al.* [2000] found that mercury fluxes ranged from -3.3 ng m^{-2} h^{-1} during full foliage to 13.2 ng m^{-2} h^{-1} for an episodic event following spring thaw. *Wallschlager et al.* [2002] also found that moisture and high biogeochemical productivity promotes conversion rates of non-volatile Hg species to those that are volatile. In the Everglades study [*Lindberg and Meyers*, 2001], fluxes were very large and were dominated by vegetation dynamics. Currently, there is little known about the role of plants in wetlands on air-surface exchange of mercury. A dynamic scheme for scaling up is needed which addresses water levels, vegetation, as well as seasonal effects.

[38] Much of Canada is covered by various types of forest. Fluxes from litter-covered forest soils were highly variable. Mercury can accumulate in forest soils and be re-released, depending on the circumstances. As previously discussed, organic matter is very important to Hg chemistry dynamics, as are microbial activity and soil moisture effects [*Beauchamp et al.*, 2002].

[39] The role of plants in mercury cycling is still being studied. *Lindberg and Meyers* [2001] showed that photosynthesis and transpiration in wetland plants is linked to Hg emissions, and *Beauchamp et al.* [2002] showed that Hg flux from a pine tree was substantial. At the same time, wet and dry deposition to forests is much greater than to soils. These competing flux mechanisms need to be understood better before fluxes can be scaled up for forests and other vegetated sites.

[40] Mercury species in geological material will also affect the mercury fluxes. Mercury in solid substrates (bedrock and soil minerals) is typically found in the Hg^{2+}

form, associated with other components of the substrate (i.e., sulphur in the form HgS, oxides, and organic matter), and is released to its volatile phase (elemental mercury Hg^0) during physical and chemical weathering. The rate of transformation of Hg^{2+} to Hg^0 depends on speciation, temperature, moisture content, exposed surface area, degree of compaction and availability of conduits for mercury to reach the atmosphere from deeper horizons.

[41] Fluxes may be underestimated if solid rock or highly compacted parent materials are tested in laboratory chambers as conditions may not be representative of natural emissions measured in situ. Fluxes measured in natural field conditions compared well with laboratory chamber fluxes measured under controlled light and temperature conditions, when using geological substrate material collected directly from the in situ field monitoring sites [*Gustin et al.*, 1999a]. These effects need further investigation, as they are particularly important to assist in scaling up efforts based on the application of laboratory measurements to bedrock geology survey maps.

[42] The log relationship between soil Hg content and TGM fluxes varies. From these studies and those of *Nacht and Gustin* [2004], it was found that when only non-mercuriferous substrates are considered, there is no significant relationship between soil Hg content and TGM flux, and that slopes of the relationship are smaller (Table 5), or even negative, relative to those found for Hg-rich geologies. Thus it would be inappropriate to extrapolate a mercury flux for the whole of Canada based on substrate-flux relationships observed in mercuriferous regions. Another obstacle is the lack of survey data describing spatial variations in Hg concentrations (and more importantly Hg speciation) in the surface layer. Additionally, the percentage of land area in Canada with anomalous (high emitting) concentrations of mercury is very small, compared to the large land area represented by low emitting substrates (background concentrations of less than 100 ppb).

[43] Environmental factors greatly influence mercury fluxes, as evidenced by diurnal trends of deposition at night and emission during the day [e.g., *Poissant et al.*, 2000; *Gårdfeldt et al.*, 2001], and seasonal trends with higher fluxes occurring at higher temperatures and solar radiation [e.g., *Carpi and Lindberg*, 1997; *Ferrara et al.*, 1997; *Lee et al.*, 2000]. Such effects have been documented in previous studies, which have established relationships between mercury flux and water temperature [*Xiao et al.*, 1991; *Boudala et al.*, 2000], soil temperature [*Carpi and Lindberg*, 1998; *Boudala et al.*, 2000], air temperature [*Poissant and Casimir*, 1998; *Poissant et al.*, 1999; *Boudala et al.*, 2000], and solar radiation [*Beauchamp et al.*, 2002; *Boudala et al.*, 2000; *Carpi and Lindberg*, 1997, 1998; *Gårdfeldt et al.*, 2001; *Gustin et al.*, 1999a, 2002; *Poissant and Casimir*, 1998; *Poissant et al.*, 2004a]. Soil moisture also affects Hg chemistry in soil, and following rain events Hg fluxes have been found to increase [*Carpi and Lindberg*, 1998; *Gustin et al.*, 1999b; *Lindberg et al.*, 1999].

[44] Scaling up emissions based on the limited Hg flux values presented here would present challenges due to the considerable variability within and between sites. Since 40% of Canada's land is north of 60°N latitude (http://www.pfc.cfs.nrcan.gc.ca), the application of the current measurements, most of which were conducted south of this

region, is limited. Additionally, most of the flux measurements were conducted from June to August, when conditions were most conducive to gas exchange due to temperature and solar radiation effects, therefore inventories of net annual mercury flux must take this into account. These temperature and solar radiation effects are inherent in flux versus substrate relationships developed through this research (Figures 2 and 3, and Table 5), and are not usually considered in inventories due to the lack of data [e.g., *Richardson et al.*, 2003]. Another limitation is that many of the studies in Atlantic Canada were conducted under warm, high-pressure systems in the summertime, reflecting only a portion of this maritime climate, where precipitation and cloudy conditions could result in very different mercury fluxes.

[45] Although these fluxes could potentially be extrapolated to similar temperature and radiation regimes, the processes related to soil and water Hg chemistry are not well understood. The species of mercury in soils and water will also influence processes driving mercury flux depending on their volatility [*Schroeder*, 1988; *Lindqvist and Schroeder*, 1989; *Wallschlager et al.*, 1995; *Carpi and Lindberg*, 1997]. The volatility of the mercury species in the substrate will affect the relationship between Hg flux and substrate Hg concentrations. Mercury deposited from the atmosphere into the soil environment can undergo various chemical and physical processes creating stable compounds which do not readily volatilize [*Schluter*, 2000]. Geogenic mercury, which is released from bedrock and parent material, is incorporated into the soil matrix, and its release will depend on the sorption efficiency of the soil. Mercury evasion from Hg-enriched soils originating from mineralized or geothermal areas must be distinguished from that originating in non-mercuriferous areas, since the composition of volatile species in the two geologies will be different. At low mercury concentrations in substrates, the availability of volatile mercury will depend on how tightly bound the Hg 2+ species are, either to soil surfaces, or in the case of shale, to the mineral matrix. For mercury incorporated into the soil, volatilization is slow, and depends on climatic conditions [*Schluter*, 2000], such as photoreduction and soil moisture, as well as soil chemistry. For mineral-bound Hg, weathering plays a key role, and under many circumstances the bound Hg will not be released. Thus emission factors need to account for the retention by soil and sediment, which depends on interdependent factors such as climatic conditions, biological activity and soil type [*Rasmussen*, 1994]; thus, at low Hg concentrations, soil sampling alone will not necessarily reflect Hg available for volatilization. Additionally, time of year, surface roughness, meteorology and ambient air concentrations will influence the fluxes from these sites through their role in deposition processes, and will affect the ability to use substrate concentrations to predict the flux.

[46] Permafrost (bedrock or soil that remains below 0°C throughout the year) underlies about half of Canada's landmass and its areal extent varies with climate change, vegetation, snowpack conditions, etc. (http://atlas.gc.ca/site/english/maps/enviroment/land/permafrost/1). Mercury fluxes from these surfaces have not been quantified. Additionally, there is a large variation in snow-covered surfaces (e.g., depth, snow type, substrate). The results from the snow studies in this project illustrate some of the relevant processes, but are not sufficient for scaling up purposes. Further research is needed to understand TGM flux from snow, as well as effects of thawing and freezing cycles, so that cycling of mercury can be understood on an annual scale.

[47] This paper has focused on gaseous mercury measurements, and has not considered particulate or reactive species of mercury. Further research will be needed to appropriately consider these mercury species in natural emission inventories.

5. Summary and Conclusions

[48] Fluxes measured in a variety of Canadian landscapes were in the range reported for similar landscapes and climates in other countries. Where noted, differences in flux values for similar substrates may be explained by differences in climatological and biogeochemical factors. Prior to undertaking these air-surface exchange measurements, there were almost no direct measurements of Hg exchange available for Canada. Although mercury emissions acquired in the various landscapes throughout these studies have made a significant contribution to understanding air-surface exchange processes in the Canadian environment, there are still many knowledge gaps related to process understanding, spatial and temporal variability, and soil and water chemistry, that must be addressed before a reliable natural emission inventory can be created.

[49] The following research areas are important for addressing some of the remaining knowledge gaps in the mercury air-surface exchange data for Canada, so that a more reliable natural emission inventory can be constructed: (1) snow studies and thaw-freeze cycles at background and Hg-rich substrates; (2) seasonal studies in forest and wetlands to constrain temporal variability; (3) lake studies for relationship in DGM, DOC, pH, etc.; (4) effects of overburden and weathering; (5) background measurements over long periods (i.e., years) to assess deposition, re-emission, and substrate activity; (6) understanding of processes/mechanisms/interactions controlling air-surface exchange for a variety of variables (e.g., rain, soil moisture, radiation, surface roughness and cover, etc.); (7) role of vegetation, particularly in forests and wetlands.

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