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Mercury Contamination of Golf Courses Due to Pesticide Use

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Management practices at golf courses require frequent pesticide applications to maintain turf quality under extremely stressful conditions produced by heavy traffic. Golf course turf usually consists of only one or two grass species, allowing disease to thrive and intensifying the need for pesticide treatments. Despite the persistence and toxicity of mercury and the availability of alternatives, mercurial fungicides are used regularly to combat snow molds, *Typhula spp.*and *Fusarium nivale.*

The persistence of mercury presents the potential for accumulation in soil as fungicide applications occur over several years. Disturbance of soils may allow remobilization to occur many years after fungicidal applications have ceased. The strong tendency of mercury to adsorb to soil complexes increases the probability of off-site contamination because pesticides bound to soil particles may be transported to aquatic systems in surface water runoff and between waterbodies in suspended solids (Environment Canada 1985). This is a particular concern at golf courses because many are located in watersheds important to recreation or groundwater supplies. The proximity of golf courses to aquatic ecosystems and ramifications for future land use decisions warrant further examination of the long-term environmental impacts of mercurial pesticide use at these sites. A study of mercury contamination at golf courses in Atlantic Canada was initiated to determine the extent of the problem, the potential for movement of mercury from application areas, and the possibility of contamination of nearby aquatic ecosystems.

MATERIALS AND METHODS

Sampling stations, which included two greens, two ponds, a fairway, and a nearby lake, were established at two golf courses in 1992. In 1993, 20 sampling stations were used on six additional courses, 11 were from greens and 9 were from watercourses. Also in 1993, 4 sampling stations in Fish Lake were established along a transect at 300 m intervals from greens at Oakfield Golf Course to the outlet of the lake (Table 1). An additional station was placed near the inlet of Fish Lake, and a reference station was located 5 km away in Grand Lake. Three soil cores were taken 2 m inset from the perimeter of greens and watercourses

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using acid-washed teflon tubes with an inside diameter of 3.2 cm At lake stations five sediment cores were collected in acid-washed teflon core tubes, in a stainless steel casing with a 1 m extension or inside a Phleger coring device. All cores were frozen immediately and stored at -20°C until analyzed. Cores were cut while frozen and dried to constant weight over 24 hr at 60°C before analysis for total mercury. For methyl mercury analysis, soil and sediment samples were thawed just prior to extraction.Two soil depths were analyzed, 0-2 cm and 7-9 cm. Five samples of three aquatic species, pickerel weed (*Pontedaria cordata*), freshwater mussels (*Anodonta sp.*), killifish (*Fundulus diaphanus*), 5 individuals per sample, were taken at the three nearshore Fish Lake stations and Grand Lake. All samples were placed in polyethylene bags, frozen immediately and stored at -20°C until analyzed. Biota samples were homogenized and finely ground prior to extraction and analysis.

Soil and sediment samples were digested with sulfuric acid, nitric acid, potassium permanganate and potassium persulfate. Excess permanganate and manganese oxides were reduced with hydroxylamine hydrochloride and the solutions were diluted to volume. Samples were further reduced with stannous chloride immediately prior to analysis by cold vapour atomic absorption spectrophotometry (Milton Roy Mercury Monitor). Soil leachates were prepared according to CGSB 164-GP-IMP (1987) (pH 5.0 $\pm$ 0.5 with acetic acid, 24 hr).

Phenylmercuric acetate (PMA) concentrations were estimated, based on the mercury content of the leachate. Portions of the leachate were analyzed for mercury directly by cold vapour atomic absorption. This represented the ionic and easily hydrolyzed mercury in the solutions. Separate solution aliquots were digested and analyzed for total mercury. The difference between the total extractable mercury and ionic extractable mercury was attributed to the presence of chemically stable, water (or dilute acid) soluble mercury-containing compounds such as phenylmercuric acetate. This procedure was verified for samples spiked with pure compound.

Methyl mercury analysis was performed in a manner similar to that described in AOAC (1984). Sediment/soil samples (5g), fish (2.5 g), mussel (2.5 g), and plant (2.5 g) were washed with 3 x 8 mL acetone and 1 x 8 mL benzene and the washings were discarded. Then 10 mL of 6 N hydrochloric acid was added to the samples, followed immediately by 5 mL benzene. Samples were shaken for 30 min and the benzene layer was removed. Samples were re-extracted with 2 x 5 mL benzene and the benzene extracts combined and reduced to 5 mL under a nitrogen stream. Gas chromatographic analysis was performed on a HP 5890 series 11 instrument with splitless injection and ECD detection. Methyl mercury chloride was chromatographed on a DB5 30 meter capillary column (without $HgCl_2$ treatment). Recovery checks were carried out on reference material DORM-1 (National Research Council).

RESULTS AND DISCUSSION

In 1992, the highest mean total mercury concentrations were found on the greens, (15 to 71 mg/kg), however watercourse sediments were also contaminated (<0.050 to 1.9 mg/kg) (Table 1). Mean PMA concentrations ranged from <0.050 to 0.45 mg/kg, with higher concentrations occurring in the 0-2 cm layer. At the six courses sampled in 1993, mean total mercury concentrations on the greens ranged from <0.030 to100 mg/kg, while those in watercourse sediments ranged from <0.030 to 0.26 mg/kg (Table 2). Mean leachable mercury concentrations were low as compared to mean total mercury concentrations, ranging from <0.050 to 0.016 mg/kg.

At ten of the thirteen greens mean soil concentrations of total mercury exceeded the Canadian Council of Ministers of the Environment interim soil remediation criteria of 10 mg/kg for industrial sites (CCME 1991), which indicated that regular applications of mercurial fungicides within limits specified on product labels have resulted in accumulation of mercury at golf courses. This was supported by several previous studies. Gilmour and Miller (1973) found that annual applications of a 30% mercuric chloride, 60% mercurous chloride formulation at a rate of 0.6 g/m^2 resulted in a minimum total mercury concentration in surface soil of 125 mg/kg. Fushtey and Frank (1981) reported maximum mercury concentrations of 197 and 119 mg/kg on golf greens, the first receiving inorganic mercury formulations over a period of 20 years, and the second receiving both inorganic and PMA applications annually for 40 years. At golf courses at least 50-years-old at the time of sampling, MacLean *et al.*(1973) noted a mean mercury concentration on greens of 53 mg/kg, and 7.5 mg/kg more than 30 m from the application area, relative to a background level of 0.05 mg/kg.

Low concentrations of PMA in relation to total mercury (Table 2) suggested PMA formulations were transformed to inorganic forms. Mercury in soil is strongly bound to organic matter, so that only trace concentrations of mercury are soluble (MacLean 1974), evident in the low leachable mercury concentrations found (Table 2). Thus, the bulk movement of mercury did not occur in the soil solution but adsorbed to soil particles.The variation in the relationship between mercury concentration and depth was partially a reflection of the age of the golf courses and differences in the intensity and frequency of pesticide applications, and no overall trend was evident (Fig.1).

Although the thatch-soil interface is typically rich in organic matter and has the potential to adsorb and retain pesticides, there was no preferential retention of mercury in the top 0-2 cm of the greens as compared to the 7-9 cm layer (Fig.1). In fact, on the greens where the highest concentrations of mercury were observed, the 7-9 cm samples had higher concentrations than the 0-2 cm samples, suggesting downward movement as observed in other studies (MacLean *et al.*1973). However, ten of the twelve watercourses examined contained more mercury in the

Table 1. Mean mercury and PMA residues in soil and sediment from golf courses, 1992 (mg/kg, uncorrected dry wt. basis, n=3, nd=not detected)

Course	Location	Depth (cm)	Total Mercury (1sd)	PMA (1sd)
Brightwood, NS	Green 8	0-2	71 (1.7)	0.21 (0.099)
		7-9	15 (6.3)	0.076 (0.038)
	Pond 8	0-2	1.9 (2.4)	nd
		7-9	0.29 (0.16)	nd
	Fairway 15	0-2	1.3 (0.70)	nd
		7-9	0.25 (0.023)	nd
Oakfield, NS	Green 12	0-2	18 (3.4)	0.45 (0.11)
		7-9	18 (10.1)	0.27 (0.22)
	Pond 12	0-2	nd	nd
		7-9	nd	nd
	Fish Lake	0-2	0.25 (0.17)	0.12 (0.12)
		7-9	0.10 (0.016)	nd
Detection Limit			0.050	0.050
Recovery (%)			100(n=3)	98(n=4)

0-2 cm samples, which suggested that no long-term deposition occurred in the watercourses, as would be expected if the mercury was removed in surface water drainage.

Methyl mercury was not detected in any of the lake sediment samples collected. Mean total mercury concentrations in lake sediments ranged from 0.011 to 0.045 mg/kg (Table 3). After variation due to pH and moisture had been removed in multiple regression analysis, the sediments from Fish Lake had significantly higher ($p<0.001$) total mercury concentrations than Grand Lake. The mercury concentration of 0.25 mg/kg in Fish Lake sediment (Table 1) was above the lowest effect level of 0.20 mg/kg established for mercury by the Ontario Ministry of Environment Sediment Quality Guidelines (Persaud *et al.* 1992). This corresponds to a 'marginally to significantly polluted' classification which has been noted to affect the use of sediments by benthic organisms.

Mercury in sediments in a headwater lake over 15 km upstream was measured at 0.3 mg/kg, attributed to historical use of mercury in an extraction process for mining gold (Environment Canada 1985). Based on the direction of flow through the system, it is possible that Grand Lake may have received input from mining wastes. Thus, it would be expected that mercury contamination would be higher in Grand Lake sediments than Fish Lake. There was more mercury in Fish Lake, suggesting the course as a source of mercury contamination. The highest concentrations of mercury were found in the middle of Fish Lake, a pattern also found by Wiener *et al.*(1990), because mercury in sediments tends to be spatially distributed in the same manner as the material to which it is adsorbed, dependent upon the configuration of the lake.

Table 2. Mean mercury residues in soil and sediment from golf courses, 1993 (mg/kg, uncorrected dry wt. basis, n=3, nd=not detected)

Course	Location	Depth (cm)	Leachable Mercury	Total Mercury (1sd)
Green Gables, PEI	Green 12	0-2	nd	0.090 (0.064)
		7-9	nd	1.2 (0.85)
	Pond 16	0-2	0.0011	0.050 (0.045)
		7-9	nd	0.030 (0.042)
Maplewood, NB	Green 3	0-2	0.0047	16.9 (8.0)
		7-9	0.0010	0.29 (0.18)
	Pond 3	0-2	nd	nd
		7-9	nd	0.11 (0.016)
	Green 4	0-2	0.0089	21 (3.3)
		7-9	nd	0.14 (0.012)
	Pond 4	0-2	nd	0.17 (0.15)
		7-9	0.0011	0.083 (0.0047)
Fundy, NB	Green 8	0-2	0.00090	3.3 (1.5)
		7-9	0.016	63 (22)
	Stream 8	0-2	0.00060	0.040 (0.057)
		7-9	0.0087	0.030 (0.042)
	Green 4	0-2	0.0017	5.2 (1.8)
		7-9	0.0099	100 (39)
	Near Brook 4	0-2	0.0010	1.5 (1.5)
		7-9	0.0059	1.1 (1.1)
Cape Breton Highlands, NS	Green 11	0-2	nd	3.6 (2.7)
		7-9	nd	5.0 (2.6)
	Brook 11	0-2	nd	0.063 (0.090)
		7-9	0.0018	0.080 (0.070)
	Green 12	0-2	0.0015	5.8 (2.5)
		7-9	0.0015	32 (14)
	Brook 12	0-2	nd	0.14 (0.10)
		7-9	nd	0.12 (0.041)
Belvedere, PEI	Green 5	0-2	0.00080	16 (5.3)
		7-9	0.0026	70 (35)
	Green 9	0-2	0.0024	31 (21)
		7-9	0.0011	24 (8.2)
	Brook 9	0-2	0.0025	0.18 (0.025)
		7-9	nd	0.080 (0.0082)
Terra Nova, NF	Green 12	0-2	0.0016	0.20 (0.14)
		7-9	nd	nd
	Green 15	0-2	0.00090	0.12 (0.019)
		7-9	nd	nd
	Ditch 8	0-2	nd	0.26 (0.12)
		7-9	nd	0.12 (0.085)
Detection Limit			0.00050	0.030
Recovery (%)			101 (n=4)	99 (n=4)

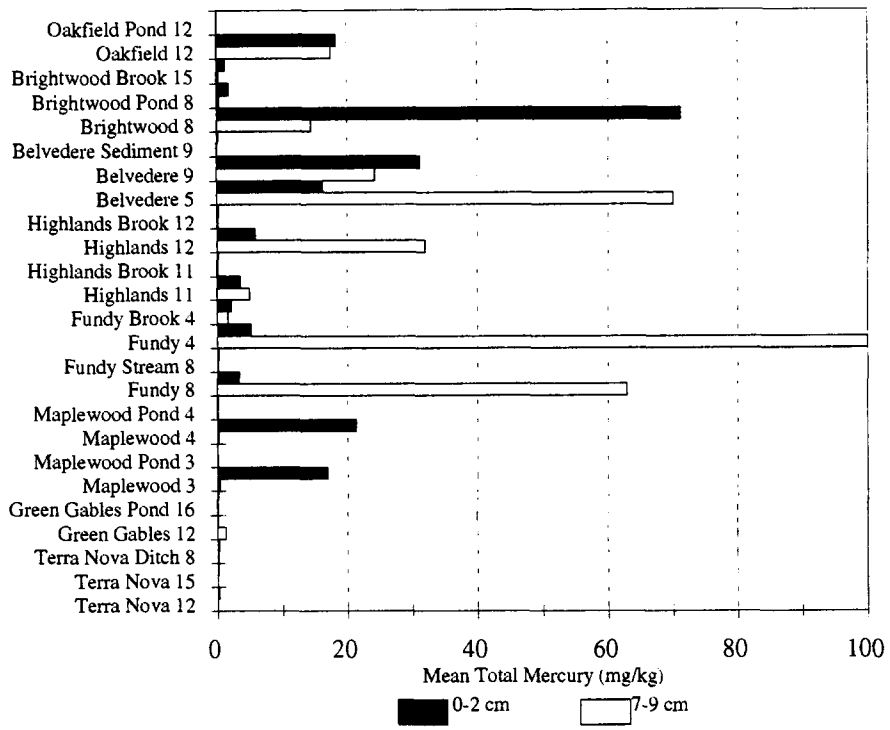

Figure 1. Mean total mercury concentrations (mg/kg) at two soil depths on golf greens and watercourses (n=3).

The dominant form of mercury in organisms is methyl mercury, which is more toxic than the inorganic forms (Zilloux *et al.* 1993). It forms strong complexes with sulfhydryl groups of proteins and bioaccumulates in greater concentrations than predicted by octanol/water distribution coefficients. Aquatic organisms may be contaminated with methyl mercury even when mercury concentrations are below detection in the water column. Methyl and total mercury were not detected in the aquatic plants examined, at a detection limit of 0.010 mg/kg (Table 4). Other studies have also indicated that removal by plants is negligible (Gilmour and Miller 1973; MacLean 1974). Both methyl and total mercury concentrations were an order of magnitude higher in mussels from Fish Lake than those from Grand Lake (Table 4), and the differences were significant (ANOVA, $p<0.010$ and $p<0.001$, respectively). Methyl mercury in mussels ranged from 30-70 % of the total mercury concentration, with the highest proportion occurring in samples collected nearest the green. Bivalves are indicative of local contamination because they are sedentary filter-feeders. Mussels at the station nearest the greens showed the highest concentrations of methyl and total mercury, and those in Grand Lake were an order of magnitude lower (Table 4), which suggested the greens as a source of mercury contamination.

Table 3. Mean mercury concentrations in sediments from Fish Lake and Grand Lake,1993 (mg/kg, uncorrected wet wt. basis, n=5, nd=not detected).

Location	Depth (cm)	Methyl Mercury	Total Mercury (1 sd)
Fish Lake, near greens	0-2	nd	0.038 (0.0034)
Fish Lake, near greens	7-9	nd	0.029 (0.0031)
Fish Lake, 300 m from greens	0-2	nd	0.045 (0.0039)
Fish Lake, 600 m from greens	0-2	nd	0.042 (0.0064)
Fish Lake, outlet	0-2	nd	0.027 (0.0048)
Fish Lake, inlet	0-2	nd	0.015 (0.0040)
Grand Lake	0-2	nd	0.011 (0.0060)
Grand Lake	7-9	nd	0.014 (0.0039)
Detection Limit		0.0010	0.0010
Recovery (%)		102 (n=2)	65 (n=2)

Table 4. Mean mercury residues in aquatic organisms from Fish Lake and Grand Lake,1993 (mg/kg, uncorrected wet wt. basis, n=5).

Organism	Location	Methyl Mercury (1sd)	Total Mercury (1sd)
Pontedaria cordata (pickerel weed)	Fish Lake, near greens	nd	nd
	Fish Lake, outlet	nd	nd
	Fish Lake, inlet	nd	nd
	Grand Lake	nd	nd
Anodonta sp. (freshwater mussel)	Fish Lake, near greens	0.10 (0.0099)	0.14 (0.011)
	Fish Lake, outlet	0.036 (0.0079)	0.12 (0.031)
	Fish Lake, inlet	0.041 (0.010)	0.10 (0.032)
	Grand Lake	0.014 (0.00063)	0.028 (0.037)
Fundulus diaphanus (banded killifish)	Fish Lake, near greens	0.15 (0.041)	0.13 (0.020)
	Fish Lake, outlet	0.11 (0.016)	0.11 (0.010)
	Fish Lake, inlet	0.11 (0.019)	0.096 (0.010)
	Grand Lake	0.14 (0.03)	0.14 (0.012)
	Detection Limit	0.010	0.010
	Recovery (%)	102 (n=3)	108 (n=4)

Fish provide an indication of mercury contamination reaching higher trophic levels, and, as observed in this study, typically contain more mercury than other biological components of aquatic ecosystems (Zilloux *et al.* 1993). Mean methyl mercury concentrations in *Fundulus* ranged from 0.11 to 0.14 mg/kg, with the highest concentrations in fish collected adjacent to the golf green (Table 4). Similarly, mean total mercury concentrations in fish decreased with distance from the green along the sampled transect in Fish Lake, from 0.130 to 0.096 mg/kg. Grand Lake fish contained comparable concentrations of methyl mercury and higher concentrations of total mercury than those in Fish Lake. Although mean methyl mercury concentrations in *Fundulus* samples were higher than total mercury concentrations due to the variation between the different analytical

techniques for total and methyl mercury, it was evident that methyl mercury comprised >95 % of the total mercury. Mercury contamination in fish did not follow the same spatial pattern as sediment concentrations. The contamination observed was above concentrations shown to adversely affect *Fundulus*. Teratological effects in *Fundulus* have been shown at 0.02 mg/kg, and changes in mercury tolerance of *Fundulus* populations at 0.05 mg/kg (Weis and Weis 1982;1984).

This study showed that use of mercurial fungicides resulted in mercury contamination of golf course soils, and supported the hypothesis that nearby aquatic ecosystems are also contaminated. Given the widespread nature of the problem and the potential for mercury to bioaccumulate as trophic levels increase, further research is required to determine the extent to which freshwater ecosystems may be impacted by past and present use of mercurial fungicides.

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