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Effect of urban sewage treatment on total and methyl mercury concentrations in effluents

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Abstract. The purpose of this study was to investigate the effect of sewage treatment on total mercury (THg) and methylmercury (MeHg) concentrations in domestic effluents and the contribution of urban sewage treatment facilities to THg and MeHg in rivers. We determined the concentrations of THg and MeHg in unfiltered samples of untreated and treated domestic sewage from the three treatment facilities and receiving river water within the City of Winnipeg. The concentrations of THg in the Red and Assiniboine rivers ranged from 3–31 ng/L. THg was related positively to suspended sediment concentrations in the rivers. The concentrations of MeHg in these rivers were usually 0.2–0.3 ng/L. THg concentrations in raw sewage varied widely, from 2–150 ng/L. Treatment removed an average of 88% of this mercury. MeHg concentrations in raw sewage were 0.5–4.3 ng/L, however, after treatment at two treatment facilities, MeHg was greatly reduced, usually to 0.1–0.4 ng/L. Most treated sewage, therefore, had MeHg concentrations that were similar to levels in the receiving rivers and the effect of discharged effluent was usually a change of about 2% or less on concentrations in the rivers. However, one of the facilities (the West End plant) was discharging higher concentrations of MeHg, up to 2 ng/L, causing calculated increases of up to 11% in the concentration of MeHg in the Assiniboine River.

Introduction

Previous studies on the effect of domestic sewage treatment on mercury concentrations have focused on total mercury (THg). Although it has been shown that domestic wastewater treatment removes most of the THg from raw sewage (Glass et al. 1990; Balogh & Liang 1995; Mugan 1996), the possibility that concentrations of methylmercury (MeHg) in treated effluents are high required attention. We hypothesized that rates of mercury methylation in the sewage treatment process could be high, resulting in significant concentrations of MeHg in treated effluents, especially in relation to ambient concentrations in receiving rivers. The primary objectives of this study were therefore to determine the effect of domestic sewage treatment on the THg and MeHg concentrations and to investigate the effect of discharges of treated sewage on the THg and MeHg concentrations in receiving rivers.

Concentrations of THg and MeHg are now quite well known in temperate lakes and reservoirs, however there has been much less work done on rivers. Therefore, a secondary objective of this study was to determine the concentration of THg and MeHg in naturally turbid, prairie rivers.

Study area and sewage treatment facilities

The City of Winnipeg, an urban center with a population of about 650,000, is located in south-central Canada, near to the north-eastern margin of the Great Plains of North America. Climate is cool continental with long, cold winters and warm summers. Mean July temperature is about 20 °C whereas mean January temperature is about −18 °C. Rivers in the region are ice-covered for about 5 months of the year.

The Red and Assiniboine rivers drain areas of the sedimentary prairie. Much of their drainage areas are covered by the glacial-lacustrine sediments of Glacial Lake Agassiz. The Red River drains parts of Manitoba, North Dakota, Minnesota, and South Dakota whereas the Assiniboine River drains parts of Manitoba, Saskatchewan, and North Dakota. Most of the drainage basins of both rivers are dominated by agricultural lands. Both rivers are naturally turbid; in 1994 suspended sediment concentrations in the Red River ranged from 50–750 mg/L and in the Assiniboine River ranged from 68–320 mg/L. The Red River has a mean annual discharge of 222 m^3/s. The Assiniboine River is smaller, with a mean annual discharge of 47 m^3/s.

The City of Winnipeg operates three domestic sewage treatment facilities (Water Pollution Control Centres – WPCCs): North End, South End and West End WPCCs (Figure 1). All three facilities provide secondary treatment of urban wastewater. Two of the WPCCs (North End and South End) use oxygen in the secondary treatment, whereas the West End WPCC uses air for secondary treatment. In addition, the West End WPCC uses lagoons after secondary treatment for further effluent conditioning. Flows at the facilities on the dates sampled ranged from 30–35 ML/day (West End), 55–65 ML/day (South End) and 210–460 ML/day (North End).

The central (older) part of the city has combined storm and sanitary sewers, whereas the outer (newer) parts of the city have separated sewers. Moderate to heavy rainfall events cause combined sewer overflows (CSOs), during which time the capacities of the sewage treatment facilities are exceeded and effluent from combined storm and sanitary sewers is discharged directly to the river. There are 18 CSO events in a typical year during the “recreation” season (May to September inclusive).

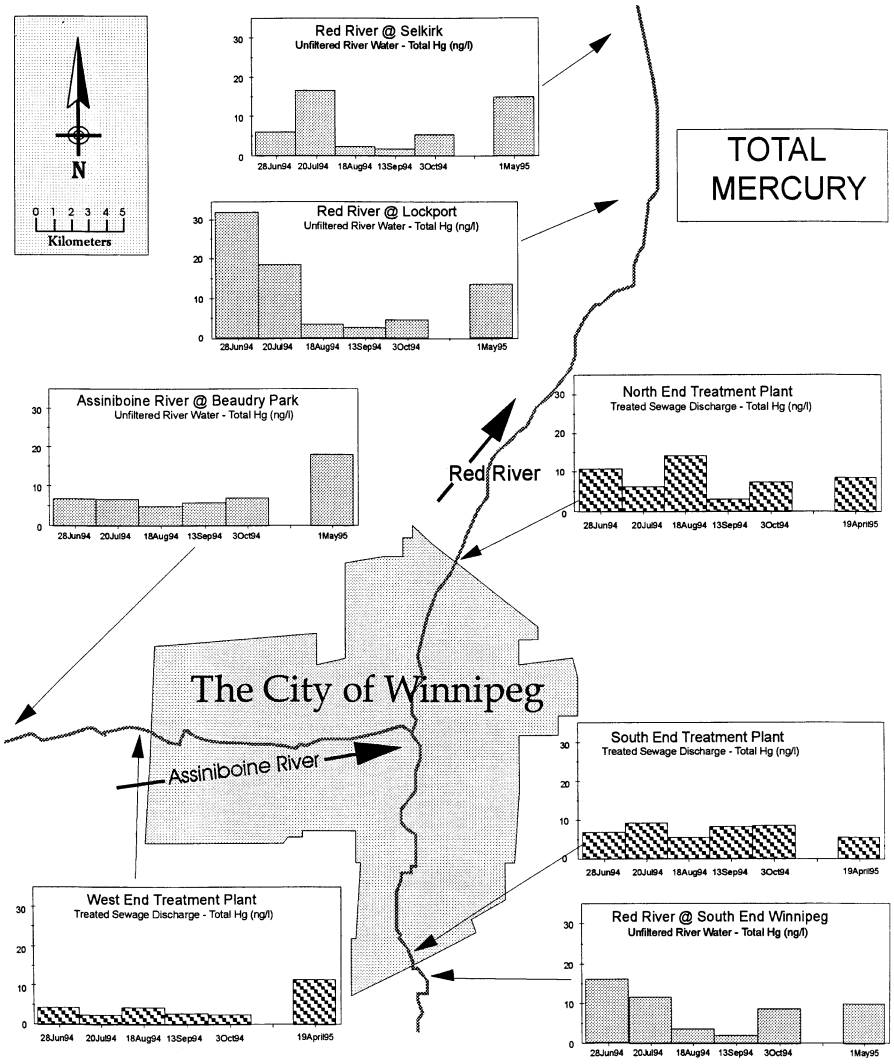

Figure 1. Total mercury concentrations in unfiltered water from the Red and Assiniboine rivers and treated sewage from Winnipeg's three sewage treatment facilities.

Methods

Water and sewage samples for THg and MeHg were taken in acid-cleaned Teflon bottles, triple-bagged, and were transported in clean coolers. The "clean hands-dirty hands" protocol was used in sampling (Gill & Fitzgerald 1987; St. Louis et al. 1994). THg samples were preserved with concentrated trace-metal grade HCl whereas samples for MeHg were frozen. Samples

were not filtered. THg of water and sludge samples were determined at Flett Research Ltd. using cold vapour atomic fluorescence (Bloom & Crecelius 1987). The detection limit of this method is 0.2–0.3 ng/L. MeHg was determined at Flett Research Ltd. using aqueous phase ethylation, a distillation step followed by chromatographic separation with atomic fluorescence (Bloom 1989; Horvat et al. 1993). The detection limit of this method was 0.01–0.02 ng/L. Most samples were taken in duplicate and the duplicate samples were analysed independently. Occasionally, three or four samples were taken and analysed. See St. Louis et al. (1994, 1996) for full details of sampling and analytical procedures. The mean standard deviation of replicate determinations of 24 river water samples analysed for THg was 0.48 (range 0.01–3.45) and the mean relative standard deviation was 4.7% (range 0.27–10.8%). The mean standard deviation of replicate determinations of 24 river water samples analysed for MeHg was 0.021 (range 0.007–0.064) and the mean relative standard deviation was 8.5% (range 2.3–18.8%). We sampled five times in early summer to autumn 1994 and once in spring 1995.

River flow and suspended sediment data were provided by Environment Canada, Water Survey Branch, Winnipeg, MB.

Results

Total and methyl mercury in the Red and Assiniboine rivers

THg in the Red River (Lockport station) varied over a wide range over the period June 1994 to May 1995, from 2.6–32 ng/L (Figure 1). There was an apparent seasonal variation in THg concentrations in the Red River; concentrations were high in the spring and early summer and low in the late summer and autumn. Similar variation was observed in suspended sediment concentrations. Suspended sediment concentrations explained 70% of the variation in THg concentrations in the Red River (Figure 2a).

Less variation in THg concentrations was observed in the Assiniboine River, where the total range in concentrations was 4.9–18.0 ng/L (Figure 1). As was found for the Red River, THg concentrations may be related to suspended sediment concentrations. In 1994, suspended sediments and THg concentrations in the Assiniboine varied little, whereas both were much higher in the spring of 1995 (Figure 2b).

MeHg concentrations in the Red and Assiniboine rivers did not vary dramatically, ranging from 0.16–0.41 ng/L at all sampling stations (Figure 3). MeHg concentrations showed no obvious seasonal trends and no relationship with suspended sediment concentrations.

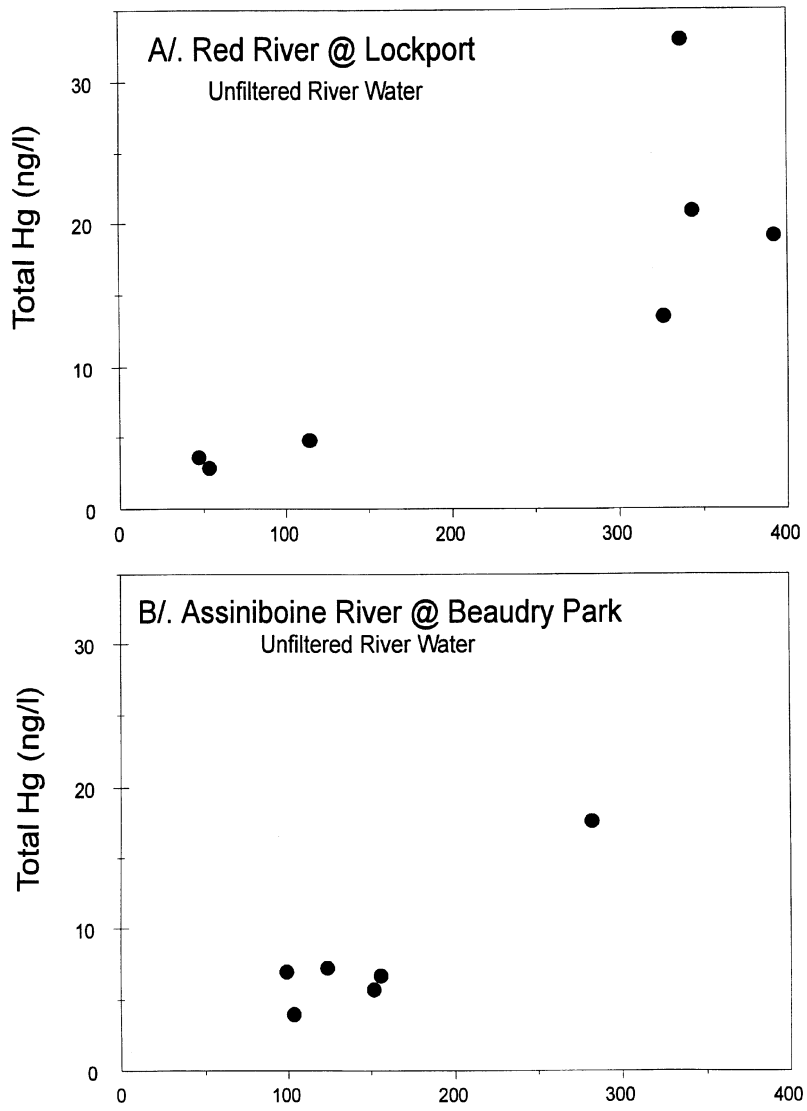

Figure 2. Relationship between total mercury concentrations and suspended sediment concentrations in the Red and Assiniboine rivers. A. Red River at Lockport. B. Assiniboine River at Beaudry Park.

Effect of sewage treatment on total and methyl mercury

THg in raw sewage varied widely, from 2–160 ng/L (Figure 4). The mean concentration was 61 ng/L. Treatment resulted in lower, rather constant THg concentrations in effluent discharged to the rivers (Figures 1 & 4). Treated

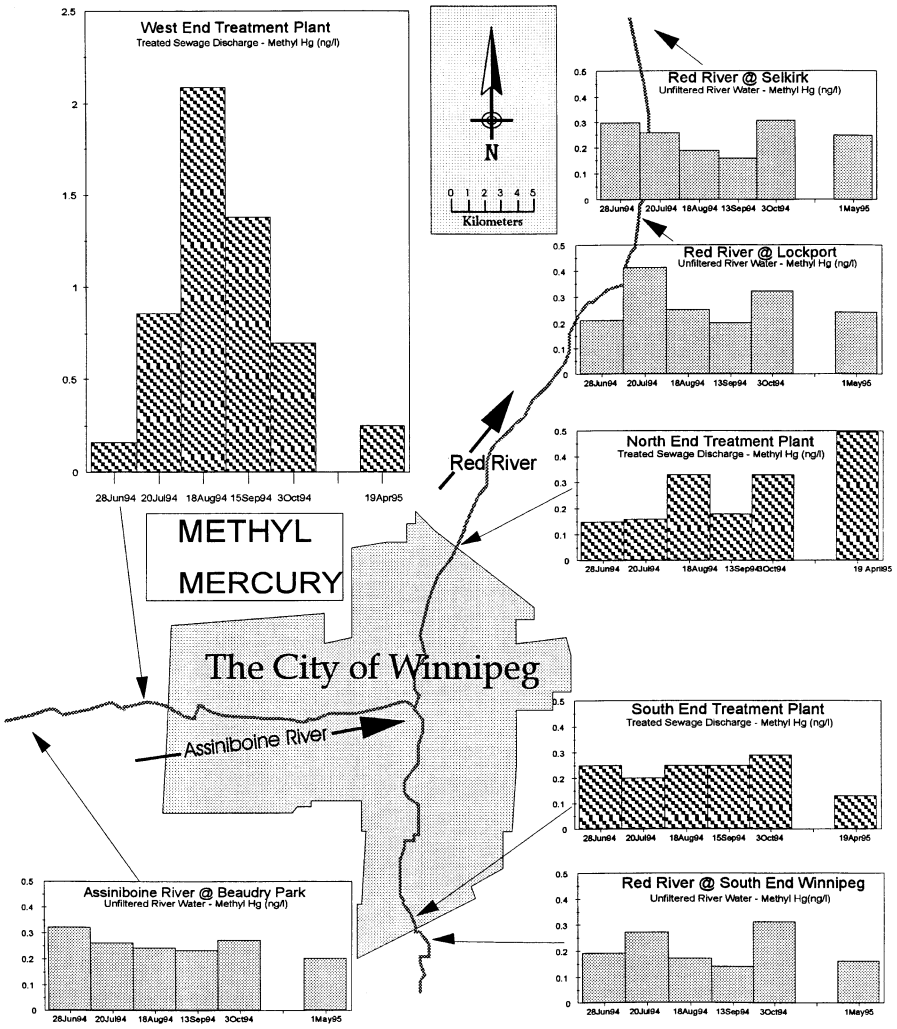

Figure 3. Methyl mercury concentrations in unfiltered water from the Red and Assiniboine rivers and treated sewage from Winnipeg's three sewage treatment facilities.

effluent ranged from 3–14 ng/L. There did not appear to be a seasonal pattern in the concentration of THg in treated effluent. Because incoming and outgoing streams were sampled at about the same time, because there is a great deal of mixing and recirculation in sewage treatment facilities, and because travel times are usually several hours, the calculation of removal proportions from individual paired samples is probably not justified. The average removal of THg by treatment, calculated as the mean THg in treated effluent divided by

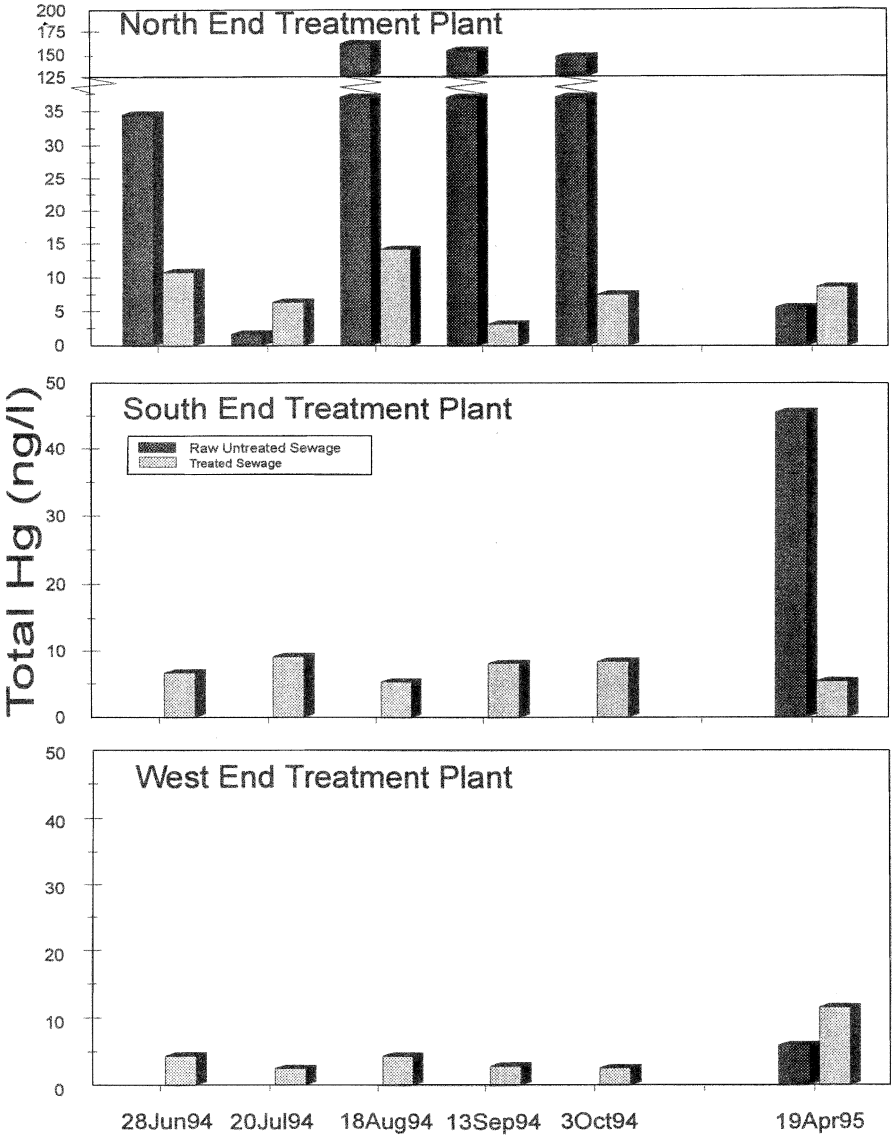

Figure 4. Total mercury concentrations in unfiltered samples of raw sewage and treated sewage for City of Winnipeg sewage treatment facilities.

the mean THg in raw sewage for all dates with paired samples for all plants, was 88% (n = 8) (Figure 4).

MeHg concentrations in raw sewage varied from 0.5–>4 ng/L, averaging 2.2 ng/L (Figure 5). MeHg concentrations in treated sewage were very low at the North End and South End WPCCs (range 0.13–0.56 ng/L; Figures 3

& 5). No seasonal trends were evident in these data. In contrast, MeHg in treated sewage from the West End facility varied considerably, up to quite high concentrations (>2 ng/L) in 1994. There was a noticeable seasonal trend in MeHg in treated sewage from the West End facility with concentrations being highest in August.

Treatment removed an average of 90% of MeHg from raw sewage (Figure 5). This average does not include, however, the summer period for the West End WPCC when MeHg in treated effluent was much higher than on those sampling days when MeHg in raw sewage was measured and approached the mean concentration in raw sewage (Figure 5).

Effect of the discharge of treated effluent on total and methyl mercury in the Red and Assiniboine rivers

THg concentrations in treated sewage from Winnipeg's three treatment facilities were usually similar to concentrations in the Red and Assiniboine rivers (Figure 1). Also, the discharged flows from the three facilities were usually small compared to river flows. Flow from the South End WPCC ranged up to 0.7% and from the North End WPCC ranged up to 2% of the flow of the Red River, and flow from the West End WPCC ranged up to 1.4% of the flow of the Assiniboine River. Therefore, effluent discharge did not result in large direct changes to THg mercury concentrations in the rivers. We calculated the contribution of treated effluents on concentrations in the receiving rivers by comparing loadings of THg and MeHg in the rivers and in effluents, calculated as the products of daily flows and sampled concentrations. The flow of treated effluent from the South End and West End WPCCs caused increases and decreases in THg concentrations of less than 2% in their respective rivers. The flow of treated effluent from the North End WPCC constituted a larger proportion of the flow of receiving river than for other treatment facilities, affecting concentrations in the Red River from a decrease of 0.5% to an increase of 6%.

MeHg in treated effluent from the South End and North End WPCCs affected concentrations in the Red River by very small amounts, always less than 2%. In the Assiniboine River, MeHg in treated effluent was often much higher than in the Assiniboine River upstream of the West End WPCC (Figure 3). Therefore, discharge of treated effluent sometimes had a moderately large effect on MeHg concentrations in the river; this change ranged from small decreases to an increase of 11%.

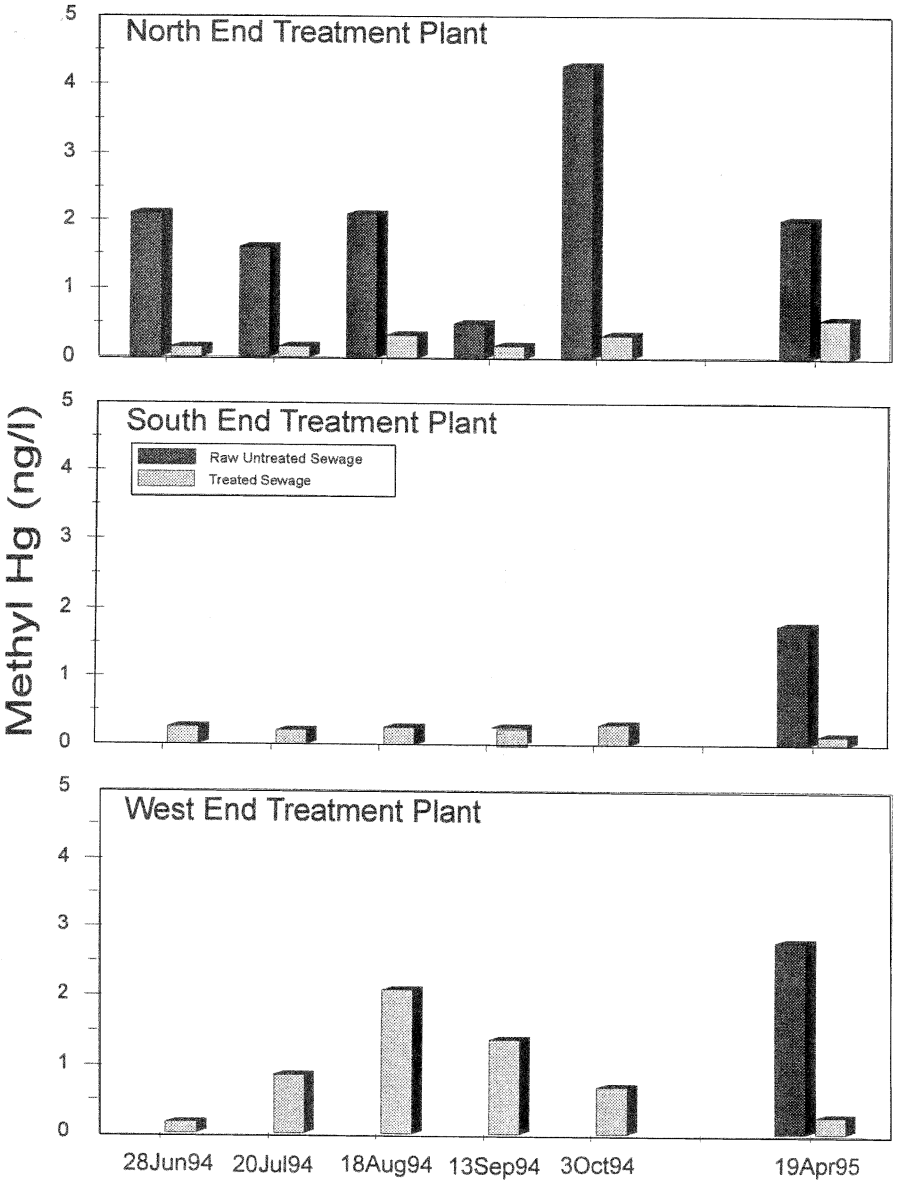

Figure 5. Methyl mercury concentrations in unfiltered samples of raw sewage and treated sewage for City of Winnipeg sewage treatment facilities.

Discussion

Effect of sewage treatment on mercury

Secondary treatment removed most of the THg and MeHg from urban sewage, with the notable exception of MeHg from the West End facility. On average,

88% of THg and 90% of MeHg was removed by treatment. Our results for THg agree with previously published studies. Mean removal of THg from Wisconsin and Minnesota facilities ranged from 84–99% (Glass et al. 1990; Mugan 1996). Mean removal from the (east) Metropolitan Wastewater Treatment Plant (St. Paul, Minnesota) was 97% (Balogh & Liang 1995; Balogh, unpubl. data). Also, high proportions of MeHg removal by treatment is consistent with studies at the St. Paul facility, where about 85% of the MeHg appeared to be removed by treatment (Balogh, unpubl. data).

Most of the THg is probably bound to solids which are removed in the treatment process. A mean reduction in THg concentrations of 59.8 ng/L and a mean reduction of 203 mg/L in suspended solids was observed at the North End WPCC. Dewatered sludge had an average THg concentration of 298 ng/g, which corresponds to 60.5 ng of THg per litre, a value that is very similar to the observed THg removal noted above.

Concentrations of THg in untreated sewage determined in this study were lower than found for other North American sewage treatment facilities. THg in inflowing sewage at the St. Paul facility ranged from 87–630 ng/L and averaged 287 ng/L (Balogh & Liang 1995; Balogh, unpublished data). Mean THg concentrations in raw sewage in other facilities in Wisconsin and Minnesota ranged from 125–820 ng/L and individual measurements ranged from extremes of 20 to 3,000 ng/L (Glass et al. 1990; Mugan 1996).

Mercury concentrations found in this study for treated effluent were very similar to those for the St. Paul plant. Treated effluent from the (east) St. Paul plant ranged from 3.2–14.6 ng/L THg and averaged 6.5 ng/L and from the (west) St. Paul plant (which receives high mercury scrubber water from incinerators) ranged from 4.2–25.4 ng/L and averaged 12.5 ng/L (Balogh, unpublished data). MeHg in untreated sewage at the St. Paul wastewater treatment plant was 1.6–2.2 ng/L and in treated sewage was 0.23–0.47 ng/L (Balogh, unpubl. data).

Concentrations of mercury in the rivers and effects of discharged effluent

THg in the Red and Assiniboine rivers ranged from 3–32 ng/L and was similar to previously reported THg concentrations in rivers. THg (filtrable plus particulate) in 11 tributary rivers of Lake Michigan ranged from about 1 to 39 ng/L (Hurley et al. 1996). Many of these watersheds are highly urbanized and industrialized. Balogh et al. (1997) found 1 to 35 ng/L THg in the Minnesota River. Gill & Bruland (1990) found concentrations of 2–12 ng/L in west coast United States rivers (excluding David Creek sites downstream of the mine), whereas Babiarz & Andren (1995) found from $<$1–9 ng/L THg in Wisconsin rivers. THg concentrations in oxic, unpolluted lake waters are usually less than those observed in the Red and Assiniboine rivers. For example, THg

in lakes at the Experimental Lakes Area, northwestern Ontario were usually less than 3 ng/L (St. Louis et al. 1996). Watras et al. (1994) found 0.7–2.1 ng/L THg in the epilimnion of seven Wisconsin lakes. Total aqueous mercury in remote Adirondack lakes was usually 1–4 ng/L (Driscoll et al. 1995). The Red and Assiniboine rivers had THg concentrations which were more similar to lakes ($<$8 ng/L) when suspended sediment concentrations were low ($<$150 mg/L).

THg concentrations in the Red River were related to suspended sediment concentrations, which ranged up to almost 400 mg/L. This implies that a significant proportion of the THg was associated with suspended sediments. In Wisconsin rivers, Babiarz & Andren (1995) found a weak relationship with total suspended particulates, which ranged from about 3–32 mg/L. Balogh et al. (1997) found a strong correlation and confirmed the association of THg with suspended sediments by filtration experiments. The concentration of MeHg in the rivers ranged from 0.16–0.41 ng/L. MeHg concentrations are generally less than about 0.3 ng/L in natural lakes in temperate and northern regions (Bodaly et al. 1997; St. Louis et al. 1996; Watras et al. 1994; Driscoll et al. 1995). The lack of relationships between suspended sediments and MeHg indicates that fluxes of MeHg in these rivers are controlled by different factors than those controlling fluxes of THg.

The discharge of treated effluent usually resulted in only small changes in THg and MeHg concentrations in the receiving rivers, although up to 11% increases in MeHg concentrations in the Assiniboine River were caused by the discharge of treated effluents of up to 2 ng/L from the West End WPCC. These high concentrations of MeHg from the West End WPCC in 1994 may have been related to the fact that the facility had just begun operations in this year. Start-up problems were experienced, including the growth of filamentous algae in secondary clarifiers. Also, this facility is the only Winnipeg plant to utilize outside sewage lagoons and these lagoons, especially if anoxic, could be the sites of significant mercury methylation.

Combined sewer overflows (CSOs) discharge a mixture of raw sewage and storm sewer water directly into the receiving rivers. Therefore, the benefit of secondary treatment on concentrations of THg and MeHg in sewage is lessened during CSO events. Although we did not measure mercury in CSO effluents, the combined effect of treated effluent and CSO effluent on river mercury concentrations would be expected to be greater than calculated for treated effluents alone. Quantitative data on CSO's could be used to calculate the total influence of treated and untreated effluents on the receiving rivers. Also, the high organic content of CSOs may have the additional effect of increasing rates of mercury methylation in the rivers.

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