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Historical variations in the stable isotope composition of mercury in a sediment core from a riverine lake: Effects of dams, pulp and paper mill wastes, and mercury from a chlor-alkali plant

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A B S T R A C T

The Wabigoon River (Ontario, Canada) was affected by dams starting in 1898 and was polluted with pulp and paper mill wastes starting in 1913 and mercury from a chlor-alkali plant from 1962 to 1975. A dated sediment core from a riverine lake was analysed to investigate resultant changes in the biogeochemistry of mercury as revealed by variations in mercury isotope ratios and sediment chemistry. A total mercury maximum formed by the mercury pollution coincided with minimums in the δ-values of the $^{198}Hg/^{202}Hg$, $^{199}Hg/^{202}Hg$, $^{200}Hg/^{202}Hg$, and $^{201}Hg/^{202}Hg$ ratios, and the δ-values decreased in the order $\delta^{201}Hg > \delta^{200}Hg > \delta^{199}Hg > \delta^{198}Hg$. Thus, mass-dependent fractionation caused depletion in lighter isotopes, implying evaporation of Hg(0) and pollution of the atmosphere as well as the river-lake system. Concurrently, mass-independent fractionation caused ^{199}Hg *enrichment*, possibly reflecting an independently documented upsurge in methylmercury production, and ^{201}Hg *depletion*, suggesting removal of methylmercury with anomalously high $^{201}Hg/^{199}Hg$ ratios by aquatic organisms and accumulation of ^{201}Hg-depleted inorganic Hg(II) in sediments. The $\delta^{201}Hg/\delta^{199}Hg$ ratio rose abruptly when mercury pollution began, reflecting the resultant increase in methylmercury production, and remained high but gradually declined as the pollution abated, paralleling trends shown by methylmercury in aquatic organisms. The $\delta^{201}Hg/\delta^{199}Hg$ ratio of pre-1962 background mercury increased ca. 1898 and ca. 1913–1929, suggesting accelerated methylmercury production due to stimulation of microbial activities by the damming of the river and the input of pulp and paper mill wastes, respectively. Other variations were linked to economic and technological factors that affected pulp and paper manufacture.

1. Introduction

The stable isotope composition of mercury (Hg) in natural environments shows significant spatial and temporal variations. Some Hg isotope signatures are traceable to particular nearby sources of Hg contamination and may be ascribed to isotope fractionation at the points of origin, but fractionation by a wide range of biotic and abiotic processes in the environment alters the original isotope signatures and may obliterate them, especially during long-range atmospheric transport of Hg. Further complexity arises from the fact that Hg isotopes are subject to both mass-dependent fractionation (MDF) and mass-independent fractionation (MIF). MIF usually affects the isotopes of odd mass number (^{199}Hg and ^{201}Hg), causing anomalous enrichment in some products of isotope-fractionating processes and depletion in others relative to the abundances that would be expected if Hg isotope fractionation were due solely to MDF. The literature on Hg isotopes in the environment and mechanisms of isotope fractionation has been reviewed elsewhere (Jackson, 2015a; Bessinger, 2014; Blum et al., 2014; Jackson et al., 2013; Jackson and Muir, 2012) and will not, therefore, be surveyed again here. Suffice it to say that variations in the isotope composition of Hg may provide important information about the sources and biogeochemical cycling of Hg. Hg isotope signatures seem to be of limited value for source identification, but they are rich repositories of information on biogeochemical and ecological phenomena, including effects of climatic variation, toxic pollutants, and other environmental factors on microbial communities in lakes (Jackson, 2013, 2015a; Jackson and Muir, 2012; Jackson et al., 2004, 2006, 2008, 2013, 2015a).

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This paper reports the results of research on historical variations in the isotope composition of Hg as recorded in a dated sediment core from a riverine lake which has been seriously affected by damming upstream from its inflow and by pulp and paper mill wastes and Hg from a chlor-alkali plant. The purpose of the research was to characterise and interpret the isotope signature of the Hg from the chlor-alkali plant and to trace temporal variations in the effects of specific industrial operations on the biogeochemistry of Hg — in particular, microbial production of the highly toxic, preferentially bioaccumulated compound methylmercury (CH_3Hg^+) — as revealed by changes in Hg isotope ratios. Chemical and biological data together with historical records of local industrial activities aided in the interpretation of the isotope data.

2. Field area, materials, and methods

2.1. The field area and the history of its degradation by human activities

2.1.1. General features of the field area

The Wabigoon River of northern Ontario (Canada) spills out of Wabigoon Lake, flows northwestward past the city of Dryden, is joined by a tributary called the Eagle River, and empties into Clay Lake at the east end of the lake, ~70 km downstream from Dryden (Fig. 1). Emerging from the west end of the lake, the river continues its northwestward course until it meets Ball Lake, thereby joining the English River, which eventually merges with the Winnipeg River, which, in turn, flows into Lake Winnipeg, Manitoba (Armstrong and Hamilton, 1973). For the most part, the rivers flow through sparsely populated country characterised by boreal forest, low relief, and Precambrian granitic rock and greenstone belts overlain by patches of Pleistocene glacio-lacustrine clay and sandy till (Jackson et al., 1980b; Parks et al., 1980).

2.1.2. The damming of the Wabigoon River and Eagle River

A timber dam was constructed across the Wabigoon River at Dryden in 1898 but was replaced by a concrete dam in 1912 (Johnston, 2014; Johnston, G., personal communication). In 1923 another dam was built between Dryden and Clay Lake, creating a small impoundment called the Wainwright Reservoir (Fig. 1), and the Eagle River (Fig. 1) was dammed at two localities in 1928 and 1938, respectively (Johnston, G., personal communication). Presumably these control structures reduced considerably the flow rate and discharge of the Wabigoon River, especially during the summer slack water season.

2.1.3. The discharge of pollutants from the pulp and paper mill

The history of the pulp and paper mill at Dryden has been detailed elsewhere (Johnston, 2014), but relevant features of it will be outlined here. In 1913 the mill began its operations, which employed the Kraft process. From 1918 to 1922 the mill prospered and expanded its activities, but, owing to subsequent financial

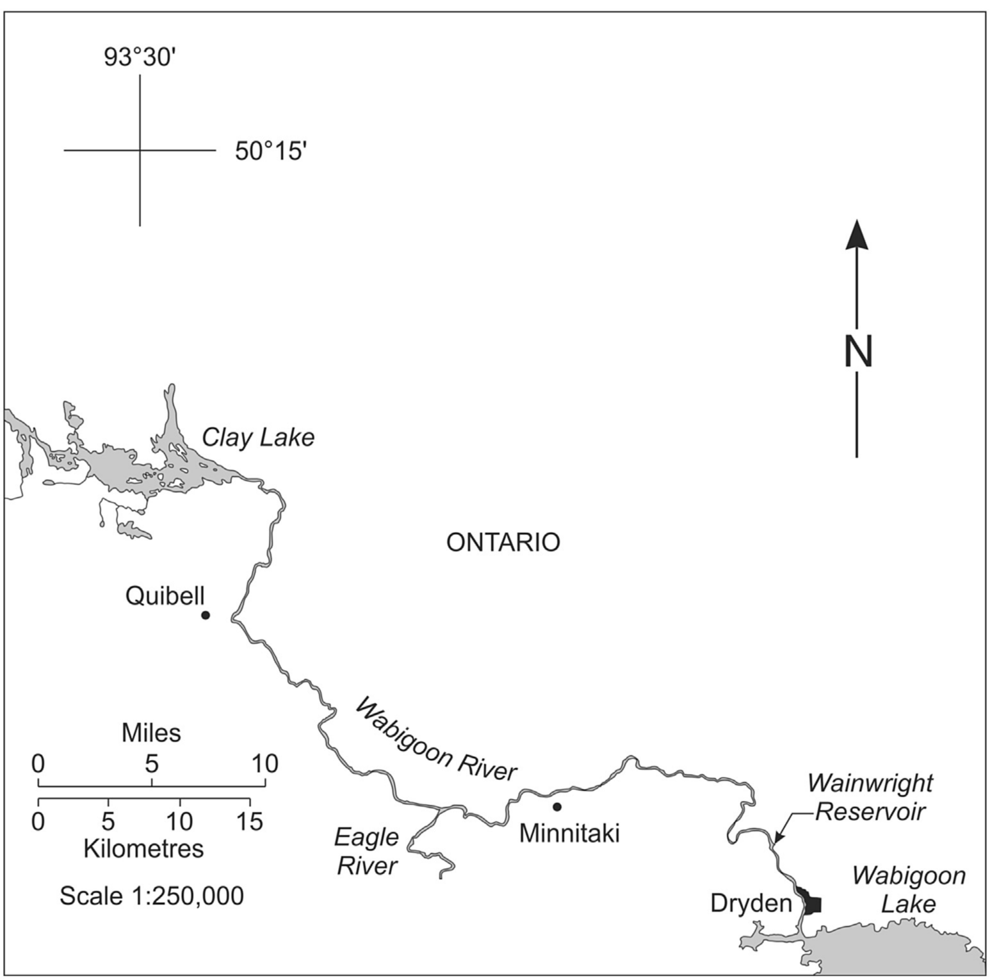

Fig. 1. Map of the field area.