Journal of Great Lakes Research 37 (2011) 124–131

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Metals in Lake Simcoe sediments and tributaries: Do recent trends indicate changing sources?

Amanda L. Landre [a,*], Jennifer G. Winter [a,1], Paul Helm [b,2], Veronique Hiriart-Baer [c,3], Joelle Young [a,4]

[a] *Sport Fish and Biomonitoring Unit, Water Monitoring and Reporting Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, ON M9P 3V6, Canada*
[b] *Great Lakes Unit, Water Monitoring and Reporting Section, Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment, Toronto, ON M9P 3V6, Canada*
[c] *Aquatic Ecosystem Management Research Division, Water Science and Technology Directorate, Science and Technology Branch, National Water Research Institute Environment Canada, 867 Lakeshore Road, Burlington, ON L7R 4A6, Canada*

ARTICLE INFO

Article history:
Received 12 September 2009
Accepted 24 August 2010
Available online 12 February 2011

Communicated by Stephanie Guildford

Index words:
Lake Simcoe
Metal
Sediment
Enrichment
Point source
Diffuse pollution

ABSTRACT

Metals released to the environment from various natural and anthropogenic sources accumulate in lake sediments, providing a record of metal emissions over time. Metal concentrations (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Rb, Sb, Sr, V, Zn) in sediments were measured across Lake Simcoe, replicating a study conducted 25 years earlier. The highest metal concentrations were found in sediment cores from Kempenfelt Bay where concentrations peaked in the 1950s through to the 1970s. Metal concentrations generally decreased from peak levels, except for Cu and Zn whose concentrations have since returned to peak levels. In recent years, concentrations of As, Cd, Cr, Cu, Pb, Sb, and Zn were still more than double their early industrial (pre-1900s) concentrations. Across the lake, concentrations of metals in the surface sediments were generally highest in Kempenfelt Bay and the main basin, and decreased with distance away from shore and towards the lake outlet. Metal concentrations in several tributaries in the watershed were highest at locations downstream from urban areas. The temporal and spatial trends in sediment metal concentrations are consistent with a shift from point source metal pollution to diffuse sources of metals including urban runoff and atmospheric pollution.

Introduction

The Lake Simcoe watershed has changed considerably over the past two centuries as land was cleared for agriculture, towns, roads and industries. The resulting negative impacts to lake water quality were first observed over 30 years ago, with deep water oxygen depletion caused by eutrophication leading to the recruitment failure of coldwater fish (Evans et al., 1995; LSEMS, 1985). Excess nutrients continue to impair the lake ecosystem and additional pollutants such as metals also cause concern. Elevated concentrations of metals including Cd, Cr, Cu, Hg, Ni, Pb and Zn have been found in Lake Simcoe sediments (Johnson and Nicholls, 1989; MOE, 1978). Metal pollution is an issue because metals are ubiquitous and persistent, and because certain metals may produce negative biological effects such as chronic toxicity and bioaccumulation (Adams and Chapman, 2007).

During the 1800s, towns were settled and early industries including mills and tanneries were established in the Lake Simcoe watershed (Magel, 1998). Land was cleared for agriculture and forestry, and peak soil erosion occurred in the 1880s (Johnson and Nicholls, 1989). Towards the 1900s, additional industries including foundries, machinery fabrication, wood processing, and printing and publishing works were founded (Bloomfield and Bloomfield, 1992). In the 1920s and 30s, wetlands surrounding the lower Holland River were dyked and drained for agriculture, and canals were built to channel the river downstream. Manufacturing peaked in the 1960s, especially near the City of Barrie where numerous metal finishing industries and tanneries operated, but has since declined and shifted to commercial and residential development as the population in the watershed has grown.

Metals in the Lake Simcoe watershed come from agriculture, industry and urban development as well as from natural sources. Agricultural wastes and older pesticides and fertilizers contain metals, as do industrial wastes from metal finishing, tanneries, plastic fabrication, microelectronics, paints, textile production and metal scrap heaps (Adriano, 2001). Residential sewage and urban runoff also contains substantial amounts of metals (Bannerman et al., 1995; Marsalek and Ng, 1989; US EPA, 1983). Fossil fuel combustion, metal smelting and waste incineration are major sources of atmospheric

---

[*] Corresponding author. Tel.: +1 647 520 9121.
E-mail addresses: amandalandre@gmail.com (A.L. Landre), jennifer.winter@ontario.ca (J.G. Winter), paul.helm@ontario.ca (P. Helm), veronique.hiriart-baer@ec.gc.ca (V. Hiriart-Baer), joelle.young@ontario.ca (J. Young).
[1] Tel.: +1 416 327 3715.
[2] Tel.: +1 416 235 6131.
[3] Tel.: +1 905 336 6447.
[4] Tel.: +1 416 327 4864.

0380-1330/$ – see front matter © 2011 International Association for Great Lakes Research. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jglr.2010.12.012

metal pollution (Nriagu and Pacyna, 1988), which may be transported to the watershed from sources hundreds of kilometers away (Steinnes and Friedland, 2006).

Metal behavior is dependent on individual characteristics including solubility, redox properties and binding affinities. Metals such as Pb and Cu have stronger affinities for binding sites on mineral and organic matter, and tend to be retained within soils or transported via particulates to stream and lake sediments more effectively than metals with lower affinities such as Ba and Sr (Stumm and Morgan, 1996; Tipping, 1998). Not all of the metals released within or deposited on the terrestrial watershed reach the lake: a portion is retained within soils, stream sediments and sewage sludges. However, impervious surfaces have very limited retention and atmospheric deposition also delivers metals directly to the lake.

Lake sediment cores are frequently used to provide a historical record of metal pollution (e.g. Couillard et al., 2008; Davis et al., 1983; Galloway and Likens, 1979; Renberg, 1986). Metals are assumed to be relatively immobile in sediments except for Mn and Fe, which are soluble and mobile under reducing conditions; As and Co are closely associated with Fe and Mn oxides and hydroxides and may also exhibit a degree of mobility in the sediments (Belzile et al., 2004; Carignan and Nriagu, 1985). Because Lake Simcoe is a large lake surrounded by a range of land uses, spatial trends in metal pollution can also be identified. Sedimentation processes remove metals from the water column relatively efficiently, so sediment concentrations should reflect inputs within a particular bay or basin (Salomons and Förstner, 1980).

Several decades ago, growing concern about the impacts of metal pollution in Lake Simcoe prompted a set of investigations. A survey of Hg concentrations in Lake Simcoe sediment cores conducted in 1977 revealed significant Hg contamination at locations closest to the urban areas of Barrie and Orillia (MOE, 1978). Five years later, a survey of metal concentrations in sediment cores showed Cd, Cr, Cu, Ni, Pb and Zn were substantially enriched compared to background levels, especially in Kempenfelt Bay (Johnson and Nicholls, 1988). In the 20 years since these studies took place, many changes have occurred across the Lake Simcoe watershed. Considerable urbanization has taken place, industries have shifted, and environmental controls have improved, but the effects of these changes on lake sediment quality with respect to metals were unknown. Therefore, we measured sediment concentrations of 17 metals (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Rb, Sb, Sr, V and Zn) at the same sites as the previous Johnson and Nicholls survey in order to:

1. investigate recent temporal trends in metal concentrations in contrast to historical concentrations;
2. evaluate the spatial patterns in recent sediment metal concentrations in relation to potential source contributions; and,
3. assess the extent that land use and other changes in the watershed have affected metal concentrations in the lake sediments.

Site description

Lake Simcoe is the largest inland lake in Southern Ontario, with a surface area of 722 km^2. The lake is dimictic, has a maximum and mean depth of 42 and 14 m respectively, and has a flushing time of approximately 11 years (based on the annual water balance from 2004 to 2007). Lake Simcoe is a hard water marl lake (mean Ca concentration 41 mg/L, mean alkalinity 116 mg/L, mean SO_4 20 mg/L) due to the limestone bedrock underlying the watershed, and whitings from $CaCO_3$ precipitation occur on occasion. Clays and organic soils are the prevalent soil types in the watershed, which covers 2899 km^2.

The population of the Lake Simcoe watershed is approximately 400,000 permanent residents (Statistics Canada, 2006) with an additional 50,000 cottagers during the summer months. Lake Simcoe receives heavy recreational use: the lake supports a year-round sport fish industry that provides over 1 million angler hours per year, and boating is especially popular since the lake forms part of the Trent–Severn waterway. Land use within the basin is primarily agricultural (47% of total area), although urban development is increasing to support some of the fastest growing municipalities in Canada, including Barrie, Newmarket and Aurora. The lake currently assimilates wastewater from 15 water pollution control plants in the watershed, although sewage from Newmarket and Aurora was diverted away from Lake Simcoe in 1984.

Methods

Sample collection

Surface sediment samples were collected in September 2008 at the same 22 locations across Lake Simcoe as the 1983 survey (Fig. 1; Johnson and Nicholls, 1988). Sonar and bulk density measurements revealed that the post-glacial and pre-industrial sedimentation rates were virtually the same, which suggests that the transects were situated in stable deposition areas. Water overlying the sediments was drained using tygon tubing, and surface sediment samples were collected using a 40 cm by 40 cm box core sampler. Macrophytes and debris were carefully removed from the samples and the top 2 cm of sediment, excluding the edges in contact with the corer, were collected using a spatula, homogenized on a glass plate and transferred to a polyethylene bottle for subsequent analysis. Sediment cores were also collected at 4 of the sampling locations: sites 3 (13.5 m depth), 6 (38.6 m depth), 13 (14.4 m depth) and 19 (26.5 m depth). At these 4 sites, the 35 cm core tubes were inserted into the box core sampler before and removed after surface sediment collection to minimize contamination and disturbance of sediments in the core. The cores were extruded taking care to minimize the effects of smearing and sliced in 1 cm intervals to 15 cm, and then 2 cm intervals to a maximum of 35 cm. The 3 slices of the same depth interval were combined in a glass jar and homogenized. The integrity of the core samples was good and there was no clear evidence of bioturbation.

Routine water samples were collected from 12 tributaries in the Lake Simcoe basin through the Provincial Water Quality Monitoring Network (PWQMN) sampling program. Sampling dates back to 1965 for some locations, but sample analysis for the full suite of metals started in October 2002. Samples are collected 8 times each year during the ice-free season (March–November). Tributary samples were collected in plastic bottles and acidified to pH 2 with trace metal grade HNO_3. The laboratory conducted tests to confirm that levels of contamination from the sample bottles and the acid preservative were below quantification levels.

Chemical analysis

The surface sediment samples were prepared and analyzed by MOE Laboratory Services. Samples were air dried, ground, homogenized and then digested with 3:1 HCl to HNO_3 ratio in a hot block for 6.5 h.

Surface sediment digests and the unfiltered, acidified tributary water samples were analyzed for metals (Al, Ba, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Sr, V, Zn) using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Digestion recoveries were measured using the certified reference standard NIST 2709; each of the reported certified metals typically had sediment digestion recoveries within +/−11%, except for V which was +31%, suggesting a possible optical interference at the measured wavelength. However, digestion recoveries for the LGC 6137 certified reference material were +/−12% for each of the reported certified metals, including V; therefore, the surface sediment results for V were considered acceptable for the purposes of this paper. The analysis of metals in water had a long-term precision of +/−10% or better as measured against an in-house composite standard.