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Changes in the long-term supply of mercury species to the upper mixed waters of a recovering lake

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We quantified internal processes that supply methylmercury from hypolimnetic reducing zones to the upper waters of a Hg-contaminated lake, Onondaga Lake, NY, USA. Diffusive transport continuously supplied methylmercury to the epilimnion under summer stratification, while fall mixing resulted in a pulsed release of methylmercury to the upper mixed waters. These processes were the main internal sources of methylmercury to the epilimnion, and together almost equaled the total external supply. The wind-driven entrainment represented an additional stochastic internal supply of methylmercury of approximately 9% in 2006. Considering more than 15 years of data, we estimate 1.8 wind-driven events occur per year. The mass of methylmercury inputs to the epilimnion exceeded the measured increase, suggesting that loss processes are important in regulating methylmercury accumulation. The relative contribution of internal sources of methylmercury to the epilimnion has decreased in recent years, shifting the importance to the external inputs.

1. Introduction

Lake ecosystems occupy a critical position for the cycling and trophic transfer of mercury (Hg). Lakes are not only sinks of total Hg (THg) inputs from atmospheric deposition and adjoining watersheds (Rudd, 1995; Selvendiran et al., 2009), but can also be sources of organic Hg to the freshwater food web (Rudd, 1995; Rolfhus et al., 2011). The fate of the Hg introduced to lakes depends on the magnitude of Hg sources (Orihel et al., 2007; Evers et al., 2007), the watershed and lake characteristics (Kamman et al., 2004; Wiener et al., 2006; Hayer et al., 2011), and the structure of the food web (Hogan et al., 2007; Eagles-Smith et al., 2008).

In temperate freshwater lakes, stable summer stratification is often associated with depletion of dissolved oxygen (DO) in the hypolimnion and enhanced net methylation of ionic Hg (Hg(II)). The hypolimnion can become enriched in methylmercury (CH_3Hg^+) from production within the water column or sediments that exceeds loss processes (Sellers et al., 2001; Todorova et al., 2009). In contrast, epilimnia remain completely mixed during the open water period and continuously replenish DO in the upper strata (Wetzel, 2001). High concentrations of CH_3Hg^+ are not sustained in epilimnion due to demethylation and photoreduction (Sellers et al., 1996; Zhang and Kim, 2010) that exceed lower production and inputs of CH_3Hg^+.

The dynamics of Hg in upper waters of lakes has been linked to both transport and biogeochemical processes. Binding of Hg with dissolved and particulate organic material increases Hg mobilization in natural and urban streams (Dittman et al., 2010; Eckley and Branfireun, 2008; Schuster et al., 2008), especially during storm events (Bushey et al., 2008). Tributary load can also be an important source of Hg species to upper waters (Muresan et al., 2008; Selvendiran et al., 2009). Besides the external drivers, internal production in the littoral sediments (Krabbenhoft et al., 1998; Guevara et al., 2009) and transport of CH_3Hg^+ from the hypolimnion (Herrin et al., 1998; Peretyazhko et al., 2005) contribute to the epilimnetic CH_3Hg^+ pool.

We investigated Hg dynamics in the epilimnion of Onondaga Lake, NY. Onondaga Lake watershed and sediments were contaminated with Hg from two chlor-alkali plants that operated in the area for more than 40 years (Effler, 1996). A mass balance study

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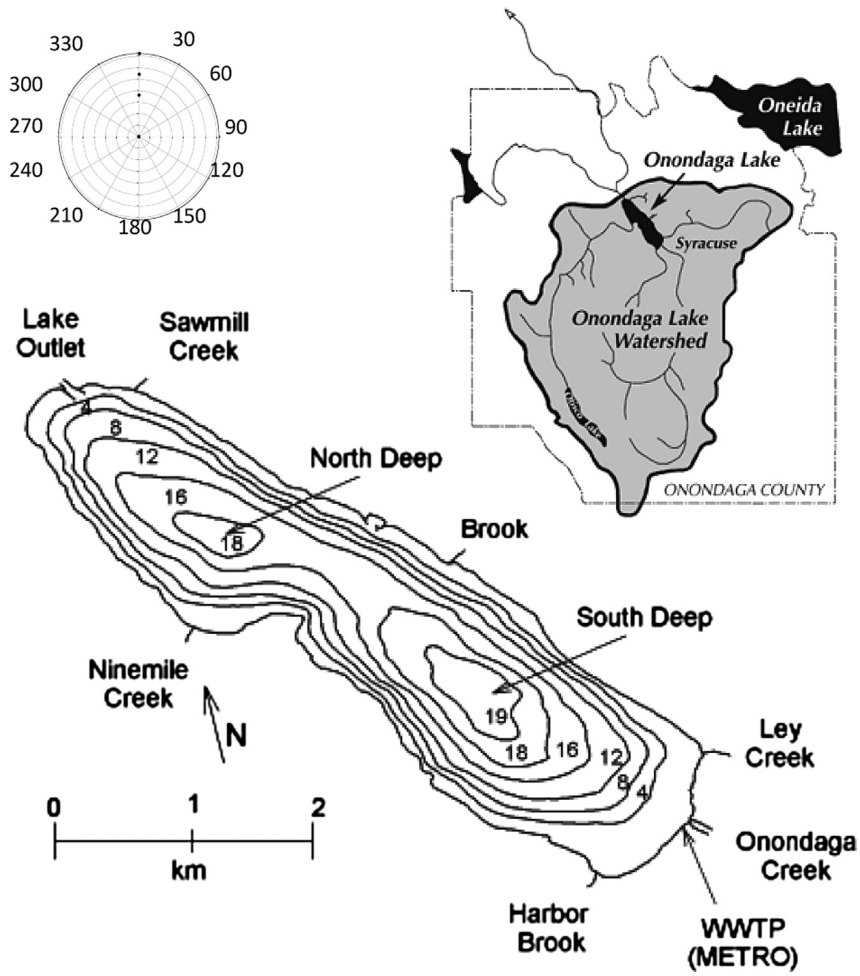

Fig. 1. Onondaga Lake, NY, USA (43° 06′ 54″N; 76° 14′ 34″W) with its watershed area (642 km^2). Arrows show the North deep and South deep basins, and the wastewater treatment plant (WWTP). Polar plot designates the orientation of the lake according to standard degree measurements. North is designated as 0°/360°. The longitudinal axis of the lake lies along 120–150° and 300–330°.

developed after the cessation of the industrial operations suggested that external sources contribute a substantial portion of the ionic Hg inputs to the lake (Henry et al., 1995). Recently, Owens et al. (2009) documented that the industrial waste, deposited on the southwestern side of the lake, continues to be a source of ionic Hg as well. Accumulation of CH_3Hg^+ is accelerated in the anaerobic hypolimnion during summer months and reaches concentrations up to 15 ng L^{-1} in the bottom layers (Todorova et al., 2009). Recent improvements in the water quality of the lake prompted substantial decreases in the length of anaerobic period, coupled with the decreases in the maximum concentrations of CH_3Hg^+ (Todorova et al., 2009; Matthews et al., 2013). However, detailed study on the effect of these changes on the epilimnetic CH_3Hg^+ concentrations and the quantification of the internal inputs of CH_3Hg^+ in Onondaga Lake has not been undertaken.

In this paper we report a multi-year dataset of THg and CH_3Hg^+ concentrations for the upper mixed waters of Onondaga Lake. We document internal drivers leading to changes in the accumulation of CH_3Hg^+ in the epilimnion, including pulse inputs from storm events, physical mixing, and diffusive transport. We consider different scales of mixing as sources of Hg to the epilimnion of the lake and differentiate among diffusive transport between epilimnion and hypolimnion, wind-driven entrainment of hypolimnetic layers, and seasonal entrainment of the hypolimnetic layers with the approach to the fall turnover. The mixing-based supplies of CH_3Hg^+ are considered in the context of the existing information on external CH_3Hg^+ sources to the lake epilimnion.

2. Materials and methods

2.1. Study system

Onondaga Lake is a seasonally stratified, eutrophic lake with a surface area of 11.7 km^2, a volume of 131 × 10^6 m^2 and a maximum depth of about 20 m (Effler, 1996). The lake is located in metropolitan Syracuse, New York, United States (43° 06′ 54″N, 76° 14′ 34″W; Fig. 1). Onondaga Lake has two major natural tributaries, Ninemile Creek and Onondaga Creek, each contributing around 38% of the total surface inflow (Effler et al., 2009). A regional wastewater treatment plant (WWTP) (Fig. 1) contributes on average 20% of the total annual inflow.

The lake has received both treated and untreated industrial and domestic waste for more than a century (Effler, 1996). The WWTP has been responsible for the hypereutrophic status of the lake with historically elevated nitrogen (N) and phosphorus (P) inputs (Effler et al., 2009, 2010). In 2004, the WWTP was upgraded with a biological aerated filter for nitrification, which treated total ammonium waste. As a result, the NO_3^- load to the lake has almost doubled and is currently 85% of the total N load (Effler et al., 2010).