

## MERCURY CYCLING IN AND EMISSIONS FROM LONG ISLAND SOUND

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### ABSTRACT

Elemental mercury ( $\text{Hg}^0$ ) emissions from Long Island Sound (LIS; 85-90 kg yr<sup>-1</sup>) are principally of anthropogenic origin (>70%), and evasional Hg losses (35% of total LIS inputs) are a significant source of Hg to the coastal/regional atmosphere (e.g. CT, NY, NJ). LIS waters are generally supersaturated with  $\text{Hg}^0$  (72-1154%), and concentrations in surface waters (61-816 fM) vary both spatially and seasonally. Biotically mediated and photochemical reduction of reactant Hg (i.e., labile species) in seawater are the principal mechanisms for the *in situ* production of elemental Hg. This production reduces the availability of labile species for the biologically mediated production of toxic methylmercury (MMHg) in coastal waters. The control that  $\text{Hg}^0$  cycling exerts on MMHg bioaccumulation is also illustrated by the mass balance. External sources (~4 kg y<sup>-1</sup>) and *in situ* production (5-10 kg y<sup>-1</sup>) of MMHg in LIS account for only about 5% of the total inputs and 10-15% of the evasional mass flux. These results provide valuable data to aid in understanding the biogeochemical cycling of Hg and MMHg in nearshore regions and assessing impact from pollutant Hg inputs.

### INTRODUCTION

We are currently conducting a long-term study of Hg in our local waters, Long Island Sound (LIS). Environmental Hg studies have typically focused on terrestrial regions, especially aquatic ecosystems. In contrast, estuaries and adjacent coastal waters, which are major repositories for natural and pollutant riverborne/watershed derived Hg species, have received scant attention. There is a vital need to increase knowledge and understanding concerning the biogeochemical cycling of Hg, and the impact of anthropogenically related inputs, in biologically productive nearshore regions. Methylmercury is of particular concern because it is considerably more toxic to organisms than other forms of Hg, and the primary exposure of humans to MMHg is by consumption of marine fish and fish products.

Long Island Sound is a large urbanized coastal embayment, and among the world's most important commercial and recreational coastal resources. The atmospheric and aquatic biogeochemical Hg cycle associated with LIS and its environs is affected not only by localized discharges (e.g., rivers, waste water treatment facilities) and tidal exchange, but from the direct and indirect (via watershed leaching) airborne transport and deposition of Hg from regional and longer range sources. Inputs of significance to LIS are: the East River (western region) with its large sewage loadings, and the Connecticut River (eastern zone) which contributes about 70% of annual input of freshwater, and whose extensive watershed and potential for leaching of atmospherically derived Hg extends northward into Canada. The Sound provides an ideal coastal laboratory in which to examine important mercury species such as  $\text{Hg}^0$  and MMHg within the multi-media framework of a broader examination into natural and human-related sources, the processes and reactions controlling the aquatic biogeochemistry of Hg, and its amplification as the MMHg species in biota.

## METHODS

Elemental Hg measurements were made during a series of 3-4 day cruises on LIS with an automated gaseous elemental mercury analyzer (AGEMS) developed by our laboratory, and using traditional methods in the laboratory (Rolffhus & Fitzgerald, in review). Earlier Hg<sup>0</sup> measurements, as well as measurement of other Hg species, were made between 1995 and 1997. Atmospheric Hg inputs to LIS were assessed by total Hg determinations in bulk deposition samplers sited at 4 locations on the north shore of the Sound over an 18 month period. Total, reactive and MMHg concentrations were determined in samples from 4 target rivers, at sites above the salt intrusion. The Connecticut River was more extensively sampled over 14 months during representative flow regimes. Additionally, Hg species determinations were made in effluent from 7 water treatment facilities in Connecticut, as well as at multiple locations in the waters of LIS over a period of 26 months (Vandal et al., in prep.).

## RESULTS AND DISCUSSION

Our research has yielded useful first-order biogeochemical mass balances (i.e., sources and sinks) for total and MMHg in LIS. The estimated current annual Hg loadings to LIS are approximately 230 kg, of which about 75% (180 kg) is of pollutant origin. The principal sources of Hg to the Sound are wastewater treatment facilities, (WTFs, ~85 kg y<sup>-1</sup>; 38%), rivers (~120 kg y<sup>-1</sup>; 52%), and direct atmospheric deposition (~26 kg y<sup>-1</sup>; 10%) (Vandal et al., in prep.; Fitzgerald et al., in press) (Figure 1). More than 85% of WTF flux (i.e., ~74 kg y<sup>-1</sup>) is estimated to be from NY sewage facilities discharging into the East River and consequently into the western Sound. Riverine fluxes at ~120 kg y<sup>-1</sup> are the major Hg source to LIS. The Connecticut River contributes about 70% of this input (~84 kg y<sup>-1</sup>). Direct wet atmospheric Hg deposition is a relatively small input to the Sound. However, deposition of Hg to the watershed and subsequent leaching is an important contributor to the Hg loadings via rivers. We suggest that the estimated Hg flux from the Connecticut River could be due entirely to its watershed if 25% of the atmospheric Hg loadings runs off.

Although the mass balance needs constraints, the principal external sources (~4 kg y<sup>-1</sup>) of MMHg to the Sound are WTFs (~1.4 kg y<sup>-1</sup>; 35%), rivers (~1.6 kg y<sup>-1</sup>; 40%), and direct atmospheric deposition at about ~0.7 kg y<sup>-1</sup> (18%) (Vandal et al., in prep.; Figure 2). Our marsh and near shore studies suggest that the major source of MMHg in LIS is internal production. Studies of net Hg methylation in two Connecticut salt marshes point to nearshore sedimentary regimes as regions of significant production (Langer et al., in press). We hypothesize that as much as 6 to 18 kg y<sup>-1</sup> of MMHg are formed through the microbial conversion of reactive mercury (Hg<sup>R</sup>) species into MMHg in shallow sedimentary regions of LIS. Net *in situ* microbially mediated MMHg production may be two to five times greater than the fluxes from rivers, sewage, and the atmosphere. The principal source of this toxic species in marine aquatic systems is *in situ* biologically-mediated conversion of Hg<sup>R</sup>. Sulfate reducing bacteria (SRB) have been implicated as the primary synthesizers. The aqueous production of Hg<sup>0</sup> competes for reactant (i.e., ionic Hg or Hg<sup>R</sup>) with the *in situ* biological synthesis of MMHg, such that water bodies with a large production of Hg<sup>R</sup> may have smaller amounts of MMHg in biota and accumulation in the sediment.

Elemental Hg is nearly always found to be supersaturated (72-1154%) in LIS (Figure 3), indicating reduction of ionic Hg (reactant). General trends include higher supersaturation during warmer months and in the middle of the Sound near the mouth of the Connecticut River (Rolffhus & Fitzgerald, in review). Supersaturation of Hg<sup>0</sup> suggests Hg is lost from the Sound to the atmosphere via evasion. Wanninkhof (1992) is currently our gas exchange “model of choice” based on its wide acceptance and successful application to other gases. Evasional flux estimates (122-822 pmol m<sup>-2</sup> d<sup>-1</sup>) for each of the

Hg<sup>0</sup> surveys in LIS waters are summarized in Figure 4. General trends include increased Hg<sup>0</sup> flux at increased Hg<sup>0</sup> concentrations during warmer months and in the central Sound, as well as at higher wind velocities. Averaged over the year for LIS, the calculated reduction rate required to maintain steady state (ave. total Hg is 6pM) and to balance evasion is 0.4% per day (Rolfhus, 1998). Laboratory measured reduction rates of 0.5 to 3% d<sup>-1</sup> for both biotic and abiotic reduction processes are more than sufficient to sustain the estimates for evasional fluxes of Hg<sup>0</sup> from LIS.

One of the most striking findings from our work is the presence of significantly large emissions of Hg<sup>0</sup> from the waters of LIS to the local/regional atmosphere. While the importance of Hg<sup>0</sup> cycling in natural waters is well known, its significance in coastal waters is just being revealed. The estimates for seasonal Hg<sup>0</sup> fluxes average 363 pmol m<sup>-2</sup> d<sup>-1</sup> which correspond to an annual Hg<sup>0</sup> emission from LIS of approximately 85-90 kg. The scale and importance of water to air Hg<sup>0</sup> volatilization is evident. For example, Hg<sup>0</sup> emissions from LIS surface waters are considerably larger than direct wet atmospheric Hg deposition as estimated from our four coastal atmospheric sampling stations (Figure 1). This production/emission cycle is remobilizing amounts of Hg comparable to the river input or our values for annual Hg fluxes from the wastewater treatment facilities (WTFs). Indeed, as much as 35% of the Hg input to LIS is transformed (reduced biotically and abiotically) and re-emitted to the atmosphere. Since most Hg entering LIS has an anthropogenic origin, a substantial pollution component is being recycled.

These findings from our LIS investigations indicate that source/receptor models for atmospheric Hg cycling, especially when applied to coastal states, must consider Hg<sup>0</sup> emissions from coastal embayments and the continental shelf. For example, if the emissions of Hg<sup>0</sup> in other coastal settings were comparable to LIS (27 g km<sup>-2</sup> y<sup>-1</sup>), then the efflux from shelf regions of the eastern U.S. (assuming a coast length of 2400 km, and shelf width of 200 km) might approach 13 Mg y<sup>-1</sup> (13 tons). This potential mobilization of Hg is extraordinarily large, and environmentally significant. Globally, the shallow coastal margins of the oceans total about 36 x 10<sup>6</sup> km<sup>2</sup>. As an upper limit, these marine regions could yield an annual water-air flux of Hg of about 1000 tons (5 Mmole), if Hg cycled in a manner similar to LIS.

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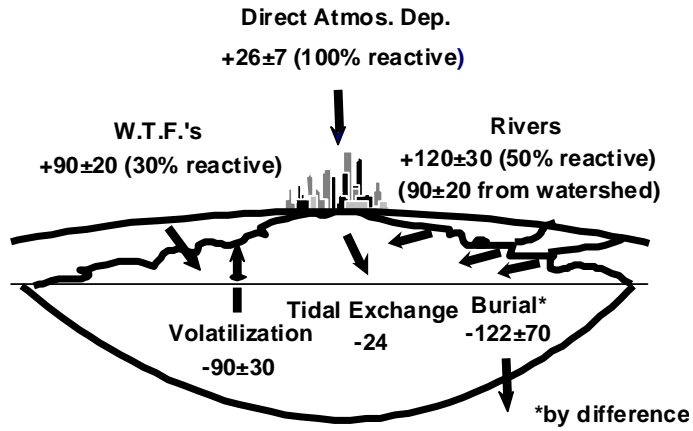


Figure 1. Total Hg Budget for LIS (kg/y)

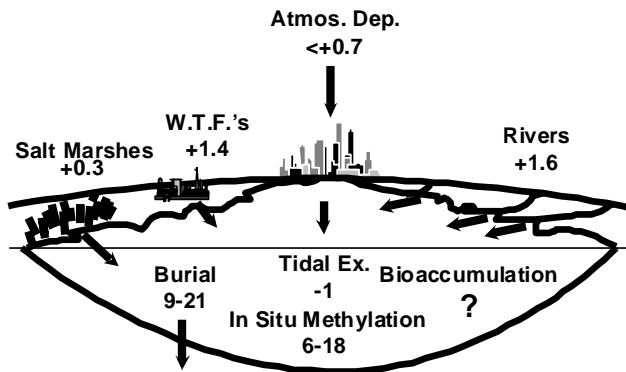


Figure 2. Methylmercury Budget for LIS (kg/y)

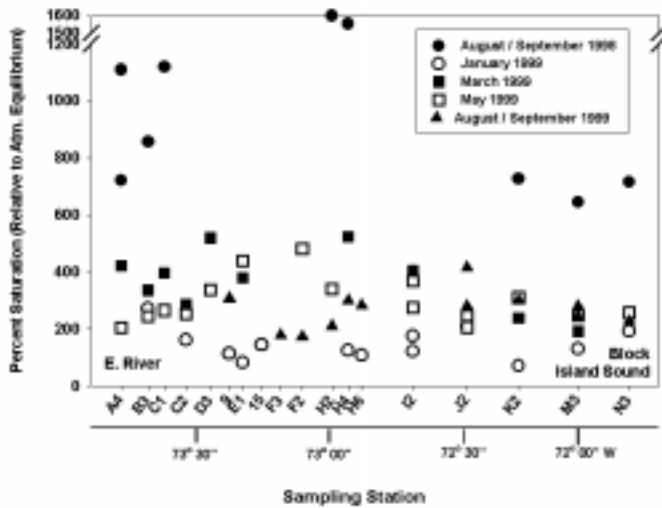


Figure 3. Elemental Hg Saturations in LIS

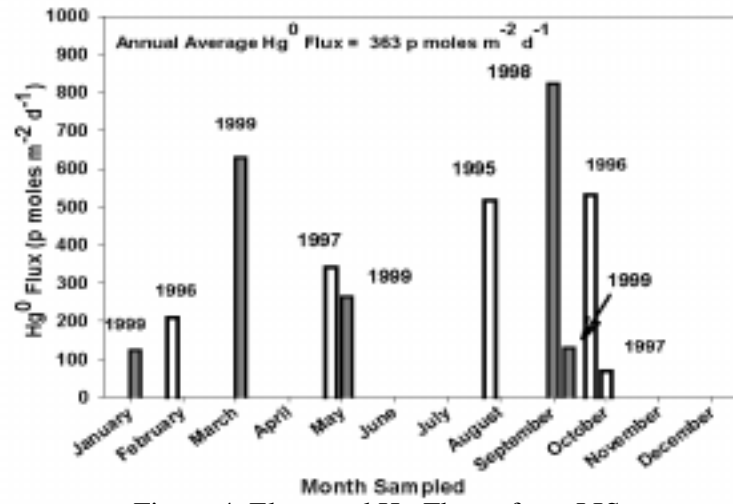


Figure 4. Elemental Hg Fluxes from LIS