



Atmospheric mercury depletion events at the Dead Sea: Spatial and temporal aspects



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HIGHLIGHTS

- ▶ AMDEs were strong in both seasons and some occurred regionally at the Dead Sea.
- ▶ Some AMDEs occurred without subsequent ozone depletion, despite halogen controls.
- ▶ Total-Hg and methyl-Hg were not enhanced despite high occurrence of AMDEs.
- ▶ Tekran 2537 measures Hg(0) only.
- ▶ Tekran speciation unit has higher blanks under higher Hg(II) concentrations.

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ABSTRACT

Atmospheric cycling over the saline Dead Sea is highly dynamic due to high atmospheric BrOx (Br + BrO) concentrations. Elevated atmospheric BrOx concentrations cause large and frequent atmospheric mercury (Hg) depletion events (AMDEs), whereby the normally dominant gaseous Hg(0) drops well below global background levels and oxidized forms – particularly Hg(II)_{gaseous} – increase dramatically. The high BrOx concentrations also cause ozone (O₃) depletion events (ODEs), and the corresponding depletions of Hg(0) and O₃ provide strong evidence that Dead Sea AMDEs are linked to active halogen chemistry. We conducted two measurement campaigns in the Dead Sea basin (summer 2009 and winter 2009/2010), and here provide: spatial and temporal data on atmospheric levels of Hg(0), Hg(II) (gaseous and particulate), and O₃; Dead Sea water methyl-Hg and total-Hg concentrations; and an evaluation of the performance of current Hg measurement techniques under the particularly high atmospheric Hg(II) concentrations found at the Dead Sea. AMDEs (Hg(0) < 1.0 ng m⁻³) occurred on 20 of 29 days in summer, of which eight events were very strong (< 0.5 ng m⁻³); in winter, they occurred on eight of 20 days, of which four were very strong. Although all AMDEs occurred when BrO levels (measured by LP-DOAS) were enhanced, only four and three of the strong AMDEs (in summer and winter, respectively) showed corresponding ODEs, while other events showed no corresponding O₃ concentration declines. This indicated that AMDEs can occur without detectable ODEs, even though BrOx chemistry is considered to drive AMDEs. We attribute these patterns to the fact that Hg concentrations seem more sensitive to active halogen chemistry than O₃ which occurs at concentrations orders of magnitude higher and also shows photochemical daytime production. A second observation site some 400 m above the Dead Sea surface showed that AMDEs and ODEs occur throughout the Dead Sea basin and are not limited to the shore, although their frequency was lower (four events with levels < 1.0 ng m⁻³ in winter). Total-Hg and methyl-Hg concentrations of the Dead Sea water were not enhanced in spite of the regular occurrence of AMDEs, with methyl-Hg concentrations below detection limits and total-Hg concentrations below 5 ppt. We further found that even at high Hg(II)_{gaseous} concentrations, the commonly-used Tekran Model 2537 Hg vapor analyzer predominantly measures Hg(0) – as opposed to total gaseous Hg (TGM: GEM + Hg(II)_{gaseous}); and that at high Hg(II)_{gaseous} levels, the Tekran speciation unit experiences enhanced system blank levels because glassware possibly has difficulty fully retaining Hg(II).

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1. Introduction

Hg is a global concern due to neurotoxic effects on humans, particularly in its methylated, organic form (Fillion et al., 2011;

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Steffen et al., 2012; USEPA, 2012). The primary route of Hg transport to remote ecosystems, one area where inorganic Hg can be methylated, is via the atmosphere (Fitzgerald et al., 1998). Atmospheric Hg consists of three main species: gaseous elemental Hg, or Hg(0); gaseous oxidized Hg, or Hg(II)_{gaseous}; and fine particulate (<2.5 μm) bound Hg, or Hg(II)_{particulate}. The predominant form of Hg in the atmosphere, Hg(0) – often comprising more than 90% – is volatile, undergoes long range transport (thousands of km), and has a relatively long atmospheric lifetime (0.5–2 years) (Brunke et al., 2010; Holmes et al., 2006; Lamborg et al., 2002; Mao et al., 2008; Steffen et al., 2008). The main sources of Hg(0) can be natural (volcanoes or geologically enriched areas) or anthropogenic (coal-fired power plants, cement production, medical waste incineration) (USEPA, 2012). Hg(II)_{gaseous} and Hg(II)_{particulate} emissions are typically produced during high temperature combustion (i.e., coal-fired energy generating units), are water soluble, and typically transported across much shorter distances (tens to hundreds of km) (e.g., Lin et al., 2012; Rothenberg et al., 2010; Schroeder and Munthe, 1998).

Under certain atmospheric conditions most often found in polar regions and at the Dead Sea, Hg(II)_{gaseous} and Hg(II)_{particulate} can be produced in situ via oxidation of Hg(0), causing dramatic drops (near 0 ng m⁻³) in Hg(0) concentrations, a process termed atmospheric mercury depletion events (AMDEs). During AMDEs, atmospheric concentrations of Hg(0) rapidly decrease to levels substantially below global background concentrations, while Hg(II)_{gaseous} and Hg(II)_{particulate} concentrations increase initially before rapidly depositing out of the atmosphere (Brooks et al., 2008, 2006; Lindberg et al., 2002; Schroeder et al., 1998; Steffen et al., 2008). Strong (Hg(0) near 0 ng m⁻³) AMDEs have been reported in many Arctic, Antarctic, and sub-polar regions (e.g., Brooks et al., 2006; Dommergue et al., 2010a; Steffen et al., 2008) where they are estimated to contribute to increased atmospheric Hg deposition loads (Skov et al., 2004). Recent data also indicate that Hg(0) depletions and enriched levels of Hg(II)_{gaseous} can occur in the high troposphere and lower stratosphere (Lyman and Jaffe, 2012; Murphy et al., 2006; Talbot et al., 2007). Due to rapid oxidation of Hg(0) to Hg(II) and its subsequent rapid removal from the atmosphere, AMDEs are important in regard to increased deposition rates and can affect the overall global atmospheric lifetime of Hg(0) (Goodsite et al., 2004; Holmes et al., 2010, 2006).

AMDEs were originally thought to occur primarily at high latitudes and low temperatures in the presence of reactive halogen species and sunlight. These halogens oxidize Hg(0) to Hg(II), producing an Hg(II)-halogen complex (3) (Goodsite et al., 2004; Holmes et al., 2006; Peleg et al., 2007; Raofie and Ariya, 2004) through an intermediate Hg(I)-halogen (2) complex that is unstable at high temperatures (Brooks et al., 2011; Dibble et al., 2012; Goodsite et al., 2004; Holmes et al., 2006; Stern et al., 2012):



An alternative pathway may include reaction of Hg with BrO, although this reaction has been considered endoergic (Dibble et al., 2012; Raofie and Ariya, 2004; Tossell, 2006):



or



or



Recent measurements at the Dead Sea have shown that very strong and frequent AMDEs also occur in the temperate and warm (>40 °C) atmosphere (Obrist et al., 2011; Peleg et al., 2007). The finding of strong AMDEs in the Dead Sea basin, an area well known for its active bromine chemistry (Matveev et al., 2001; Tas et al., 2012, 2005, 2006), indicates an importance of halogen chemistry for the destruction of atmospheric Hg(0) at temperatures higher than encountered in Polar Regions. We previously suggested that AMDEs at the Dead Sea were caused by reactive bromine species (BrOx: Br plus BrO) since they temporally coincide with BrO formation and ODEs (Obrist et al., 2011; Peleg et al., 2007). In fact, the local atmosphere at the Dead Sea is highly enriched in BrOx due to, high ambient temperatures, high Br⁻ concentrations in the Dead Sea water (enriched more than 100 times compared to regular ocean water), and pollution (Smoydzin and von Glasow, 2009; Tas et al., 2005, 2006, 2008). The formation of these high BrOx levels and corresponding depletions of O₃ has been extensively characterized by observational and modeling studies (Matveev et al., 2001; Smoydzin and von Glasow, 2009; Tas et al., 2005, 2006, 2008). Expanding box model simulations to include Hg(0) oxidation, Tas et al. (2012) estimated that BrOx accounts for 85–90% of Hg(0) oxidation at the Dead Sea (on a 24-h average) and that the combined effects of other oxidants (including O₃, OH, and NO₃) may be in the range of 4–8%. Further, Tas et al. (2012) suggested that BrO in particular may be the dominant oxidant at the Dead Sea – with more than an 80% contribution to oxidation – as opposed to Br which is generally considered the main oxidant for AMDEs in Polar regions (Brooks et al., 2011; Goodsite et al., 2004; Holmes et al., 2010, 2006). It is noteworthy that chlorine is considered less significant in the region due to the high Br⁻ to Cl⁻ ratio of the Dead Sea (note that Br⁻/Cl⁻ ratios are 9 times higher than in regular ocean water; Tas et al., 2005).

The goal of the present study is to describe in detail spatial and temporal patterns of AMDEs observed in the boundary layer of the Dead Sea basin. We provide the following: (i) a comparison of AMDEs along the Dead Sea shore of two campaigns, one performed during summer 2009 and a second during winter 2009/2010, to document temporal aspects of Dead Sea AMDEs; (ii) Hg(0) and O₃ depletion data from a second site 400 m above the Dead Sea water surface to characterize spatial patterns of AMDEs; (iii) Hg concentrations (total-Hg and methyl-Hg) of the Dead Sea water to assess implications of Dead Sea AMDEs on Hg enrichment in Dead Sea water; and (iv) an assessment of the performance of current analyzer technology used to quantify AMDEs under the extremely high Hg(II)_{gaseous} levels (peak of 800 pg m⁻³ and exceeding 300 pg m⁻³ on a regular basis) and strong diurnal cycling that occur at the Dead Sea.

2. Methods

2.1. Measurement locations

The Dead Sea is separated into two basins by the Lisan Peninsula where an artificial channel allows water to be pumped from the northern to the southern basin. The Dead Sea is one of the most saline lakes in the world with high concentrations of bromide (Br⁻;

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