Environ. Sci. Technol. **2007**, *41,* 7280−7285

Mercury Depletion Events in the Troposphere in Mid-Latitudes at the Dead Sea, Israel

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The occurrence of mercury depletion events (MDE) in the Polar Regions during the spring periods has raised global concern due to the biomagnifications of the deposited mercury into the aquatic food chain. However, it now appears that MDE is not limited to the Polar Regions and can also occur at mid-latitudes. Diurnal cycles of mercury, ozone, and BrO behavior based on short-time resolution measurements are presented for the Dead Sea, Israel, for Summer 2006. The results show that mercury depletion events occur almost daily, accompanied always by the presence of BrO and concurrent ozone destruction. The intensity of the MDE corresponded to increasing BrO levels. Mercury depletions of more than 40% were observed when BrO levels rose above 60−70 ppt. Based on the present measurements and supported by theoretical considerations, it appears that BrO_x (BrO + Br) is the primary species responsible for the mercury depletion at the Dead Sea. The present study also suggests, especially at low ozone levels, that the Br atom may play a major role in conversion of the gaseous elemental mercury to the reactive species, $HgBr_2$. The implications of the present study are that even at low BrO levels (<10 ppt), mercury depletion may well occur at other mid-latitude sites and thus needs to be taken into consideration in the global mercury cycle.

Introduction

In 1995, Canadian researchers (*1*) first observed significant depletion of gaseous elemental mercury (GEM) in the Arctic at Alert, Canada. This phenomenon, now termed mercury depletion events (MDE), has since been observed in other Arctic sites in Canada (*2*), Alaska (*3*), Norway (*4*), Greenland (*5*), and Antarctica (*6*, *7*). The occurrence of MDE strongly resembles previously observed depletion events of ozone (O_3) in these areas (*8*). In fact, MDE strongly correlate to O_3 depletions, suggesting that similar mechanisms are responsible for both. It is known that O_3 depletion is highly correlated with elevated concentrations of reactive halogen species (RHS), specifically atomic bromine (*8*) and bromide oxide (*9*) with the bromine atom causing catalytic destruction of O_3 (*10*). Bromine atoms originate from photolysis of Br_2 that is recycled by self-reaction of BrO or via reaction of BrO with hydroperoxide. The autocatalytic formation of Br species leads to an exponential increase of gas-phase bromine and is referred to as "Bromine Explosion" (*11*−*13*). Lindberg et al. (*14*) suggested a similar process, involving a reactive halogen species (RHS) as the cause for observed MDE. The scheme proposed (*14*) was heterogeneous and required a frozen aerosol or snow surface for the depletion of gaseous elemental mercury (GEM), Hg^0. Both bromine and chlorine atoms as well as halogen oxide radicals (i.e., BrO and ClO) produced during O_3 destruction may serve as primary oxidants to produce water-soluble reactive gaseous mercury (RGM) such as $HgBr_2$ or HgO. The reactive halogens are produced by oxidation of halides (Cl^- and Br^-). The depletion of GEM is accompanied by the formation of RGM and particulate mercury (Hg−P) (*14*−*16*). Thus, unlike O_3, which is destroyed during depletion events, GEM is not destroyed but is converted to RGM and Hg−P which have high deposition velocities and are readily deposited to surfaces after formation. Hence, during and after the occurrence of MDE, snow mercury levels become significantly enhanced (*4*, *14*, *15*). The deposited mercury can then enter the biogenic cycle, where the mercury is enriched and thus MDE are a potential health hazard (*14*).

It is important to note that the occurrence of RHS, specifically BrO, is not limited to the high latitudes. Even higher BrO mixing ratios, >150 ppt or a factor 10-fold higher than that in the Arctic, have been observed in the Dead Sea during the summer (*17*, *18*). BrO levels of 6 ppt have also been reported in the Great Salt Lake (*19*) and up to 20 ppt have also been detected in the Salar de Uyuni in Bolivia (*20*). Along with high levels of BrO, researchers at the Dead Sea observed—for the first time outside high latitudinal regions—significant O_3 destruction (*18*). O_3 destruction was observed over most of the Dead Sea valley, levels dropping regularly from noontime values of 50−80 ppb down to 10−30 ppb and on occasion to below the detection limit of 2 ppb (*21*). The O_3 depletion correlated with the enhanced BrO levels (*21*, *22*).

The occurrence of high BrO levels together with O_3 depletion events outside of Polar Regions suggests that MDE might be more abundant than previously supposed. To test this hypothesis, mercury concentrations were monitored at the Dead Sea during Summer 2006 to study MDE at mid-latitudes.

Experimental Techniques and Site Conditions

Measurements were performed at Ein Bokek (latitude 31.37° N, longitude 31.20° E), a holiday resort area, situated midway along the Dead Sea. The Dead Sea's geographical position is between 31°50′ N and 31° N, 35°30′ E; its dimensions are about 75 km long and 15 km wide and situated on the eastern border of Israel at approximately 400 m below sea level (for further details see Matveev et al. (*18*)). The region, except for the Dead Sea Salt Works situated some 25 km south of the measuring site, is essentially a recreation region. The Dead Sea Works has its own power plant (110 MW) that operates on heavy fuel oil. This power plant is the main source of anthropogenic pollution in the region apart from limited pollution emitted by vehicles traveling (1−2 thousand per day) on the road bordering the Dead Sea. The Dead Sea is one of the most saline lakes in the world containing more than 8 g/L bromide and 300 g/L chloride (*18*) in contrast to 0.065 g/L bromide and 19 g/L chloride in standard ocean

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10.1021/es070320j CCC: $37.00
Published on Web 10/05/2007

water. This high bromide content in the waters is probably the main reason why high levels of BrO are repeatedly observed in the region (*18*).

The instrumentation for the present study was situated at a resort hotel on the top floor, some 20 m above the water and about 25 m inland from the Dead Sea. Measurements were performed for total gaseous mercury (TGM) using a mercury vapor analyzer (Tekran model 2537A). Quality assurance for mercury is essential at such low levels and has been described in detail in a previous paper (Valente et al. (*23*)). The instrument was operated with a 5 min integrated sampling frequency at a flow rate of 1 L/min and automatically calibrated daily against an internal certified permeation tube. In addition, the instrument has an alternate filter and flow path, which allows for daily zero of the monitor. The span and zero values obtained during the daily automatic calibrations remained constant throughout the entire measuring campaign. The instrument was calibrated, before beginning the campaign, by injection of a mercury standard using the Tekran model 2505 saturated mercury calibration unit. No loss in the gold trap efficiencies were observed throughout the study as evident by the stable readings of the area values obtained during the calibration spans. Acid-cleaned new Teflon tubing was used for sampling the inlet air with a 0.45 μm PTFE particulate filter in front of the monitor.

A study performed by Temme et al. (*7*) has shown that the Tekran model 2537A detects not only the gaseous elemental mercury but that reactive gaseous mercury (RGM) can pass through a heated Teflon sampling line and a PTFE particulate filter to be amalgamated on the gold cartridge and subsequently detected as Hg^0. The result of the above study (*7*) showed that, at least for Antarctic conditions, the Tekran 2537A measures a "sum parameter" of both gaseous inorganic mercury species (GEM + RGM), even at periods with relatively high RGM concentrations. While under "normal" conditions, the contribution of RGM to the TGM was less than 10%, under MDE this was much higher. The TGM results reported in the present study represent therefore the upper limits of GEM that under non-MDE conditions will be close to TGM levels.

Ozone was measured by the UV absorption method using a Thermo Electron Corporation model 48C monitor. The ozone monitor was calibrated daily against certified standards as well as for zero stability. BrO was measured using the differential optical absorption spectroscopy (DOAS) technique (Hoffmann model HMT-DOAS Measuring System). The DOAS instrument used a 10 km light path traveling west to east over the Dead Sea. Using the above setup, it is possible to detect BrO down to less than 10 ppt. The DOAS setup and general evaluation procedure for the optical spectra have been described previously (*18*).

The measurements at the Dead Sea were performed from June 26 to July 3, 2006. Additional TGM measurements, for comparison with Dead Sea data, were performed at an urban Jerusalem site (The Hebrew University) from June 8 to June 18, 2006. The Jerusalem site is situated some 60 km NE of the Dead Sea site and at an elevation of 800 m ASL.

Results

The diurnal results for total gaseous mercury (TGM) at Jerusalem and the Dead Sea, grouped into hourly bins with standard deviations and average symbols, are shown in Figure 1. The Jerusalem TGM data ranged between 1.5 and 8 ng m^{-3} (average 2.29 $\pm$ 0.87 ng m^{-3}, $n = 2915$), in comparison to the Dead Sea where levels ranged between 0.8 and 4 ng m^{-3} (average 1.97 $\pm$ 0.39 ng m^{-3}, $n = 2250$). For Jerusalem, the TGM levels increased at noon, averaging ~3 ng m^{-3}, while at the Dead Sea, an opposite trend was observed with decreasing noon time TGM levels, averaging ~1.5 ng m^{-3}. For comparison, a consensus from the literature for various rural and remote sites in the northern hemisphere indicates that GEM averaged near 1.7 $\pm$ 0.3 ng m^{-3} as compared to 5.2 $\pm$ 0.35 ng m^{-3} for urban sources (*23*). The Dead Sea site cannot be considered a remote site, but is influenced by regional mercury transported into the area and maybe also by local sources emitted from the Dead Sea Salt Works.

Figure 2 shows the mercury, BrO, and ozone levels as measured at the Dead Sea for the entire measuring campaign. The results for the entire measuring period show that drops in TGM and O_3 were more pronounced when BrO concentrations were higher. The data indicate a daily occurrence of MDE in the Dead Sea Basin, very similar in pattern to that observed in the Arctic and Antarctic and show that MDE can also occur in mid-latitudinal areas. Careful examination of the entire data set showed that the decreases in mercury levels (and the decrease in O_3) were not necessarily completely synchronized with increases in BrO, but that BrO increases can sometimes occur after the decreases in O_3 and GEM. Regression analysis gave a square of the correlation coefficient (R^2) between Hg and BrO as 0.24 while between Hg and O_3 a value of 0.35 was obtained. A typical 1 day (July 3, 2006) detailed example of a mercury depletion event as observed at the Dead Sea (Ein Bokek) together with concurrent O_3 and BrO values is shown in Figure 3. As observed, the BrO levels start to increase significantly around 9 a.m. with values increasing to almost 50 ppt. As BrO concentrations increased above 20 ppt, a significant drop of TGM and of O_3 were observed. The TGM values dropped to below 1.5 ng m^{-3} for about 1 h, with a concurrent decrease in O_3 values to ~20 ppb.

Drops in TGM concentrations at the Dead Sea were observed in general to be shorter in duration (several hours) and less pronounced, maximum 60% depletion, compared to sites in the high latitudes where GEM concentrations frequently fell below 1 ng m^{-3} and at times below the measurement limits (<0.1 ng m^{-3}) of the mercury analyzer (*4*). Mercury concentrations at the Dead Sea also showed a very "spiky" pattern with high variability of TGM. Similar variability of TGM during and after depletion an event has been observed by others in high latitudes (*4*, *5*, *14*) and was attributed to re-emissions of GEM from surfaces (*24*). The less pronounced depletion and high variability of TGM in the Dead Sea Basin could well be due to the high variability in BrO production as shown both by experiment (*22*) and by model simulations (*25*). Additionally, a very dynamic pattern of oxidation and reduction processes, more pronounced due to warmer temperatures, higher solar loads, and the presence of anthropogenic atmospheric pollutants as compared with that in the remote locations in the high latitudes might also affect the mercury depletion pattern.

Discussion

The chemical mechanisms responsible for mercury depletion at the Polar Regions and in the upper free troposphere are still the subject of speculation and controversy. A summary of the state of the knowledge on the above topic resulting from a recent international expert panel convened to discuss the progress and uncertainties in attributing the sources of mercury in deposition has been presented in a recent paper (*26*). Model simulations have assumed that hydroxyl radicals (OH) and gaseous ozone were the main global oxidants of GEM (*27*, *28*). However, it has recently been shown (*29*) that the oxidation of Hg^0 by OH is much slower than previously reported and therefore the OH radical mechanism is now believed to be insignificant under atmospheric conditions. Further recent model simulations have shown (*27*) that the determined reaction rate of Hg^0 with O_3 appears to be too slow to be the main oxidant of Hg^0. Nor can it alone explain the GEM

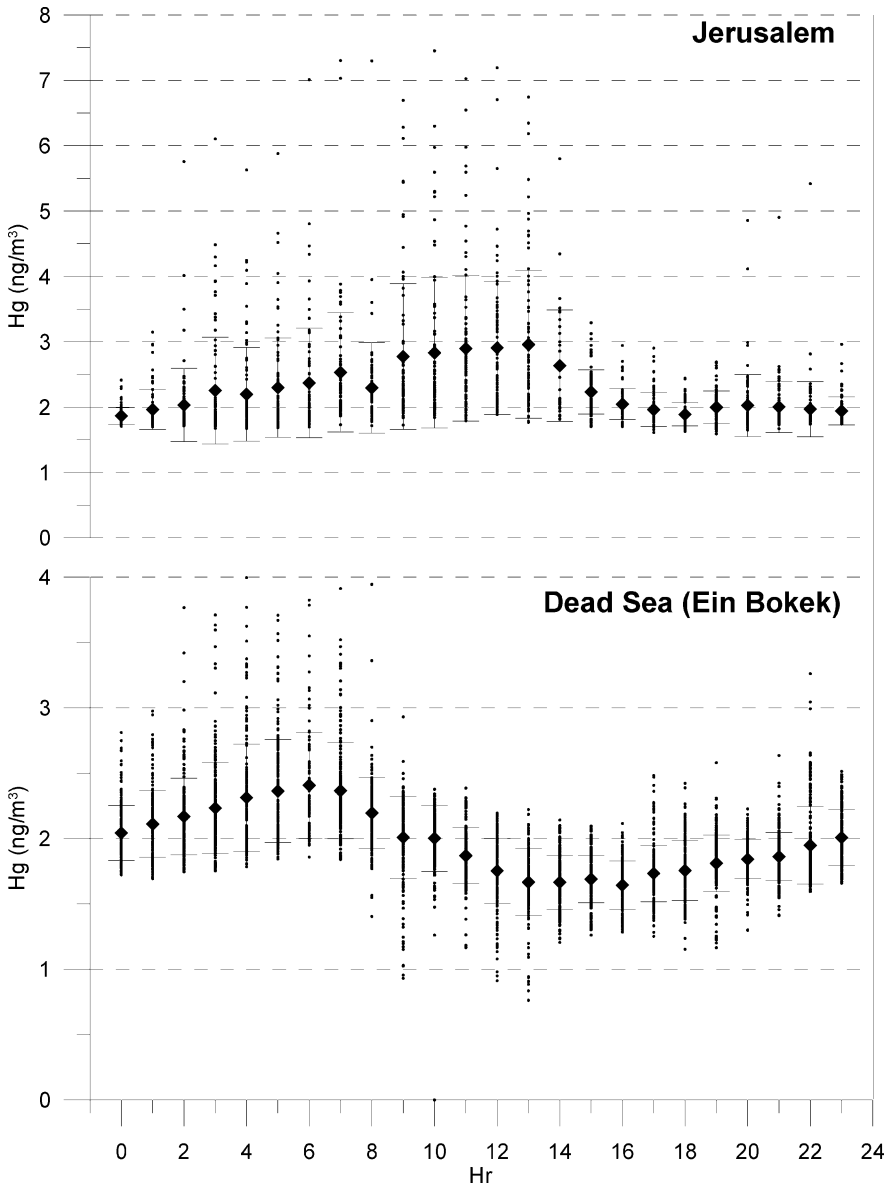

FIGURE 1. Total gaseous mercury (TGM) at Jerusalem and the Dead Sea—in hourly bins with standard deviations and average symbols.

temporal and spatial variations or the observed diurnal cycle of gaseous Hg(II) (*30*).

A homogeneous mechanism for Hg−Br chemistry in the troposphere (*31*) based on theoretical kinetic calculations has shown that gas-phase oxidation of Hg^0 by Br atoms might be able to explain the MDE in the Arctic springtime boundary layer. Several mechanisms have been proposed to explain the oxidation of GEM (*14*, *32*) to form HgO and/or $HgBr_2$:

$$Br + O_3 \rightarrow BrO + O_2 \quad (1)$$

$$BrO + Hg \rightarrow HgO + Br \quad (2)$$

$$Br + Hg \leftrightarrow HgBr \quad (3)$$

$$HgBr + Br \rightarrow HgBr_2 \quad (4)$$

Calculations (*33*) have shown that all the possible reactions of BrO with gaseous Hg^0 are endoergic, particularly the one producing gaseous HgO. On the other hand, the reactions of GEM with either one or two Br radicals are exoergic. The compound suggested (*33*) as being most probably formed in reactive gaseous mercury is $HgBr_2$. This compound is also stable photolytically in sunlight, while species such as HgO and HgBr will decompose rapidly in visible light. It has been demonstrated (*31*) that the recombination of Hg with Br is surprisingly fast for an atom−atom recombination, in agreement with other studies (*31*). The addition of a second bromine to HgBr was also predicted to be a very fast reaction (*32*). It was further shown *(31)* that the crucial factor that determines the lifetime to convert Hg^0 to Hg^{II} is the rate at which HgBr thermally decomposes back to Hg and Br (reaction (3) is reversible). It was therefore concluded (*31*, *34*) that a mechanism based on oxidation of Hg^0 by atomic bromine, followed by addition of a second atom in competition with thermal dissociation, must seriously be considered as a possible mechanism capable of accounting for the observed rate of Hg^0 removal, both in Artic depletion events and on a global scale in the free troposphere. However, as summarized by the expert panel recently convened (*26*), other possible mechanisms involving O_3 and OH cannot be neglected.

As shown earlier, mercury depletion at the Dead Sea is paralleled with ozone destruction and both decrease as BrO levels increase. Thus, it appears that BrO may play a central role in MDE. Figure 4 shows the variation in percentage of mercury depletion (based on the TGM values) as related to

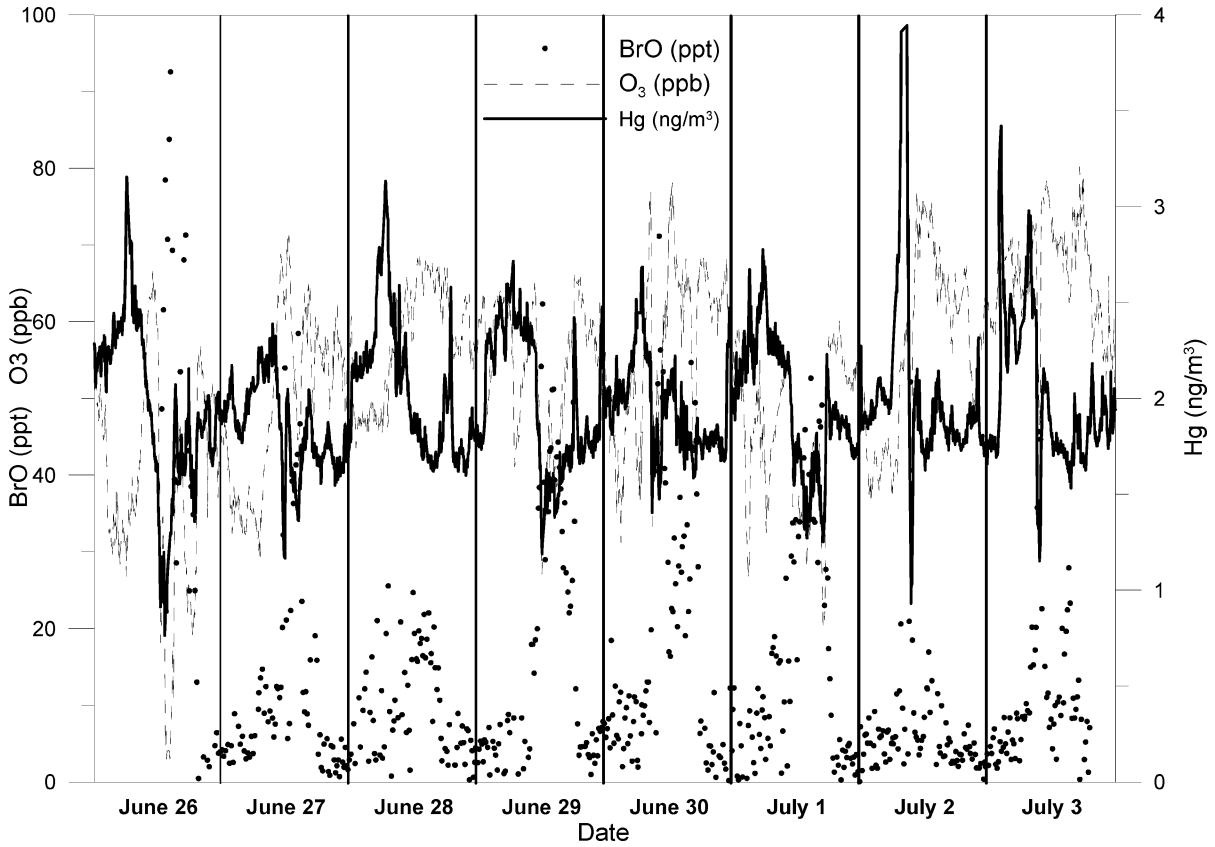

FIGURE 2. Mercury, BrO, and O_3 levels at the Dead Sea. June 26–July 3, 2006.

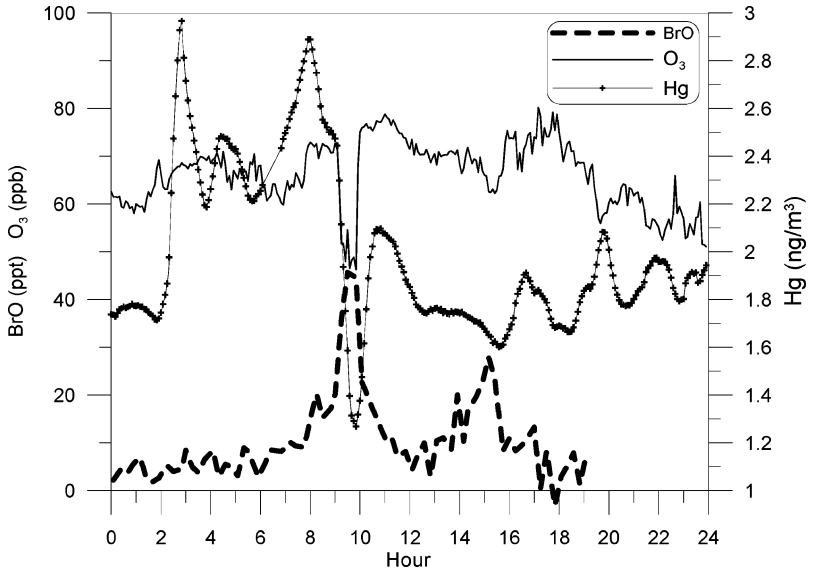

FIGURE 3. Mercury depletion event observed at Ein Bokek at the Dead Sea, July 3, 2006.

increasing BrO and ozone levels (grouped in concentration bins with standard deviations and average symbols). The percentage depletion was calculated with respect to the average TGM level for the time period when BrO formation is not active. At BrO levels below ~30 ppt, MDE are minimal, averaging only several percent. Obviously, an accurate value depends on the Hg^0 value taken as the Dead Sea background level. Increased mercury depletion begins at BrO levels above 30 ppt, reaching average maximum depletion of around 40% as BrO levels rise above 70 ppt. The MDE increase strongly as ozone levels drop below 50 ppb, with maximum depletion at ozone levels below 10 ppb. It should also be pointed out, as explained previously, that the measured TGM represents in fact the sum of GEM and RGM and therefore the true GEM values should be even lower, indicating even higher depletion values.

Since direct measurements of the free Br radical were not possible in the present study, theoretical calculations were performed in an attempt to evaluate the Br levels present during BrO formation, under summer conditions, at the Dead Sea. Measurement-based modeling studies using a One-Dimensional Chemical Transport Model, as described in detail by Tas et al. (*25*), have shown that the Br/BrO ratio at the Dead Sea increases exponentially from less than 0.01 at ozone levels above 20 ppb to ratios of 0.1 at 10 ppb and to 0.5 and higher at ozone levels below 5 ppb. Thus, as the

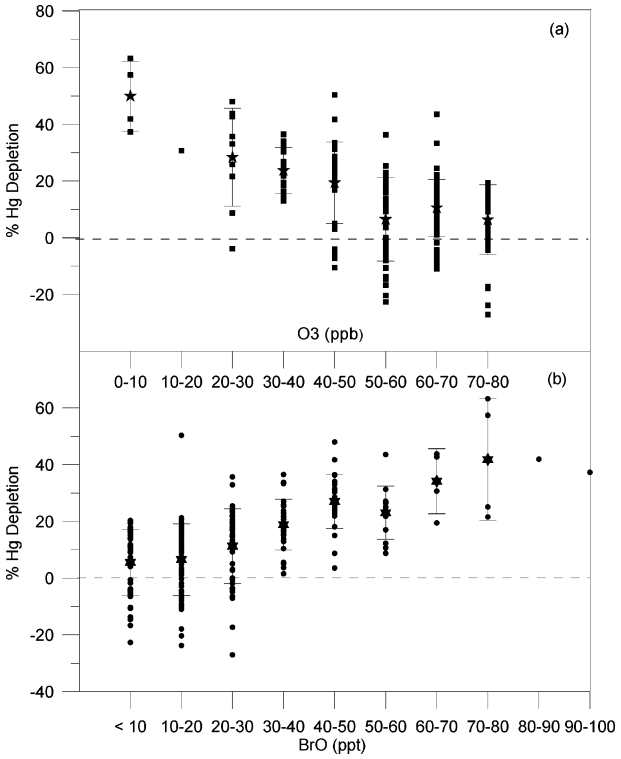

FIGURE 4. Effect of BrO and O_3 on percentage of Hg depletion—in concentration bins with standard deviations and average symbol.

ozone levels decrease to below 20 ppb, the Br atom might well play an increasing part in the mercury depletion mechanism.

Midday mercury depletion events accompanied by increasing BrO levels and ozone depletion have been demonstrated to occur at the Dead Sea in Israel, during the summer period. The extent of mercury depletion is related to the BrO level, or maybe more correctly to the BrO_x (Br + BrO) level. While the conditions (both climatic and physical) at the Dead Sea are far different than those in the Polar Region, it appears that the phenomenon of mercury depletion may be similar for both regions. This, in spite of the fact that the dissociation rate of HgBr, formed in reaction (*3*), is extremely temperature-sensitive, doubling every 6 K (at 273 K), (*31*), and thus reducing the $HgBr_2$ formation via reaction (*4*). The heterogeneous mechanism suggested for mercury depletion at the Polar Regions (*14*) may not be as effective at the Dead Sea since frozen aerosols or snow surfaces are obviously not present in this area, although the presence of aerosols (such as sulfates (*22*)) might also provide the surfaces required for heterogeneous reactions.

Our results suggest that limited mercury depletion (several percent) may occur even at low BrO levels (<10 ppt). Since low levels of RHS have been observed to occur in large areas of the mid-latitude marine boundary layer, with BrO concentrations ranging from <1 to 3.6 ppt (*35*), reactive bromine chemistry could potentially impact atmospheric mercury processes in most of the marine boundary layer. This is supported by studies performed both in the Mediterranean Sea (*36*) and the North Pacific Ocean (*37*) that showed the presence of RGM, resulting from GEM depletion, in these regions averaged 7.9 and 9.5 pg m^{-3}, with maximum values of 30.1 and 92.4 pg m^{-3}, respectively. The above studies agree with the proposition that, at least in mid-latitude areas, it is the reactive halogen species that cause RGM production and hence GEM depletion.

The implications of MDE occurring in mid-latitudes due to oxidation by atmospheric bromine may be important for understanding global cycling of mercury and mercury deposition loads to terrestrial and aquatic ecosystems, as also recently proposed by Holmes et al. (*34*), based on their model calculations.

Acknowledgments

This work was supported by a grant awarded by The Israel Science Foundation (Grant 662/2004). The assistance of the Dead Sea Works (environmental division) in site logistics is greatly appreciated.

Literature Cited

(1) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. A.; Lu, J. Y.; Steffen, A. Artic springtime depletion of mercury. *Nature* **1998**, *394*, 331−332.
(2) Poissant, L.; Pilote, M. Time series analysis of atmospheric mercury in Kuujjuarapik/Whapmagoostui (Quebec). *J. Phys. IV* **2003**, *107*, 1079−1082.
(3) Lindberg, S. E.; Brooks, S.; Lin, C.-J.; Scott, K.; Meyers, T.; Chambers, L.; Landis, M.; Stevens, R. Formation of reactive gaseous mercury in the Artic: Evidence of oxidation of Hg^0 to Hg^{II} compounds after Artic sunrise. *Water Air Soil Pollut. Focus* **2001**, *1*, 295−302.
(4) Berg, T.; Bartnicki, J.; Munthe, J.; Lattila, H.; Hrehoruk, J. Atmospheric mercury species in the European Artic: Measurements and modeling. *Atmos. Environ.* **2001**, *35*, 2569−2582.
(5) Skov, H.; Christensen, J. H.; Goodsite, M. E.; Heidam, N. Z.; Jensen, B.; Wahlin, P.; Geernaert, G. Fate of elemental mercury in the Arctic during atmospheric mercury depletion episodes and the load of atmospheric mercury to the Artic. *Environ. Sci. Technol.* **2004**, *38*, 2373−2382.
(6) Ebinghaus, R.; Kock, H. N.; Temme, C.; Einax, J. W.; Lowe, A. G.; Richter, A.; Burrows, J. P.; Schroeder, W. H. Antarctic springtime depletion of atmospheric mercury. *Environ. Sci. Technol.* **2002**, *36*, 1238−1244.
(7) Temme, C.; Einax, J. W.; Ebinghaus, R.; Schroeder, W. H. Measurements of atmospheric mercury species at a coastal site in the Antarctic and over the South Atlantic Ocean. *Environ. Sci. Technol.* **2003**, *37*, 22−31.
(8) Bottenheim, J. W.; Gallant, A. C.; Brice, K. A. Measurements of NO_y species and O_3 at 2°N latitude. *Geophys. Res. Lett.* **1986**, *13*, 113−116.
(9) Hausmann, M.; Platt, U. Spectroscopic measurement of bromine oxide and ozone in the high Arctic during polar sunrise experiment. *J. Geophys. Res.* **1994**, *99*, 25399−25414.
(10) Platt, U.; Hönninger, G. The role of halogen species in the troposphere. *Chemosphere* **2003**, *52*, 325−338.
(11) Fan, S.-M.; Jacob, D. J. Surface ozone depletion in the Artic spring sustained by bromine reactions on aerosols. *Nature* **1992**, *359*, 522−524.
(12) Vogt, R.; Crutzen, P. J.; Sander, R. A. A mechanism for halogen release from sea salt aerosol in the remote marine boundary layer. *Nature* **1996**, *383*, 327−330.
(13) Platt, U.; Moortgat, K. Heterogeneous and Homogeneous Chemistry of Reactive Halogen Compounds in the Lower Troposphere. *J. Atmos. Chem.* **1999**, *34*, 1−8.
(14) Lindberg, S. E.; Brooks, S.; Lin, C.-J.; Scott, K. J.; Landis, M. S.; Stevens, R. K.; Goodsite, M.; Richter, A. Dynamic oxidation of gaseous mercury in the Artic troposphere at Polar sunrise. *Environ. Sci. Technol.* **2002**, *36*, 1245−1256.
(15) Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, A.; Welch, H. E.; Martin, K.; Lockhart, W. L.; Hunt, R. V.; Boila, G.; Richter, A. Magnification of atmospheric mercury deposition to Polar Regions in springtime: The link to troposphere ozone depletion chemistry. *Geophys. Res. Lett.* **2001**, *28*, 3219−3222.
(16) Sprovieri, F.; Pirrone, N.; Landis, M. S.; Stevens, R. K. Oxidation of gaseous elemental mercury to gaseous divalent mercury during 2003 Polar sunrise at Ny-Alesund. *Environ. Sci. Technol.* **2005**, *39*, 9156−9165.
(17) Hebestreit, K.; Stutz, J.; Rosen, D.; Matveev, V.; Peleg, M.; Luria, M.; Platt, U. DOAS measurements of tropospheric bromine oxide in mid-latitudes. *Science* **1999**, *283*, 55−57.
(18) Matveev, V.; Peleg, M.; Rosen, D.; Siman Tov-Alper, D.; Hebestreit, K.; Stutz, J.; Platt, U.; Blake, D.; Luria, M. Bromine oxide-ozone interaction over the Dead Sea. *J. Geophys. Res.* **2001**, *106*, 10375−10387.
(19) Stutz, J.; Ackermann, R.; Fast, J. D.; Barrie, L. Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah. *Geophys. Res. Lett.* **2002**, *29*, 1380.

(20) Hönninger, G.; Bobrowski, N.; Palenque, E. R.; Torrez, R.; Platt, U. Reactive bromine and sulfur emissions at Salar de Uyuni, Bolivia. *Geophys. Res. Lett.* **2004**, *31*, L04101, doi:10.1029/2003GL018982.

(21) Tas, E.; Matveev, V.; Zingler, J.; Luria, M.; Peleg, M. Frequency and extent of ozone destruction episodes over the Dead Sea, Israel. *Atmos. Environ.* **2003**, *37*, 4769−4780.

(22) Tas, E.; Peleg, M.; Mattveev, V.; Zingler, J.; Luria, M. Frequency and extent of bromine oxide formation over the Dead Sea. *J. Geophys. Res.* **2005**, *1220*, D11304; doi:10.1029/2004JD005665.

(23) Valente, R. J.; Shea, C.; Humes, K. L.; Tanner, R. L. Atmospheric mercury in the Great Smoky Mountains compared to regional and global levels. *Atmos. Environ.* **2007**, *41*, 1861−1873.

(24) Ferrari, C. P.; Gauchard, P.-A.; Dommergue, A.; Magand, O.; Bahlmann, E.; Nagorski, S.; Temme, C.; Ebinghaus, R.; Steffen, A.; Banic, C.; Berg, T.; Planchon, F.; Barbante, C.; Cescon, P.; Boutron, C. F. Snow-to-air exchanges of mercury in an Arctic seasonal snow pack in Ny-Ålesund, Svalbard. *Atmos. Environ.* **2005**, *39*, 7633−7645.

(25) Tas, E.; Peleg, M.; Pedersen, D. U.; Matveev, V.; Pour Biazar, A.; Luria, M. Measurement-based modeling of bromine chemistry in the boundary layer: 1. Bromine chemistry at the Dead Sea. *Atmos. Chem. Phys.* **2006**, *6*, 5589−5604.

(26) Lindberg, S.; Bullock, R.; Ebinghaus, R.; Engstrom, D.; Feng, X.; Fitzgerald, W.; Pirrone, N.; Prestbo, E.; Seigneur, C. A synthesis of progress and uncertainties in attributing the sources of mercury in deposition. *Ambio* **2007**, *36*, 19−32.

(27) Bergan, T.; Rodhe, H. Oxidation of elemental mercury in the atmosphere: Constraints imposed by global scale modeling. *J. Atmos. Chem.* **2001**, *40*, 191−212.

(28) Selin, N. E.; Jacob, D. J.; Park, R. J.; Yantosca, R. M.; Strode, S.; Jaegle, L.; Jaffe, D. Chemical cycling and deposition of atmospheric mercury: Global constraints from observations. *J. Geophys. Res.* **2006**, *112*, D02308, doi: 10.1029/2006JD007450.

(29) Calvert, J. G.; Lindberg, S. E. Mechanisms of mercury removal by O_3 and OH in the atmosphere. *Atmos. Environ.* **2005**, *39*, 3355−3367.

(30) Hedgecock, I. M.; Trunfio, G. A.; Pirrone, N.; Sprovieri, F. Mercury chemistry in the MBL: Mediterranean case and sensitivity studies using the AMCOTS (Atmospheric Mercury Chemistry over the Sea) model. *Atmos. Environ.* **2005**, *39*, 7217−7230.

(31) Goodsite, M. E.; Plane, J. M. C.; Skov, H. A theoretical study of the oxidation of Hg^0 to $HgBr_2$ in the troposphere. *Environ. Sci. Technol.* **2004**, *38*, 1772−1776.

(32) Ariya, P. A.; Khalizoz, A.; Gidas, A. Reaction of gaseous mercury with atomic and molecular halogens: Kinetics, product studies, and atmospheric implications. *J. Phys. Chem. A* **2002**, *106*, 7310−7320.

(33) Tossell, J. A. Calculation of the energetics for oxidation of gas-phase elemental Hg by Br and BrO. *J. Phys. Chem. A* **2003**, *107*, 7804−7808.

(34) Holmes, C. D.; Jacob, D. J.; Yang, X. Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere. *Geophys. Res. Lett.* **2006**, *33*, L20808; doi: 10.1029/2006GL027176.

(35) Leser, H.; Hönninger, G.; Platt, U. MAX-DOAS measurements of BrO and NO_2 in the marine boundary layer. *Geophys. Res. Lett.* **2003**, *30*, 1537; doi: 10.1029/2002GL015811.

(36) Sprovieri, F.; Pirrone, N.; Gardfeldt, K.; Sommar, J. Mercury speciation in the marine boundary layer along a 6000 km cruise path around the Mediterranean Sea. *Atmos. Environ.* **2003**, S63−S71.

(37) Laurier, F. J. G.; Mason, R. P.; Whalin, L.; Kato, S. Reactive gaseous formation in the North Pacific Ocean's marine boundary layer: A potential role of halogen chemistry. *J. Geophys. Res.* **2003**, *108* (D17), 4529; doi: 10.1029/2003JD003625.

Received for review February 8, 2007. Revised manuscript received August 16, 2007. Accepted August 22, 2007.

ES070320J