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## Two new sources of reactive gaseous mercury in the free troposphere

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# Oxidation of elemental Hg in anthropogenic and marine airmasses

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**Abstract.** Mercury (Hg) is a neurotoxin that bioaccumulates in the food chain. Mercury is emitted to the atmosphere primarily in its elemental form, which has a long lifetime allowing global transport. It is known that atmospheric oxidation of gaseous elemental mercury (GEM) generates reactive gaseous mercury (RGM) which plays an important role in the atmospheric mercury cycle by enhancing the rate of mercury deposition to ecosystems. However, the primary GEM oxidants, and the chemical composition of RGM are poorly known. Using speciated mercury measurements conducted at the Mt. Bachelor Observatory since 2005 we present two previously unidentified sources of RGM to the free troposphere (FT). Firstly, we observed elevated RGM concentrations, large RGM/GEM-ratios, and anti-correlation between RGM and GEM during Asian long-rang transport events, demonstrating that RGM is formed from GEM by in-situ oxidation in some anthropogenic pollution plumes in the FT. During the Asian pollution events the measured RGM/GEM-enhancement ratios reached peak values, up to  $\sim 0.20$ , which are significantly larger than ratios typically measured ( $\text{RGM/GEM} < 0.03$ ) in the Asian source region. Secondly, we observed very high RGM levels – the highest reported in the FT – in clean air masses that were processed upwind of Mt. Bachelor Observatory over the Pacific Ocean. The high RGM concentrations (up to  $700 \text{ pg m}^{-3}$ ), high RGM/GEM-ratios (up to 1), and very low ozone levels during these events provide observational evidence indicating significant GEM oxidation in the lower FT in some conditions.

## 1 Introduction

During the last decade the measurements of atmospheric mercury (Hg) have developed substantially. Speciated Hg measurements, including gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and particle bound mercury (PBM) (Landis et al., 2002), are providing important information about mercury sources, transformation and subsequent deposition (e.g., Talbot et al., 2008; Peterson et al., 2009; Gustin and Jaffe, 2010; Sprovieri et al., 2010). Mercury is mainly emitted to the atmosphere in its elemental form, which has a long lifetime allowing global transport (Jaffe et al., 2005; NRC, 2010). Atmospheric oxidation of GEM generates gas- and particle-phase oxidized Hg compounds (thought to be primarily inorganic Hg(II) species) that deposit quickly as they are more reactive, more water-soluble, and less volatile (Schroeder and Munthe, 1998; Lin and Pehkonen, 1999; Holmes et al., 2009; NRC, 2010). The spatial distribution of mercury deposition in many instances might thus depend more on atmospheric conditions (e.g. wind direction, oxidant concentrations, temperature) than on proximity to mercury sources (Chand et al., 2008; Sprovieri et al., 2010; Holmes et al., 2010; Rothenberg et al., 2010).

Information on transport and transformation of Hg in the free troposphere (FT) is scarce due to a poor understanding of sources of RGM and lack of long-term measurements at high elevations. The few Hg observations above the boundary layer (BL) demonstrate that the upper troposphere/lower stratosphere (UT/LS) is depleted in GEM and enriched in reactive mercury ( $\text{RM} = \text{RGM} + \text{PBM}$ ; Murphy et al., 2006; Swartzendruber et al., 2006, 2008; Talbot et al., 2007, 2008; Lyman and Jaffe, 2011). Oxidation of GEM in the FT is not

well understood. Previous studies have shown that oxidation of GEM in the stratosphere (coupled with stratosphere to troposphere transport) is one source of RGM above the BL (Murphy et al., 2006; Swartzendruber et al., 2006; Lyman and Jaffe, 2011). However, based on previous studies and calculations this source accounts for only a small fraction of tropospheric RGM (Lyman and Jaffe, 2011). Although halogen species might also play a role in GEM oxidation in the FT, the existing observations and model studies have not clearly proven this. Therefore, the sources and RGM formation mechanisms in the bulk of the global atmosphere remain poorly characterized. Using observations of speciated mercury (GEM, RGM, and PBM), submicron aerosol scattering ( $\sigma_{\text{sp}}$ ), trace gases (ozone,  $\text{O}_3$ ; carbon monoxide, CO) and meteorology from the Mt. Bachelor Observatory (MBO), we describe in this paper two sources of RGM observed in the FT.

## 2 Experimental

### 2.1 Mt. Bachelor observatory

The Mount Bachelor Observatory (MBO) is located on the summit of Mt. Bachelor in central Oregon, USA (43.981° N, 121.691° W, 2.7 km a.s.l.). The site is approximately 180 km east of the Pacific coast. Past work has demonstrated that MBO is suitable for observing FT airmasses with minimal influence from North American anthropogenic emissions (Jaffe et al., 2005; Weiss-Penzias et al., 2006; Ambrose et al., 2011; Fischer et al., 2011).

### 2.2 Measurements

Speciated Hg (gaseous elemental mercury (GEM), reactive gaseous mercury (RGM), and particle bound mercury (PBM)) measurements have been conducted at MBO since 2005 using a Tekran 2537A Hg vapor analyzer and a Tekran 1130/1135 Hg speciation system. A detailed description of the sampling system can be found in Swartzendruber et al. (2006). Briefly, a Teflon-coated aluminum (Al) cyclone inlet (URG Corp.), coupled to a Teflon-coated Al high-volume inlet (URG), was used for sampling. The flow through the high-volume inlet was maintained between 50 and 100  $\text{std L min}^{-1}$  (standard pressure of 1.01 bar and temperature of 273.15 K). The speciation system sampled 7.5  $\text{std L min}^{-1}$  from the high-volume inlet. A KCl coated annular denuder was used to collect RGM and a quartz fiber filter was used to collect PBM. Downstream of the speciation system the Tekran 2537A sampled an additional 0.65  $\text{std L min}^{-1}$  from the airstream and measured GEM at 5 min intervals. The total flow through the cyclone inlet yielded a particle size cut of 2.5  $\mu\text{m}$ . To improve the detection limit, RGM and PBM samples were collected for 3 h prior to analysis. During the RGM and PBM analysis cycle (60 min) GEM was not measured. The Hg instruments were calibrated with the elemental mercury ( $\text{Hg}^0$ ) permeation source internal

to the Tekran 2537A. The emission rate of the permeation source was verified by injections of  $\text{Hg}^0$  from a Tekran 2505 saturated  $\text{Hg}^0$  vapor source, using a gas-tight microliter syringe (Hamilton). The measured Hg concentrations are expressed as mass concentrations,  $\text{ng m}^{-3}$  or  $\text{pg m}^{-3}$ , at standard temperature and pressure (273.15 K, 1.01 bar). There are uncertainties about the calibration and interferences in the Tekran RGM measurements (Lyman et al., 2010; Gustin et al., 2013; Ambrose et al., 2013). Nonetheless, until these issues can be definitively resolved, we assume the Tekran RGM measurements represent all oxidized forms of Hg in the atmosphere, similar to most researchers.

Aerosol measurements conducted at MBO since 2004 are described in detail by Fischer et al. (2011). Briefly, a Radiance Research nephelometer (M903) was used to measure scattering coefficient at mid-visible wavelength (530 nm). Aerosol concentrations were estimated from the scattering coefficients ( $\sigma_{\text{sp}}$ ) using a dry mass scattering efficiency value of 3.0 (Hand and Malm, 2007). The cutoff diameter was changed from 1  $\mu\text{m}$  to 2.5  $\mu\text{m}$  at the beginning of 2010. The rotating drum impactor, developed at the University of California, (Raabe et al., 1988; Perry et al., 2004) was used to measure the elemental composition (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pb) of ambient aerosols at the following size classes (aerodynamic diameter,  $D_a$ ) > 5.0, 5.0–2.5, 2.5–1.1, 1.1–0.75, 0.75–0.56, 0.56–0.34, 0.34–0.26, and 0.26–0.09  $\mu\text{m}$ . The elemental composition of samples collected to mylar-substrates was analyzed using a synchrotron X-ray fluorescence (S-XRF) technique (Haller and Knochel, 1996; Perry et al., 2004). The blank values were determined by analyzing the blank portions of both ends of the used mylar substrates.

Measurements of CO and  $\text{O}_3$  are described in Ambrose et al. (2011). Briefly,  $\text{O}_3$  and CO concentrations were measured with a Dasibi 1008-RS analyzer and a TECO 48C Trace Level Enhanced analyzer, respectively (Weiss-Penzias et al., 2006, 2007; Jaffe et al., 2005). A Vaisala PTB101B transmitter was used to measure pressure and a Campbell Scientific HMP45C probe was used to monitor the ambient temperature ( $T$ ) and relative humidity (RH).

### 2.3 Back trajectory modeling

We calculated 10-day air mass backward trajectories for each high RGM event to establish the transport history of the associated air masses. Trajectories were calculated using the NOAA Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, v4.9, Draxler and Rolph, 2012) and global meteorological data from the Global Data Assimilation System (GDAS) archive, having a horizontal resolution of  $1^\circ \times 1^\circ$ , 3 h time resolution, and a vertical resolution of 23 pressure surfaces between 1000 and 20 hPa. Trajectories were initialized from the summit of MBO for the hours

during each event when the highest RGM/GEM-ratios were observed.

## 2.4 Statistical analysis

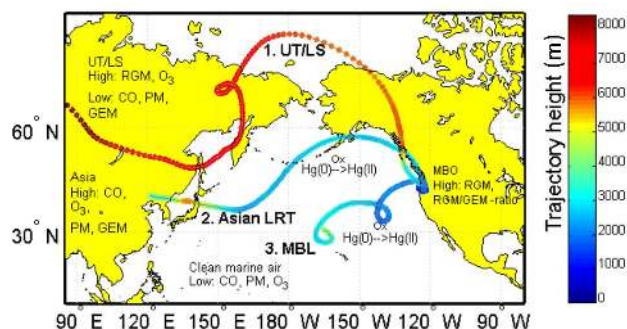
Due to error in both  $x$  and  $y$  variables and the relatively small number of RGM observations during each event, correlations between measured compounds were calculated using the Williamson-York Iterative Bivariate Fit method (Cantrell et al., 2008).

## 3 Results

RGM measurements in the FT are scarce and thus the identification of mercury sources and characterization of the global mercury cycle has been a challenge. Previous studies have shown that transport of RGM from the stratosphere (type 1. UT/LS event) is one source of RGM above the BL (Murphy et al., 2006; Swartzendruber et al., 2006; Lyman and Jaffe, 2011). During UT/LS (type 1) events an increase in RGM and ozone concentrations and a clear correlation between RGM and ozone is typically observed. Also, during these events, a decrease in GEM, CO and aerosol concentrations is observed, coinciding with the RGM and  $O_3$  enhancements (Swartzendruber et al., 2006). Using mercury (GEM, RGM, PBM), aerosol (scattering and elemental composition) and trace gas (CO,  $O_3$ ) measurements conducted at MBO since 2005 we describe here two additional sources of RGM to the FT. Figure 1 shows a conceptual model of the three types of RGM sources to the lower FT (1, UT/LS; 2, Asian long-range transport (ALRT); 3, marine boundary layer (MBL)) observed at MBO. Type 1 (UT/LS) events were identified previously by Swartzendruber et al. (2006) and will not be discussed here. Type 2 (ALRT) and type 3 (MBL) events are described in Sects. 3.1 and 3.2.

### 3.1 Anthropogenic RGM events (Type 2)

Type 2 events suggest in-situ oxidation of GEM to RGM (yielding RGM/GEM-ratios up to 0.18) in anthropogenic pollution plumes that were transported from Asia. This is important because oxidation of GEM in long-range transported pollution plumes in the FT has not been observed previously (Jaffe et al., 2005; Swartzendruber et al., 2006; Faïn et al., 2009). Previous studies conducted in urban areas have shown that point source emissions affect the GEM and RGM concentrations in downwind areas (Lynam and Keeler, 2005; Rothenberg et al., 2009). However, these studies did not suggest in-situ production of RGM. During springtime, meteorological conditions are favorable for transpacific transport and Asian pollution plumes are repeatedly observed at MBO (Jaffe et al., 2005; Weiss-Penzias et al., 2006; Ambrose et al., 2011). Increasing anthropogenic Hg emissions in developing Asian countries (Pacyna et al., 2010; Fu et al., 2012), coupled with formation of RGM during long-range transport



**Fig. 1.** Sources of RGM in the free troposphere as measured at MBO: 1, UT/LS (Swartzendruber et al., 2006; Ambrose et al., 2011); 2, ALRT (this paper); and 3, clean marine boundary layer (MBL) air masses processed in the FT above the Pacific Ocean (this paper). The HYSPLIT airmass back trajectories of three events (UT/LS: 22 April 2006; ALRT: 17 April 2008; MBL: 9 May 2007) are used to show a typical pathway of airmasses during each event type. Trajectories are colored by height. The typical chemical composition of airmasses (ozone ( $O_3$ ), CO, and particulate matter (PM) concentrations) are shown for the areas where the trajectories originate. Key features of the Hg observations at MBO are also shown.

will enhance Hg deposition in downwind regions, such as North America.

Here we present as an example one clear ALRT event (Fig. 2) with total Hg (THg = GEM + RGM + PBM) and RGM concentrations substantially elevated above typical background FT levels. Atmospheric concentrations of Hg species and trace gases, aerosol scattering values, and correlations between main components are shown for each event in Table 1. During ALRT events airmass back trajectories show transport from Asia in  $\leq 10$  days (Fig. 3). In addition, the THg/CO correlation slopes (with values between 0.0051 and 0.0081  $\text{ng m}^{-3} \text{ppbv}^{-1}$ ; Fig. 4) were consistent with the ratios measured previously in Asian plumes (Jaffe et al., 2005; Weiss-Penzias et al., 2007). The THg/CO correlation slopes measured for North American pollution are typically significantly smaller than for Asian LRT. Weiss-Penzias et al. (2007) reported an average THg/CO slope of 0.0011  $\text{ng m}^{-3} \text{ppbv}^{-1}$  for North American pollution. Furthermore, aerosol scattering (20–48  $\text{Mm}^{-1}$ ), CO (162–200 ppbv), and  $O_3$  (72–80 ppbv) were enhanced to levels typically measured in Asian pollution plumes at MBO (Jaffe et al., 2005; Weiss-Penzias et al., 2007; Ambrose et al., 2011) (Table 1). Also, the  $O_3$ /CO correlation slopes (unitless) for these events (0.1–0.3) were in the range of values that are typically seen in Asian pollution plumes with no UT/LS influence (Price et al., 2004). During ALRT events PBM concentrations were low ( $< 15 \text{ pg m}^{-3}$ ), amounting to  $< 15\%$  of reactive mercury (see Sect. 3.3 for more information).

During ALRT events RGM was correlated with the anthropogenic pollution tracers (CO or  $\sigma_{\text{sp}}$  and  $O_3$ ; see Table 1). Furthermore, RGM and GEM were anti-correlated in

**Table 1.** Chemical characteristics of ALRT (type 2) and MBL (type 3) high-RGM events observed at MBO.

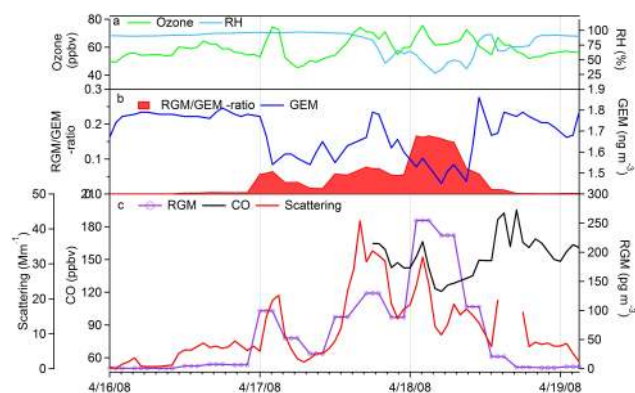
Event time period (UTC) <sup>a</sup>	Max RGM (pg m <sup>-3</sup> )	Avg. GEM (ng m <sup>-3</sup> )	Avg. THg (ng m <sup>-3</sup> )	Max RGM/ GEM (%)	Max CO (ppbv)	Max O <sub>3</sub> (ppbv)	Max $\sigma_{sp}$ (Mm <sup>-1</sup> )	R <sup>b</sup> (RGM vs. GEM)	R <sup>b</sup> ( $\sigma_{sp}$ vs. RGM)	R <sup>b</sup> (CO vs. RGM)	R <sup>b</sup> ( $\sigma_{sp}$ vs. CO)
ALRT											
16 Apr 17:00–18 Apr 14:00, 2008 <sup>c</sup>	255	1.61 ± 0.07	1.73 ± 0.08	16	164	71	23.4	-0.67*	0.67*	–	–
12 May 07:00–13 May 03:00, 2006	235	1.68 ± 0.09	1.80 ± 0.04	15	153	69	19.5	-0.77	0.94**	0.53	0.75
28 Apr 00:00–29 Apr 21:00, 2007 <sup>d</sup>	290	1.65 ± 0.10	1.80 ± 0.08	18	157	77	9.5	-0.68*	0.32	0.60*	0.79**
MBL											
8 May 22:00–10 May 15:00, 2007	706	0.91 ± 0.28	1.40 ± 0.05	105	89	42	1.9	-0.97**	-0.76**	-0.82**	0.88**
21 Jun, 2007, 01:00–21:00	547	0.89 ± 0.10	1.37 ± 0.03	67	63	23	1	-0.92*	-0.81	-0.78	0.98**
7 Jul 11:00–10 Jul 04:00, 2007	388	1.25 ± 0.14	1.39 ± 0.09	40	82	43	1.7	-0.81*	-0.37	-0.61*	0.90**
10 May 01:00–12 May 01:00, 2011	275	1.12 ± 0.25	1.27 ± 0.12	31	90	42	1.5	-0.92**	-0.34	-0.79**	0.06

<sup>a</sup> The event time period includes the maximum RGM enhancement and up to 14 h preceding and following a discernible increase in RGM associated with the peak enhancement. Correlation parameters were calculated for this time period ( $n = 5-15$ ); the mean and maximum values for each chemical parameter correspond with only the times for which RGM was > 10 % of Max RGM ( $n = 2-6$ ).

<sup>b</sup> Pearson correlation coefficient; \*,  $p < 0.05$ ; \*\*,  $p < 0.01$ ; no star,  $p > 0.05$ .

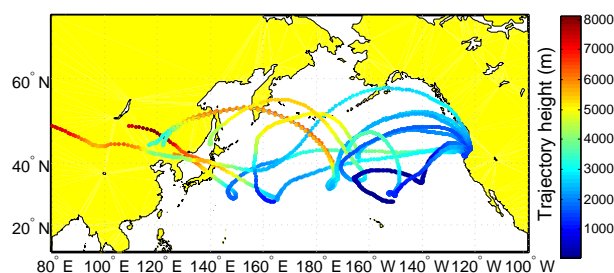
<sup>c</sup> Some CO data are missing for this event, which would tend to reduce the statistical significance of correlations between CO and other parameters. Thus correlations between CO and other measured compounds are not included in the table.

<sup>d</sup> One 3-h averaged measurement (04:00 UTC on 29 April) with a possible UT/LS influence was excluded when calculating the values presented here.

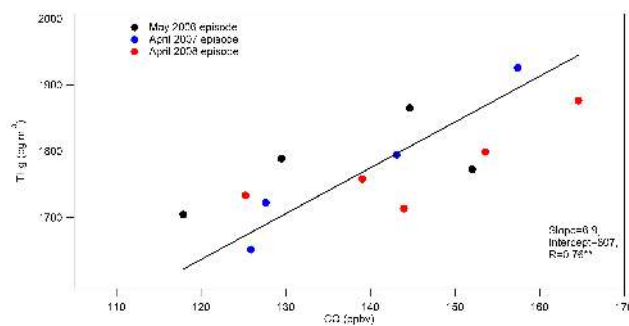


**Fig. 2.** Time series of (a) O<sub>3</sub> and relative humidity (RH); (b) RGM/GEM-ratio and GEM; (c) RGM, submicron aerosol scattering ( $\sigma_{sp}$ ), and CO measured at MBO during a type 2 (ALRT) high-RGM event in spring 2008. All data are 1-h averages, except RGM and RGM/GEM-ratios that are 3-h averages (resolution of the RGM measurement). Measurements of RGM are plotted for each hour of collection. ( $1 \text{ ng m}^{-3} \approx 0.12$  parts per trillion by volume at 1.01 bar and 273 K).

the ALRT plumes. The RGM enhancements corresponded with GEM depletions of  $0.2-0.4 \text{ ng m}^{-3}$  (Fig. 2). This indicates that we are seeing the effects of conversion of GEM to RGM in-situ, rather than primary Asian RGM. Depletion of GEM in anthropogenic pollution plumes has only been seen previously in the BL (Weiss-Penzias et al., 2003; Lynam and Keeler, 2005). Several studies have measured RGM and GEM concentrations in China and in Asian pollution plumes in the Western Pacific BL (Jaffe et al., 2005; Chand et al., 2008; Fu et al., 2012). The RGM/GEM-ratios observed in previous studies were typically below 0.03. In contrast, for the three ALRT events presented in this paper the peak RGM/GEM-ratio was between 0.15 and 0.18, showing that

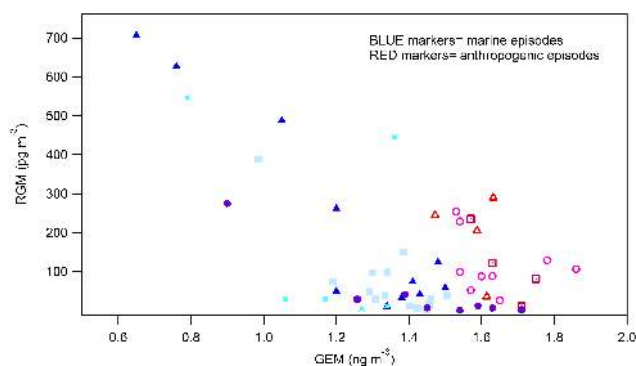


**Fig. 3.** Ten-day HYSPLIT airmass back trajectories for three Asian long-range transport (ALRT) high-RGM events. Trajectories were initialized at times during each event when the highest RGM/GEM-ratios were observed.



**Fig. 4.** Elevated CO and THg concentrations and THg/CO enhancement ratios measured during May 2006, April 2007, and April 2008 high-RGM events are suggestive of Asian long-range transport (ALRT). Due to the small number of data points during each individual event, we calculated the slope by using all data during episodes combined. The THg/CO correlation slope for the combined events is similar to Asian emission ratios measured previously (Jaffe et al., 2005; Weiss-Penzias et al., 2007).



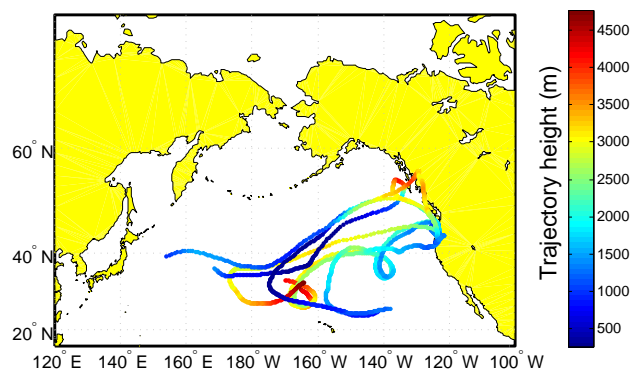


**Fig. 5.** A negative correlation was observed between RGM and GEM during high-RGM events. Elevated total mercury (THg) and RGM concentrations (peak RGM values of 200–700  $\text{pg m}^{-3}$ , elevated by up to  $\sim 0.2$ – $0.7 \text{ ng m}^{-3}$  and a factor of  $\sim 20$ – $70$  above typical background FT levels) were observed during MBL events. The GEM concentrations were higher during ALRT events (THg = 1.65–1.80  $\text{ng m}^{-3}$ ; 1 nanogram per cubic meter  $\approx 0.12$  parts per trillion by volume at 1.01 bar and 273 K). In general, the MBL events (type 3) show stronger inverse correlations between RGM and GEM compared to ALRT events (type 2).

the measured RGM is a significant fraction of THg (Table 1, Fig. 2). Previous studies have shown that for primary RGM emissions a positive correlation between RGM and GEM is typically observed, whereas for in-situ oxidation an anti-correlation between RGM and GEM is expected (Swartzendruber et al., 2006; Sillman et al., 2007). The anti-correlation between RGM and GEM (Table 1, Fig. 5) and elevated RGM/GEM-ratios in ALRT plumes observed at MBO suggest that the source of RGM during these events was in-situ oxidation during FT transport. Previous studies have shown that the lifetime of RGM is longer in the FT than in the BL due to the absence of removal mechanisms (Munthe et al., 2003; Selin et al., 2007). Therefore, conditions in the FT are expected to be more favorable for accumulation and transport of secondary (e.g. photochemical) RGM.

### 3.2 Marine boundary layer events (type 3)

The second RGM source we have observed (type 3; marine boundary layer) occurs in very clean air masses. The air mass back trajectories show that these air masses had circled above the Pacific Ocean for at least 10 days prior to arriving at MBO (Figs. 1 and 6). Here we present as an example one clear MBL event (Fig. 7). During MBL events a simultaneous increase in RGM and decrease in CO, aerosol scattering, and  $\text{O}_3$  was observed (Table 1). The low CO and aerosol scattering values (Fig. 7, Table 1) measured during these time periods suggest minimal influence from anthropogenic emissions or from biomass burning (Munthe et al., 2003; Weiss-Penzias et al., 2007). The  $\text{O}_3$  and water vapor mixing ratios ( $\sim 30$ – $45$  ppbv and  $3$ – $4 \text{ g kg}^{-1}$ , respectively) during the events do not indicate transport from the UT/LS; rather, the composi-

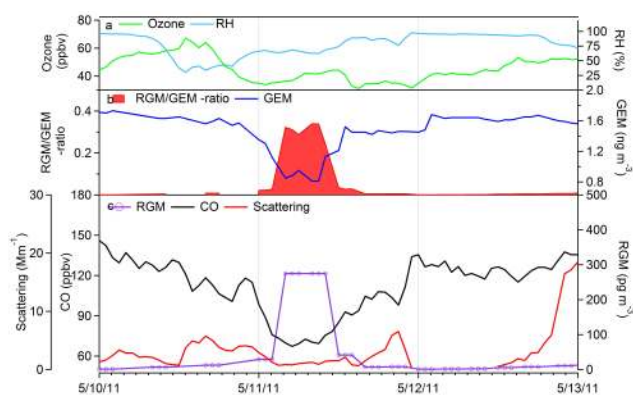


**Fig. 6.** Ten-day HYSPLIT airmass back trajectories for the marine boundary layer (MBL) high-RGM events. Trajectories were initialized at times during each event when the highest RGM/GEM-ratios were observed.

tion of these air masses is more consistent with an influence from the clean sub-tropical MBL.

The RGM concentrations observed during MBL events were very high (200–700  $\text{pg m}^{-3}$ ) compared to anthropogenic pollution plumes (200–300  $\text{pg m}^{-3}$ ) (Table 1). Such high RGM levels have only been measured in the BL near emission sources and locations with high concentrations of oxidants (e.g., those encountered at the Dead Sea; Obrist et al., 2010). To our knowledge such high levels have not been previously observed in the FT. Much lower THg concentrations were measured during MBL events (1.2–1.4  $\text{ng m}^{-3}$ ) when compared to anthropogenic pollution plumes (1.7–1.8  $\text{ng m}^{-3}$ ). As for Type 2 events, PBM concentrations were low ( $< 12 \text{ pg m}^{-3}$ ), amounting to  $< 15\%$  of reactive mercury. A clear anti-correlation between RGM and GEM was observed during MBL events (Table 1, Fig. 7) indicating in-situ GEM oxidation. Furthermore, the large RGM/GEM-ratios (0.31–1.05, Table 1) demonstrate an efficient process for GEM oxidation and transport of RGM in the FT. It is notable that the large RGM enhancements in these air masses far exceed those previously observed in UT/LS influenced air masses (Swartzendruber et al., 2006; Ambrose et al., 2011).

Aerosol chemical composition was measured with rotating DRUM impactors during the MBL event observed in May 2011. A small increase in aerosol sea salt ( $\text{Na}^+$  and  $\text{Cl}^-$ ) concentration was measured, further indicating that the air mass likely originated from the marine boundary layer. Sea salt aerosol may be an important sink for RGM in the MBL (Malcolm et al., 2009), thus explaining smaller ambient RGM concentrations observed in the studies conducted in marine regions (Laurier et al., 2003; Laurier and Mason, 2007; Holmes et al., 2009).



**Fig. 7.** Time series of (a) O<sub>3</sub> and relative humidity (RH); (b) RGM/GEM-ratio and GEM; (c) RGM, submicron aerosol scattering ( $\sigma_{sp}$ ), and CO measured at MBO during a type 3 (MBL) high-RGM event in spring 2011. All data are 1-h averages, except RGM and RGM/GEM-ratios that are 3-h averages (resolution of the RGM measurement). Measurements of RGM are plotted for each hour of collection.

### 3.3 Particle bound mercury (PBM)

During the measurement period (2005–2011) the PBM concentrations were usually low (below  $30 \text{ pg m}^{-3}$ ) in the FT. Elevated PBM concentrations ( $30\text{--}45 \text{ pg m}^{-3}$ ) were mainly observed during biomass burning episodes (Finley et al., 2009), when the emissions originated from the boundary layer. During RGM events described in this paper PBM concentrations were low ( $< 15 \text{ pg m}^{-3}$ ), amounting to less than 15 % of RM ( $= \text{RGM} + \text{PBM}$ ). The contribution of PBM is clearly lower than expected based on RM partitioning coefficients derived from measurements in the BL at low altitude sites (Rutter and Schauer, 2007b; Amos et al., 2012). However, previous studies have demonstrated that partitioning of RM (and other semivolatile species) between the gas and aerosol phase depends on conditions such as temperature (Rutter and Schauer, 2007b; Amos et al., 2012); aerosol concentration and composition (Rutter and Schauer, 2007a; Amos et al., 2012); and possibly also relative humidity (Pankow et al., 1994; Xiu et al., 2009; Kim et al., 2012). Furthermore, previous studies suggest that heterogeneous reactions at surfaces potentially play a key role in Hg chemistry (Subir et al., 2012). The conditions in the FT (e.g., dry air; low temperature and pressure; high solar radiation intensity; Jaffe et al., 2005; Weiss-Penzias et al., 2006), are substantially different than in the boundary layer; therefore, RM partitioning behavior likely also differs between the FT and BL. If partitioning of RM to PBM is enhanced in the presence of an aerosol aqueous phase, the lower relative humidity in the FT will likely favor partitioning of RM to RGM more so than in the BL. Also, due to below freezing temperatures in the free troposphere, it is likely that aerosol particles will incorporate ice rather than liquid water. Although the interfa-

cial chemistry of Hg on ice surfaces is poorly known (Subir et al., 2012), it appears that the uptake of RGM to ice is less efficient than for liquid water (Sigler et al., 2009). We note that previous studies have also measured low PBM concentrations in the free troposphere (Murphy et al., 2006).

### 3.4 Oxidation mechanisms

Oxidation of Hg<sup>0</sup> in the atmosphere is not well understood (Calvert and Lindberg, 2005; Hynes et al., 2009). For instance, the gas-phase oxidation of Hg<sup>0</sup> by O<sub>3</sub>, hydroxyl radical (HO<sup>•</sup>), or nitrate radical (NO<sub>3</sub><sup>•</sup>) is expected to be negligibly slow under atmospheric conditions (Calvert and Lindberg, 2005; Hynes et al., 2009; Dibble et al., 2012); however, laboratory kinetics studies consistently indicate that a gas-phase mechanism exists for O<sub>3</sub> and that the associated kinetics can be treated as second order (Rutter et al., 2012). In light of apparent inconsistencies between the results of past experimental and computational studies, it has been suggested that Hg<sup>0</sup> oxidation mechanisms may be mediated by complex or unstable intermediate species and by surfaces (Tossell, 2003, 2006; Hynes et al., 2009; Subir et al., 2011, 2012).

Gaseous halogen species, in particular bromine atom (Br<sup>•</sup>), likely play an important role in atmospheric Hg<sup>0</sup> oxidation (Ariya et al., 2002, 2004; Tossell, 2003; Goodsite et al., 2004, 2012; Hedgecock and Pirrone, 2004; Donohoue et al., 2006; Murphy et al., 2006; Holmes et al., 2009, 2010; Hynes et al., 2009; Obrist et al., 2010; Mao et al., 2010; Stephens et al., 2012). There exists some observational evidence that bromine oxide (BrO<sup>•</sup>) may also be an important Hg<sup>0</sup> oxidant under some conditions, although theoretical predictions suggest that a purely gas-phase mechanism is unlikely (Tossell, 2003, 2006; Raofie and Ariya, 2004; Shepler et al., 2007; Stephens et al., 2012; Tas et al., 2012). Recent computational work suggests that the HgBr radical formed in the initial step of gas-phase Br-initiated Hg<sup>0</sup> oxidation is much less stable against thermal dissociation than previously estimated, but can form stable products with more atmospheric radicals than previously considered (Dibble et al., 2012; Goodsite et al., 2012). While the kinetics of Br-initiated Hg<sup>0</sup> oxidation is better understood than for O<sub>3</sub>, HO<sup>•</sup>, and NO<sub>3</sub><sup>•</sup>, the global distribution of Br radicals is highly uncertain.

The three main sources of RGM observed at MBO represent contrasting air mass types: dry upper tropospheric air with high O<sub>3</sub> and RGM concentrations (type 1); aged Asian anthropogenic emissions with elevated Hg concentrations (type 2); and clean air with background Hg and a potential contribution from natural oceanic emissions (type 3). Thus, it is likely that the oxidation mechanisms converting GEM to RGM are different in each case. Production of RGM in type 1 events (Swarzendruber et al., 2006) is likely associated in part with Br<sup>•</sup> chemistry in the UT/LS region, where the abundance of Br<sup>•</sup> is expected to be large and cold temperatures favor the stability of HgBr<sup>•</sup> (Goodsite et al., 2004,

2012; Holmes et al., 2010; Lyman and Jaffe, 2011; Dibble et al., 2012; Parrella et al., 2012).

During the ALRT events (type 2) the occurrence of simultaneous increases in RGM and tracers of anthropogenic pollution (CO or  $\sigma_{sp}$ ) suggests that the oxidant responsible for RGM production might also be associated with anthropogenic pollution, although the mechanisms are unclear. Ozone, HO $\cdot$ , and NO $_3\cdot$  may all play a role in Hg $^0$  oxidation during these events. We note that halogen chemistry could also contribute to the RGM associated with type 2 events. For instance, previous studies have indicated that chlorine atom (Cl $\cdot$ ) can be generated from the interaction of pollution plumes with chloride (Cl $^-$ ) containing aerosols, and this process is known to enhance the oxidizing capacity of the atmosphere (Lawler et al., 2009; Thornton et al., 2009). Oxidation via heterogeneous chemistry involving aerosol particles is also a possible mechanism (Subir et al., 2012), and would be consistent with the observed correlation between the RGM and aerosol concentrations.

For type 3 (MBL) events a clear anti-correlation between RGM and O $_3$  was observed, indicating that O $_3$  is not likely to be the primary oxidant. Also, as these events are only seen in clean air masses, it seems unlikely that the oxidant would have an anthropogenic origin (e.g., NO $_3\cdot$ ). We believe reactive halogens are the most likely oxidants, although O $_3$ /HO $\cdot$  cannot be entirely ruled out. Zonally averaged HO $\cdot$  concentrations during spring and summer are largest in the lower troposphere at northern mid-latitudes (Spivakovsky et al., 2000). Modeled Hg $^0$  oxidation is also greatest in this region when HO $\cdot$  and O $_3$  are assumed to be the only oxidants (Holmes et al., 2010). For the MBL events, air mass backward trajectories consistently indicate transport from low latitudes in the lower FT and MBL of the North Pacific. In the marine boundary layer, RGM enhancements have been reported (Laurier and Mason, 2007; Chand et al., 2008; Holmes et al., 2009), but these never reached the levels we observed in the FT. A possible explanation for the very high RGM concentrations observed during MBL events at MBO is that RGM that accumulates on aqueous super-micron sea-salt aerosol in the MBL (Rutter and Schauer, 2007a; Malcolm et al., 2009) subsequently partitions back to the gas phase when lofted to the lower FT. This would occur if lower relative humidity in the FT, and subsequent evaporation of the aerosol aqueous phase, also favors partitioning of water-soluble sea salt-bound PBM to RGM. Furthermore, low relative humidity in the FT would favor partitioning of halogens to the gas phase, due to evaporation of the aerosol aqueous phase and associated decrease in pH (Lawler et al., 2009, 2011), potentially facilitating gas-phase Hg $^0$  oxidation reactions during transport in the FT.

## 4 Conclusions

Mercury is an important global pollutant, with a complex atmospheric cycle. Current models provide a rough outline of the global budget, but the atmospheric chemistry is poorly understood. Studies in the FT are needed to fully understand the global transport and chemical cycle of Hg. Using long-term Hg observations at the Mt. Bachelor Observatory we have identified two sources of RGM in the atmosphere, which suggest stronger coupling between BL emissions and FT oxidation than previously recognized. For type 2 events, Hg and its oxidants (or oxidant precursors) are likely first lofted from the Asian BL to the FT. Subsequently, GEM is effectively converted to RGM in the FT on relatively short timescales (several days) during long-range transport to downwind regions. The RGM generated will eventually be entrained back to the BL (Lyman and Gustin, 2009; Weiss-Penzias et al., 2009), deposited and incorporated to biota. For type 3 events, Hg $^0$  oxidation by halogens – possibly mediated by sea salt aerosol in the MBL – or O $_3$ /HO $\cdot$  results in very high RGM that can subsequently undergo long range transport in the FT. We believe also that changes in RM gas-particle partitioning during transport could also contribute to the high observed RGM concentrations during MBL events. Results of this study offer new directions for process oriented studies of the atmospheric mercury cycle.

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