

The influence of ozone on atmospheric emissions of gaseous elemental mercury and reactive gaseous mercury from substrates

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Abstract

Experiments were performed to investigate the effect of ozone (O_3) on mercury (Hg) emission from a variety of Hg-bearing substrates. Substrates with Hg(II) as the dominant Hg phase exhibited a 1.7 to 51-fold increase in elemental Hg (Hg^0) flux and a 1.3 to 8.6-fold increase in reactive gaseous mercury (RGM) flux in the presence of O_3 -enriched clean (50 ppb O_3 ; 8 substrates) and ambient air (up to 70 ppb O_3 ; 6 substrates), relative to clean air (oxidant and Hg free air). In contrast, Hg^0 fluxes from two artificially Hg⁰-amended substrates decreased by more than 75% during exposure to O_3 -enriched clean air relative to clean air. Reactive gaseous mercury emissions from Hg⁰-amended substrates increased immediately after exposure to O_3 but then decreased rapidly. These experimental results demonstrate that O_3 is very important in controlling Hg emissions from substrates. The chemical mechanisms that produced these trends are not known but potentially involve heterogeneous reactions between O_3 , the substrate, and Hg. Our experiments suggest they are not homogeneous gas-phase reactions. Comparison of the influence of O_3 versus light on increasing Hg^0 emissions from dry Hg(II)-bearing substrates demonstrated that they have a similar amount of influence although O_3 appeared to be slightly more dominant. Experiments using water-saturated substrates showed that the presence of high-substrate moisture content minimizes reactions between atmospheric O_3 and substrate-bound Hg. Using conservative calculations developed in this paper, we conclude that because O_3 concentrations have roughly doubled in the last 100 years, this could have increased Hg^0 emissions from terrestrial substrates by 65–72%.

1. Introduction

Volatilization of mercury (Hg) from natural substrates (i.e., soils and rocks) has been shown to be a significant source of atmospheric Hg (McCarthy, 1972; Zhang et al., 2001; Gustin, 2003). Understanding the magnitude and mechanisms controlling these emissions is necessary for predicting the effectiveness of controls on anthropogenic sources (e.g., coal-fired power plants and chloralkali plants). In an effort to estimate Hg emissions from natural sources, several studies have tried to model Hg emissions from substrates (Scholtz et al., 2003; Tsiros and Dimopoulos, 2003; Bash et al., 2004). These models rely on an understanding of the dominant controls on Hg emission. Previous studies have identified light intensity (Gustin et al., 2002; Bahlmann et al., 2004a), temperature (Poissant et al., 1999), and soil moisture (Bahlmann et al., 2004b; Gustin and Stamenkovic, 2005) as being highly correlated with elemental Hg (Hg^0) flux and the most influential parameters. Concentrations of reactive gaseous mercury (RGM), oxidized forms of gaseous mercury (e.g., $HgCl_2$, $HgBr_2$, HgO), are also positively correlated with these parameters suggesting that they similarly influence emission and/or RGM formation (Lindberg and Stratton, 1998; Poissant et al., 2004). It is noteworthy that the exact chemical structures of molecules classified as RGM are yet to be confirmed. Diel Hg^0 flux from natural substrates generally follows the daily pattern of light intensity with low fluxes in early morning, peaking at midday, and then declining with sunset (Gustin, 2003). However, Zhang and Lindberg (1999) observed similar temporal variations of Hg^0 emission from soil samples during exposure to ambient air in a dark, constant temperature laboratory environment and suggested soil surface exchange with an unknown chemical substance in ambient air. During laboratory experiments similar to Zhang and Lindberg's, we observed several large releases of Hg^0 from a sample of mine tailings that correlated strongly ($R^2 = 0.98$; $p < 0.05$) with concentrations of ozone (O_3) in the incoming ambient air. These results prompted further study of substrates containing different Hg species exposed to air sources with varied chemistry under controlled conditions. This paper presents the results of this work.

2. Methods

Elemental Hg and RGM fluxes were measured from eight dry substrates (75–150 g; 60 cm² surface area) placed in 10 cm diameter petri dishes using a 13.5 L (3400 cm² surface area) dynamic Plexiglas gas exchange chamber (Fig. 1). Airflow through the chamber was 20–71 L min⁻¹ for all experiments resulting in a residence time of 38 s. Natural and synthetic Hg(II)-bearing and Hg⁰-amended substrates were used. A description of the substrates is provided in Table 1. Samples were exposed to clean air (oxidant and Hg free), O_3 -enriched (50–72 ppb) clean air, and ambient Reno, Nevada, USA, air (0 to 70 ppb O_3) for 24 h exposures except for the Hg⁰-1 sample (See Table 1), which was only exposed to clean

air for 12 h. Experiments were conducted in the dark at near constant chamber temperature (22.5 ± 1 °C). Ambient air was pulled from outside the laboratory using PTFE tubing. To avoid removal of tropospheric oxidants in ambient air during transport into the chamber, no pump or particle filter was placed in inlet lines. However, the travel time through the PTFE tube (~0.5 s) was long enough that some atmospheric oxidants were probably removed (e.g., HO₂ Levievel et al., 2004).

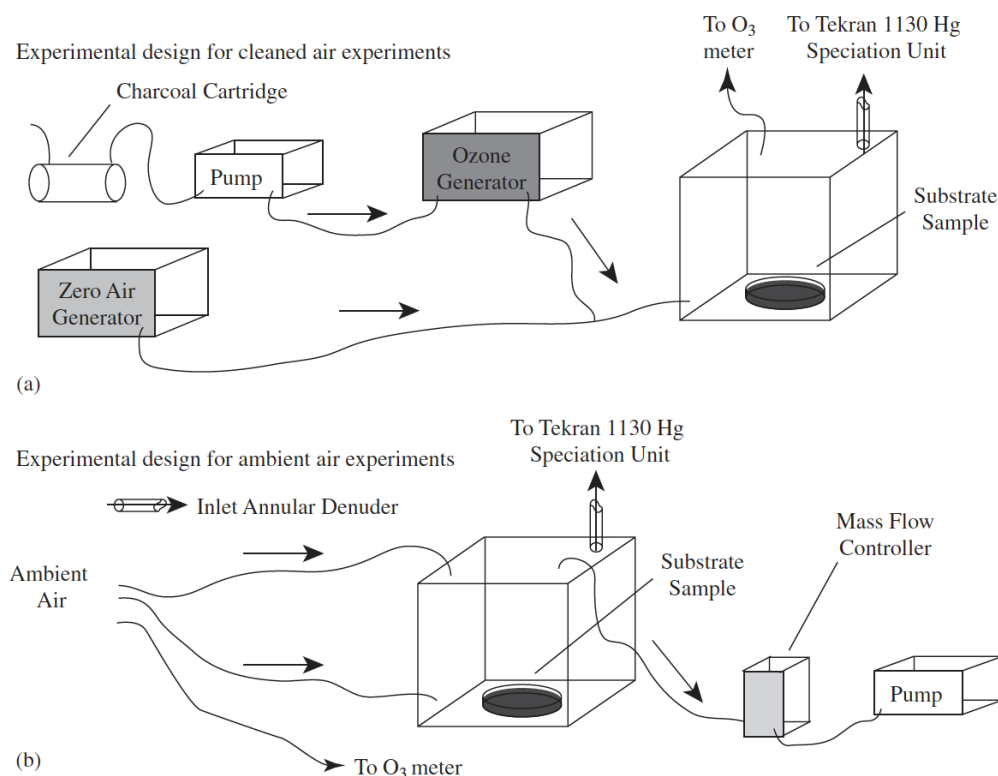


Fig. 1. Experimental design of the dynamic flux chamber for (a) clean air and (b) ambient air experiments.

Table 1
Description and mercury concentration of substrates used in study

Substrate	Description	Total Hg (ng g ⁻¹)
<i>Hg(II)-bearing substrates</i>		
Enriched-1	Naturally Hg-enriched mine waste (dominated by HgS). Hydrothermally altered andesite, Washington Hill prospect, Nevada, USA	229,000
Enriched-2	Fe-Ag-S associated Hg in mine tailings ^a , Bessel Mill, Carson River Superfund Site, Nevada, USA	347,000
Unenriched-1	Mollisol soil from Norman, Oklahoma, USA	5
Unenriched-2	Aridisol soil from Washoe County, Nevada, USA	18
Synthetic-HgCl ₂	Clean quartz sand (Fisher brand) amended with HgCl ₂ (Aldrich, CAS no. 7487-94-7)	313
Synthetic-HgS	Clean quartz sand (Fisher brand) amended with HgS (Aldrich, CAS no. 1344-48-5)	24,400
<i>Hg⁰-amended substrates</i>		
Hg ⁰ -1	Natural beach sand from Pyramid Lake, Nevada amended with Hg ⁰ (Fisher brand, CAS no. 7439-97-6)	21,000
Hg ⁰ -2	Clean quartz sand (Fisher Brand) amended with Hg ⁰ (Fisher brand, CAS no. 7439-97-6)	420,000

^aSubstrate mercury speciation described in Sladek and Gustin, (2003).

Clean air was generated using an Aadco pure air generator (model 737R-10) or iodated charcoal filters (Hg and O₃ concentrations were less than the detection limits of the respective analyzers). Purity specifications for the Aadco pure air generator are 0.1 ppb O₃, hydrocarbons, CH₄, NO_x, H₂S, SO₂, COS, CO, CO₂, SF₆, and fluorocarbons. Ozone was

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supplied via an O₃ generator developed by the Desert Research Institute, Reno, Nevada. Concentrations of Hg⁰ and RGM in the chamber were measured using a Tekran 2537A CVAFS Hg analyzer in conjunction with a Tekran 1130 gaseous Hg speciation unit (Landis et al., 2002). This system measured concentrations of Hg⁰ in 5 min intervals in air after it passed through a KCl-coated annular denuder that collected RGM. After 90 min of sampling Hg⁰, the denuder was heated to 550 °C and RGM trapped on the denuder was released as Hg⁰ into the Tekran 2537A through an automated process (Landis et al., 2002). No Hg was collected from the flux chamber during the 30-min RGM analysis and a counter flow of air from the 1130 unit back into the chamber changed the flow dynamics. The first Hg⁰ concentration measured after the RGM analysis process was removed allowing for the chamber to equilibrate.

Fluxes were calculated using the following equation:

$$F = \frac{Q(C_o - C_i)}{A}$$

where F is the flux of Hg⁰ (ng m⁻² h⁻¹) or RGM (pg m⁻² h⁻¹), C_o is the concentration of Hg⁰ (ng m⁻³) or RGM (pg m⁻³) at the outlet of the chamber, C_i is the concentration of Hg⁰ (ng m⁻³) or RGM (pg m⁻³) at the inlet of the chamber, and A is the surface area of the substrate sample (m²). Positive fluxes represent net emission from the substrate while negative fluxes indicate that Hg is being deposited. For data collected during exposure to clean and O₃-enriched clean air, a C_i of 0 was used because RGM and Hg⁰ concentrations in clean air were below detection. During exposures to ambient air, the Hg⁰ C_i used was an average of the previous 24-h-air concentrations, because a second Tekran Hg analyzer was not typically available to simultaneously measure Hg concentrations in the incoming ambient air. The exception was the experiment with the unenriched-1 substrate where a second Tekran Hg analyzer was used to simultaneously measure ambient air Hg⁰ concentrations. Ambient air concentrations were <20% of Hg⁰ (24-h-averages = 1.82 ± 0.31 to 4.01 ± 1.66) measured in an air chamber during exposure of substrate samples, except for the unenriched-1 substrate where they accounted for 490% of the Hg⁰ measured in the chamber outlet. Twelve-hour average concentrations of RGM were determined using manual denuders for collection of RGM at the chamber inlet during ambient air experiments (cf. Landis et al., 2002). Ambient air RGM concentrations (12-h integrated averages 3–98 pg m⁻³) were less than 20% of the RGM measured in the chamber except for the Hg⁰-1 substrate experiment when they approached 50%. Reactive gaseous mercury concentrations measured simultaneously in ambient air (annual denuders) and the empty chamber (Tekran 1130 unit) were not significantly different ($p < 0.01$), indicating that negligible RGM was lost during transport into the chamber.

To verify that RGM measured inside the chamber was being emitted from the substrates and was not forming in the chamber via a homogenous reaction between O₃ and Hg⁰, gaseous Hg⁰ from a Dynacal permeation tube was introduced to the chamber with clean and ambient air. Elemental Hg concentrations in the chamber for these experiments were, ~25 ng m⁻³ (clean air), ~100 ng m⁻³ (ambient air), and ~330 ng m⁻³ (clean air). The presence of O₃ had no effect on the concentrations of Hg⁰ or RGM measured ($p > 0.01$). This agrees well with kinetic data that indicate the homogenous gas-phase reaction is relatively slow (Hg⁰ lifetime 12.5 days assuming [O₃] 50 ppb; Pal and Ariya, 2004).

All data were corrected for the chamber blank measured 8 h prior to each experiment (Hg⁰ flux blank 2.5–75.1 ng m⁻² h⁻¹; RGM flux blank 25–724 pg m⁻² h⁻¹). Because Hg⁰ and O₃ both absorb light at 254 nm, we tested for false-positives on the Tekran 2537A analyzer by sampling Hg-free O₃-enriched air; no Hg⁰ was detected by the analyzer. The Tekran 2537A analyzer was calibrated weekly using an internal permeation source or manual injections of Hg⁰. Efficiency of the gold traps in the instruments was checked regularly by running standard additions of Hg⁰ in ambient air, particularly when two Tekrans were concurrently used. Replicates of enriched-1, enriched-2, synthetic-HgCl₂, and Hg⁰-2 exposures to clean and O₃-enriched clean air and enriched-1, enriched-2, and synthetic-HgCl₂ exposures in ambient air exhibited similar fluxes and responses, indicating a precision for our experiments of 490% for clean and O₃-enriched clean air experiments to 465% for ambient experiments.

Temperatures (Vaisala CS500) inside the chamber were monitored and collected in 5 min intervals using a Campbell Scientific CR21X or CR10X datalogger. Ozone concentrations were measured using a laboratory-calibrated Monitor Labs Model 8810 O₃ analyzer and collected in 5 min intervals. Ozone concentrations during experiments using O₃-enriched clean air were near constant, deviating less than 2 ppb over 24 h. Total Hg content of substrates was determined using thermal decomposition and cold vapor atomic absorbance spectrophotometry using a Milestone DMA-80 (EPA method 7473) or aqua regia digestion and cold vapor atomic absorbance using a Varian SpectraAA model 220 (EPA method 245.5). Standard reference material NIST San Joaquin standard no. 2709 was used to check instrument calibration and recovery; precision ranged from 91–105% ($n = 4$).

One set of experiments using the enriched-1 substrate exposed to clean and O₃-enriched clean air were run in the dark and in the light. The light passing through the chamber ranged from 315 to 900 nm. Light intensity was 500 W m⁻² inside the chamber (Li-Cor LI200). Although an external fan was applied to cool the chamber, air inside the chamber increased from ~23 °C in the dark to 28 °C when the light was applied. The experiment was replicated and similar patterns were observed for both experiments.

To examine the influence of soil moisture, the enriched-1 substrate sample was fully saturated (70% water by weight)

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with ultraclean water (Milli-Q[®] 18.2 mO, Hg 0.1 ng L⁻¹) and placed into the dynamic flux chamber for 24 h and exposed to clean air. At the end of the 24-h period, the substrate sample was re-saturated to the original soil moisture (70%) and O₃ was added to the chamber for another 24 h. A replicate of this experiment produced similar results.

Statistical tests were run using Stata 8 and Vista[™] 6.4. Non-parametric Mann–Whitney tests were used to determine significant differences between unpaired datasets ($p < 0.01$). Twenty-four hour integrated Hg emissions were calculated using an iterative trapezoidal method model (tolerance < 0.01 , QtiPlot).

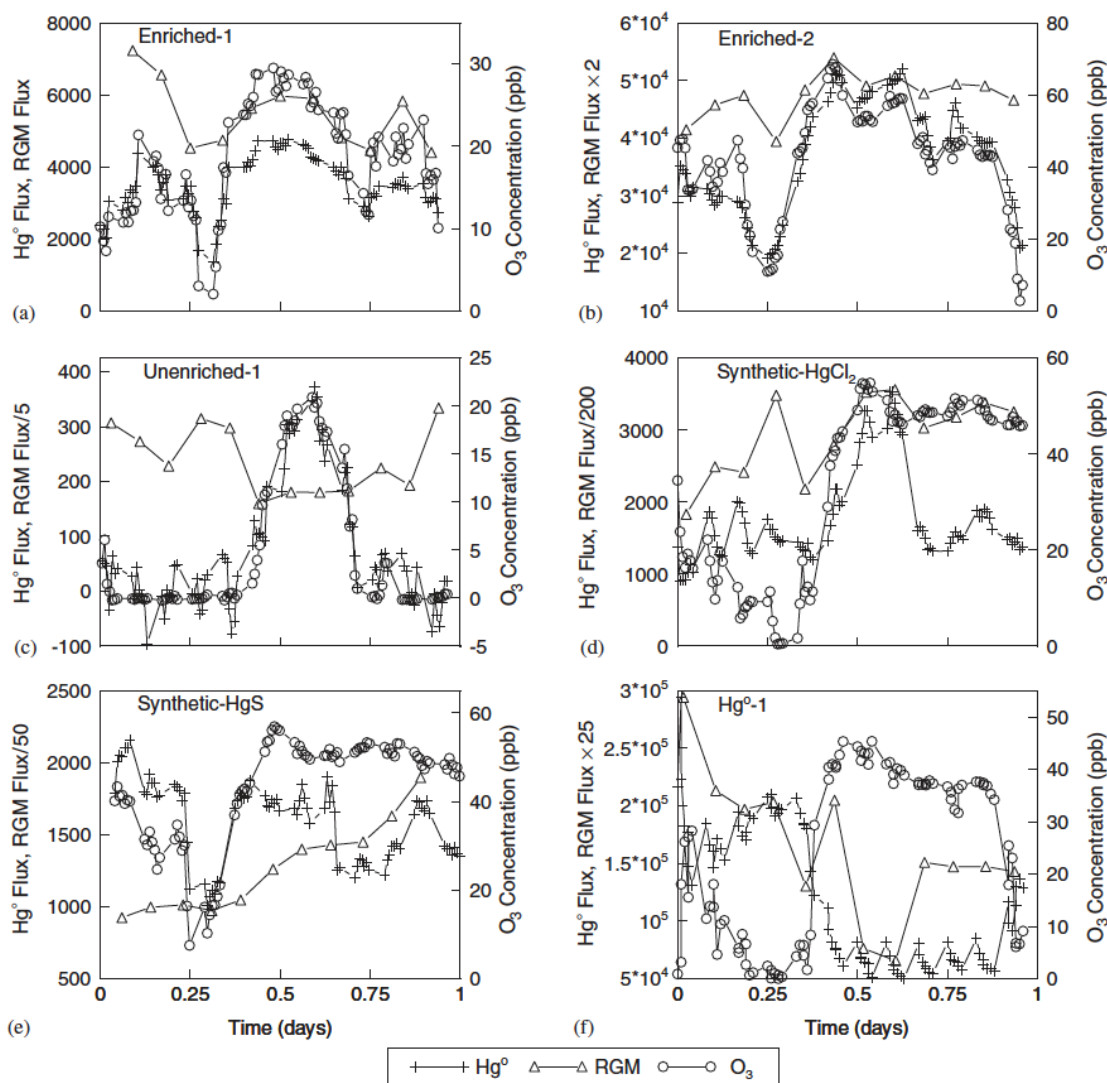


Fig. 3. Elemental mercury and RGM fluxes during exposure of $\text{Hg}(\text{II})$ -bearing (e-f) and Hg° -amended sand substrates (f) to ambient air. Concentrations of O_3 in ambient air, shown on right y-axis. Data corrected for chamber blanks and ambient air concentrations of Hg° and RGM. Experiments started at midnight. Replicate experiments showed a precision of $>65\%$. Scales vary between plots.

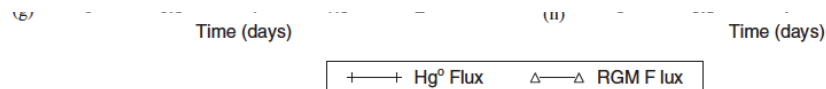


Fig. 2. Elemental mercury and RGM fluxes during exposure of $\text{Hg}(\text{II})$ -bearing (a-f) and Hg° -amended substrates (g,h) to clean air, followed by O_3 -enriched clean air. Descriptions of substrates provided in Table 1. Data to the left of the gray vertical bar collected in clean air while data to the right were collected in O_3 -enriched air (50 ppb). Cyclic patterns in the Hg° data are a result of changes in the turnover rate in the chamber due to reduced air-flow during denuder analysis. Replicate experiments showed a precision of $>90\%$. Scales vary between plots.

3. Results

Fluxes of Hg⁰ and RGM measured for eight substrate samples during exposure to clean air for 24 h (except for the Hg⁰-1 substrate which was only exposed to clean air for 12 h) followed by a 24 h exposure to O₃-enriched clean air are shown in Fig. 2. Reactive gaseous mercury flux data points are plotted in the middle of each 90 min integrated sampling period. Elemental mercury and RGM flux for six of the substrates during exposure to ambient air over a 24 h period are shown in Fig. 3.

All five Hg(II)-bearing substrates showed a significant ($p < 0.01$) 1.8 to 45-fold increase in Hg⁰ emissions (24 h average) during exposure to O₃-enriched clean air relative to clean air alone (Figs. 2a–f, Table 2). The high-Hg substrates (enriched-1, enriched-2, synthetic-HgCl₂, and synthetic-HgS) exhibited an immediate large release of Hg⁰ with an initial O₃ exposure and then an asymptotic decline to a flux elevated above pre-exposure fluxes. Fluxes from the two low-Hg substrates (unenriched-1 and unenriched-2) exhibited a similar response but the data are more variable due to low Hg⁰ concentrations in the chamber. Termination of O₃ exposure produced an almost immediate decrease in Hg⁰ emissions (data not shown).

Table 2
 Twenty-four-hour integrated emission of Hg⁰ and RGM fluxes from substrates during exposure to different air sources

	Hg ⁰ flux in clean air (ng d ⁻¹)	Hg ⁰ flux in clean air w/ O ₃ (ng d ⁻¹)	Hg ⁰ flux in ambient air (ng d ⁻¹)	R ² value Hg ⁰ flux vs O ₃ ^a (for ambient air)	RGM flux in clean air (pg d ⁻¹)	RGM flux in clean air w/ O ₃ (pg d ⁻¹)	RGM flux in ambient air (pg d ⁻¹)
<i>Hg(II)-bearing substrates</i>							
Enriched-1	25	450 ^b	480 ^b	0.88 ^d	280	1,700 ^b	720 ^b
Enriched-2	98	840 ^b	5000 ^b	0.83 ^d	580	780 ^b	3200 ^b
Unenriched-1	3.6	8.4 ^b	10 ^b	0.88 ^d	1300	2300 ^b	160 ^c
Unenriched-2	7.1	12 ^b	—	—	200	270 ^b	—
Synthetic-HgCl ₂	52	210 ^b	240 ^b	0.22 ^d	25,000	91,000 ^b	81,000 ^b
Synthetic-HgS	5.2	230 ^b	210 ^b	0.04	1100	9100 ^b	9000 ^b
<i>Hg⁰-amended substrates</i>							
Hg ⁰ -1	28,000	1900 ^c	16,000 ^c	0.83 ^d	1200	810	870
Hg ⁰ -2	9800	2300 ^c	—	—	2000	2600 ^b	—

^aCorrelation between O₃ concentrations and Hg⁰ flux during exposure to ambient air.

^bIndicates flux is significantly greater than flux for the same substrate in clean air ($p < 0.01$).

^cIndicates flux is significantly smaller than flux for the same substrate in clean air ($p < 0.01$).

^dSignificant at $p < 0.01$.

Elemental mercury emissions from Hg(II)-bearing substrate samples exposed to ambient air were also significantly greater ($p < 0.01$) than those measured during contact with clean air, except for the unenriched-2 substrate (Table 2, Figs. 3a–e). A significant correlation ($p < 0.01$) between Hg⁰ fluxes and ambient O₃ concentrations was observed for all Hg(II)-bearing substrates except for synthetic-HgS (Table 2).

Exposure of the substrates to O₃-enriched clean air produced RGM emissions that were 1.3 to 8.6 times greater than those measured in clean air ($p < 0.01$). Reactive gaseous mercury emissions increased immediately with initial exposure to O₃ then either continued to increase slightly (Figs. 2a,f) or decreased asymptotically to a lower but still elevated flux (Figs. 2b–e). During exposure to ambient air, RGM fluxes measured from all of the Hg(II)-bearing substrates, except for the unenriched-1 substrate, were significantly greater than those observed in clean air although ambient O₃ concentrations and RGM flux were often only weakly correlated.

Unlike the Hg(II)-bearing substrates, exposure of Hg⁰-amended substrates to O₃ in clean air resulted in immediate reduction in Hg⁰ emissions by 75–92% ($p < 0.01$, 24 h average) relative to those measured in clean air (Figs. 2g–h, Table 2). This reduction in emission exhibited a pattern of asymptotic decrease with continued O₃ exposure. Upon termination of O₃ contact with the Hg⁰-2 substrate, Hg⁰ emissions quickly returned to pre-O₃ exposure values (data not shown). A similar decrease in Hg⁰ flux with increasing O₃ concentrations (r^2 0.88, $p < 0.01$) was also observed during ambient air exposures of the Hg⁰-1 substrate sample (Fig. 3f, Table 2).

Exposure of Hg⁰-amended sands to O₃ in clean air produced an immediate pulse of RGM followed by an asymptotic decrease to lower fluxes. The resulting RGM fluxes from the Hg⁰-2 substrate sample were significantly larger during exposure to O₃ than in clean air ($p < 0.01$) but were not significantly different for the Hg⁰-1 substrate sample ($p < 0.01$). Reactive gaseous mercury fluxes did not vary significantly between ambient air and clean air exposures ($p < 0.01$) and were fairly insensitive to changes in ambient concentrations of O₃.

Greater emissions of Hg⁰ and RGM were observed from the enriched-1 substrate in light with clean and O₃-enriched clean air than in the dark (Fig. 4). In the presence of O₃, change from dark to light conditions produced a large initial spike in Hg⁰ and RGM emissions both of which decreased quickly. Based on a Mann–Whitney test, the measured Hg⁰ fluxes in the presence of O₃ and light were not significantly statistically different ($p < 0.05$, ~3% increase) than from those measured in O₃ and dark (Fig. 4). In contrast, adding O₃ during exposure of the sample to light produced a 5.7-fold increase in Hg⁰

flux. This suggests that for this substrate, O_3 is a more important factor controlling emissions than light.

Emissions of Hg^0 and RGM in clean air from the water-saturated enriched-1 substrate were significantly less than those from the dry substrate (Fig. 5). As water evaporated and average substrate moisture content decreased from 70% to 42% and the immediate surface became dry, emissions increased to greater than those observed during dry conditions. At the end of the 24 h exposure to clean air, the substrate sample was re-saturated and O_3 was added to the chamber. Initially, emissions of Hg^0 and RGM were greatly inhibited as in clean air; however, as water evaporated from the substrate such that it was no longer saturated, fluxes increased to well above those observed when the sample was dry and continued to increase as the water content in the sample decreased.

4. Discussion

The enhanced emission of Hg^0 from $Hg(II)$ -bearing substrates observed in the presence of O_3 -enriched clean and ambient air relative to clean air (Figs. 2a–f, 3a–e; Table 2) demonstrates that O_3 interaction with the substrate either increases the conversion rate of $Hg(II)$ to Hg^0 which is subsequently emitted or promotes the volatilization of existing Hg^0 . As previously discussed in the methods section, heterogeneous reaction of Hg^0 with O_3 to produce RGM and false-positives of O_3 on the Tekran 2537A Hg analyzer were shown to not occur in these experiments.

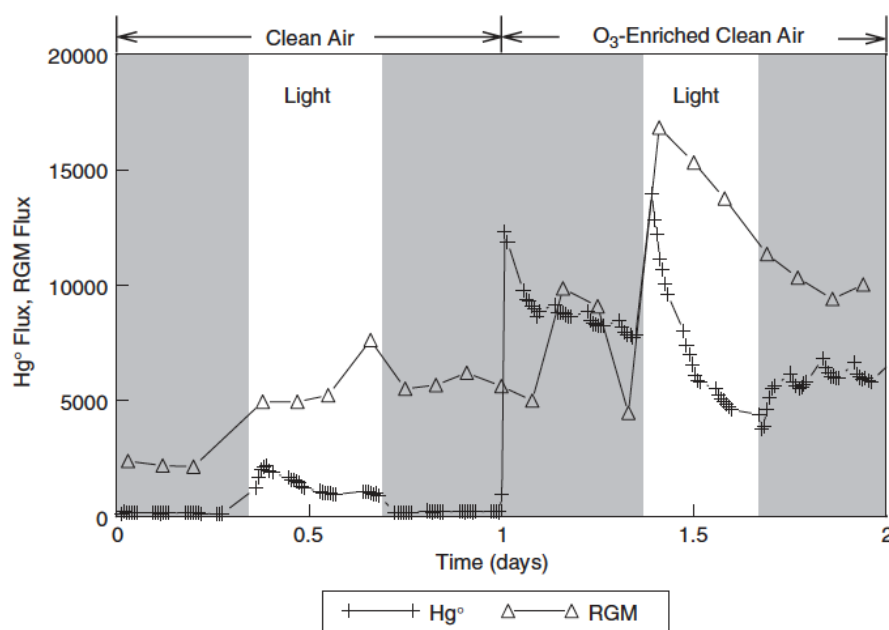


Fig. 4. Elemental mercury and RGM fluxes during exposure of the enriched-1 substrate to clean air, followed by O_3 -enriched air with and without the presence of light. Periods, when the sample was exposed to light, are denoted by the white background.

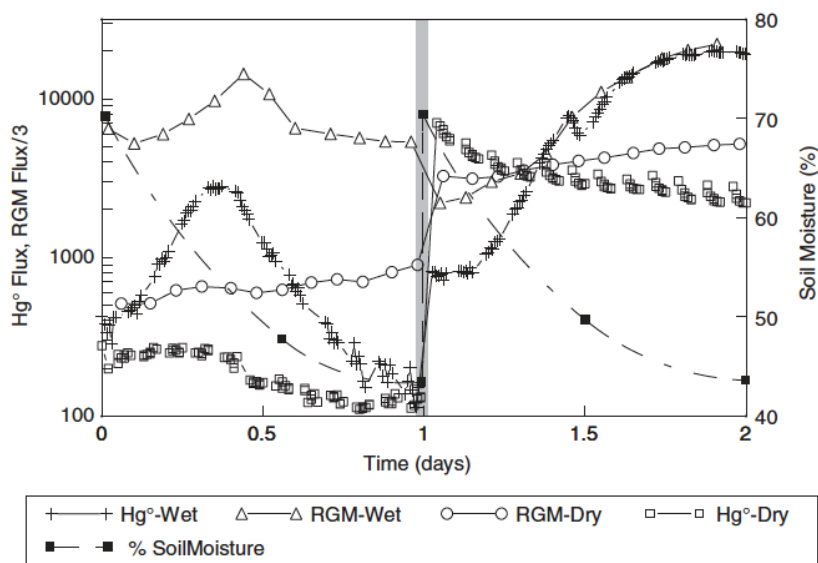


Fig. 5. Elemental mercury and RGM fluxes during exposure of the water-saturated enriched-1 substrate to clean air, followed by O₃-enriched air. Gray vertical bar indicates when 50 ppb O₃ was introduced to chamber and the sample was resaturated. The Hg°-dry and RGM-dry data were collected when the substrate sample was air dry while the Hg°-wet and RGM-wet data collected when the substrate was exposed to water.

For all but the synthetic-HgCl₂ sample, the Hg(II)-bearing substrates used in this study contained Hg(II) principally bound to reduced sulfur [S²⁻] (Table 1). Other research has shown that O₃ catalytically decomposes on substrate surfaces and can potentially oxidize reduced species, including sulfur, through heterogeneous reactions (Oyama, 2000; Ullerstam et al., 2002; Michel et al., 2003; Usher et al., 2003). The oxidation of S has been shown to be counterbalanced by the reduction of Hg(II) to Hg⁰ in the aqueous phase (Munthe et al., 1991). Similar reactions may be occurring on these substrate surfaces where O₃ is oxidizing the S²⁻ in HgS molecules and the oxidized S species are reducing Hg(II) to Hg⁰, but the exact mechanism is not known. Because emission increases, Hg⁰ formed from this process is also transported across the substrate–air interface for Hg⁰ in substrate appears to be oxidized and immobilized as discussed below. The source of increased emissions of Hg⁰ from synthetic-HgCl₂ substrate in the presence of O₃ is not known. However, it is unlikely to be a similar reaction based on the near complete lack of reaction between O₃ and dry salt-bound Cl observed in experimental settings similar to those of our system (Alebic-Juretic et al., 1992).

A second possible hypothesis is that O₃ is displacing Hg⁰ from the surface of these substrates increasing emissions. Elemental mercury is thought to be created from Hg(II)-bearing minerals via photo-reduction and other reductive processes (Carpi and Lindberg, 1997). A similar displacement mechanism involving water molecules displacing surface-bound Hg⁰ has been cited as a mechanism for increased emission of Hg from desert soils during precipitation events (Lindberg et al., 1999). However, results from the reaction of the Hg⁰-amended substrates show that O₃ inhibits Hg⁰ emissions. This suggests that either this mechanism is not occurring or differences in the distribution and/or behavior of the Hg⁰ in Hg(II)-bearing versus the Hg⁰-amended substrates used influenced their reaction with O₃.

During exposure to a near constant concentration of O₃, the Hg(II)-bearing substrates often exhibited a pattern of an immediate large release of Hg⁰ with initial O₃ exposure, and then an asymptotic decline to a lower flux (Figs. 2a–f). There are two potential explanations for this pattern. Michel et al. (2003) reported an initial high-uptake rate of O₃ on mineral dusts with a decline over time during multiple hour exposures. Michel et al. (2003) and Oyama (2000) suggested that after the initial exposure of the substrate surface to O₃, a significant fraction of the active sites became deactivated with initial coverage by O₃ and/or accumulation of slowly decaying peroxide complexes. In our experiment, a similar process could occur with the pool of available Hg⁰ or easily reducible Hg(II) on the substrate surface becoming unavailable for emission by accumulation of O₃ and surface-oxygen complexes that saturate surface sites. After periods of low-O₃ exposure, Oyama (2000) found that the surface sites become available again. Variations of Hg⁰ emissions in ambient air following O₃ trends suggest that this may also occur. A second potential mechanism for the observed trends in the data is that the available reservoir of Hg⁰ and/or easily reducible Hg(II) is relatively small and is depleted during extended periods of high-O₃

exposure. During periods of low- O_3 exposure the reservoir of Hg available for release may be regenerated, by such processes as atmospheric deposition or movement of Hg^0 to the surface.

The strong relationship between ambient air O_3 concentrations and Hg^0 fluxes for the enriched-1, enriched-2, unenriched-1, and unenriched-2 Hg(II)-bearing samples in ambient air (Figs. 3a–c; Table 2) suggests that tropospheric O_3 concentrations could have control on Hg^0 emissions from Hg(II)-bearing substrates. Weaker correlations were observed for O_3 and Hg^0 emissions for the synthetic-HgS and synthetic- $HgCl_2$ substrates in ambient air. This may be due to the fact that these were pure substrates, while in natural substrates O_3 may react with other minerals present in heterogeneous processes (Usher et al., 2003).

During exposure to ambient air, fluxes of RGM generally mimicked the temporal trend of O_3 concentration for the enriched-1, enriched-2, and synthetic- $HgCl_2$ substrates (Figs. 3a,b,d). Emissions were significantly elevated relative to clean air exposures (p<0.01; Table 2). The unenriched-1 and the synthetic-HgS substrates exhibited little relationship between the RGM emissions and ambient O_3 concentrations (Figs. 3c,e). One potential explanation for weak relationships between O_3 and RGM in ambient air is that other atmospheric oxidants with temporal concentration patterns different from O_3 may also be influencing RGM emissions from substrates.

The significant decrease in Hg^0 emissions from Hg^0 -amended substrates during exposure to O_3 -enriched clean and ambient air relative to clean air (Figs. 2g–h, 3f; Table 2) suggests that in contrast to Hg(II)-bearing substrates, O_3 inhibits volatilization of pure Hg^0 . Since homogeneous oxidation of the Hg^0 via reaction with O_3 in air was apparently not occurring during these experiments, a heterogeneous oxidation of Hg^0 on the substrate surface is probable. Conversion of Hg^0 to oxidized species of Hg that exhibit significantly lower volatilization rates would decrease Hg^0 emissions from the substrate. Because removal of O_3 from the experiment resulted in a rapid return of Hg^0 emissions to pre- O_3 exposure conditions, the oxidized form of Hg on the substrate surface must be fairly unstable, and the reaction easily reversible. We suggest that oxidation of Hg^0 to less volatile Hg(I) compounds is occurring and inhibiting Hg^0 emissions from the substrate. However, because Hg(I) is not stable, removal of O_3 results in Hg(I) reverting to Hg^0 . A similar mechanism has been proposed to explain the dynamics of Hg^0 to Hg(II) transformations in arctic snow (Lindberg et al., 2002; Poulain et al., 2004).

Exposure of the Hg^0 -amended substrates to O_3 in clean air resulted in an immediate pulse of RGM, followed by an asymptotic decrease to fluxes lower than those exhibited in pure clean air (Figs. 2g,h). This response is not well understood. One hypothesis is that initially, some of the Hg^0 in the samples may have been oxidized to volatile Hg(II)-species (e.g., $HgCl_2$) on the substrate surface. These species may be initially released in a pulse from the substrate during exposure to O_3 in a process similar to that observed for the Hg(II)-bearing samples. As hypothesized in the preceding paragraph, it is suggested that relatively very little of the Hg^0 is likely to be converted to Hg(II)-species, this available pool is quickly depleted and RGM emissions subsequently decline upon continued reaction with O_3 .

Temporal variations in Hg flux are thought to be primarily controlled by changes in light intensity, temperature, and soil moisture (Lindberg et al., 1999; Poissant et al., 1999; Gustin et al., 2002; Bahlmann et al., 2004a,b; Gustin and Stamenkovic, 2005). The ratios of the average Hg^0 flux from the enriched-1 substrate in light versus dark and in clean versus O_3 -enriched clean air (8.1 versus 18 from Table 3; respectively), were similar. However, results from our experiment (Fig. 4) suggest that for this substrate, O_3 is a more important factor controlling emissions than light. Light to dark, O_3 -enriched clean air to clean air, and ambient air and clean air average Hg^0 flux ratios based on the results of this study (Table 2) and from literature for the same substrates are provided in Table 3. For the enriched-1, enriched-2, and synthetic-HgS substrates, Hg^0 emissions were more significantly elevated during exposure to O_3 and ambient air than light. The ratios also demonstrate that Hg^0 -1 is both strongly influenced by light and O_3 /ambient air but the effect is the opposite for the latter. These results suggest that O_3 is at least as important as light in controlling Hg^0 emissions from dry-unvegetated Hg(II)-bearing substrates.

Interpretation of the experimental results discussed above suggests that the increase of Hg^0 and RGM emissions from substrates during exposure to atmospheric O_3 is most likely due to a heterogeneous reaction at the substrate–air interface. An alternate hypothesis is replacement of Hg^0 by O_3 similar to one mechanism proposed for enhanced emission due to water addition (Lindberg et al., 1999). The latter mechanism seems less likely given that Hg^0 emissions from the Hg^0 -amended substrates decreased during exposure to O_3 and ambient air relative to clean air.

Table 3
 Ratios of average Hg⁰ flux measurements for substrate samples in light versus dark conditions and cleaned air versus O₃-enriched air and ambient air conditions

Substrate	Light:dark ^a	O ₃ :clean air	Ambient air:clean air
<i>Hg(II)-bearing substrates</i>			
Enriched-1	8.1 ^c	18.1	19.2
Enriched-2	6.7 ^a	8.3	51.2
Unenriched-1	1.5–35, median = 3.7 ^b	2.3	2.9
Synthetic-HgCl ₂	9 ^a	4.1	4.8
Synthetic-HgS	5.6 ^a	45.4	43.2
<i>Hg⁰-amended substrate</i>			
Hg ⁰ -1	1.35 ^a	0.08	0.59

^aData from Gustin et al., (2002).

^bUnpublished data from M. Xin.

^cIn the absence of O₃.

5. Implications and conclusions

Concentrations of some atmospheric oxidants such as O₃ have increased over the last 100 years as a result of human activity (Volz and Kley, 1988; Hough and Derwent, 1990). This increase has been shown to dramatically affect biogeochemical systems (Takemoto et al., 2001; Loya et al., 2003). In this paper we demonstrated that increased concentrations of tropo- spheric O₃ could produce an increase in emissions of Hg⁰ and RGM from Hg(II)-bearing dry substrates. Although Hg⁰-amended substrates were used in this study, most natural soils are dominated by Hg(II) phases (Andersson, 1979). We can crudely estimate the global contribution of increasing O₃ concentrations on Hg⁰ emissions from substrates over the last 100 years with a simple calculation. Because we demonstrated that saturated soil moisture conditions inhibit the reaction between ambient O₃ and surface-bound Hg we conservatively assume that only non-polar arid and semi- arid regions of the land surface are affected by this reaction, or roughly 36% of the entire terrestrial surface (Goudie and Wilkinson, 1977). Using regression equations developed for all of the Hg(II)-substrate samples, a doubling in O₃ concentration from 10 to 20 ppb (Volz and Kley et al., 1988) would produce an anticipated 1.8 to 2-fold increase in Hg⁰ flux. This simple model assumes that (1) if the surface pool is the dominant control on emissions, the available Hg⁰/easily reducible Hg(II) reservoir is not depleted when O₃ concentrations are high and (2) if saturation of substrate surface sites by reaction with O₃ is the primary driver, that surfaces are adequately regenerated during low-O₃ concentrations. The fact that Hg⁰ emissions from the Hg(II)-bearing substrates are well correlated with O₃ concentrations during ambient air exposures and that atmospheric inputs could keep the surface pool from being depleted in low-Hg soils suggests that these assumptions could be met in natural systems. Applying this increase results in an increase in natural Hg⁰ emissions from terrestrial substrates of 65–72%. Although crude, these calculations demonstrate that changes in concentrations of O₃ may significantly affect the magnitude of terrestrial source mercury emissions to the atmosphere over time. Predictions for future global changes indicate that concentrations of O₃ are likely to increase and that arid regions are increasing in size. Given this situation, terrestrial source Hg emissions from substrates are likely to continue to increase with time.

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