Chemical sources and sinks of Hg(II) in the remote atmospheric marine boundary layer

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Hg-halogen chemistry

Simultaneous O₃ and Hg⁰ depletion event

Spitzbergen

Hg⁰ lifetime for April

Global lifetime due to Hg-Br reaction:

\[ \tau_{\text{Hg}^0} = 200 \text{ d} \quad \text{(range: 160 – 510 d)} \]

Gas-phase reaction mechanism

\[ \begin{align*}
Hg^0 & \overset{k_1}{\rightarrow} Br \\
& \overset{k_2}{\rightarrow} HgBr \\
HgBr & \overset{k_3}{\rightarrow} Br, OH, ... \\
HgBrX & \end{align*} \]
Rapid MBL cycling?

Atmosphere

Marine Boundary Layer

River

Dry Particle + 9.7

Net Evasion 7.3

Hg\textsuperscript{II} 5.7

Hg\textsuperscript{0} 13

Hg\textsuperscript{II} 1.3

Mason and Sheu, 2002

RGM-O\textsubscript{3} Anticorrelation

Max. daily RGM, pg m\textsuperscript{3}

Ozone, ppbv

- Atlantic Subtropics
- Pacific Subtropics
- Pacific Midlatitudes
- Okinawa

following Laurier and Mason, 2007
RGM diurnal cycles - regular features

Major features
- Fast morning rise
- Peak 11:00-13:00 LT
- Fast decline in afternoon
- No significant change 20:00-4:00 LT
- Amplitudes 1-3X mean

Data from Laurier et al., 2004
Jaffe et al., 2005
Laurier and Mason, 2007
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Free troposphere

Marine boundary layer

Hg⁰ → Hg(II) → MeHg → Hg(p)

O₃, OH, Br, Cl

aq. photoreduction

Dry & Wet Deposition

Sea salt aerosol

Entrainment

\[
\frac{d[RGM]_{MBL}}{dt} = P - L + \frac{F_{\text{entrain}}}{Z_{MBL}} - \frac{F_{\text{dep}}}{Z_{MBL}}
\]

\[
F_{\text{entrain}} = \rho_{\text{entrain}} ( [RGM]_{FT} - [RGM]_{MBL} )
\]

\[
F_{\text{dep}} = [RGM]_{MBL} \left( \nu_{\text{dry}}(u) + H F_{\text{ss}}(u) \right)
\]

Holmes et al., in prep.
Sources and sinks of Hg(II) in the marine boundary layer

\[ \frac{d[RGM]_{MBL}}{dt} = P - L + \frac{F_{\text{entrain}}}{Z_{MBL}} - \frac{F_{\text{dep}}}{Z_{MBL}} \]

\[ F_{\text{entrain}} = v_{\text{entrain}} ([RGM]_{FT} - [RGM]_{MBL}) \]

\[ F_{\text{dep}} = [RGM]_{MBL} (v_{\text{dry}}(u) + H' F_{\text{ss}}(u)) \]

Holmes et al., in prep.
Site-specific simulations

Holmes et al., in prep.

\[ \tau_{\text{Hg}(II)} = 6.5 \text{ h} \]

\[ \tau_{\text{Hg}(II)} = 8.1 \text{ h} \]

\[ \tau_{\text{Hg}(II)} = 2.6 \text{ h} \]

\[ \tau_{\text{Hg}(II)} = 0.7 \text{ h} \]
RGM Budget

\[ \tau_{Hg(II)} = 8.1 \text{ h} \]
\[ \tau_{Hg^0, \text{chem.}} = 100 \text{ d} \]

\[ \tau_{Hg(II)} = 6.5 \text{ h} \]
\[ \tau_{Hg^0, \text{chem.}} = 127 \text{ d} \]

\[ \tau_{Hg(II)} = 2.6 \text{ h} \]
\[ \tau_{Hg^0, \text{chem.}} = 86 \text{ d} \]

\[ \tau_{\text{air, entrain}} = 28 \text{ h} \]

Holmes et al., in prep.
Conclusions and Implications

- Loss of RGM at numerous MBL sites is controlled by wind-driven sea salt aerosols.
- Hg+Br supplies 20-40% of MBL RGM in the midlatitudes and subtropics.
- Hg+Cl contributes less than 1% of RGM.
- Entrainment supplies 30-50% of MBL RGM.
- ~1% of marine Hg⁰ emissions are immediately oxidized in the MBL vs. 40% suggested by Mason and Sheu (2002).
- Hg(II) deposition should be fastest in high-latitude storm tracks.

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Holmes et al., in prep.