Improved Mechanistic Model of the Atmospheric Redox Chemistry of Mercury

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Shah et al., ES&T, 2021
Standard Br-initiated Hg redox chemistry

Two-step oxidation; aqueous-phase reduction

\[
\begin{align*}
\text{Hg}^0 \xrightarrow{+\text{Br}} \text{BrHg}^+ \\
\text{BrHg}^+ \xrightarrow{+\text{Y}} \text{Hg}^{\text{II}G} \\
\text{Hg}^{\text{II}G} \xrightarrow{h\nu} \text{Hg}^{\text{II}P}
\end{align*}
\]

in clouds & particles in presence of OA

Instantaneous equilibrium

Oxidation by OH and O$_3$ is included in some models, but this has been questioned

(Goodsite et al. 2004; Dibble et al. 2012; Horowitz et al. 2017)
Major developments in Hg chemistry

Gas-phase photolysis of Hg\textsuperscript{I} & Hg\textsuperscript{II}
Saiz-Lopez et al. (2018; 2019)

Oxidation of Hg\textsuperscript{0} initiated by OH
Dibble et al. (2019)

New redox reactions of Hg\textsuperscript{I} & Hg\textsuperscript{II}
Lam et al. (2019); Khiri et al., (2020); Saiz-Lopez et al. (2020)

Experimental constraints on Hg\textsuperscript{II}(aq) reduction rate
Saiz-Lopez et al. (2018); Yang et al. (2019)
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\[
\text{Hg}^0 + \text{OH} \rightarrow \text{HOHg}^\text{I} + \text{Y}
\]

\[
\text{HOHg}^\text{I} + \text{Y} \rightarrow \text{Hg}^\text{II}
\]

Behaves similar to BrHg\textsuperscript{I}

New rate is 100x slower than previous estimate
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Dibble et al. (2019)

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Experimental constraints on HgII(aq) reduction rate
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Experimental constraints on Hg\textsuperscript{II}(aq) reduction rate
Saiz-Lopez et al. (2018); Yang et al. (2019)

Hg\textsuperscript{II}(aq) photoreduction rate in rainwater

Reduction rate in GEOS-Chem

Measured reduction rates
Effect of new Hg chemistry in a different model

Saiz-Lopez et al., 2020

Run #2: includes most updates ➔ Hg lifetime: 20 months
Run #1: Standard chemistry

Too much Hg in the model

Too little Hg deposition
Main Hg redox pathways in the new mechanism

Improved multiphase chemistry

Aerosol processing

Cloud processing

Hg(II) gas (X=2Cl⁻, etc.)
Global Hg lifetime consistent with observations

**Global tropospheric Hg budget**

- **Hg^0** (3.9 Gg) → 10.4 → **Hg^{II}** (0.1 Gg)
  - **Hg^{II}X**: 49%
  - **Hg^{II}P**: 22%
  - **Hg^{II}(OH)_2**: 19%
  - **BrHg^{II}OH**: 9%

**Tropospheric Hg lifetime**: 5.5 months

**Masses in Gg**
**Rates in Gg a^-1**
Hg\textsuperscript{0} is oxidized to Hg\textsuperscript{II} by Br and OH at equal rates.
**Hg^0** distribution consistent with observations

**Surface Hg^0 concentrations**

Obs: 167±48  
Model: 154±28

**Observed spatial variation captured**

**Zonal distribution of Hg**

- **Hg^0**
  - Small vertical gradient as seen in aircraft obs.

- **Hg^{II}**
  - Underestimated
Hg$^{II}$ deposition matches the observed patterns.

Wet deposition underestimated.
Conclusions

1. New mechanism includes recent advances in Hg chemistry and captures the important features of Hg observations.

2. Major uncertainties: (i) Br concentrations and Hg\(^0\)+Br rate, (ii) reactions of Hg\(^1\), (iii) Hg\(^{II}\)(aq) speciation and reduction rate.