Improved Mechanistic Model of the Atmospheric Redox Chemistry of Mercury

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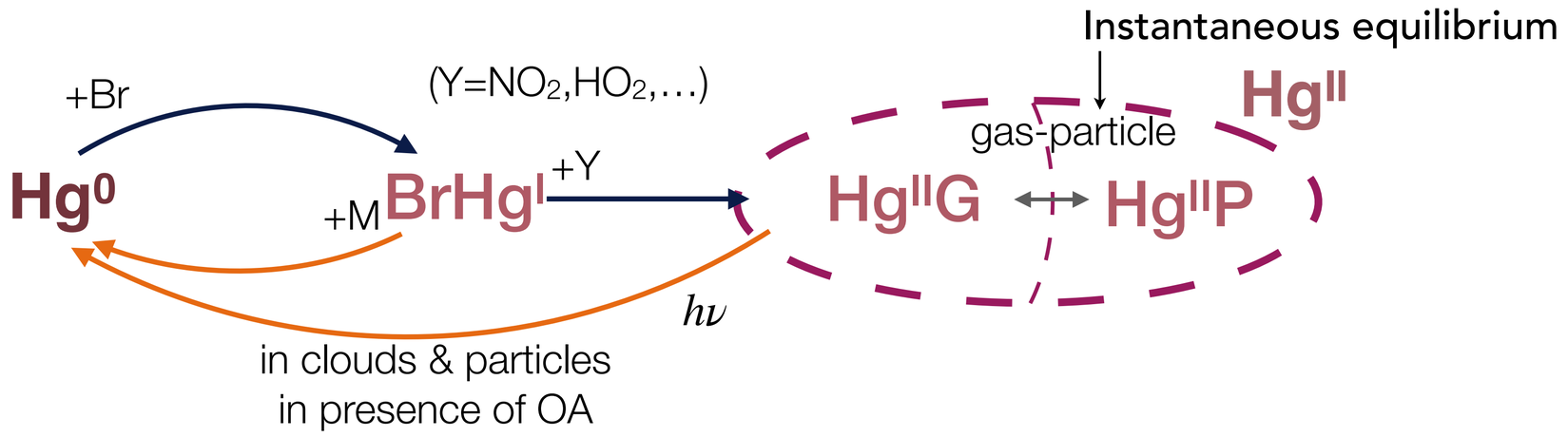
Shah et al., *ES&T*, 2021

Standard Br-initiated Hg redox chemistry

Two-step oxidation; aqueous-phase reduction



(Goodsite et al. 2004; Dibble et al. 2012; Horowitz et al. 2017)

Oxidation by OH and O_3 is included in some models, but this has been questioned

Major developments in Hg chemistry

Gas-phase photolysis of Hg^{I} & Hg^{II}

Saiz-Lopez et al. (2018; 2019)

Oxidation of Hg^{0} initiated by OH

Dibble et al. (2019)

New redox reactions of Hg^{I} & Hg^{II}

Lam et al. (2019); Khiri et al., (2020); Saiz-Lopez et al. (2020)

Experimental constraints on Hg^{II}(aq) reduction rate

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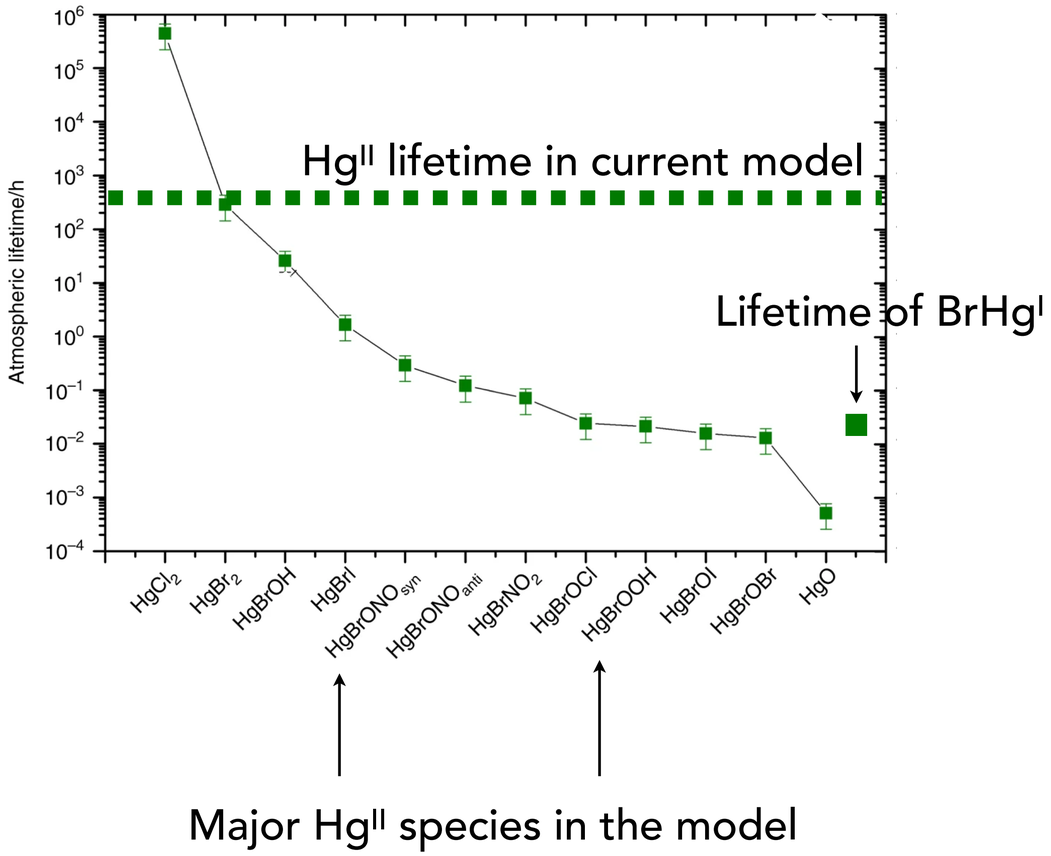
Photolysis lifetime of Hg^{II} and Hg^{I} species



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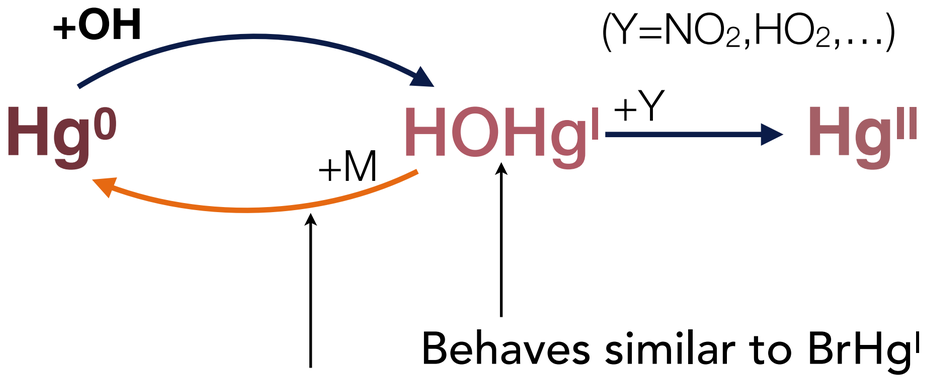

New rate is 100x slower than previous estimate

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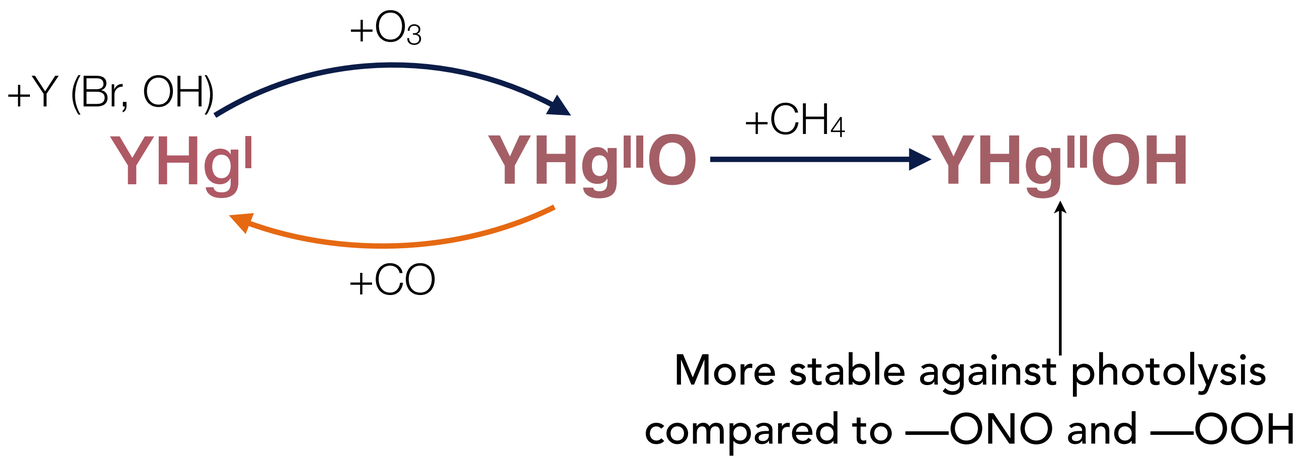

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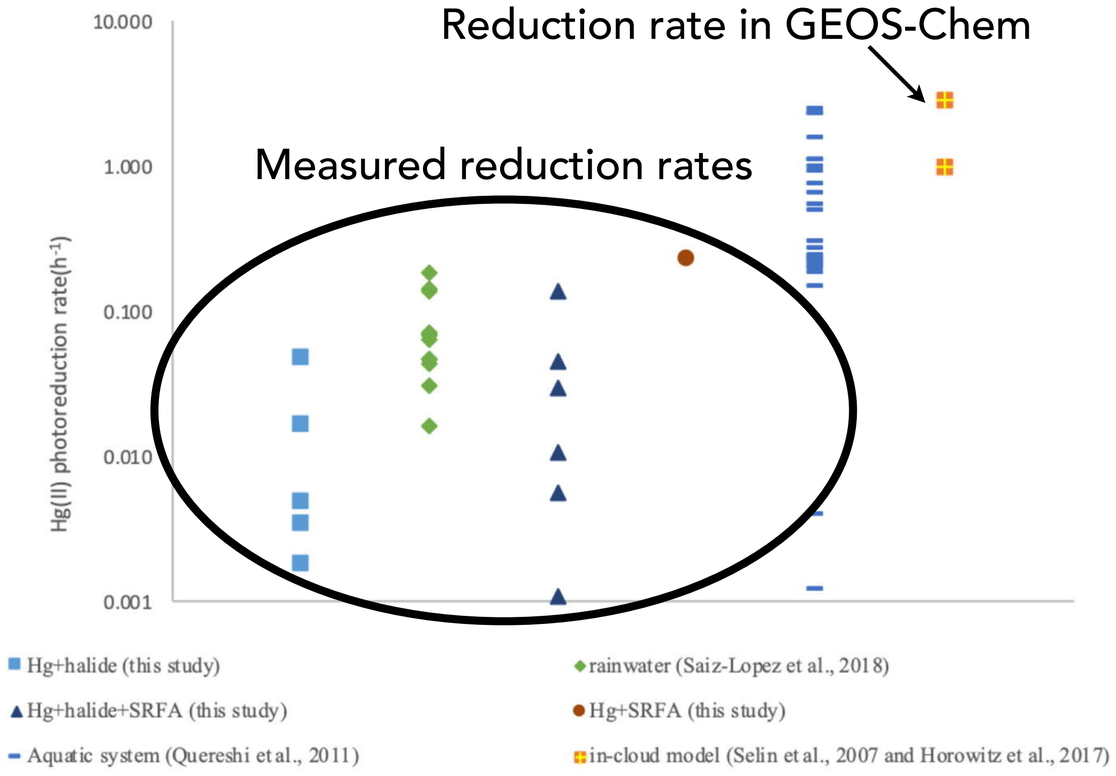
$Hg^{II}(aq)$ photoreduction rate in rainwater



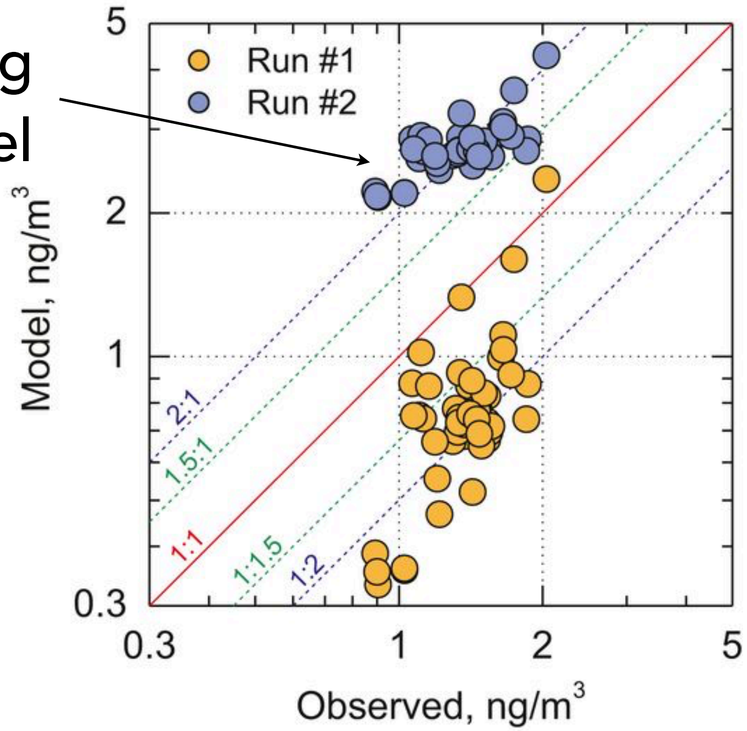
Effect of new Hg chemistry in a different model

Saiz-Lopez et al., 2020

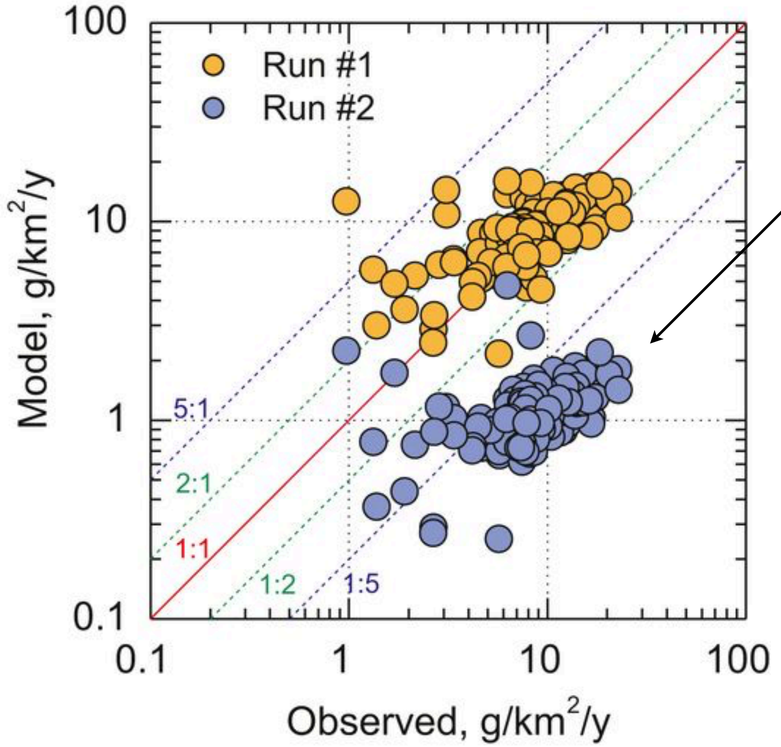
Run #2: includes most updates ➡ Hg lifetime: 20 months
Run #1: Standard chemistry

Too much Hg in the model

Surface Hg concentrations

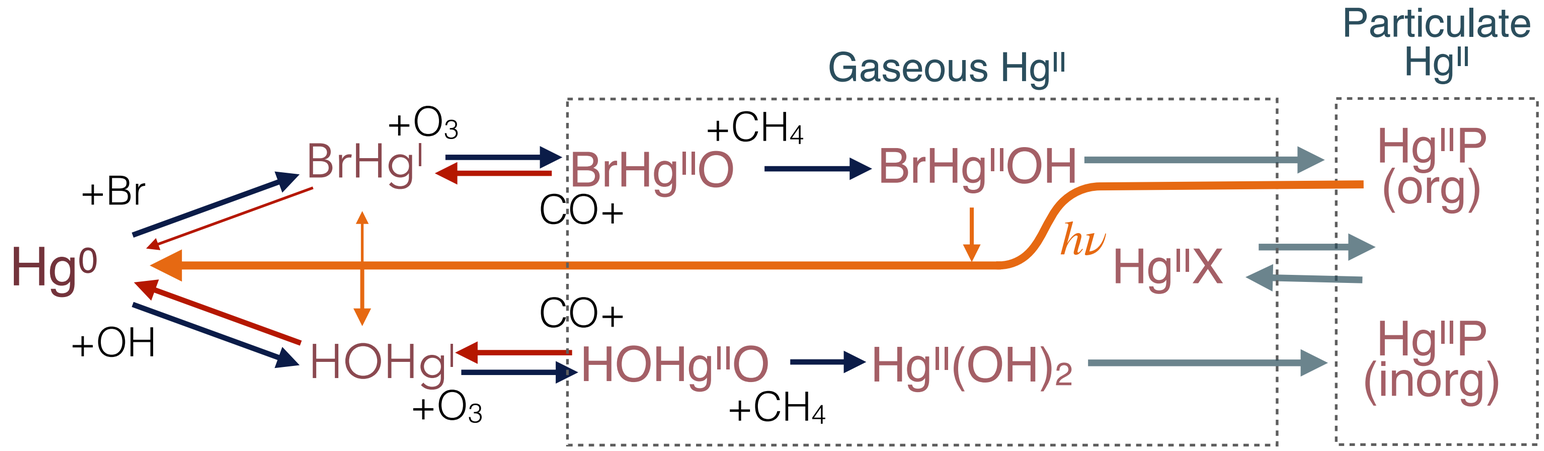


Hg wet deposition



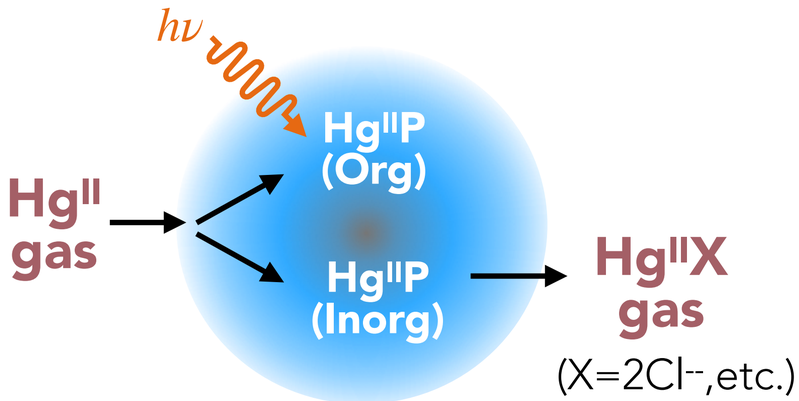
Too little Hg deposition

Main Hg redox pathways in the new mechanism

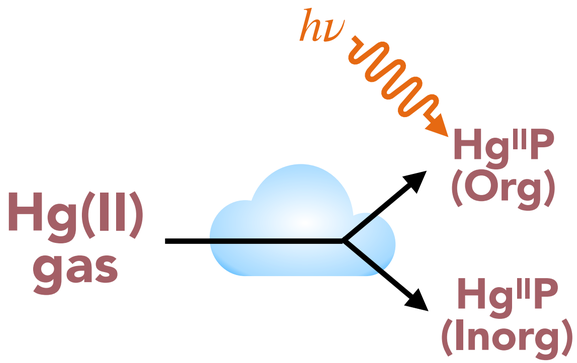


Improved multiphase chemistry

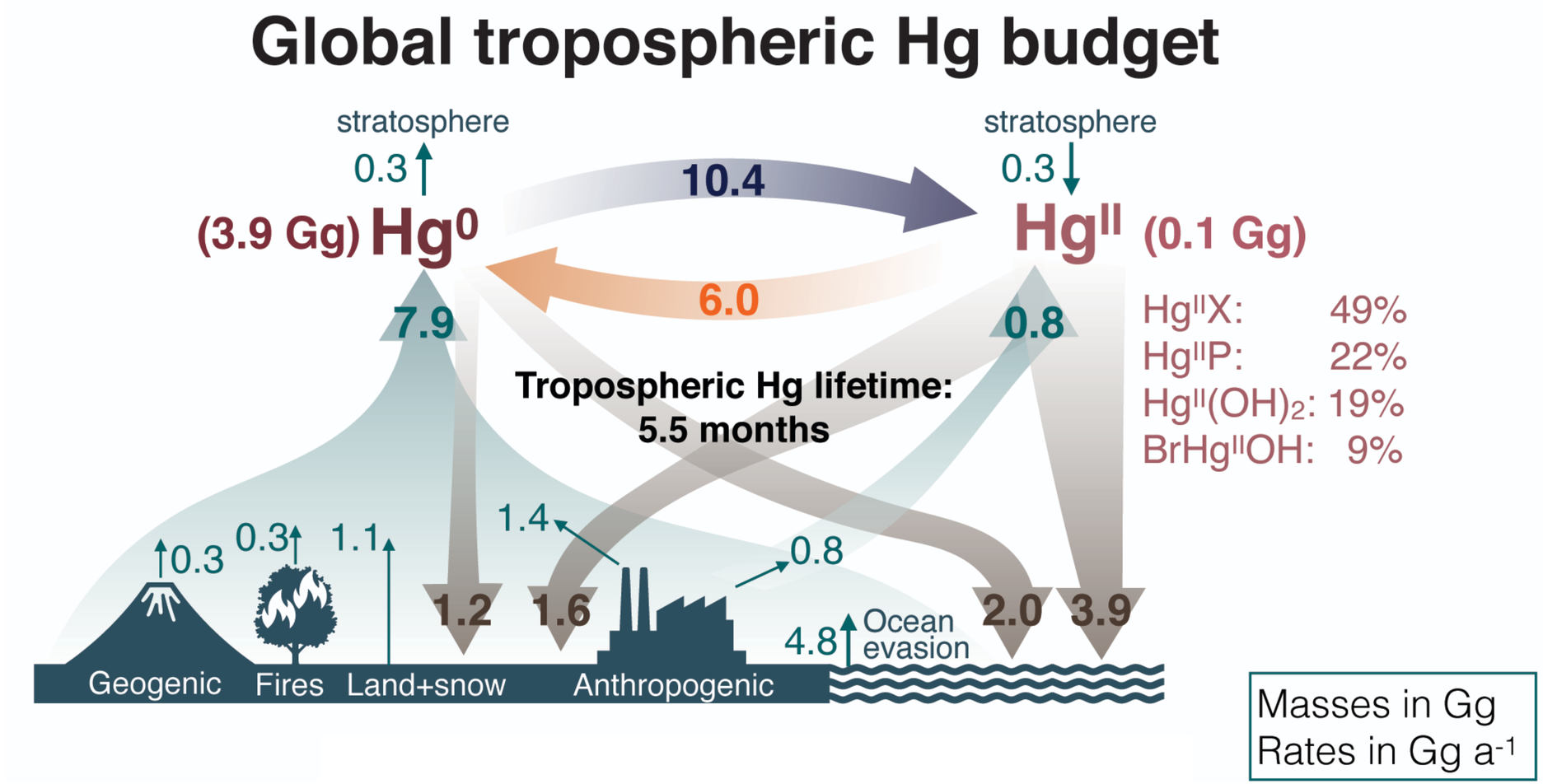
Aerosol processing



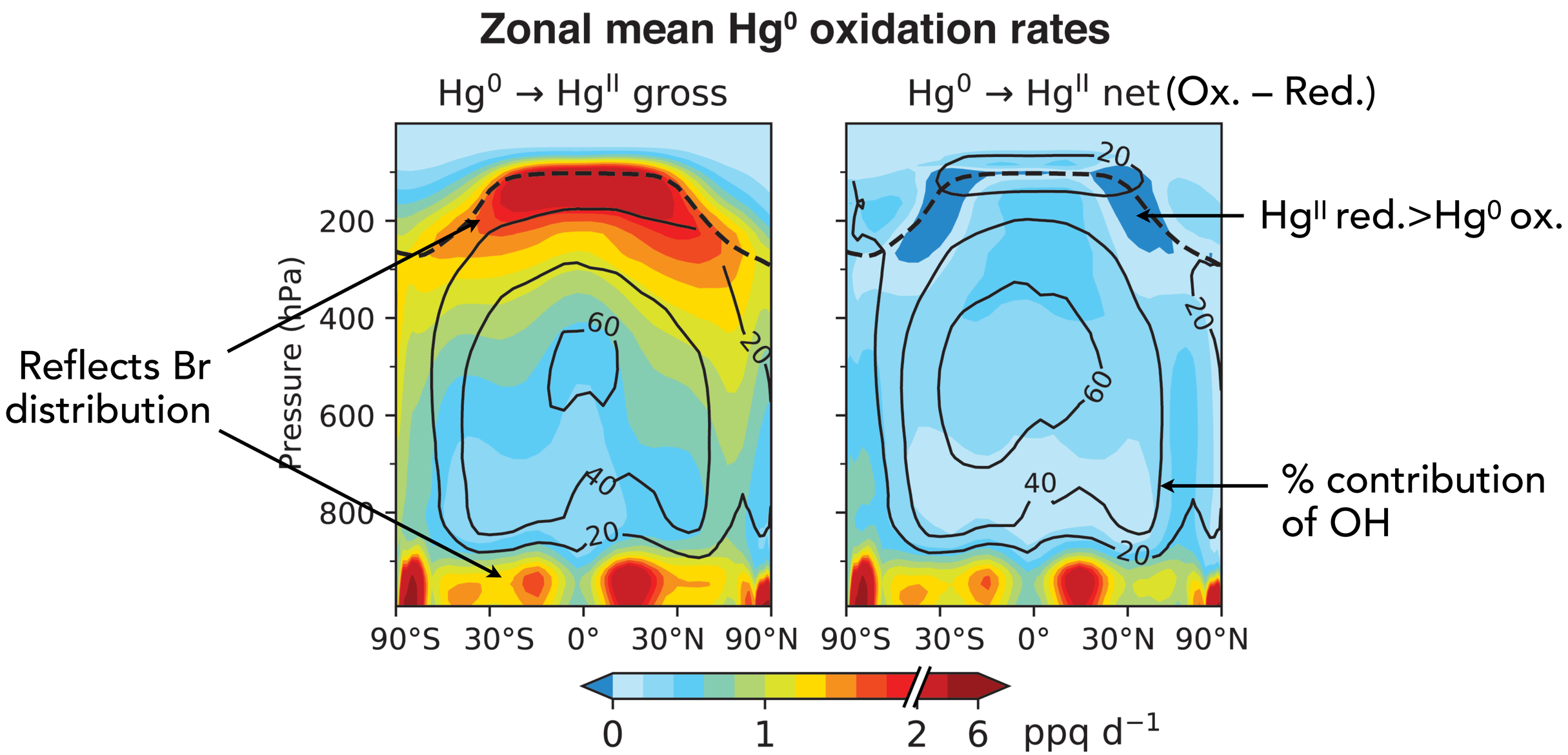
Cloud processing



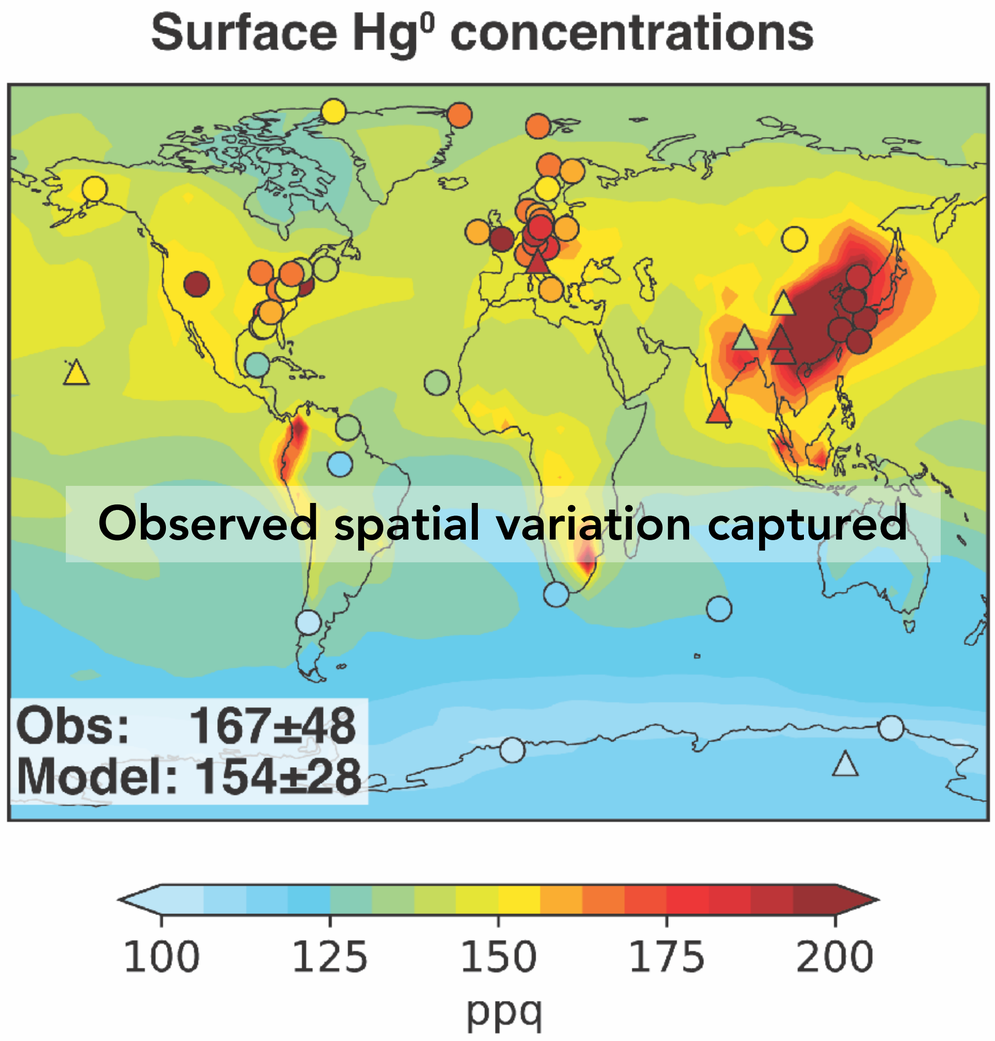
Global Hg lifetime consistent with observations

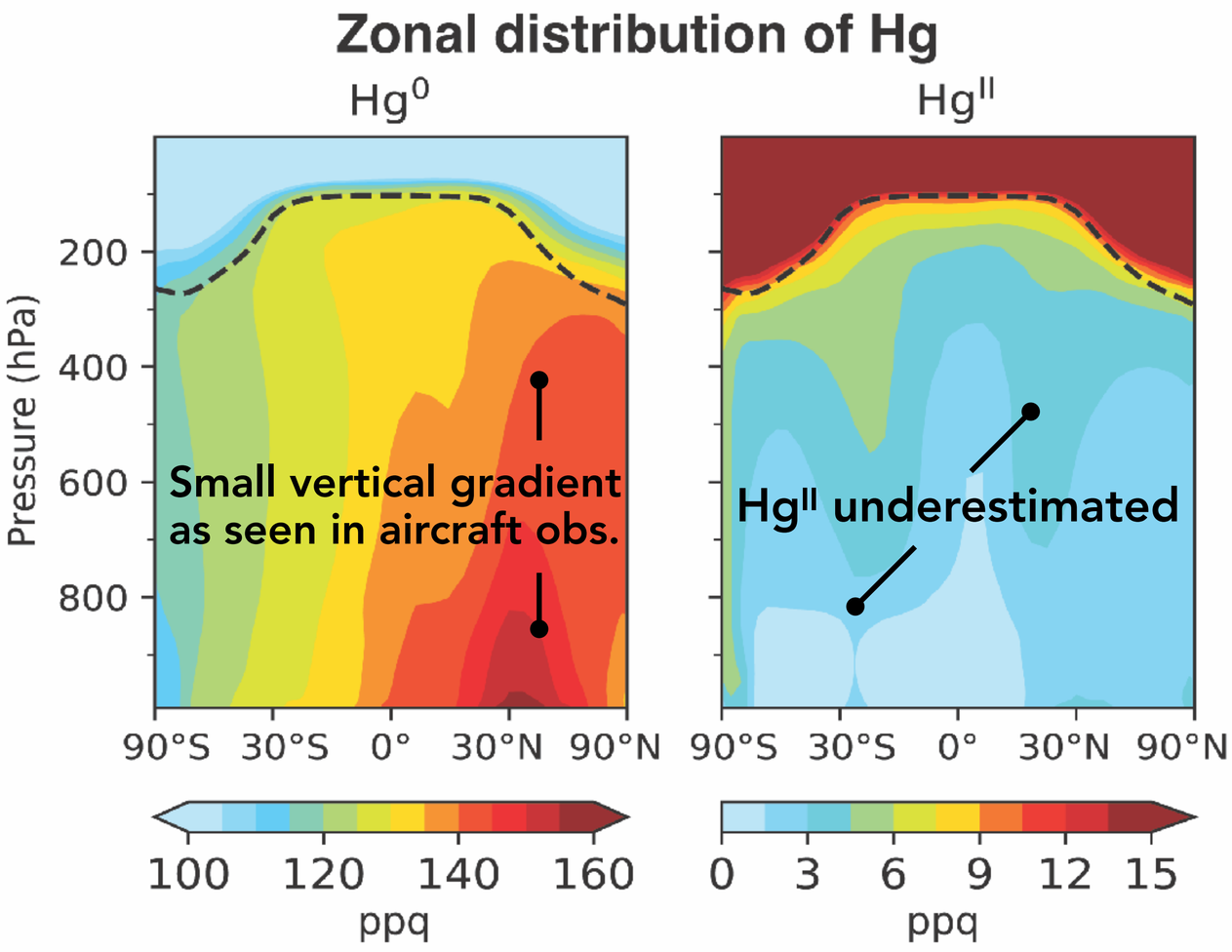


Hg^0 is oxidized to Hg^{II} by Br and OH at equal rates

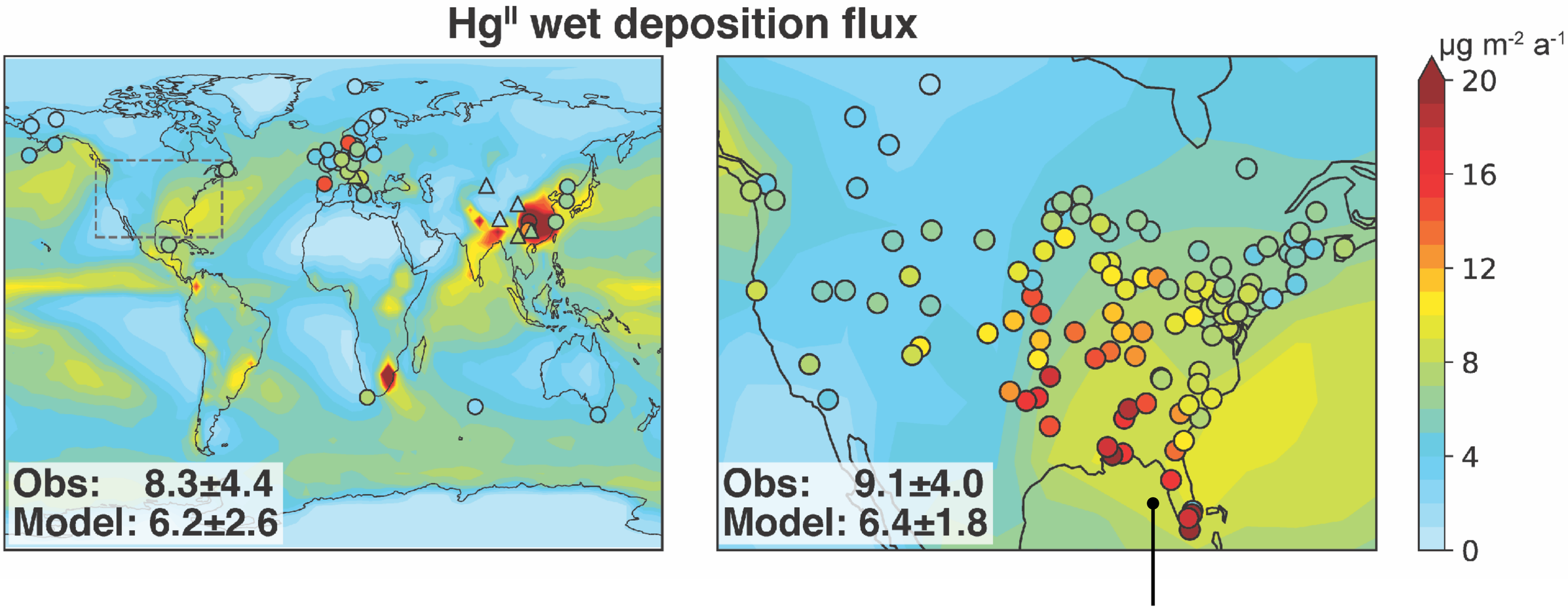


Hg^0 distribution consistent with observations





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^I, (iii) Hg^{II}(aq) speciation and reduction rate