Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols

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Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols

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Abstract. The hydroperoxyl radical (HO\textsubscript{2}) is a major precursor of OH and tropospheric ozone. OH is the main atmospheric oxidant, while tropospheric ozone is an important surface pollutant and greenhouse gas. Standard gas-phase models for atmospheric chemistry tend to overestimate observed HO\textsubscript{2} concentrations, and this has been tentatively attributed to heterogeneous uptake by aerosol particles. It is generally assumed that HO\textsubscript{2} uptake by aerosol involves conversion to H\textsubscript{2}O\textsubscript{2}, but this is of limited efficacy as an HO\textsubscript{2} sink because H\textsubscript{2}O\textsubscript{2} can photolyze to regenerate OH and from there HO\textsubscript{2}. Joint atmospheric observations of HO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} suggest that HO\textsubscript{2} uptake by aerosols may in fact not produce H\textsubscript{2}O\textsubscript{2}. Here we propose a catalytic mechanism involving coupling of the transition metal ions Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO\textsubscript{2} to H\textsubscript{2}O in aqueous aerosols. The implied HO\textsubscript{2} uptake and conversion to H\textsubscript{2}O significantly affects global model predictions of tropospheric OH, ozone, carbon monoxide (CO) and other species, improving comparisons to observations in the GEOS-Chem model. It represents a previously unrecognized positive radiative forcing of aerosols through the effects on the chemical budgets of major greenhouse gases including methane and hydrofluorocarbons (HFCs).

1 Introduction

HO\textsubscript{2} in the troposphere cycles rapidly with other members of the hydrogen oxide radical family (HO\textsubscript{x} ≡ OH + H + HO\textsubscript{2} + organic peroxy and oxy radicals). This cycling determines OH levels and ozone production. The main sources of HO\textsubscript{x} are photolysis of ozone in the presence of water vapor and photolysis of carbonyls. The sinks involve formation of peroxides, HNO\textsubscript{3}, and water. Peroxides and HNO\textsubscript{3} can photolyze, returning HO\textsubscript{x}. Formation of water is a terminal sink. HO\textsubscript{2} is in general the dominant component of HO\textsubscript{x}, so that the budget of HO\textsubscript{2} is largely defined by that of HO\textsubscript{x}.

Uptake of HO\textsubscript{2} by aqueous aerosols is promoted by its high solubility in water (Henry’s law constant 2.0 × 10\textsuperscript{3} M atm\textsuperscript{-1} at 298 K) and aqueous-phase dissociation to O\textsuperscript{−}\textsubscript{2} (pK\textsubscript{a} = 4.7), with rapid ensuing ionic redox chemistry. The efficacy of uptake is commonly measured by the reactive uptake coefficient, \(\gamma(\text{HO}_2)\), defined as the fraction of HO\textsubscript{2} collisions with aerosol surfaces resulting in reaction. Direct reaction of HO\textsubscript{2}(aq) with O\textsuperscript{−}\textsubscript{2} produces H\textsubscript{2}O\textsubscript{2} but the corresponding \(\gamma(\text{HO}_2)\) is relatively low, ranging from 0.01 for acidic aerosols (Thornton and Abbatt, 2005) to 0.2 for neutralized aerosols (Thornton and Abbatt, 2005; Taketani et al., 2008). Higher values of \(\gamma(\text{HO}_2)\), approaching unity, have been measured for Cu-doped aerosols where Cu(I)/Cu(II) redox cycling catalyzes HO\textsubscript{−}\textsubscript{2}/O\textsuperscript{−}\textsubscript{2} conversion to H\textsubscript{2}O\textsubscript{2} (Mozurkewich et al., 1987; Cooper and Abbatt, 1996; Thornton and Abbatt, 2005; Taketani et al., 2008). Model calculations suggest that other aerosol transition metal ions (TMI), including Fe(II)/Fe(III) and Mn(II)/Mn(III), can drive similar chemistry (Graedel et al., 1986). Uptake of HO\textsubscript{2} by non-aqueous inorganic aerosol appears to be very slow (Cooper and Abbatt, 1996; Taketani et al., 2008), but can be significant for carbonaceous aerosols (up to 0.13 for levoglucosan particles) (Bedjanian et al., 2005; Taketani et al., 2010).
Standard gas-phase models for atmospheric chemistry tend to overestimate observed HO\textsubscript{2} concentrations, and this has been tentatively attributed to heterogeneous uptake by aerosol particles. As shown in Table 1, HO\textsubscript{x} loss by HO\textsubscript{2} uptake is significant where HO\textsubscript{2} concentrations are relatively low (HO\textsubscript{2} is typically less than 10 ppt) and/or aerosol loading is high. In contrast, HO\textsubscript{x} loss by HO\textsubscript{2} uptake is less apparent where HO\textsubscript{2} concentration is a few tens of ppt such as urban areas (Mao et al., 2010b) and forests (Mao et al., 2012). To a large extent this is because HO\textsubscript{2} loss through HO\textsubscript{2} + HO\textsubscript{2} and HO\textsubscript{2} + RO\textsubscript{2} is quadratic on HO\textsubscript{x} concentrations.

All the laboratory and model mechanisms for HO\textsubscript{2} uptake by aerosol involve conversion to H\textsubscript{2}O\textsubscript{2} (Mozurkewich et al., 1987; Hanson et al., 1992; Gershenzon et al., 1995; Cooper and Abbatt, 1996; Remorov et al., 2002; Bedjanian et al., 2005; Thornton and Abbatt, 2005; Taketani et al., 2008; Thornton et al., 2008; Loukhovitskaya et al., 2009; Taketani et al., 2009; Macintyre and Evans, 2011), but this is of limited efficacy as an HO\textsubscript{2} sink because H\textsubscript{2}O\textsubscript{2} can photolyze to regenerate OH and from there HO\textsubscript{2}. Joint atmospheric observations of HO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} suggest that HO\textsubscript{2} uptake by aerosols may in fact not produce H\textsubscript{2}O\textsubscript{2} (de Reus et al., 2005; Mao et al., 2010a). Previous proposed mechanisms for the conversion of HO\textsubscript{2} to H\textsubscript{2}O, including Br\textsubscript{2} + HO\textsubscript{2} (Matthew et al., 2003), HSO\textsubscript{4}\textsuperscript{-} + HO\textsubscript{2} (Cooper and Abbatt, 1996), and the HO\textsubscript{2}-HSO\textsubscript{4} complex (Miller and Francisco, 2001) are not catalytic and thereby less efficient. Here we propose a catalytic mechanism involving coupling of the transition metal ions (TMI) Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO\textsubscript{2} to H\textsubscript{2}O in aerosols (Fig. 1).

### 2 Cu-Fe-HO\textsubscript{x} cycling

Cu and Fe are ubiquitous components of crustal and combustion aerosols. Concentrations in rural air are in the range 3–300 ng m\textsuperscript{-3} for Cu and 55–14 500 ng m\textsuperscript{-3} for Fe (Schroeder et al., 1987). The submicron size fraction generally associated with combustion aerosols accounts for 25–100 % of Cu mass and 15–50 % of Fe mass (Tables S1 and S2 in the Supplement). Joint measurements of Cu and Fe in fine particles (PM\textsubscript{2.5}) show that the molar Cu/Fe ratio is typically below 0.1 (Table S3, Fig. S3). While Cu tends to fully dissolve at pH<5 (Deguillaume et al., 2005), the solubility of Fe varies greatly, ranging from less than 1 % in soils to 81 % in oil combustion products (Schroth et al., 2009). Observations indicate that the dissolved Cu to Fe molar ratio (hereinafter “Cu/Fe”) is typically 0.01–0.1 (Table S4 in the Supplement). Cu-catalyzed HO\textsubscript{2} loss to H\textsubscript{2}O in acid aerosols proceeds by Reactions (RA1)–(RA2), with similar reactions involving O\textsubscript{2} for higher-pH conditions:

### Table 1. Field evidence for HO\textsubscript{2} aerosol uptake\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>HO\textsubscript{2} Conc (pptv)\textsuperscript{b}</th>
<th>Estimated γ(HO\textsubscript{2})</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mauna Loa, Hawaii</td>
<td>remote rural</td>
<td>15\textsuperscript{c}</td>
<td>0.5–1</td>
<td>To reduce HO\textsubscript{2} by more than a factor of 2</td>
<td>Cantrell et al. (1996)</td>
</tr>
<tr>
<td>Southern Ontario, Canada</td>
<td></td>
<td>10</td>
<td>~1</td>
<td>To reduce HO\textsubscript{2} by 50 %</td>
<td>Plummer et al. (1996)</td>
</tr>
<tr>
<td>Oki Island, Japan</td>
<td>remote plume in free troposphere</td>
<td>10</td>
<td>N/A</td>
<td>30 %–50 % loss of peroxy radicals onto aerosols</td>
<td>Kanaya et al. (2000)</td>
</tr>
<tr>
<td>TRACE-P aircraft campaign</td>
<td></td>
<td>10</td>
<td>~1</td>
<td>30 %–50 % loss of peroxy radicals onto aerosols</td>
<td>Cantrell et al. (2003a)</td>
</tr>
<tr>
<td>TOPSE aircraft campaign</td>
<td>remote</td>
<td>5</td>
<td>N/A</td>
<td>30 %–50 % loss of peroxy radicals onto aerosols</td>
<td>Cantrell et al. (2003b)</td>
</tr>
<tr>
<td>Remote marine boundary layer near Australia</td>
<td></td>
<td>8</td>
<td>1</td>
<td>No H\textsubscript{2}O\textsubscript{2} formed from HO\textsubscript{2} uptake. Also needs uptake for H\textsubscript{2}O\textsubscript{2}</td>
<td>Sommariva et al. (2004); Haggerstone et al. (2005)</td>
</tr>
<tr>
<td>Saharan dust plume</td>
<td>plume</td>
<td>15\textsuperscript{c}</td>
<td>1</td>
<td>No H\textsubscript{2}O\textsubscript{2} formed from HO\textsubscript{2} uptake. Also needs uptake for H\textsubscript{2}O\textsubscript{2}</td>
<td>de Reus et al. (2005)</td>
</tr>
<tr>
<td>Mace Head, Ireland</td>
<td>remote</td>
<td>6</td>
<td>1</td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Sommariva et al. (2006); Kanaya et al. (2007); Parker et al. (2009); Commave et al. (2010)</td>
</tr>
<tr>
<td>Rishiri Island, Japan</td>
<td>remote</td>
<td>6</td>
<td>1</td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Sommariva et al. (2006); Kanaya et al. (2007); Parker et al. (2009); Commave et al. (2010)</td>
</tr>
<tr>
<td>Jungfraujoch research station\textsuperscript{d}</td>
<td>remote</td>
<td>6</td>
<td>1</td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Sommariva et al. (2006); Kanaya et al. (2007); Parker et al. (2009); Commave et al. (2010)</td>
</tr>
<tr>
<td>Biomass burning plumes in West Africa</td>
<td>plume</td>
<td>N/A</td>
<td></td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Sommariva et al. (2006); Kanaya et al. (2007); Parker et al. (2009); Commave et al. (2010)</td>
</tr>
<tr>
<td>Arctic spring</td>
<td>remote</td>
<td>5</td>
<td>~1</td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Mao et al. (2010a); Olson et al. (2012); Olson et al. (2012)</td>
</tr>
<tr>
<td>Arctic summer</td>
<td>remote</td>
<td>10</td>
<td>~1</td>
<td>Modelled HO\textsubscript{2} is higher than measured HO\textsubscript{2} by a factor of 5.</td>
<td>Mao et al. (2010a); Olson et al. (2012); Olson et al. (2012)</td>
</tr>
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\textsuperscript{a} γ(HO\textsubscript{2}) for all aerosol inferred from photochemical modeling of observed HO\textsubscript{2} concentrations.

\textsuperscript{b} noontime mean or median value

\textsuperscript{c} estimated from the measured total peroxy radicals (HO\textsubscript{2} + RO\textsubscript{2}).

\textsuperscript{d} estimated for the uptake on snow surface.
Cu(I) + HO₂ → Cu(II) + O₂ + H^+  \hspace{1cm} \text{(RA1)}

Cu(I) + HO₂ → Fe(II) + H₂O₂  \hspace{1cm} \text{(RA2)}

Cu(I) + O₂ → Cu(II) + HO₂  \hspace{1cm} \text{(RA3)}

Here the destruction of HO₂ is buffered by the production of HO₂ via (Reaction RA3) (Ervens et al., 2003). Fe-catalyzed HO₂ loss proceeds by a similar cycle though the rate constant of Fe(III) + HO₂ is two orders of magnitude lower than for Cu(II) (Mozurkewich et al., 1987).

The coupled Cu-Fe catalytic cycle for aqueous-phase HO₂ loss involves (Reaction RA1) and

Cu(I) + Fe(III) → Cu(II) + Fe(II)  \hspace{1cm} \text{(RA4)}

with three likely pathways for Fe(II) to close the cycle:

Fe(II) + HO₂ → Fe(III) + H₂O₂  \hspace{1cm} \text{(RA5)}

Net : HO₂ + HO₂ → H₂O₂ + O₂  \hspace{1cm} \text{(RA6)}

Fe(II) + H₂O₂ → Fe(III) + OH⁺ + OH⁻  \hspace{1cm} \text{(RA6)}

Net : HO₂ + H₂O₂ → OH⁻ + O₂ + H₂O  \hspace{1cm} \text{(RA7)}

Fe(II) + OH^- → Fe(III) + OH⁻  \hspace{1cm} \text{(RA7)}

Net : HO₂ + OH⁻ → O₂ + H₂O  \hspace{1cm} \text{(RA7)}

The electron transfer reaction Cu(I) + Fe(III) (Reaction RA4) is rapid with a rate constant of 1.3–3 × 10⁴ M⁻¹ s⁻¹ (Bjergbakke et al., 1976; Sedlak and Hoigné, 1993). It has been found previously to regulate the observed diurnal pattern of the Fe(II)/Fe(III) ratio in cloud water (Ervens et al., 2003; Deguillaume et al., 2004). Aerosol chemistry models suggest that (Reaction RA1) is the dominant sink for Cu(II) (Jacob et al., 1989), and we show below that (Reaction RA4) is then the dominant sink for Cu(I) over the expected range of Cu/Fe ratios. The implications for HOₓ depend on the fate of Fe(II). (Reaction RA5) converts HOₓ to H₂O₂ while (Reaction RA7) converts HOₓ to H₂O. (Reaction RA6) also effectively leads to HOₓ loss by converting H₂O₂ to H₂O.

3 Formulation of HO₂ reactive uptake by aerosols

We conducted box model simulations of aqueous aerosol chemistry to examine the effect of Cu-Fe-HO₂ cycling by (Reaction RA1)-(Reaction RA7) on the HOₓ chemical budget. The chemical mechanism mainly draws from Jacob (2000), Chemical Aqueous Phase Radical Mechanism (CAPRAM) 2.4 (Ervens et al., 2003) and Deguillaume et al. (2004), with a number of modifications and updates (Tables S8 and S9 in the Supplement). A few complexes are included to take into account the speciation of Fe and Cu: Fe(OH)⁺, Fe(OH)₂⁺, Fe(SO₄)²⁻, Fe(OH)²⁺, and CuSO₄(aq). Our simulations are for T = 298 K as kinetic data are often not available at low temperatures.

Modeling aerosol aqueous chemistry must account for ionic strength corrections. We use the Aerosol Inorganic Model (Clegg et al., 1998), to calculate the ionic strength and activity coefficients for major ions (i.e. NH₄⁺, H⁺, HSO₄⁻, SO₄²⁻) (Table S6). Activity coefficients for trace metal ions and neutral species are calculated based on specific ion interaction theory or estimated following Ross and Noone (1991) (supplemental material, summarized in Table S7). We also account for the salting out effect on Henry’s law constants. We assume Henry’s law equilibrium for H₂O₂, O₃, and O₂ because of their long lifetimes. Gas uptake of OH is small compared to its aqueous production, in part due to its low Henry’s law constant (25 M atm⁻¹ at 298 K) (Klasing et al., 1985; Hanson et al., 1992), and in part due to its much lower gas phase concentration than that of HO₂ (Mao et al., 2009). We thus calculate OH(aq) from aqueous-phase steady state in this model. Concentrations of total dissolved Cu and Fe are held fixed throughout the simulation at their initial values.

The HO₂ uptake and volatilization rates Rᵢₙ and Rᵢₒᵤₜ (molecules cm⁻³ s⁻¹) for a monodisperse aqueous aerosol of radius a can be approximated as (Schwartz, 1986):

\[ Rᵢₙ = \left( \frac{a}{D_g} + \frac{4}{vα} \right)^{-1} A n_{HO₂} \]  \hspace{1cm} (1)

and

\[ Rᵢₒᵤₜ = \left( \frac{a}{D_g} + \frac{4}{vα} \right)^{-1} A \frac{[HO₂]_{surf}}{H_2O} \]  \hspace{1cm} (2)
where $n_{\text{HO}_2}$ is the gas phase concentration of HO$_2$, $A$ is the aerosol surface area per unit volume of air, $v$ is the mean molecular speed, $\alpha$ is the mass accommodation coefficient assumed here to be unity (Thornton and Abbatt, 2005), $D_\text{g}$ is the HO$_2$ gas phase diffusion constant (0.25 cm$^2$ s$^{-1}$), $[\text{HO}_2]_{\text{surf}}$ is the concentration at the aerosol surface, and $H^*$ is the effective Henry’s law constant corrected for ionic strength and acid dissociation.

The chemical loss rate of aqueous HO$_2$ is the difference between $R_{\text{in}}$ and $R_{\text{out}}$. $\gamma(\text{HO}_2)$ is then defined as the ratio of chemical loss rate to $R_{\text{in}}$. Given the short lifetime of aqueous HO$_2$ ($\sim 10^{-5}$ s) against reaction with Cu(II) by (Reaction RA1), the bulk concentration $[\text{HO}_2]_{\text{bulk}}$ and surface concentration $[\text{HO}_2]_{\text{surf}}$ may differ substantially (Schwartz and Freiberg, 1981; Schwartz, 1986). On the basis of the solution to a steady state diffusion equation, their relationship can be expressed as (Jacob, 1986):

$$[\text{HO}_2]_{\text{surf}} = \frac{P_{\text{HO}_2}}{k_l^f} + ([\text{HO}_2]_{\text{bulk}} - \frac{P_{\text{HO}_2}}{k_l^f}) \cdot [3(\coth q - \frac{1}{q})]^{-1} \tag{3}$$

where $k_l^f$ is the first-order loss constant of HO$_2$, $P_{\text{HO}_2}$ is the aqueous-phase production rate of HO$_2$, and $q = \alpha \left(\frac{k_l^f}{D_{\text{aq}}^f}\right)^{1/2}$ is the diffuso-reactive parameter (Schwartz and Freiberg, 1981), in which $D_{\text{aq}}$ is the HO$_2$ aqueous phase diffusion constant. $P_{\text{HO}_2}$ is mainly from (Reaction RA3).

### 4 Atmospheric model simulations

Figure 2 shows the aqueous-phase chemical budgets of O$_2$($-I \equiv \text{HO}_2(aq) + \text{O}_2^-$), H$_2$O$_2$, dissolved Cu, and dissolved Fe for a 0.35 µm (dry radius) NH$_4$HSO$_4$ aerosol at RH = 85%, with dissolved Cu of $2.9 \times 10^{-3}$ M and Cu/Fe = 0.05 (molar). The concentration of Cu is estimated from the measured size distribution of Cu in rural aerosols with total Cu of 3.1 ng m$^{-3}$ (Ross and Noone, 1991). Reactions responsible for less than 1% of total production or loss are not shown. In particular, we find that Fe(III) + Cu(I) completely dominates over other pathways for Fe(III) reduction including photolysis and Fe(III) + HO$_2$.

In contrast to cloud chemistry (Jacob, 2000), the HO$_x$ budget in aerosols is mainly controlled by TMI chemistry because TMI concentrations are so high. Aqueous OH production and loss are dominated by (Reaction RA6) and (Reaction RA7) respectively. Aqueous HO$_2$ production within the aerosol accounts for less than 2% of its loss as (Reaction RA4) dominates over (Reaction RA3). The major sinks of aqueous HO$_2$ are (Reaction RA1) and (Reaction RA5). As shown in Fig. 2, 70% of HO$_2$ taken up from the gas phase is chemically lost, with the remainder volatilizing. Therefore $\gamma(\text{HO}_2)$ under these conditions is equal to 0.7.

The Cu/Fe ratio is a critical factor in this model calculation. When Cu/Fe $> 1$, (Reaction RA2) and (Reaction RA3) are the dominant sinks for Cu(I), leading to the conversion of HO$_2$ to H$_2$O$_2$. Aerosol pH is also critical. Acid-base dissociation of HO$_2$(aq)/O$_2^-$ at higher pH decreases the HO$_2$
dependence of \( Y_{2} \) and this can be expressed as a positive or negative Hg phase can lead to either production or loss of Hg. This is in part due to the enhanced loss of aqueous Hg by (Reaction RA1) and Fe(III) + O\(_{2}\)(−I), resulting in suppressed production of HgO by (Reaction RA5). On the other hand, at higher pH, the oxidation of Fe(II) is enhanced by Fe(OH)\(^{2+}\) + HgO which is five orders of magnitude faster than Fe\(^{2+}\) + HgO. (Reaction RA6) and (Reaction RA7) then become the dominant sinks for Fe(II) and may lead to a reactive uptake of HgO by (Reaction RA2). This pathway becomes unimportant at lower Cu/Fe.

Figure 3c examines the sensitivity of \( \gamma(\text{HO}_2) \) to a decrease of Cu concentrations from the \( 2.9 \times 10^{-3} \) M assumed in the standard simulation, keeping a fixed Cu/Fe=0.05. We find that the sensitivity is weak as long as Cu remains above \( 5 \times 10^{-4} \) M (corresponding to a Cu solute mass fraction of \( 8.0 \times 10^{-5} \)), consistent with the threshold value (mass fraction of \( 1-2 \times 10^{-4} \)) for Cu-only chemistry noted in Thornton et al. (2008). For example, at pH=3, \( \gamma(\text{HO}_2) \) only decreases from 0.85 to 0.61 with a five-fold decrease of Cu concentrations. This weak response is mainly because uptake of HO\(_2\) is limited by diffusion in the aqueous phase, reflecting its very fast reaction with Cu(II). As Cu(II) concentrations drop to values sufficiently low for HO\(_2\) to become well-mixed into the aerosol, \( \gamma(\text{HO}_2) \) then decreases rapidly with decreasing Cu. This dependence of \( \gamma(\text{HO}_2) \) on Cu concentrations also appears to be consistent with laboratory measurements (Mozurkewich et al., 1987).

The aerosol budget can be significantly different in the presence of organic species in aerosols. First, TMI can readily form complexes with organic ions, such as oxalate, glyoxalate, and pyruvate (Moorhead and Sutin, 1966; Cooper and DeGraff, 1972; Zuo and Hoigne, 1994; Okochi and Brimblecombe, 2002; Deguillaume et al., 2005). While these organic complexes are in general less reactive towards HO\(_2\) (Bielski et al., 1985), the slight increase of \( Y_{\text{H}_2\text{O}_2} \) at Cu/Fe = 0.1 while pH increases from 0 to 3 is mainly due to the enhanced HgO production by (Reaction RA2). This pathway becomes unimportant at lower Cu/Fe.

Fig. 3. Impacts of Cu-Fe-HO\(_2\) cycling on aerosol chemistry for the model calculations described in the text. (A) and (B): pH dependence of the HO\(_2\) reactive uptake probability \( \gamma(\text{HO}_2) \) and the corresponding HgO yield for a dissolved Cu concentration of \( 2.9 \times 10^{-3} \) M and different Cu/Fe molar ratios. (C): dependence of \( \gamma(\text{HO}_2) \) on Cu concentrations for different pH values with Cu/Fe = 0.05.

volutilization flux as the reaction rate constants of Cu or Fe with O\(_{2}^−\) can be two orders of magnitude faster than with HO\(_2\)(aq). The speciation of Cu and Fe is affected by pH, and we account for some of the complexation equilibria as described in Sect. 3. Organic complexes may be important for Cu (Thornton et al., 2008) but we have no kinetic data for them. Precipitation of Fe(OH)\(_3\) could take place at pH > 4, but we assume this to be negligible due to high ionic strength (activity coefficient A(Fe\(^{3+}\)) = 0.01) and slow kinetics.

Figure 3a shows the pH dependence of our calculated \( \gamma(\text{HO}_2) \) for ammonium-sulfate aerosol at various Cu/Fe ratios. Aerosol pH is held fixed throughout each simulation. For a given Cu/Fe, \( \gamma(\text{HO}_2) \) approaches unity with increasing pH, reflecting enhanced chemical loss of O\(_{2}^−\) and therefore reduced volutilization flux. This pH dependence of \( \gamma(\text{HO}_2) \) is consistent with laboratory measurements. Mozurkewich et al. (1987) found higher \( \gamma(\text{HO}_2) \) with neutral Cu-doped aerosols (LiNO\(_2\)) \( \gamma(\text{HO}_2) = 0.94 \) than acidic Cu-doped aerosols (NH\(_4\)HSO\(_4\)) \( \gamma(\text{HO}_2) = 0.40 \). At fixed pH, \( \gamma(\text{HO}_2) \) increases with decreasing Cu/Fe ratio, resulting from the suppressed HO\(_2\) production by (Reaction RA3) and enhanced HO\(_2\) loss by Fe(III) + O\(_{2}^−\) (−I).

The TMI chemistry initiated by HO\(_2\) uptake from the gas phase can lead to either production or loss of HO\(_2\) (Fig. 1), and this can be expressed as a positive or negative HO\(_2\) yield \( (Y_{\text{H}_2\text{O}_2}) \) associated with \( \gamma(\text{HO}_2) \). Figure 3b shows the pH dependence of \( Y_{\text{H}_2\text{O}_2} \) over a range of Cu/Fe ratios. \( Y_{\text{H}_2\text{O}_2} = 0.5 \) indicates that all HO\(_2\) is converted to HO\(_2\), \( Y_{\text{H}_2\text{O}_2} = 0 \) indicates that all HO\(_2\) is converted to HgO, and \( Y_{\text{H}_2\text{O}_2} < 0 \) indicates a reactive uptake of HO\(_2\). When Cu/Fe ≤ 0.05, \( Y_{\text{H}_2\text{O}_2} \) decreases with increasing pH. This is in part due to the enhanced loss of aqueous HO\(_2\) by (Reaction RA1) and Fe(III) + O\(_{2}^−\)(−I), resulting in suppressed production of HO\(_2\) by (Reaction RA5). On the other hand, at higher pH, the oxidation of Fe(II) is enhanced by Fe(OH)\(^{2+}\) + HO\(_2\) which is five orders of magnitude faster than Fe\(^{2+}\) + HO\(_2\). (Reaction RA6) and (Reaction RA7) then become the dominant sinks for Fe(II) and may lead to a reactive uptake of HO\(_2\) \( (Y_{\text{H}_2\text{O}_2} < 0) \). The slight increase of \( Y_{\text{H}_2\text{O}_2} \) at Cu/Fe = 0.1 while pH increases from 0 to 3 is mainly due to the enhanced HO\(_2\) production by (Reaction RA2). This pathway becomes unimportant at lower Cu/Fe.
Fig. 4. Effect of HO$_2$ reactive uptake on non-cloud aerosols ($\gamma$(HO$_2$) = 1 producing H$_2$O) on surface air concentrations of OH, HO$_2$, CO, and O$_3$ in the GEOS-Chem model. Values are annual means for 2005 and are calculated by difference with a simulation including no HO$_2$ uptake.

5 Global implications for atmospheric oxidant chemistry

We examine the potential global implications of Cu-Fe-HO$_x$ cycling by incorporating the corresponding HO$_2$ uptake in the GEOS-Chem global model of aerosol-oxidant chemistry (v9-01-01, http://www.geos-chem.org). Values in Fig. 3a indicate $\gamma$(HO$_2$) in the range 0.4–1 for typical rural aerosol Cu concentrations and Cu/Fe ratios at 298 K. At such high values, uptake of HO$_2$ can become diffusion-limited with little residual sensitivity to $\gamma$(HO$_2$) (Fig. S1 in the Supplement). There are several reasons why such high $\gamma$(HO$_2$) values might not be representative of the global troposphere. As shown in Fig. 3c, $\gamma$(HO$_2$) becomes insignificant for [Cu] <1 $\times$ 10$^{-4}$ M, and the importance of such a threshold was previously noted by Thornton et al. (2008) for Cu-only chemistry. Cu concentrations could be much lower than assumed here in the remote troposphere and at high altitudes. There remain large uncertainties in the aerosol phase and mixing state. Also Cu and Fe may not be chemically available across aerosol types or size ranges due to their distribution, speciation and solubility (Furutani et al., 2011). On the other hand, the higher solubility of HO$_2$ at colder temperatures than the 298 K assumed here would increase $\gamma$(HO$_2$) (Mao et al., 2010a). As pointed out in Table 1, field studies suggest the need for $\gamma$(HO$_2$) $\sim$1 to explain HO$_2$ observations, and there is some evidence that H$_2$O$_2$ is not the product. Other mechanisms than the Cu-Fe-HO$_x$ redox chemistry described here could contribute to HO$_2$ conversion to H$_2$O in aqueous aerosols (Sect. 2 in the Supplement).

The standard GEOS-Chem model includes a parameterization of $\gamma$(HO$_2$) taken from Thornton et al. (2008) for HO$_2$ uptake by pure water. The resulting $\gamma$(HO$_2$) is typically less than 0.1 and the product is H$_2$O$_2$, with no significant effects on global oxidant chemistry. Here we investigated the implications for oxidant chemistry of assuming as an upper limit $\gamma$(HO$_2$) = 1 for all aerosols. We further assume Y$_{H_2O_2}$ = 0 (Fig. 3b), since observations suggest that the dissolved Cu/Fe ratio is usually below 0.1 (Table S4); in fact, it appears from Fig. 3b that Y$_{H_2O_2}$ is more likely to be negative than positive. Previous comparisons to aircraft and satellite observations suggest that GEOS-Chem provides a reasonable representation of aerosol loadings in the global troposphere (Drury et al., 2010; van Donkelaar et al., 2010; Fisher et al., 2011; Wang et al., 2011).

Figure 4 shows the difference of annual mean (2005) simulated surface air concentrations of OH, HO$_2$, CO, and O$_3$ for the GEOS-Chem simulation with fast aerosol conversion of HO$_2$ to H$_2$O ($\gamma$(HO$_2$) = 1, Y$_{H_2O_2}$ = 0) compared to a simulation with no HO$_2$ uptake. The effects are largest in the extratropical northern hemisphere and over the Southern Ocean, where aerosol loading is high and gas-phase photochemistry is slow. Surface OH and HO$_2$ concentrations decrease there by 20-30% and 40-60% respectively; the decrease in OH is partly compensated by an increase
Fig. 5. Seasonal variation of CO concentrations at remote surface sites in northern extratropics. Climatological observations from NOAA/GMD (1988–2007) are shown in black. GEOS-Chem model values are shown in red with no HO\(_2\) uptake and in green with \(\gamma(\text{HO}_2) = 1\) producing H\(_2\)O.

The decrease of OH concentrations drives an annual mean increase of model CO concentrations by 20-30 ppb in the extratropical northern hemisphere, with maximum effect in spring. As shown in Fig. 5, this largely corrects the long-standing seasonal GEOS-Chem bias in that part of the world (Alvarado et al., 2010; Fisher et al., 2010; Kopacz et al., 2010). A similar CO bias in the extratropical northern hemisphere is found in other global models (Shindell et al., 2006) and may be similarly corrected.

Surface ozone concentrations decrease in general by 3–10 ppb over North America and Eurasia. Similar results over North America were reported in a previous study (Horowitz et al., 1998). The largest decreases (up to 20 ppb) are in East Asia and help to correct model overestimates of surface ozone in that region (Wang et al., 2008). Comparison with surface ozone observations in the US from the Clean Air Status and Trends Network (CASTNet) shows a decrease of mean model bias from +7 to +3 ppb (Fig. S2). The production rate of global tropospheric ozone decreases from 5280 Tg yr\(^{-1}\) to 4800 Tg yr\(^{-1}\), and the loss rate decreases from 4660 Tg yr\(^{-1}\) to 4240 Tg yr\(^{-1}\). As a result, the change in global tropospheric ozone burden is rather small (about 1% decrease from 373 Tg to 369 Tg).

HO\(_2\) conversion to H\(_2\)O in aqueous aerosols thus improves the simulation of tropospheric oxidant chemistry in GEOS-Chem and could improve other models as well. Anthropogenic aerosol concentrations are expected to decrease globally in the coming decades as a result of policies for improving air quality (Meinshausen et al., 2011). Our work suggests that this could have a detrimental effect on ozone air quality (Fig. 4) by decreasing HO\(_x\) radical scavenging. It could also lead to a previously unrecognized, indirect negative radiative forcing from aerosols by decreasing the lifetimes of the long-lived greenhouse gases methane and...
hydrofluorocarbons (HFCs). The resulting negative radiative forcing from aerosol decrease would partly offset the positive radiative forcing from decreased aerosol and cloud scattering.

In summary, we have presented an aqueous chemical mechanism for rapid conversion of HO$_2$ to H$_2$O in aerosols, and have explored its potential impact on atmospheric chemistry. Although there are large uncertainties regarding the mechanism, there is evidence from field observations that this rapid conversion does take place, and implementing it in GEOS-Chem shows large effects. A better understanding of aqueous HO$_2$ chemistry in atmospheric aerosols requires substantial work in many aspects. Measurements of aerosol Cu and Fe speciation would be of particular value as speciation could greatly affect the kinetics. More information is needed for the remote troposphere on Cu and Fe concentrations, solubility, and internal mixing across aerosol types. Redox coupling involving other TMI present in atmospheric aerosols (Heal et al., 2005) should be investigated (Marcus, 1993). Better characterization of aqueous-phase kinetics is needed including reaction rate constants and complexation equilibria with ionic strength and temperature dependences. Furthermore, organic compounds have been found to be abundant in aerosols (Ervens and Volkamer, 2010). Oxidation of organic species provides a sink for OH in aerosols, while photoreduction and Fenton reaction of organic complexes could provide a source. In future studies, the aqueous chemical mechanism could be improved by including organic compounds and halogen species, such as in CAPRAM (Ervens et al., 2003).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/13/509/2013/acp-13-509-2013-supplement.pdf.

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References


