

Supplemental material

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S1. Field evidence of HO₂ uptake and its product

The importance of HO₂ uptake on HO_x radical budget depends not only on aerosol surface area, but also on ambient HO_x and NO_x concentrations. Gas phase HO_x loss is in general dominated by three pathways:



In particular, HO_x loss through (RG1) and (RG2) is quadratic on HO_x concentrations, while HO_x loss through HO₂ uptake is only first-order on ambient HO_x. Therefore HO_x loss by HO₂ uptake can only be significant at relatively low level of both HO_x and NO_x concentrations.

We summarize previous field evidence of HO₂ uptake in Table S1. We find that field evidence of HO₂ uptake are mainly from the locations where the gas-phase photochemistry controlling HO_x levels is slow (HO₂ is typically less than 10 ppt) or aerosol loading is high. In fact, a recent study by Fuchs et al. (2011) found a significant interference (up to 50%) in HO₂ measurements by laser-induced fluorescence technique, further supporting the previously unrecognized role of HO₂ uptake.

Three previous studies suggest that the product from HO₂ uptake is unlikely to be H₂O₂. The first study is TOPSE aircraft campaign, in which both overestimates of total peroxy radicals (HO₂ + RO₂) and H₂O₂ were found when comparing box model calculations to observations (Cantrell et al., 2003; Wang et al., 2003). In particular, the overestimate of H₂O₂ cannot be attributed to wet scavenging (Wang et al., 2003). The second study is the measurements of total peroxy radical and H₂O₂ in dust events, in which H₂O₂ observations can be explained by the box model with HO₂ uptake with no formation of H₂O₂ and a reactive uptake for H₂O₂ (de Reus et al., 2005). The third study is the ARCTAS aircraft campaign, in which joint atmospheric observations of HO₂ and H₂O₂ suggest that HO₂ uptake by aerosols may not produce H₂O₂ (Mao et al., 2010).

S2. Other suggested mechanisms for HO₂ uptake

Several mechanisms have been proposed for the fate of HO₂ in aerosol phase. Although these mechanisms are not catalytic, they may still facilitate HO₂ loss in the aerosol phase.

The first mechanism is proposed by Copper and Abbatt (1996), suggesting that HO₂ could react with HSO₄⁻, and form the peroxymonosulfate radical SO₅⁻:

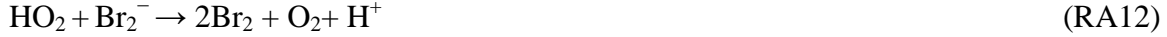


Mao et al. (2010) suggests that SO₅⁻ can then react with O₂⁻, HCOO⁻, and HSO₃⁻, to produce the peroxide HSO₅⁻ (peroxymonosulfate), followed by (RA9) and (RA10) (Jacob, 1986), leading to the conversion to water:



The second mechanism involves the formation of an HO₂ complex. Miller and Francisco (Miller and Francisco, 2001) found from quantum chemical calculations that a stable HO₂-H₂SO₄ complex can be formed in both gas and aerosol phase. But the fate of this complex is unknown.

HO₂ can be also consumed by reactive halogen species in the aerosol phase (Matthew et al., 2003)



This mechanism may be efficient for sea salt aerosols.

S3. GEOS-Chem model

GEOS-Chem is a global 3-D chemical transport model driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-5) of the NASA Global Modeling and Assimilation Office (GMAO) (Bey et al., 2001). We apply here GEOS-Chem version 9-01-01 (<http://www.geos-chem.org/>) to examine the impact of Cu-Fe-HO_x redox mechanism ($\gamma(\text{HO}_2) = 1$ with producing H₂O) on gas phase chemistry. The standard GEOS-Chem simulation of ozone-NO_x-HO_x-VOC-aerosol chemistry is described for example by Mao et al. (2010).

GEOS-Chem simulates aerosol mass concentrations for several aerosol components: sulfate-nitrate ammonium (Park et al., 2004; Fisher et al., 2011), size-resolved mineral dust (Fairlie et al., 2007), fine and coarse sea salt (Alexander et al., 2005), and black carbon and organic carbon (Park et al., 2003; Wang et al., 2011). For each aerosol component, the model calculates an effective area-weighted radius (r_e) dependent on local relative humidity (RH) (Chin et al., 2002).

Gas uptake by each aerosol component is then represented following Martin et al. (2003) by a first-order uptake rate constant k :

$$k = -\left(\frac{r_e}{D_g} + \frac{4}{v\gamma}\right)^{-1} A \quad (1)$$

where v is the mean molecular speed of the gas, D_g is the gas-phase molecular diffusion coefficient, γ is the reactive uptake coefficient for the gas, and A is the aerosol surface area per unit volume of air calculated from the mass concentration and effective radius of that aerosol component. D_g is calculated as a function of molecular weight, temperature, and air density. The standard model includes aerosol uptake of NO₂, NO₃, and N₂O₅ (Jacob, 2000; Evans and Jacob, 2005).

S4. Gas-phase diffusion limitation

We here address the importance of gas-phase diffusion limitation on the resulting HO₂ uptake rate calculated by Eq. (1). With $\gamma(\text{HO}_2)$ closer to 1, gas-phase diffusion, the first term on the right-hand side of Eq.(1), becomes comparably important as the interfacial mass transport, i.e., the second term on the right-hand side of Eq. (1).

Figure S1 shows the ratio of interfacial mass transport to gas-phase diffusion, as a function of $\gamma(\text{HO}_2)$ and aerosol effective radius (corrected by hygroscopic growth factor). For example, when $\gamma(\text{HO}_2) = 1$, gas-phase diffusion rate is equivalent to the interfacial mass transport rate at $r_e = 0.3 \mu\text{m}$, suggesting that gas-phase diffusion then becomes the limiting step for any aerosol with effective radius larger than $0.3 \mu\text{m}$. The gas-phase diffusion limitation has to be taken into account for evaluating the impact of HO_2 uptake on a global scale.

S5. Measurements of aerosol Cu and Fe

S5.1 Size distribution of Cu and Fe mass in ambient aerosols

Cu and Fe have been extensively measured in ambient aerosols. Table S2 and S3 show the measured mass fraction of aerosol Cu and Fe in ambient aerosols.

We find in Table S2 that Cu mass is mainly in submicron aerosols, indicating that combustion is indeed the major source of aerosol Cu. In fact, previous measurements in remote and urban sites both show that a large fraction of aerosol Cu is in ultrafine particles ($<0.1 \mu\text{m}$) (Lannefors et al., 1983; Li and Winchester, 1993). The Cu concentrations we use here assume 0.56 ng m^{-3} in the size bin of $0.5\text{-}1 \mu\text{m}$, only accounting for 22% of Cu mass in submicron aerosols.

In contrast, aerosol Fe may largely originate from dust, but Table S3 still suggests a significant portion in submicron aerosols.

S5.2 Measurements in PM2.5

We show from Table S4 the measurements of Cu and Fe in PM2.5 aerosols. Cu/Fe ratio is typically below 0.1 for aerosols in urban, rural and remote conditions. Similar results are found from the long-term measurements from IMPROVE sites over continental US (Fig S4).

S5.3 Aqueous measurements of dissolved Cu and Fe

Table S5 shows the aqueous measurements of dissolved Cu and Fe from cloud and rain droplets. We find that dissolved Cu/Fe molar ratio is typically 0.01-0.1.

S5.4 Organic complexes

Organic complexes are not included in the model owing to paucity of kinetic data. As a major species among identified water soluble organic compounds (Mader et al., 2004), oxalate can readily form complexes with TMI, while formate and acetate have much less tendency owing to their lower complexation constants (Deguillaume et al., 2005). For less soluble organics, we consider them to be unimportant, because of liquid-liquid phase separation into an organic-rich and an aqueous electrolyte phase (Zuend et al., 2010).

Oxalic acid has first and second acid dissociation constants (pK_a) of 1.2 and 4.2, with stability constant of 6.2, 3.0 and 9.4 (at zero ionic strength) for CuC_2O_4 , $\text{Fe}(\text{C}_2\text{O}_4)$ and $\text{Fe}(\text{C}_2\text{O}_4)^+$ respectively (Sedlak and Hoigné, 1993). Observed aerosol oxalate concentrations are comparable to that of aerosol iron (Sorooshian et al., 2006). We here focus on oxalic acid as a representative species of dicarboxylic acids (DCA), and similar conclusion can be extended to other DCA, such as malonic and succinic acids (Furukawa and Takahashi, 2011).

Fe-oxalato complexes appear to be a small fraction of total Fe. Recent measurement of oxalate metal complexes suggested that the major fraction (60 – 80%) of aerosol oxalate is chelated with Ca, Zn, and Mg, despite their much lower stability constant (3.0, 4.9 and 3.4) and comparable concentrations to Fe (Furukawa and Takahashi, 2011). This is consistent with the fast cycling between photolysis of Fe(III)-oxalato complexes (photolysis rate $\sim 10^{-2} \text{ s}^{-1}$) (Zuo and Hoigné, 1992), and $\text{Fe}(\text{II})\text{C}_2\text{O}_4 + \text{H}_2\text{O}_2$ that is three orders of magnitude faster than $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ (Sedlak and Hoigné, 1993), leading to a rapid loss of $\text{C}_2\text{O}_4^{2-}$.

The kinetic data of Cu-oxalato complexes are unknown. We estimate that $\text{Cu}(\text{C}_2\text{O}_4)$ is a small fraction (< 0.5) of dissolved copper, given the high solubility of Cu oxalate relative to Ca and Zn (Furukawa and Takahashi, 2011). In addition, organically complexed copper can also be a significant sink for HO_2/O_2^- (Voelker et al., 2000). Therefore we conclude that organic complexation has limited impact on Cu-Fe- HO_x cycling, given the weak response of $\gamma(\text{HO}_2)$ to Cu concentrations.

S6. Activity coefficient for aerosol chemistry

Activity coefficient must be taken into account for calculation of aerosol chemistry. We follow Ross and Noone (1991) to calculate the activity coefficient for the ions in our simulation. For an ion(x) of charge z , the activity coefficient (A_x) is

$$\log(A_x) = -z_x^2 D - \sum_y \varepsilon(x, y, l) m_y$$

where

$$D = \frac{0.5109\sqrt{l}}{1 + 1.5\sqrt{l}}$$

Here l is ionic strength, m_y is molality of the solution, and ε is the interaction coefficient for the correction in concentrated solutions.

$$\varepsilon(x, y, l) = \frac{(\log(A_{\mp}) + z_x z_y D)(z_x + z_y)^2}{4l}$$

The activity coefficient for free ion Cu^{2+} can be written as:

$$\log(A_{Cu^{2+}}) = -4D - \varepsilon(Cu^{2+}, SO_4^{2-})[SO_4^{2-}]$$

$\varepsilon(Cu^{2+}, SO_4^{2-})$ was calculated using the mean activity coefficients tabulated in Robinson and Stokes (2002), which varies at different ionic strength. When ionic strength is greater than 1.4m, the mean activity coefficient is adopted from Baes et al. (1993).

The activity coefficient is implemented for example as:

$$K = \frac{A(CuSO_4)[CuSO_4]}{A(Cu^{2+})[Cu^{2+}]A(SO_4^{2-})[SO_4^{2-}]}$$

Here K is the equilibrium constant for $Cu(SO_4)(aq)$ at indefinite dilution. $A(CuSO_4)$ is the mean activity coefficient for $CuSO_4$.

We also correct the Henry's law constant of O_2 , O_3 , HO_2 and H_2O_2 , by the activity coefficient A as a result of salting out effect (Millero and Sohn, 1992):

$$H^* = \frac{H}{A}$$

where H is the Henry's law constant at zero ionic strength.

Tables

Table S1 Mass fraction of Cu in four size bins in ambient aerosols

| | Type | <1.0 μm | 1.0-2.5 μm | 2.5-10.0 μm | >10.0 μm | Reference |
|---------------------------|--------|------------|---------------|----------------|-------------|---------------------------------------|
| Central England, UK | rural | 48% | 24% | 24% | 4% | Allen et al. (2001) |
| Auchencorth, UK | rural | 28% | 15% | 45% | 22% | Allen et al. (2001) |
| New York City, USA | urban | 25% | 50% | 15% | 10% | Bernstein and Rahn (1979) |
| Birmingham, UK | urban | 71% | 16% | 13% | | Birmili et al. (2006) |
| Suburban Vienna, AT | rural | 58% | | | | Horvath et al. (1996) |
| Central Vienna, AT | urban | 57% | | | | Horvath et al. (1996) |
| Ponce South, PR | urban | 52% | 28% | 16% | 4% | Infante and Acosta (1991) |
| Ponce West, PR | urban | 58% | 11% | 22% | 9% | Infante and Acosta (1991) |
| Ponce East, PR | urban | 26% | 33% | 20% | 20% | Infante and Acosta (1991) |
| Ponce North, PR | urban | 100% | | | | Infante and Acosta (1991) |
| Ponce Center, PR | urban | 29% | 45% | 17% | 9% | Infante and Acosta (1991) |
| Kola Peninsula, Russia | remote | 46% | | | 10% | Kelley et al.(1995) |
| Thessaloniki, Greece | urban | 46% | 14% | 25% | 15% | Samara and Voutsas (2005) |
| Southeastern US | rural | 99% | | | | Goforth and Christoforou (2006) |
| Sweden | rural | 80% | 9% | 11% | | Lannefors et al. (1983) |

Table S2 Mass fraction of Fe in four size bins in ambient aerosols

| | Type | <1.0 μm | 1.0-2.5 μm | 2.5-10.0 μm | >10.0 μm | Reference |
|-------------------------|-------|-----------------------|--------------------------|---------------------------|------------------------|---------------------------------------|
| Central England, UK | rural | 15% | 30% | 40% | 15% | Allen et al. (2001) |
| New York City, USA | urban | 21% | 1% | 46% | 32% | Bernstein and Rahn (1979) |
| Birmingham, UK | urban | 35% | 32% | 32% | | Birmili et al. (2006) |
| Suburban Vienna, AT | rural | 50% | | | | Horvath et al. (1996) |
| Central Vienna, AT | urban | 36% | | | | Horvath et al. (1996) |
| Ponce South, PR | urban | 28% | 32% | 15% | 25% | Infante and Acosta (1991) |
| Ponce West, PR | urban | 29% | 7% | 23% | 41% | Infante and Acosta (1991) |
| Ponce East, PR | urban | 20% | 41% | 21% | 18% | Infante and Acosta (1991) |
| Ponce North, PR | urban | 42% | 36% | 0 | 22% | Infante and Acosta (1991) |
| Ponce Center, PR | urban | 28% | 17% | 21% | 34% | Infante and Acosta (1991) |
| Thessaloniki, Greece | urban | 25% | 12% | 34% | 29% | Samara and Voutsas (2005) |
| Southeastern US | rural | 22% | | | | Goforth and Christoforou (2006) |

Table S3 Measurements of aerosol Cu and Fe in PM2.5 (Unit: ng m⁻³)

| | Type | Fe | Cu | Cu/Fe | |
|--|--------|------------------|------------------|-------|--------------------------|
| Background in Edinburgh | urban | 27.6 | 1.4 | 5.1% | Heal et al. (2005) |
| Birmingham | urban | 114 | 30.2 | 26.5% | Harrison and Yin (2000) |
| Toronto | urban | 55 | 2.5 | 4.5% | Lee et al. (2003) |
| Background in Switzerland | urban | 200 | 11 | 5.5% | Bukowiecki et al. (2009) |
| Mexico City ^a | urban | 1600 | 57 | 3.6% | Mugica et al. (2009) |
| Background in Beijing | urban | 480 | 20 | 4.2% | Sun et al. (2006) |
| Beijing Summer | urban | 650 | 40 | 6.2% | Sun et al. (2004) |
| Beijing Winter | urban | 1040 | 80 | 7.7% | Sun et al. (2004) |
| Downey, Los Angels | urban | 150.9 | 3.5 | 2.3% | Singh et al. (2002) |
| Gosan, Korea | urban | 453 ^b | 4.8 ^b | 1.1% | Kim et al. (2011) |
| Diesel transport routes in Korea | urban | 1198 | 67.3 | 5.6% | Kuo et al. (2009) |
| eastern Transvaal, South Africa ^c | rural | 101 | 0.62 | 0.6% | Maenhaut et al. (1996) |
| Fire plume in South Africa | rural | 162 | 7 | 4.3% | Formenti et al. (2003) |
| Amazon forest dry season | remote | 28.2 | 1.6 | 5.7% | Artaxo et al. (2002) |
| Amazon forest wet season | remote | 21.4 | 0.33 | 1.5% | Artaxo et al. (2002) |
| Amazon pasture dry season | remote | 162 | 2.1 | 1.3% | Artaxo et al. (2002) |
| Amazon pasture wet season | remote | 26 | 0.22 | 0.8% | Artaxo et al. (2002) |
| Upper troposphere in Arctic | remote | 185 | 19 | 10.3% | Li and Winchester (1993) |
| Middle troposphere in Arctic | remote | 85 | 20 | 23.5% | Li and Winchester (1993) |
| Ground | remote | 10 | 1 | 10.0% | Li and Winchester (1993) |

^a Average over three periods.

^b Only measured at PM10, averaged over seven years (2000-2006).

^c Average over three sites : Skukuza, Pretoriuskop, Palmer.

^d Only measured at PM10.

Table S4 Aqueous measurements of dissolved Cu and Fe

| | type | dissolved Fe (μM) | dissolved Cu (μM) | Cu/Fe | aqueous phase | reference |
|-------------------------|---------|--------------------------------|--------------------------------|----------|---------------|------------------------------------|
| Darmstadt, Germany | urban | 0.22 | 0.03 | 13.6% | rain | Hofmann et al. (1991) |
| Gross-Rohrheim, Germany | rural | 0.25 | 0.03 | 12% | rain | Hofmann et al. (1991) |
| Plynlimon, Wales | rural | 0.72 | 0.08 | 11% | cloud | Wilkinson et al. (1997) |
| Plynlimon, Wales | rural | 0.078 | 0.026 | 33% | rain | Wilkinson et al. (1997) |
| Plynlimon, Wales | rural | 1.34 | 0.13 | 10% | rain | Cawse (1980) ^a |
| Tour du Valat, France | coastal | 0.29 | 0.02 | 6.9% | rain | Guieu et al. (1997) |
| Jaipur, India | urban | 5.3 | 0.32 | 6.0% | rain | Manoj et al. (2000) |
| Kota, India | urban | 4.1 | 0.12 | 2.9% | rain | Manoj et al. (2000) |
| Paradize, New Zealand | remote | 0.037 | 0.002 | 0.5% | rain | Halstead et al. (2000) |
| Bakersfield, CA | urban | 0.2 – 0.4 | 0.008 – 0.015 | 3% – 4% | fog / stratus | Siefert et al. (1998) ^b |
| Great Dun Fell, UK | rural | 0.06 – 1.6 | 0.0042 – 0.031 | 2% - 20% | cloud | Sedlak et al. (1997) |

^a Data is from Wilkinson et al. (1997).

^b Dissolved TMI was measured by filter.

Table S5 Nomenclature of species in box model

| Nomenclature | Species |
|--------------|--|
| Fe(II) | Fe^{2+} , $\text{Fe}(\text{OH})^+$ |
| Fe(III) | Fe^{3+} , $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{SO}_4)^+$, $\text{Fe}(\text{OH})^{2+}$ |
| Fe(IV) | FeO^{2+} |
| Cu(I) | Cu^+ |
| Cu(II) | Cu^{2+} , $\text{CuSO}_4(\text{aq})$ |

Table S6 Activity coefficients produced from AIM for NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ aerosols

| Dry radii (μm) | RH (%) | Wet Volume $\times 10^{-13}$ (cm^3) | Ionic Strength | $m(\text{H}^+)^{\text{a}}$ | $m(\text{NH}_4^+)$ | $m(\text{SO}_4^{2-})$ | $m(\text{HSO}_4^-)$ | $A(\text{SO}_4^{2-})^{\text{b}}$ | $A(\text{H}^+)$ |
|-----------------------------|--------|--|----------------|----------------------------|--------------------|-----------------------|---------------------|----------------------------------|-----------------|
| 0.35 | 85 | 7.90 | 7.84 | 1.74 | 4.36 | 1.74 | 2.63 | 0.010 | 1.020 |
| 0.35 | 85 | 8.65 | 12.2 | 0.102 | 8.43 | 3.90 | 0.32 | 0.0162 | 0.255 |
| 0.35 | 85 | 8.25 | 13.2 | 1.14(-2) ^c | 8.85 | 4.39 | 0.0328 | 0.0159 | 0.203 |
| 0.35 | 85 | 8.21 | 13.3 | 1.16(-3) | 8.89 | 4.44 | 3.29(-3) | 0.0159 | 0.199 |
| 0.35 | 85 | 8.20 | 13.3 | 1.37(-4) | 8.90 | 4.45 | 3.89(-4) | 0.0159 | 0.198 |
| 0.35 | 85 | 8.20 | 13.3 | 1.37(-5) | 8.90 | 4.45 | 3.89(-4) | 0.0159 | 0.198 |

^a Molality with unit mol/kg solvent.

^b Activity coefficient.

^c Read 1.14(-2) as 1.14×10^{-2} .

Table S7 Activity coefficients used in the box model

| | Activity coefficient |
|---|---------------------------------|
| Univalent ions | |
| Cu^+ , $\text{Fe}(\text{OH})^+$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{SO}_4)^+$, O_2^- | 0.6 |
| Bivalent ions | |
| Cu^{2+} , Fe^{2+} , $\text{Fe}(\text{OH})^{2+}$, and FeO^{2+} | Calculated as Cu^{2+} |
| Trivalent ions | |
| Fe^{3+} | 0.01 ^a |
| Neutral species | |
| HO_2 , OH , O_2 , O_3 , H_2O_2 , Cl | $10^{0.1 \cdot I}$ ^b |

^a lowest estimate from Millero et al. (2009).

^b I is the ionic strength. This calculation is following Ross and Noone (1991).

Table S8 Kinetic data for the simulation of TMI chemistry in aqueous aerosols

| Reactants | Products | No. | k_{298} | Ea/R | Reference |
|---|---|-----|-----------|------|---------------------------------|
| Fe chemistry | | | | | |
| $\text{H}_2\text{O}_2 + \text{Fe}^{2+}$ | $\text{Fe}^{3+} + \text{OH} + \text{OH}^-$ | R1 | 70 | 5050 | Christensen et al. (1993) |
| $\text{H}_2\text{O}_2 + \text{FeO}^{2+}$ | $\text{Fe}^{3+} + \text{HO}_2 + \text{OH}^-$ | R2 | 9.5(3) | 2800 | Jacobsen et al. (1997) |
| $\text{H}_2\text{O}_2 + \text{Fe}(\text{OH})^+$ | $\text{Fe}(\text{OH})^{2+} + \text{OH} + \text{OH}^-$ | R3 | 1.9(6) | 6200 | Moffett and Zika (1987) |
| $\text{H}_2\text{O}_2 + \text{Fe}^{3+}$ | $\text{Fe}^{2+} + \text{HO}_2 + \text{H}^+$ | R4 | 2.0(-3) | | Walling and Goose (1973) |
| $\text{H}_2\text{O}_2 + \text{Fe}(\text{OH})^{2+}$ | $\text{Fe}^{2+} + \text{HO}_2 + \text{H}_2\text{O}$ | R5 | 2.0(-3) | | estimated ^a |
| $\text{O}_2^- + \text{Fe}^{2+} + 2\text{H}^+$ | $\text{H}_2\text{O}_2 + \text{Fe}^{3+}$ | R7 | 1.0(7) | | Rush and Bielski (1985) |
| $\text{O}_2^- + \text{Fe}^{3+}$ | $\text{Fe}^{2+} + \text{O}_2$ | R8 | 1.5(8) | | Rush and Bielski (1985) |
| $\text{O}_2^- + \text{Fe}(\text{OH})^{2+}$ | $\text{Fe}^{2+} + \text{O}_2 + \text{OH}^-$ | R9 | 1.5(8) | | Rush and Bielski (1985) |
| $\text{O}_2^- + \text{Fe}(\text{OH})^{2+}$ | $\text{Fe}^{2+} + \text{O}_2 + 2\text{OH}^-$ | R10 | 1.5(8) | | Rush and Bielski (1985) |
| $\text{HO}_2 + \text{Fe}^{2+} + \text{H}^+$ | $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ | R11 | 1.2(6) | 5050 | Jayson et al. (1973b) |
| $\text{HO}_2 + \text{FeO}^{2+}$ | $\text{Fe}^{3+} + \text{O}_2 + \text{OH}^-$ | R12 | 2.0(6) | | Jacobsen et al. (1998) |
| $\text{HO}_2 + \text{Fe}(\text{OH})^{2+}$ | $\text{Fe}^{2+} + \text{O}_2 + \text{H}_2\text{O}$ | R13 | 1.3(5) | | Ziajka et al. (1994) |
| $\text{OH} + \text{Fe}^{2+}$ | $\text{Fe}(\text{OH})^{2+}$ | R14 | 4.6(8) | 1100 | Christensen and Sehested (1981) |
| $\text{OH} + \text{FeO}^{2+} + \text{H}^+$ | $\text{Fe}^{3+} + \text{H}_2\text{O}_2$ | R15 | 1.0(7) | | Loegager et al. (1992) |
| $\text{O}_3 + \text{Fe}^{2+}$ | $\text{FeO}^{2+} + \text{O}_2$ | R16 | 8.2(5) | | Loegager et al. (1992) |
| $\text{FeO}^{2+} + \text{H}_2\text{O}$ | $\text{Fe}^{3+} + \text{OH} + \text{OH}^-$ | R17 | 1.3(-2) | 4100 | Jacobsen et al. (1998) |
| $\text{FeO}^{2+} + \text{Fe}^{2+} + \text{H}_2\text{O}$ | $2\text{Fe}^{3+} + 2\text{OH}^-$ | R18 | 7.2(4) | 842 | Jacobsen et al. (1997) |
| $\text{Cl}_2^- + \text{Fe}^{2+}$ | $\text{Fe}^{3+} + 2\text{Cl}^-$ | R22 | 1.0(7) | 3060 | Thornton and Laurence (1973) |
| $\text{O}_2^- + \text{Fe}(\text{SO}_4)^+$ | $\text{Fe}^{2+} + \text{SO}_4^{2-} + \text{O}_2$ | R33 | 1.5(8) | | Rush and Bielski (1985) |
| $\text{HO}_2 + \text{Fe}(\text{SO}_4)^+$ | $\text{Fe}^{2+} + \text{SO}_4^{2-} + \text{O}_2 + \text{H}^+$ | R34 | 1.0(3) | | Rush and Bielski (1985) |
| $\text{Fe}^{3+} + \text{SO}_4^{2-}$ | $\text{Fe}(\text{SO}_4)^+$ | R44 | 3.2(3) | | Jayson et al. (1973a) |
| $\text{Fe}(\text{SO}_4)^+$ | $\text{Fe}^{3+} + \text{SO}_4^{2-}$ | R45 | 2.7(1) | | Jayson et al. (1973a) |

| | | | | |
|---|---|------|----------|-------------------------------|
| Cu chemistry | | | | |
| OH + Cu ⁺ | Cu ²⁺ + OH ⁻ | R48 | 3.0(9) | Goldstein et al. (1992) |
| O ₂ + Cu ⁺ | Cu ²⁺ + O ₂ ⁻ | R50 | 4.6(5) | Bjergbakke et al. (1976) |
| H ₂ O ₂ + Cu ⁺ | Cu ²⁺ + OH + OH ⁻ | R51 | 7.0(3) | Berdnikov (1973) |
| HO ₂ + Cu ⁺ + H ⁺ | Cu ²⁺ + H ₂ O ₂ | R52 | 3.5(9) | Berdnikov (1973) |
| O ₂ ⁻ + Cu ⁺ + H ⁺ | Cu ²⁺ + H ₂ O ₂ | R53 | 9.4(9) | Piechowski et al. (1993) |
| HO ₂ + Cu ²⁺ | Cu ⁺ + O ₂ + H ⁺ | R54 | 1.0(8) | Rabani et al. (1973) |
| O ₂ ⁻ + Cu ²⁺ | Cu ⁺ + O ₂ | R55 | 8.0(9) | Rabani et al. (1973) |
| HO ₂ + Cu(SO ₄) | Cu ⁺ + O ₂ + HSO ₄ ⁻ | R117 | 1.0(7) | estimated |
| O ₂ ⁻ + Cu(SO ₄) | Cu ⁺ + O ₂ + SO ₄ ²⁻ | R118 | 1.0(8) | estimated |
| Cu-Fe coupling | | | | |
| Fe ³⁺ + Cu ⁺ | Cu ²⁺ + Fe ²⁺ | R87 | 1.3(7) | Bjergbakke et al. (1976) |
| Fe(OH) ²⁺ + Cu ⁺ | Cu ²⁺ + Fe ²⁺ + OH ⁻ | R88 | 3.0(7) | Sedlak and Hoigné (1993) |
| Fe(OH) ₂ ⁺ + Cu ⁺ | Cu ²⁺ + Fe ²⁺ + 2OH ⁻ | R89 | 1.3(7) | estimated ^a |
| Fe(SO ₄) ⁺ + Cu ⁺ | Cu ²⁺ + Fe ²⁺ + SO ₄ ²⁻ | R116 | 1.8(6) | estimated ^b |
| Odd hydrogen | | | | |
| OH + HO ₂ | H ₂ O + O ₂ | R93 | 7.0(9) | Sehested et al. (1968) |
| OH + O ₂ ⁻ | OH ⁻ + O ₂ | R94 | 1.0(10) | Sehested et al. (1968) |
| OH + H ₂ O ₂ | H ₂ O + HO ₂ | R95 | 2.7(7) | Christensen et al. (1982) |
| HO ₂ + HO ₂ | H ₂ O ₂ + O ₂ | R99 | 8.6(5) | Bielski (1978) |
| HO ₂ + O ₂ ⁻ | H ₂ O ₂ + O ₂ + OH ⁻ | R100 | 1.0(8) | Bielski (1978) |
| O ₃ + O ₂ ⁻ + H ₂ O | OH + 2O ₂ + OH ⁻ | R101 | 1.5(9) | Sehested et al. (1983) |
| Photolysis | | | | |
| O ₃ + H ₂ O | H ₂ O ₂ + O ₂ | P1 | 2.98(-4) | Graedel and Weschler (1981) |
| H ₂ O ₂ | 2OH | P2 | 4.81(-6) | Graedel and Weschler (1981) |
| Fe ³⁺ + H ₂ O | Fe ²⁺ + OH + H ⁺ | P9 | 6.41(-6) | Benkelberg and Warneck (1995) |
| Fe(OH) ²⁺ | Fe ²⁺ + OH | P10 | 5.63(-3) | Benkelberg and |

| | | | | | |
|---------------------------------------|--|-----|-----------|-------|-----------------------------|
| | | | | | Warneck (1995) |
| Equilibria | | | | | |
| $\text{Fe}^{2+} + \text{H}_2\text{O}$ | $\text{Fe}(\text{OH})^+ + \text{H}^+$ | E1 | 3.22(-10) | | Mesmer (1971) |
| $\text{Fe}^{3+} + \text{H}_2\text{O}$ | $\text{Fe}(\text{OH})^{2+} + \text{H}^+$ | E2 | 6.0(-3) | | Brandt and van Eldik (1995) |
| HO_2 | $\text{O}_2^- + \text{H}^+$ | E14 | 2.05(-5) | | Bielski (1978) |
| H_2O_2 | $\text{HO}_2^- + \text{H}^+$ | E15 | 1.6(-12) | -3700 | Hoffmann et al. (1985) |
| $\text{Cu}^{2+} + \text{SO}_4^{2-}$ | $\text{Cu}(\text{SO}_4)$ | E20 | 2.3(2) | | Casas et al. (2000) |

^a Estimated following Deguillaume et al. (2004)

^b: use the lowest value measured in H_2SO_4 solution when $\text{pH}=1.6$, assuming $\text{Fe}(\text{III})$ is dominated by $\text{Fe}(\text{SO}_4)^+$.

Table S9 Henry's law constants for species in box model

| Species | K_{298} (M atm ⁻¹) | $\Delta H_{298}^{\circ}/R$ (K) | reference |
|-------------------------------|----------------------------------|--------------------------------|-----------------------------------|
| HO ₂ | 2.0(3) | 6600 | Schwartz (1984) |
| H ₂ O ₂ | 7.4(4) | 6615 | Lind and Kok (1986) |
| O ₂ | 1.2(-3) | 1620 | |
| O ₃ | 1.1(-2) | 2300 | Kosak-Channing and Helz (1983) |

Note: Read 2.0 (3) as 2.0×10^{-3} . The Henry's Law constant K at temperature T is

$$K = K_{298} \exp\left[\frac{-\Delta H_{298}^{\circ}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \text{ where } T_0 = 298 \text{ K.}$$

Figures

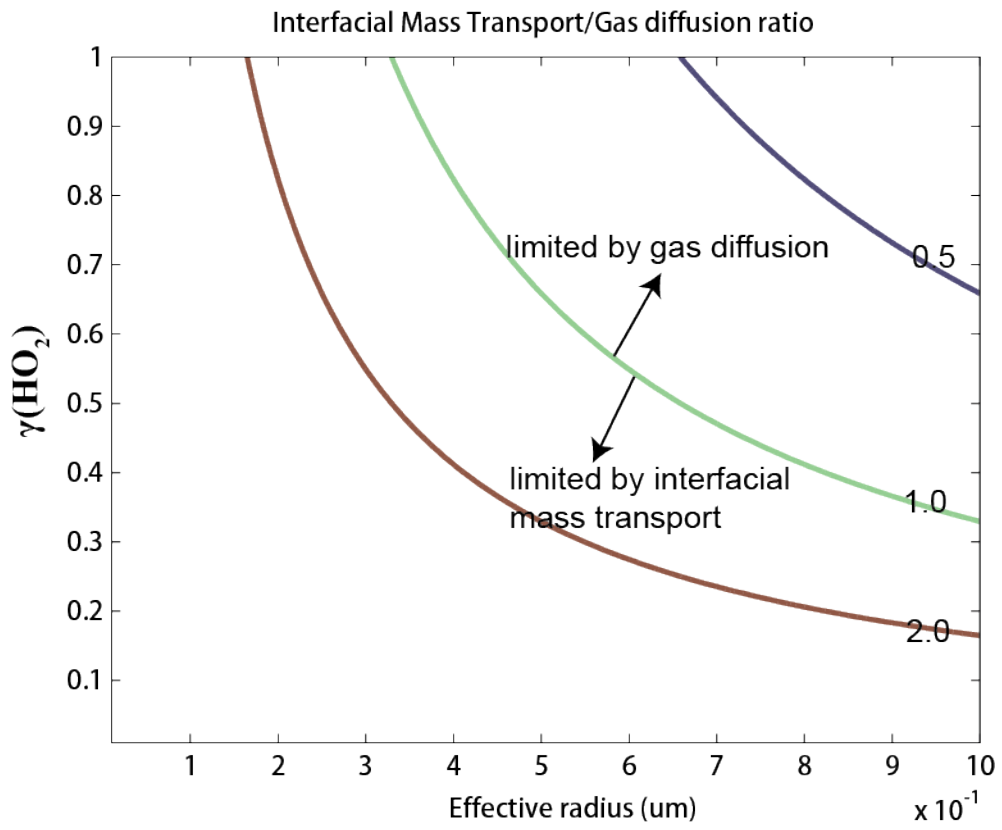


Figure S1 Ratio of interfacial mass transport to gas diffusion as a function of $\gamma(\text{HO}_2)$ and aerosol effective radius (corrected by hygroscopic growth factor).

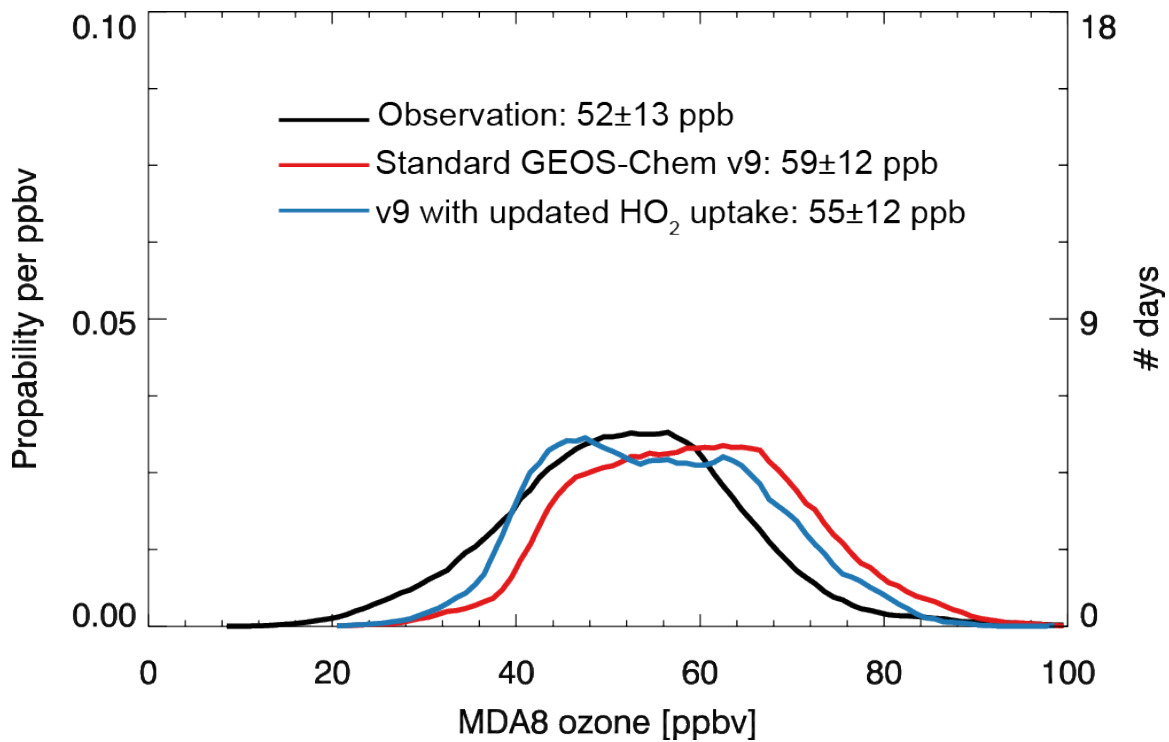


Figure S2 Probability distributions of daily 8-h max ozone concentrations in March-August 2006 for 80 CASTNet sites in the US. Observations (black) are compared to standard GEOS-Chem simulations (red) and GEOS-Chem with updated HO₂ uptake (blue).

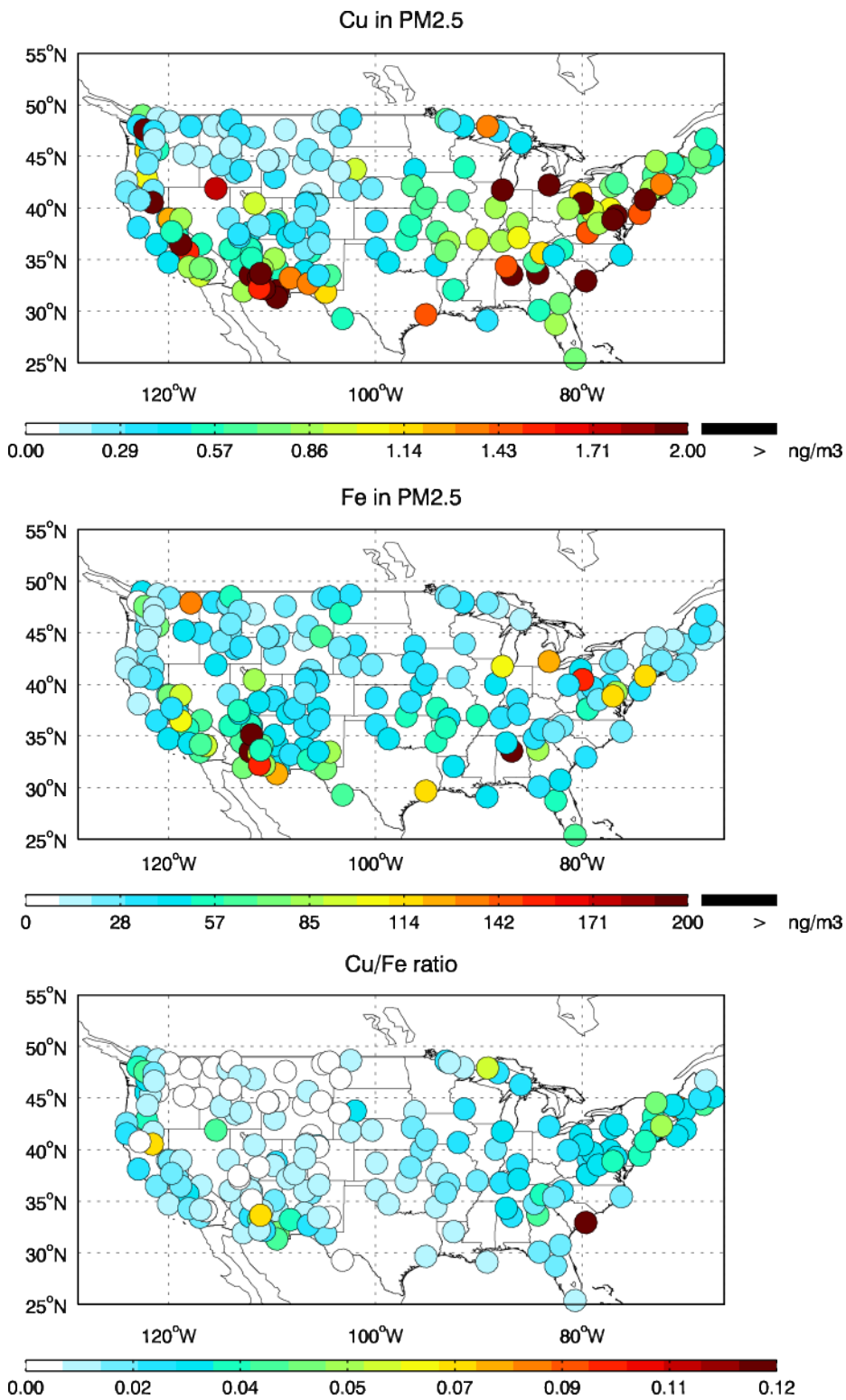


Figure S3 Mean concentrations of measured Cu and Fe in PM 2.5 from the IMPROVE sites in continental US during the period of 1988-2004.

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