Supplemental material

Content

S1. Field evidence of HO_2 uptake and its product

The importance of HO_2 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:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad \text{(RG1)}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \quad \text{(RG2)}$$

$$NO_2 + OH + M \rightarrow HNO_3 + M \quad \text{(RG3)}$$

In particular, HO_x loss through (RG1) and (RG2) is quadratic on HO_x concentrations, while HO_x loss through HO_2 uptake is only first-order on ambient HO_x. Therefore HO_x loss by HO_2 uptake can only be significant at relatively low level of both HO_x and NO_x concentrations.

We summarize previous field evidence of HO_2 uptake in Table S1. We find that field evidence of HO_2 uptake are mainly from the locations where the gas-phase photochemistry controlling HO_x levels is slow (HO_2 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 HO_2 measurements by laser-induced fluorescence technique, further supporting the previously unrecognized role of HO_2 uptake.

Three previous studies suggest that the product from HO_2 uptake is unlikely to be H_2O_2. The first study is TOPSE aircraft campaign, in which both overestimates of total peroxy radicals (HO_2 + RO_2) and H_2O_2 were found when comparing box model calculations to observations (Cantrell et al., 2003; Wang et al., 2003). In particular, the overestimate of H_2O_2 cannot be attributed to wet scavenging (Wang et al., 2003). The second study is the measurements of total peroxy radical and H_2O_2 in dust events, in which H_2O_2 observations can be explained by the box model with HO_2 uptake with no formation of H_2O_2 and a reactive uptake for H_2O_2 (de Reus et al., 2005). The third study is the ARCTAS aircraft campaign, in which joint atmospheric observations of HO_2 and H_2O_2 suggest that HO_2 uptake by aerosols may not produce H_2O_2 (Mao et al., 2010).

S2. Other suggested mechanisms for HO_2 uptake

Several mechanisms have been proposed for the fate of HO_2 in aerosol phase. Although these mechanisms are not catalytic, they may still facilitate HO_2 loss in the aerosol phase.

The first mechanism is proposed by Copper and Abbatt (1996), suggesting that HO_2 could react with HSO_4^-, and form the peroxymonosulfate radical SO_5^-:

$$HO_2 + HSO_4^- \rightarrow SO_5^- + H_2O \qquad \text{(RA8)}$$

Mao et al. (2010) suggests that SO_5^- can then react with O_2^-, $HCOO^-$, and HSO_3^-, to produce the peroxide HSO_5^- (peroxymonosulfate), followed by (RA9) and (RA10) (Jacob, 1986), leading to the conversion to water:

$$HSO_5^- + OH \rightarrow SO_5^- + H_2O \qquad \text{(RA9)}$$

$$HSO_5^- + HSO_3^- + H^+ \rightarrow 2SO_4^{2-} + 2H^+ \qquad \text{(RA10)}$$

The second mechanism involves the formation of an HO_2 complex. Miller and Francisco (Miller and Francisco, 2001) found from quantum chemical calculations that a stable HO_2-H_2SO_4 complex can be formed in both gas and aerosol phase. But the fate of this complex is unknown.

HO_2 can be also consumed by reactive halogen species in the aerosol phase (Matthew et al., 2003)

$$HO_2 + Br_2^- \rightarrow Br_2 + HO_2^- \qquad \text{(RA11)}$$

$$HO_2 + Br_2^- \rightarrow 2Br_2 + O_2 + H^+ \qquad \text{(RA12)}$$

This mechanism may be efficient for sea salt aerosols.

S3. Gas-phase diffusion limitation

Gas uptake by aerosols can be represented as a first-order uptake rate constant *k* (Jacob, 2000) :

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

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.

We here address the importance of gas-phase diffusion limitation on the resulting HO_2 uptake rate calculated by Eq. (1). With $\gamma(HO_2)$ 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 $\gamma(HO_2)$ and aerosol effective radius (corrected by hygroscopic growth factor). For example, when $\gamma(HO_2) = 1$, gas-phase diffusion rate is equivalent to the interfacial mass transport rate at $r_e = 0.3$ µm, suggesting that gas-phase diffusion then becomes the limiting step for any aerosol with effective radius larger than 0.3 µm. The gas-phase diffusion limitation has to be taken into account for evaluating the impact of HO_2 uptake on a global scale.

S4. Measurements of aerosol Cu and Fe

S4.1 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 um) (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 0.5-1 um, 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.

S4.2 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).

S4.3 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. 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 change 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 Voutsa (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 Voutsa (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+}, $Fe(OH)^{+}$
Fe(III)	Fe^{3+}, $Fe(OH)_2^{+}$, $Fe(SO_4)^{+}$, $Fe(OH)^{2+}$
Fe(IV)	FeO^{2+}
Cu(I)	Cu^{+}
Cu(II)	Cu^{2+}, $CuSO_4$(aq)

Table S6 Activity coefficients produced from AIM for NH_4HSO_4 and $(NH_4)_2SO_4$ aerosols

Dry radii (μm)	RH (%)	Wet Volume ×10^{-13} (cm^3)	Ionic Strength	m(H^+)[a]	m(NH_4^+)	m(SO_4^{2-})	m(HSO_4^-)	A(SO_4^{2-})[b]	A(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^+, $Fe(OH)^+$, $Fe(OH)_2^+$, $Fe(SO_4)^+$, O_2^-	0.6
Bivalent ions	
Cu^{2+}, Fe^{2+}, $Fe(OH)^{2+}$, 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	$10^{0.1*l}$ [b]

[a] lowest estimate from Millero et al. (2009).

[b] *l* 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					
$H_2O_2 + Fe^{2+}$	$Fe^{3+} + OH + OH^-$	R1	70	5050	Christensen et al. (1993)
$H_2O_2 + FeO^{2+}$	$Fe^{3+} + HO_2 + OH^-$	R2	9.5(3)	2800	Jacobsen et al. (1997)
$H_2O_2 + Fe(OH)^+$	$Fe(OH)^{2+} + OH + OH^-$	R3	1.9(6)	6200	Moffett and Zika (1987)
$H_2O_2 + Fe^{3+}$	$Fe^{2+} + HO_2 + H^+$	R4	2.0(-3)		Walling and Goose (1973)
$H_2O_2 + Fe(OH)^{2+}$	$Fe^{2+} + HO_2 + H_2O$	R5	2.0(-3)		estimated[a]
$O_2^- + Fe^{2+} + 2H^+$	$H_2O_2 + Fe^{3+}$	R7	1.0(7)		Rush and Bielski (1985)
$O_2^- + Fe^{3+}$	$Fe^{2+} + O_2$	R8	1.5(8)		Rush and Bielski (1985)
$O_2^- + Fe(OH)^{2+}$	$Fe^{2+} + O_2 + OH^-$	R9	1.5(8)		Rush and Bielski (1985)
$O_2^- + Fe(OH)^{2+}$	$Fe^{2+} + O_2 + 2OH^-$	R10	1.5(8)		Rush and Bielski (1985)
$HO_2 + Fe^{2+} + H^+$	$Fe^{3+} + H_2O_2$	R11	1.2(6)	5050	Jayson et al. (1973a)
$HO_2 + FeO^{2+}$	$Fe^{3+} + O_2 + OH^-$	R12	2.0(6)		Jacobsen et al. (1998)
$HO_2 + Fe(OH)^{2+}$	$Fe^{2+} + O_2 + H_2O$	R13	1.3(5)		Ziajka et al. (1994)
$OH + Fe^{2+}$	$Fe(OH)^{2+}$	R14	4.6(8)	1100	Christensen and Sehested (1981)
$OH + FeO^{2+} + H^+$	$Fe^{3+} + H_2O_2$	R15	1.0(7)		Loegager et al. (1992)
$O_3 + Fe^{2+}$	$FeO^{2+} + O_2$	R16	8.2(5)		Loegager et al. (1992)
$FeO^{2+} + H_2O$	$Fe^{3+} + OH + OH^-$	R17	1.3(-2)	4100	Jacobsen et al. (1998)
$FeO^{2+} + Fe^{2+} + H_2O$	$2Fe^{3+} + 2OH^-$	R18	7.2(4)	842	Jacobsen et al. (1997)
$Cl_2^- + Fe^{2+}$	$Fe^{3+} + 2Cl^-$	R22	1.0(7)	3060	Thornton and Laurence (1973)
$O_2^- + Fe(SO_4)^+$	$Fe^{2+} + SO_4^{2-} + O_2$	R33	1.5(8)		Rush and Bielski (1985)
$HO_2 + Fe(SO_4)^+$	$Fe^{2+} + SO_4^{2-} + O_2 + H^+$	R34	1.0(3)		Rush and Bielski (1985)
$Fe^{3+} + SO_4^{2-}$	$Fe(SO_4)^+$	R44	3.2(3)		Jayson et al. (1973b)
$Fe(SO_4)^+$	$Fe^{3+} + SO_4^{2-}$	R45	2.7(1)		Jayson et al. (1973b)

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)
$H_2O_2 + Cu^+$	$Cu^{2+} + OH + OH^-$	R51	7.0(3)	Berdnikov (1973)
$HO_2 + Cu^+ + H^+$	$Cu^{2+} + H_2O_2$	R52	3.5(9)	Berdnikov (1973)
$O_2^- + Cu^+ + H^+$	$Cu^{2+} + H_2O_2$	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				
$OH + HO_2$	$H_2O + O_2$	R93	7.0(9)	Sehested et al. (1968)
$OH + O_2^-$	$OH^- + O_2$	R94	1.0(10)	Sehested et al. (1968)
$OH + H_2O_2$	$H_2O + HO_2$	R95	2.7(7)	Christensen et al. (1982)
$HO_2 + HO_2$	$H_2O_2 + O_2$	R99	8.6(5)	Bielski (1978)
$HO_2 + O_2^-$	$H_2O_2 + O_2 + OH^-$	R100	1.0(8)	Bielski (1978)
$O_3 + O_2^- + H_2O$	$OH + 2O_2 + OH^-$	R101	1.5(9)	Sehested et al. (1983)
Photolysis				
$O_3 + H_2O$	$H_2O_2 + O_2$	P1	2.98(-4)	Graedel and Weschler (1981)
H_2O_2	2OH	P2	4.81(-6)	Graedel and Weschler (1981)
$Fe^{3+} + H_2O$	$Fe^{2+} + OH + H^+$	P9	6.41(-6)	Benkelberg and Warneck (1995)
$Fe(OH)^{2+}$	$Fe^{2+} + OH$	P10	5.63(-3)	Benkelberg and

					Warneck (1995)
Equilibria					
$Fe^{2+} + H_2O$	$Fe(OH)^{+} + H^{+}$	E1	3.22(-10)		Mesmer (1971)
$Fe^{3+} + H_2O$	$Fe(OH)^{2+} + H^{+}$	E2	6.0(-3)		Brandt and van Eldik (1995)
HO_2	$O_2^{-} + H^{+}$	E14	2.05(-5)		Bielski (1978)
H_2O_2	$HO_2^{-} + H^{+}$	E15	1.6(-12)	-3700	Hoffmann et al. (1985)
$Cu^{2+} + SO_4^{2-}$	$Cu(SO_4)$	E20	2.3(2)		Casas et al. (2000)

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[a] Estimated following Deguillaume et al. (2004)

[b]: use the lowest value measured in H_2SO_4 solution when pH=1.6, assuming Fe(III) is dominated by $Fe(SO_4)^{+}$.

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

Species	K_{298} (M atm^{-1})	$\Delta H°_{298}/R$ (K)	reference
HO_2	2.0(3)	6600	Schwartz (1984)
H_2O_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

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

Figures

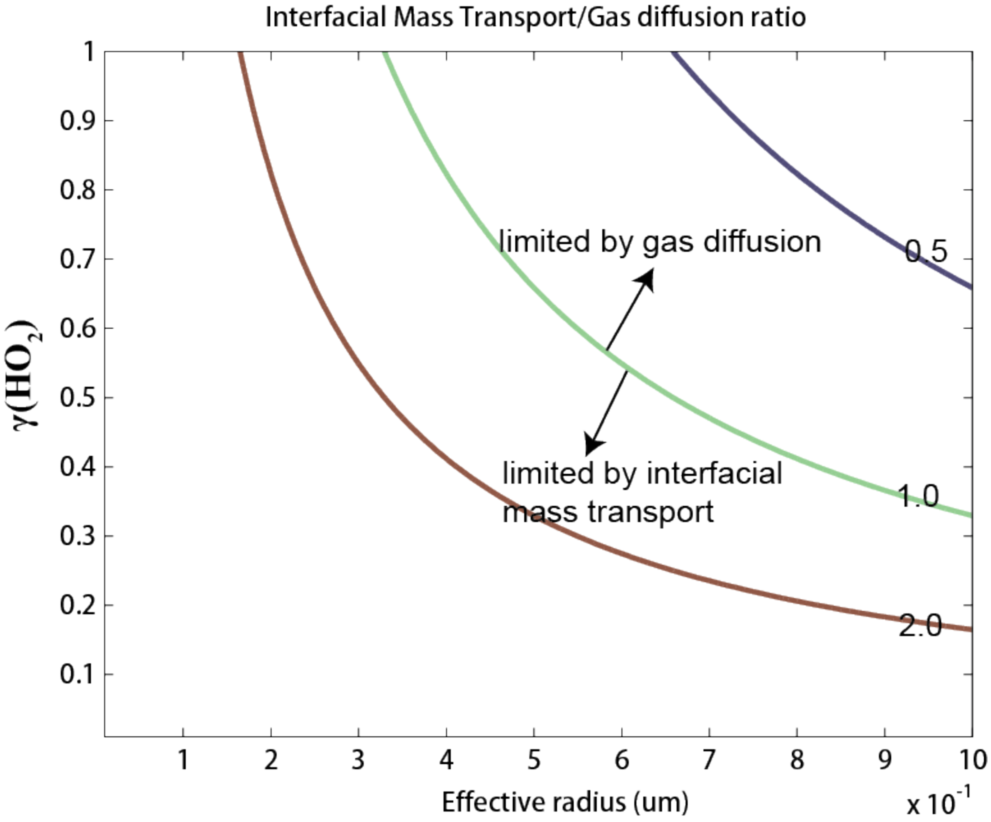

Figure S1 Ratio of interfacial mass transport to gas diffusion as a function of γ(HO_2) and aerosol effective radius (corrected by hygroscopic growth factor).

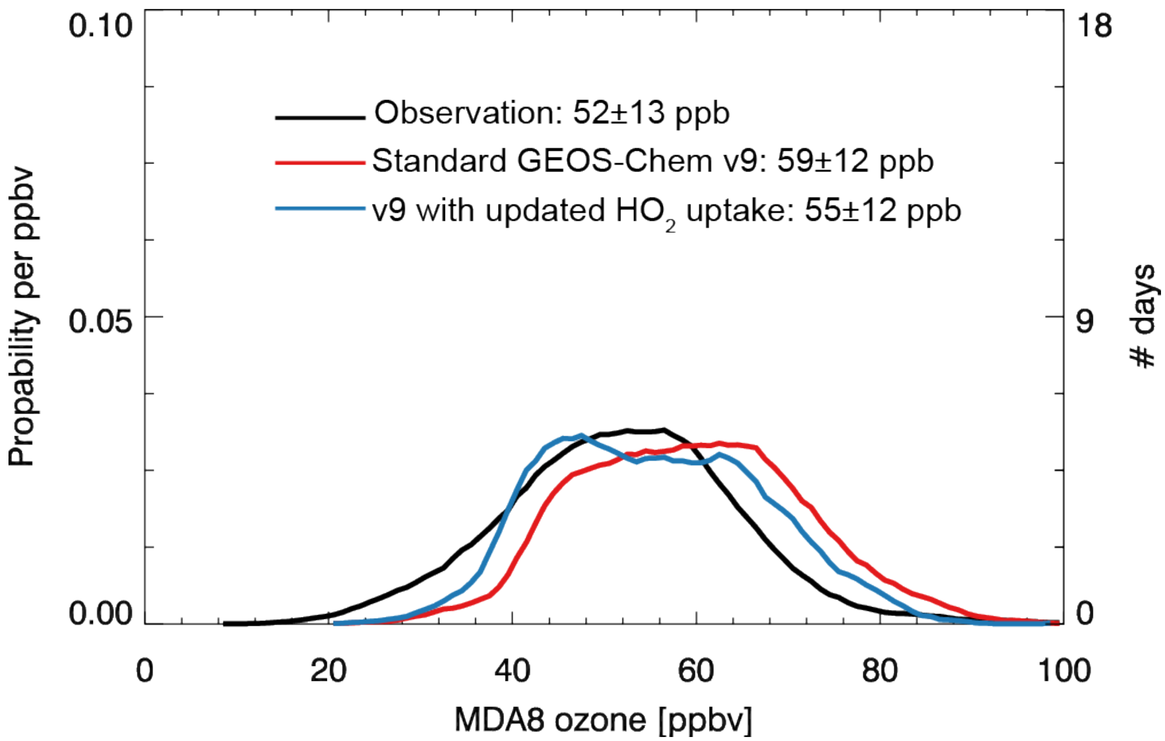

Figure S2 Probability distributions of daily 8-h max ozone concentrations in March-August 2006 for 80 CASTNet sites in the US. Obervations (black) are compared to standard GEOS-Chem simulations (red) and GEOS-Chem with updated HO_2 uptake (blue).

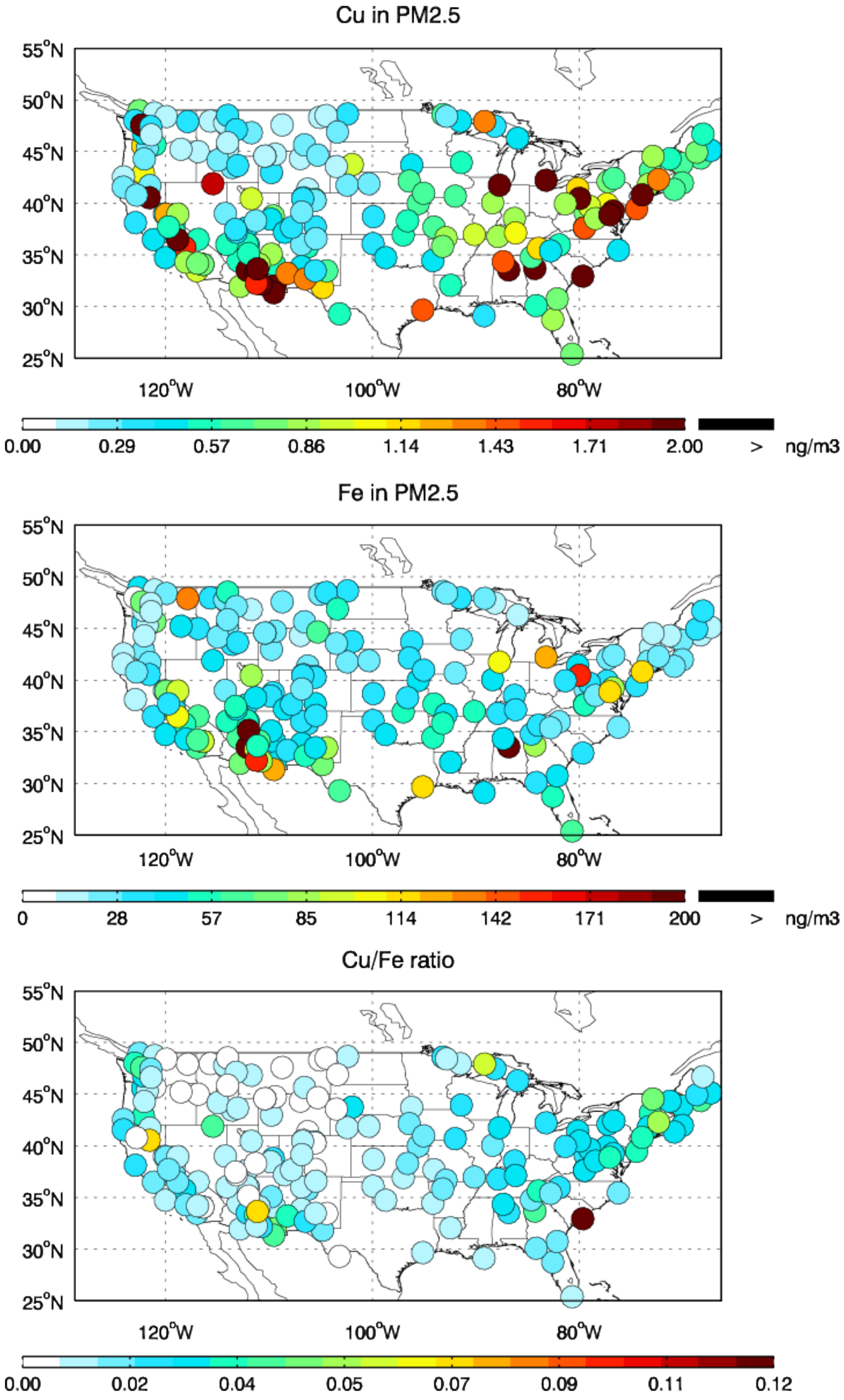

Figure S3 Mean concentrations of measured Cu and Fe in PM 2.5 from the IMPROVE sites in continental US during the period of 1988-2004.

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