Chemistry of hydrogen oxide radicals (HO$_x$) in the Arctic troposphere in spring

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Abstract. We use observations from the April 2008 NASA ARCTAS aircraft campaign to the North American Arctic, interpreted with a global 3-D chemical transport model (GEOS-Chem), to better understand the sources and cycling of hydrogen oxide radicals (HO$_x$$\equiv$H+OH+peroxy radicals) and their reservoirs (HO$_y$$\equiv$HO$_x$+peroxides) in the spring-time Arctic atmosphere. We find that a standard gas-phase chemical mechanism overestimates the observed HO$_2$ and H$_2$O$_2$ concentrations. Computation of HO$_x$ and HO$_y$ gas-phase chemical budgets on the basis of the aircraft observations also indicates a large missing sink for both. We hypothesize that this could reflect HO$_2$ uptake by aerosols, favored by low temperatures and relatively high aerosol loadings, through a mechanism that does not produce H$_2$O$_2$. We implemented such an uptake of HO$_2$ by aerosol in the model using a standard reactive uptake coefficient parameterization with $\gamma$(HO$_2$) values ranging from 0.02 at 275 K to 0.5 at 220 K. This successfully reproduces the concentrations and vertical distributions of the different HO$_x$ species and HO$_y$ reservoirs. HO$_2$ uptake by aerosol is then a major HO$_x$ and HO$_y$ sink, decreasing mean OH and HO$_2$ concentrations in the Arctic troposphere by 32% and 31% respectively. Better rate and product data for HO$_2$ uptake by aerosol are needed to understand this role of aerosols in limiting the oxidizing power of the Arctic atmosphere.

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1 Introduction

Radiative forcing by aerosol and tropospheric ozone pollution transported from mid-latitudes may be an important driver of recent Arctic warming (Quinn et al., 2008; Shindell et al., 2008). This pollution is strongest in spring (Scheuer et al., 2003) and is modulated by chemical reactions serving as sources or sinks of aerosols and ozone. The Arctic photochemical environment in spring is characterized by polar sunrise, low sun angles, intense cold, and underlying ice surface. Considerable attention has focused on halogen radical photochemistry under these conditions as a rapid sink for ozone (Simpson et al., 2007), but this appears to be important only in the shallow boundary layer where sea ice provides a halogen radical source (Wagner et al., 2001). Hydrogen oxide radicals (HOx≡H+OH+peroxy radicals) have a more pervasive effect in the tropospheric column but the chemistry of these radicals in the Arctic spring has received little study. The OH radical is the principal atmospheric oxidant, affecting both aerosols and ozone in complex ways. Peroxy radical reactions with nitric oxide (NO) are the main chemical source of tropospheric ozone. We use here observations from the April 2008 NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) aircraft campaign (Jacob et al., 2010), interpreted with a global 3-D chemical transport model (GEOS-Chem CTM), to better understand the sources and cycling of HOx radicals in the springtime Arctic atmosphere.

HOx radicals originate from water vapor. The main pathway involves oxidation by the high-energy O(1D) atom produced from photolysis of ozone:

\[ O_3 + hv \rightarrow O(1D) + O_2 \quad (R1) \]

\[ O(1D) + H_2O \rightarrow 2OH \quad (R2) \]

The OH atoms cycle with peroxy radicals, driving various HOx-catalyzed mechanisms for atmospheric oxidation and ozone formation and loss. Oxidation of methane and other volatile organic compounds (VOCs) yields formaldehyde (HCHO), which photolyzes to produce additional HOx radicals and amplify the original source:

\[ HCHO + hv \rightarrow H + HCO \quad (R3) \]

\[ H + O_2 + M \rightarrow HO_2 + M \quad (R4) \]

\[ HCO + O_2 \rightarrow HO_2 + CO \quad (R5) \]

Loss of HOx eventually takes place by radical-radical reactions. The OH+HO2 reaction produces water vapor in which the case is terminal, but the peroxy+peroxy reactions produce reservoir species such as hydrogen peroxide (H2O2) and methyl hydrogen peroxide (CH3OOH). The peroxides can photolyze to return HOx radicals. Alternatively, they can be converted to water by reacting with OH or deposited resulting in a terminal HOx sink. It is useful to define an expanded hydrogen oxides family HOx≡HOx+reservoirs (Jaegle et al., 2001), where the reservoirs include mainly peroxides but also some other minor reservoir species such as nitrous acid (HONO). The HOx budget can then be understood on the basis of the HOx budget and the chemical cycling within the HOx family, governed in part by reactions involving nitrogen oxide radicals (NOy≡NO+NO2) (Jaegle et al., 2001). The lifetime of HOx against conversion to water vapor by reaction of OH with HO2 or peroxides is of the order of a few days, so that transport of HOx reservoir species on convective and synoptic scales can modulate the supply of HOx radicals (Jaegle et al., 1997; Prather and Jacob, 1997; Mueller and Brasseur, 1999).

Past studies of HOx chemistry in Arctic spring have mainly been from surface sites. They have pointed out the importance of HOx radical production from photochemically driven snow emissions of H2O2 (Hutterli et al., 2001; Jacob et al., 2002), HCHO (Sumner and Shepson, 1999; Sumner et al., 2002), and HONO (Zhou et al., 2001). They have identified a large photochemical emission of NOx from snow (Honrath et al., 1999; Ridley et al., 2000) that plays an important role in HOx cycling (Yang et al., 2002; Chen et al., 2004). Another unique aspect of HOx chemistry in the boundary layer is the interaction with halogen radicals. These interactions include HOx production from Br+HCHO (Evans et al., 2003), additional HOx reservoirs such as HOBr (Bloss et al., 2005), and additional processes for cycling between HOx and OH (Simpson et al., 2007).

The Arctic boundary layer is very shallow (~100 m) and capped by a strong thermal inversion (Kahl, 1990). The atmosphere above is more relevant for the impacts of HOx chemistry on the Arctic troposphere. It had received little exploration prior to ARCTAS, due to the requirement of an aircraft with comprehensive chemical payload. The Tropospheric Ozone Production about the Spring Equinox (TOPSE) aircraft campaign conducted a series of flights in the North American Arctic from February to May of 2000 including measurements of total peroxy radicals (Cantrell et al., 2003a), HCHO (Fried et al., 2003), and peroxides (Snow et al., 2003) up to 8 km altitude. Photochemical model calculations constrained with these data found (R1) and (R3) to be the major HOx sources (Wang et al., 2003). However, the model greatly overestimated the observed concentrations of peroxy radicals and H2O2 (Cantrell et al., 2003b; Wang et al., 2003) while underestimating HCHO (Fried et al., 2003).

Observations from the ARCTAS aircraft expand greatly on TOPSE in terms of both coverage and chemical payload. ARCTAS vertical profiles extend from the boundary layer to the stratosphere. The payload included measurements of HOx radicals by two independent methods to resolve experimental uncertainty (Chen et al., 2010). It also included an extensive suite of HOx precursors, reservoirs, and related species. As we will see, this ensemble of observations offers strong constraints and a new perspective on the factors controlling HOx concentrations in the Arctic spring troposphere.
2 Data and model

2.1 The ARCTAS campaign

The ARCTAS spring campaign took place from 1 to 21 April, 2008 (Jacob et al., 2010). It included a DC-8 aircraft with a detailed chemical and aerosol payload and a P-3 aircraft with a detailed aerosol and radiation payload. Both were based in Fairbanks, Alaska (65° N, 148° W). We focus our attention on the DC-8 chemical data but will also make reference to the P-3 aerosol data. The DC-8 conducted nine flights in the North American Arctic totaling 73 flight hours. These included sorties out of Fairbanks as well as transit flights to and from Thule, Greenland (77° N, 69° W) and Iqaluit, Nunavut (64° N, 69° W). Almost all the data were collected north of 60° N. All flights included frequent vertical profiling from 100 m to 12 km altitude.

One of the major goals of ARCTAS was to better understand radical photochemistry in the Arctic. The DC-8 payload included measurements of HOx radicals, NOx radicals, H2O2, CH3OOH, HNO3, O3, H2O, VOCs, HCHO, aerosol composition, and photolysis frequencies (Jacob et al., 2010). OH and HO2 concentrations were measured by two independent techniques, Laser Induced Fluorescence (LIF) and Chemical Ionization Mass Spectrometry (CIMS). There were instrumental difficulties with the CIMS HO2 measurement but intercomparison for OH shows a median ratio [OH]CIMS/ [OH]LIF=0.73 (R=0.51), which agrees within the stated accuracies (32% for LIF, 65% for CIMS) (Chen et al., 2010). We rely on the LIF measurements here as they covered 96% of the flight hours. We use 1-min average data with reported accuracies in parentheses: OH (32%), HO2 (32%), H2O2 (±40%+100 pptv), CH3OOH (±76%+50 pptv), ozone (3%), HCHO (12%±26 pptv), NO (10%±5 pptv), NO2 (5%±5 pptv), HNO3 (30%±15 pptv). We also make use of fine aerosol data including sulfate (34%) and ammonium (34%). The NO2 LIF measurement includes methylperoxynitrate (CH3OONO2) decomposing in the inlet and this represents a significant positive artifact in the upper troposphere (Browne et al., 2010). We correct for it here by using local CH3OONO2/NO2 ratios from the GEOS-Chem simulation. Mean ratios are 0.03 at 0–3 km, 0.17 at 3–6 km, and 1.4 above 6 km.

Several halogen-catalyzed ozone and mercury depletion events were observed during ARCTAS (Salawitch et al., 2010), but all were confined below 500 m. No obvious signature of either bromine or chlorine radical chemistry was found above 500 m from the measured soluble bromide (Liao et al., 2010), BrO (Neuman et al., 2010) or VOC indicators (Fried et al., 2010). We neglect the effect of halogen chemistry in our modeling of the ARCTAS HOx data but will comment on its possible role in the boundary layer.

2.2 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 8-01-04 (http://acmg.seas.harvard.edu/geos/index.html) to simulation of the ARCTAS period (April 2008). The GEOS-5 meteorological data have 6-h temporal resolution (3-h for surface variables and mixing depths) with 0.5°×0.667° horizontal resolution and 72 vertical layers from the surface to 0.01 hPa. We regrid here the meteorological data to 2° latitude × 2.5° longitude for input to GEOS-Chem. The model is initialized with a 1-year simulation from January 2007 to January 2008 with 4°×5° resolution, and from January 2008 on with 2°×2.5° resolution. Our analysis of the GEOS-Chem simulation focuses on HOx chemistry. The same GEOS-Chem simulation is applied in companion papers to interpretation of ARCTAS observations for CO (Fisher et al., 2010a), sulfate (Fisher et al., 2010b), and carbonaceous aerosols (Wang et al., 2010). The latter two studies show that the model reproduces well the observed aerosol concentrations, lending some confidence in the computation of scavenging and heterogeneous uptake.

We use the standard GEOS-Chem simulation of ozone-NOx-HOx-VOC-aerosol chemistry as described for example by Park et al. (2006). We updated the chemical mechanism with compiled data from the Jet Propulsion Laboratory (Sander et al., 2006) (hereinafter “JPL06”) and the International Union of Pure and Applied Chemistry (Atkinson et al., 2006) (hereinafter “IUPAC06”). We implemented the Fast-JX radiative transfer code for calculation of photolysis rate constants (Wild et al., 2000; Bian and Prather, 2002), including updates to absorption cross-sections and quantum yields from JPL06. Total ozone columns used as input to Fast-JX are from daily measurements by the Ozone Monitoring Instrument (OMI) satellite instrument with 1°×1° resolution (ftp://toms.gsfc.nasa.gov/pub/omi/data/ozone/Y2008/). The range of ozone columns during ARCTAS was 380–430 Dobson Units. Fast-JX includes a background climatology of zonal mean profiles of monthly ozone and temperature (Wild et al., 2000). Surface albedo used in Fast-JX is from the Total Ozone Mapping Spectrometer (TOMS) satellite monthly climatology with 1°×1.25° resolution (Herman and Celarier, 1997).

A major topic of this paper will be the role of HO2 uptake by aerosol. GEOS-Chem simulates aerosol mass concentrations for several aerosol components: sulfate-nitrate-ammonium (Park et al., 2004), 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). For each aerosol component, the model calculates an effective area-weighted radius (r_e) dependent on local relative humidity (RH) (Köpke et al., 1997; Chin et al., 2002).
Gas uptake by each aerosol component is then represented following R. V. Martin et al. (2003) by a first-order uptake rate constant $k$:

$$k = \left( \frac{r_c}{D_g} + \frac{4}{v r} \right)^{-1} A$$  \hspace{1cm} (1)

where $v$ is the mean molecular speed of the gas, $D_g$ is the gas-phase molecular diffusion coefficient, $r$ 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. We ignore heterogeneous chemistry of HOx radicals in clouds because the aircraft sampled almost exclusively in clear sky and the regional effects of clouds on the HOx budget are limited by the small mass fraction of the atmosphere actually occupied by cloud (Jacob, 2000).

The standard model includes aerosol uptake of NO$_2$, NO$_3$, and N$_2$O$_5$ (Jacob, 2000; Evans and Jacob, 2005) and aqueous-phase reaction of H$_2$O$_2$ with SO$_2$ in cloud (Park et al., 2004). Earlier versions also included aerosol uptake of HO$_2$ (R. V. Martin et al., 2003), but this was removed in v7-04-06 (and hence in the v8-01-04 version that we used) on the basis of laboratory data indicating low $\gamma$ values in the absence of transition metal catalysts (Thornton and Abbatt, 2005; Sauvage et al., 2007). More recent standard versions of GEOS-Chem (v8-02-01 and beyond), developed after this work was initiated, include HO$_2$ uptake following Thornton et al. (2008). As we will show below, the ARCTAS observations suggest an important role for aerosol uptake of HO$_2$ under the cold, low-light, and relatively aerosol-rich conditions of Arctic spring.

Anthropogenic emissions in GEOS-Chem are as described in van Donkelaar et al. (2008). A prominent feature of ARCTAS flights was the influence of Siberian fire plumes (Warneke et al., 2009). Daily biomass burning emissions for 2008 with $1^\circ \times 1^\circ$ resolution are specified from the Fire Locating and Monitoring of Burning Emissions (FLAMBE) emission inventory (Reid et al., 2009) constrained by GOES and MODIS fire count data. Further details on model emissions are given by Fisher et al. (2010a).

The model wet deposition scheme is described by Liu et al. (2001). It includes wet scavenging in convective updrafts as well as grid-resolved first-order rainout and washout. Of particular interest here is the representation of peroxide and HCHO scavenging. For warm clouds ($T > 268$ K), H$_2$O$_2$, CH$_3$OOH, and HCHO are scavenged by liquid water based on their Henry’s law constants. For mixed clouds ($248 < T < 268$ K), precipitation is assumed to take place by riming of liquid cloud droplets with retention efficiencies $R_{H_2O_2} = 0.05$, $R_{CH_3OOH} = 0.02$, and $R_{HCHO} = 0.02$ (Mari et al., 2000). In cold clouds ($T < 248$ K), scavenging of H$_2$O$_2$ takes place by co-condensation on ice surfaces while scavenging of CH$_3$OOH and HCHO are considered negligible (Mari et al., 2000).

Dry deposition is calculated using a standard resistance-in-series scheme (Wesely, 1989) applied to the local surface. For snow and ice the deposition velocity of H$_2$O$_2$ is in the range 0.1–0.3 cm s$^{-1}$, while dry deposition of CH$_3$OOH and HCHO are negligible. Snow emission could offset dry deposition for the above species (Frey et al., 2005, 2006) but is not taken into account here as its effect would be confined to the shallow boundary layer. For the same reason we find dry deposition to be unimportant from a tropospheric column perspective.

All comparisons between model and observations use model output sampled along the flight tracks and at the flight time with 15-min time resolution. We exclude all measurements in the stratosphere as diagnosed by an ozone/CO molar ratio greater than 1.25. This excludes 72% of the data above 10 km, 41% of the data at 8–10 km, and 9% of the data at 6–8 km. We also exclude all measurements at latitudes lower than 60° N. In order to assess the effect of GEOS-Chem errors for species driving HO$_x$ chemistry (such as ozone, CO, NO), we compare results to those of a gas-phase photochemical box model (Olson et al., 2004) constrained locally by the ARCTAS observations (Olson et al., 2010). Similar comparisons between GEOS-Chem and this box model have been conducted in previous aircraft campaigns (Olson et al., 2004; Hudman et al., 2007; Zhang et al., 2008).

Previous comparisons of the GEOS-Chem HO$_x$ simulation to aircraft LIF measurements from the same Pennsylvania State University group have been reported for the NASA INTEX-A campaign over North America (summer 2004) and the NASA INTEX-B campaign over the North Pacific (spring 2006). Hudman et al. (2007) reported a model overestimate of 30–60% for both HO and HO$_2$ in INTEX-A, but subsequent recalibration of the measurements resolved the discrepancy (Ren et al., 2008). Zhang et al. (2008) found no model bias for HO$_2$ in INTEX-B but a 27% high bias for OH. The global mean (mass-weighted) tropospheric OH concentration in our ARCTAS simulation is $10.3 \times 10^5$ molecules cm$^{-3}$, consistent with the multimodel annual mean of $11.1 \pm 1.7 \times 10^5$ molecules cm$^{-3}$ from the intercomparison by Shindell et al. (2006).

### 3 Median distributions

Figure 1 presents median vertical profiles of OH, HO$_2$, H$_2$O$_2$, CH$_3$OOH, NO, NO$_2$, HCHO and HNO$_3$ concentrations for 1 km vertical bins during ARCTAS. We compare here the observed profiles (black) to results from the standard GEOS-Chem simulation not including HO$_2$ uptake by aerosols (dashed green line). Also shown in Fig. 1 are model simulations including HO$_2$ uptake, which will be discussed in Sect. 4. Most data were collected under sunlit conditions, between 08:00 and 18:00 local time. Stratospheric data were excluded as described in Sect. 2. Mean observed temperature and relative humidity (RH) relative to liquid water are 256 K
and 73% at 0–3 km, 243 K and 48% at 3–6 km, and 226 K and 48% above 6 km, consistent with the model. Mean observed \( J(O^{1}D) \) and \( J(NO_{2}) \) agree with the model within 25% and 10% respectively.

Observed concentrations of OH are relatively low (20 ppqv=5×10^5 molecules cm\(^{-3} \) in surface air) reflecting the low water vapor, low solar elevation, and thick ozone columns characteristic of Arctic spring. The model reproduces the vertical gradient of the observed OH and its concentrations at 1–6 km within 15%, but is too low by 40% in the surface layer (0–1 km) and too high by 40% in upper troposphere (>6 km). The discrepancy in the surface layer may be due to the effect of halogen chemistry, while the discrepancy in the upper troposphere can be explained by HO\(_2\) aerosol uptake as described in Sect. 4.

Observed concentrations of HO\(_2\), H\(_2\)O\(_2\), and CH\(_3\)OOH show little altitude dependence, consistent with TOPSE (Wang et al., 2003) but in contrast to measurements in the tropics and northern mid-latitudes that show decreases with altitude driven by water vapor (Cohan et al., 1999; O’Sullivan et al., 1999; Hudman et al., 2007; Snow et al., 2007; Zhang et al., 2008). The model reproduces this lack of vertical structure in the Arctic spring observations and attributes it in part to a strong vertical gradient of UV radiation (low solar angles, thick ozone columns) compensating for the water vapor gradient, and in part to influx of peroxides from northern mid-latitudes in the upper troposphere.

The standard simulation overestimates HO\(_2\) by up to a factor of 2, with the largest discrepancy in the upper troposphere. H\(_2\)O\(_2\) is also underestimated. This cannot be explained by model error in the species driving HO\(_2\) production, as Olson et al. (2010) find a similar discrepancy for HO\(_2\) in their box model results constrained by ARCTAS observations. They further show that the discrepancy cannot be resolved by adjusting observed concentrations within their measurement uncertainties. A similar overestimate of HO\(_2\) and H\(_2\)O\(_2\) was previously found in TOPSE when comparing box model calculations to observations (Cantrell et al., 2003b; Wang et al., 2003). We propose below that aerosol uptake of HO\(_2\) leading to a terminal sink for HO\(_2\) could explain the discrepancy between model and observations.

Median observed NO\(_x\) concentrations increase from 16 pptv in the boundary layer to 21 pptv in the upper troposphere (>6 km). The model is consistent within the measurement uncertainty (15%±10 pptv), increasing from 13 pptv in the boundary layer to 28 pptv in the upper troposphere. April observations from TOPSE at 60–80° N showed a mean NO concentration of 6 pptv (Wang et al., 2003), consistent with the ARCTAS observations and with the model. A sensitivity model simulation with no fuel emissions shows a 40% mean decrease of NO\(_x\) along the ARCTAS flight tracks, while a sensitivity simulation with no biomass burning emissions shows only a 5% decrease. We conclude that a large fraction of the NO\(_x\) in ARCTAS was anthropogenic.
Peroxyxnitric acid (HNO$_4$) is an important reservoir for HO$_2$ in the upper troposphere at northern mid-latitudes (Jaeglé et al., 2001). ARCTAS observations are below the detection limit in the lower troposphere due to thermal dissociation but increase to 30 pptv in the upper troposphere. The model reproduces the observed concentrations and vertical gradient within the measurement uncertainty.

Observed HCHO decreases with altitude, from 140 pptv near the surface to 25 pptv in the upper troposphere. TOPSE observations by a similar absorption spectrometer using a tunable lead-salt diode laser averaged 95 pptv below 0.2 km and 60 pptv at 6–8 km (Fried et al., 2003). A different laser source, based on tunable difference frequency generation (DFG), was employed in ARCTAS (Weibring et al., 2007; Richter et al., 2009). Model values decrease from 50 pptv near the surface to 30 pptv in the upper troposphere. The discrepancy below 3 km is outside the stated precision of the measurements (26 pptv). Olson et al. (2010) find a similar discrepancy in their box model simulation of the ARCTAS data, and Fried et al. (2003) also reported a low model bias relative to the TOPSE data. Previous GEOS-Chem evaluation with observed HCHO vertical profiles at northern mid-latitudes by the same investigator show no such discrepancy (Palmer et al., 2003; Millet et al., 2006). Halogen radical chemistry and snow emissions of HCHO could provide additional HCHO sources in the boundary layer. However, this does not explain discrepancies between 0.5 and 3 km given the short lifetime of HCHO (hours). Inlet artifact can be ruled out because zero air was added to the inlet every minute as instrument background signal. Singh et al. (2000) suggested a heterogeneous conversion from CH$_3$OH to HCHO, but we find no correlation between these two species below 4 km ($R<0.01$). As pointed out in Sect. 5, the source of HO$_x$ and HO$_y$ implied by the observed HCHO appears inconsistent with independent calculations of HO$_x$ and HO$_y$ sinks from the ARCTAS observations, leading to an even higher overestimate of HO$_2$.

4 HO$_2$ uptake by aerosols

4.1 Parameterization of uptake

A prominent feature of the comparison between model and observations in Fig. 1 is the overestimate of HO$_2$. Such a discrepancy between model and observations has been reported in a number of previous studies and tentatively attributed to HO$_2$ uptake by aerosols (Cantrell et al., 1996a; b; Plummer et al., 1996; Jaeglé et al., 2000; Kanaya et al., 2000; Sommariva et al., 2004; de Reus et al., 2005; Sommariva et al., 2006). This uptake has been reported in a number of laboratory studies but rates and mechanism are uncertain (Jaeglé, 2000). It could be particularly important in the Arctic because of the low temperature, relatively high aerosol, and slow photochemical cycling.

Figure 2 summarizes literature data of the HO$_2$ reactive uptake coefficient $\gamma$(HO$_2$) or different surface types. $\gamma$(HO$_2$) is defined as the fraction of HO$_2$ collisions with the aerosol surface resulting in reaction. Consistently high values ($\gamma$(HO$_2$)>0.2) are observed for Cu-doped aqueous surfaces. Soluble copper is known to drive rapid catalytic conversion of HO$_2$ to H$_2$O$_2$ by redox chemistry (Jacob, 2000). Other values for aqueous surfaces at room temperature are also relatively high ($\gamma$(HO$_2$) in the range 0.07–0.2) except for concentrated H$_2$SO$_4$ ($\gamma$(HO$_2$)<0.01). However, $\gamma$(HO$_2$) for concentrated H$_2$SO$_4$ increases rapidly with decreasing temperature and exceeds 0.2 at 240 K. Reactive uptake coefficients in general increase with decreasing temperature, reflecting negative temperature dependences of both the mass accommodation coefficient $\alpha$ on the surface and the solubility constant (Kolb et al., 1995). Solid surfaces do not take up HO$_2$ significantly. To our knowledge no data are available for $\gamma$(HO$_2$) on organic surfaces.

A high reactive uptake probability ($\gamma$(HO$_2$)>0.1) is needed for aerosol uptake to compete in the atmosphere with other chemical sinks for HO$_x$. This requires that the aerosol be aqueous, which cannot be directly determined from the ARCTAS observations. Aerosol measurements aboard the P-3 show that non-refractory submicron...
particles contributed more than 90% of total surface area (McNaughton et al., 2010). High-resolution Aerosol Mass Spectrometer (AMS; DeCarlo et al., 2006) measurements aboard the DC-8 show an average mass composition for non-refractory submicron particles of 58% sulfate, 32% organic aerosol, 6% ammonium, 3% nitrate, and 0.7% chloride (Cubison et al., 2008). An ammonium vs. sulfate molar plot for the AMS data (Fig. 3) shows dominance of the acidic NH₄HSO₄ form, although in some cases the aerosol was close to sulfuric acid while in other cases it was fully neutralized as (NH₄)₂SO₄. Because of metastability of the aqueous phase, both NH₄HSO₄ and (NH₄)₂SO₄ are expected to remain aqueous over the range of RH values experienced in ARCTAS (Onasch et al., 1999; S. T. Martin et al., 2003; Colberg et al., 2004). Sulfuric acid is aqueous under all conditions. In addition, Parsons et al. (2004) found that the crystallization RH of ammonium sulfate aerosol decreases as the organic fraction increases. We assume therefore that the aerosol surface area in ARCTAS was mainly contributed by aqueous particles.

To investigate the role of HO₂ uptake by aerosol in our ARCTAS simulations, we included the γ(HO₂) parameterization of Thornton et al. (2008) as implemented in the most recent standard versions of GEOSS-Chem (v8-02-01 and beyond). This parameterization describes HO₂ uptake by aqueous aerosol as driven by acid-base dissociation followed by the HO₂(aq)+O₂⁻ reaction at an assumed pH 5, producing H₂O₂ that then volatilizes to the gas phase. It is clearly inconsistent with the prevailing acidic conditions observed in ARCTAS (Fig. 3), and is also theoretically incorrect since it describes HO₂ uptake as a second-order process while the γ(HO₂) parameterization intrinsically describes a first-order process. Nevertheless, as shown in Fig. 2 (solid line), it yields values of γ(HO₂), that are consistent with those measured in the laboratory for acidic surfaces, ranging from less than 0.05 near the surface to 0.4 in the upper troposphere. Its temperature dependence (mainly driven by the Henry’s law constant for HO₂) is consistent with the laboratory data for concentrated H₂SO₄ (Fig. 2). We adopt the Thornton et al. (2008) scheme here to compute γ(HO₂) for want of anything better and because it fits the overall laboratory data for acid aerosols.

The fate of HO₂ in aerosol phase is generally assumed to involve conversion to H₂O₂ followed by H₂O volatilization (Jacob, 2000). However, this would exacerbate the overestimate of H₂O₂ in ARCTAS (Fig. 1). One possible solution would be protonation of H₂O₂ to HOOH⁺, a very strong oxidant (Oiestad et al., 2001), which would rapidly react and convert to H₂O. However, this requires normal acidity (pH<0) to be effective (Bach and Su, 1994). Such a mechanism could conceivably take place in concentrated H₂SO₄ aerosols, but not in the less acidic aerosol that prevailed under ARCTAS conditions (Fig. 3).
similar potential for bonding with HO$_2$ molecules (C. Miller, personal communication, 2009). The fate of these complexes is unknown. They must not decompose to the original reactants if they are to represent an actual HO$_x$ or HO$_2$ sink. One possibility would be conversion to SO$_5^-$ by Reaction (R6), with subsequent chemistry forming HSO$_5^-$ and eventually returning water as described above.

4.2 Application to the ARCTAS simulation

Figure 1 shows the results of two simulations, one with HO$_2$ aerosol uptake producing H$_2$O$_2$ ($\gamma$(HO$_2$→0.5H$_2$O$_2$), dashed blue line), and the other with HO$_2$ aerosol uptake leading to a permanent HO$_3$ sink as postulated above ($\gamma$(HO$_2$→products), red line). Mean aerosol surface area in the model corrected by hygroscopic growth factors (R. V. Martin et al., 2003) is 26 $\mu$m$^2$ cm$^{-3}$ at 0–3 km, 33 $\mu$m$^2$ cm$^{-3}$ at 3–6 km and 19 $\mu$m$^2$ cm$^{-3}$ above 6 km. The model agrees with the measurements of aerosol surface area aboard the P-3 within a factor of 2. The simulation with $\gamma$(HO$_2$→0.5H$_2$O$_2$) worsens the overestimate of H$_2$O$_2$, as aerosol uptake now competes with other HO$_x$ sinks such as OH+HO$_2$ and CH$_3$O$_2$+HO$_2$ that do not produce H$_2$O$_2$. The correction to HO$_2$ is also insufficient in the upper troposphere as H$_2$O$_2$ can be recycled to HO$_x$ by photolysis. The simulation with $\gamma$(HO$_2$→products) provides a much better fit to the observations for both HO$_2$ and H$_2$O$_2$, though H$_2$O$_2$ is now too low in the middle troposphere. It also improves the fit for OH, while not significantly affecting the fits for the other species. OH concentrations decrease by up to 36% in the upper troposphere.

Figure 4 shows scatterplots of simulated vs. observed OH, HO$_2$, H$_2$O$_2$, and CH$_3$OOH concentrations for the model simulation with $\gamma$(HO$_2$→products) and the ensemble of tropospheric observations in ARCTAS. The slopes of the reduced-major-axis regression lines are within the measurement accuracy for all species. Correlation coefficients for OH ($R=0.61$) and HO$_2$ ($R=0.81$) are only slightly improved from the gas-phase-only simulation ($R=0.58$ and $R=0.78$ respectively). Correlations are weak for H$_2$O$_2$ ($R=0.45$) and CH$_3$OOH ($R=0.50$), which might reflect the narrow dynamic range. The HO$_2$ variability is mostly correlated with solar zenith angle in both the observations and the model ($R=-0.8$ in both cases), with additional significant correlations with water vapor ($R=0.3$ observed, $R=0.4$ model) and temperature ($R=0.3$ observed, $R=0.4$ model) above 4 km. The correlation of HO$_2$ concentrations with temperature offers some supporting evidence for a sink from aerosol uptake. The DC-8 did not include measurements of aerosol surface area that we could correlate to HO$_2$ concentrations, but in the model we find that temperature is a much stronger driver of $\gamma$(HO$_2$) variability than aerosol surface area. No correlation is found between HO$_2$ and NO$_x$ concentrations in either the model or the observations.

5 Budget of HO$_x$ radicals in Arctic spring

We now proceed to quantify the budgets of HO$_x$ and HO$_2$ in Arctic spring as constrained by the ARCTAS observations and derived from the model. We use for that purpose the model including terminal loss of HO$_x$ from reactive uptake of HO$_2$ by aerosols as described in Sect. 4.1. Even though the process is uncertain, it represents our best hypothesis for explaining the HO$_x$ and peroxide observations in ARCTAS.

Figure 5 shows the median vertical profiles of major HO$_x$ source and sink terms computed from the observed ARCTAS concentrations, gas-phase reaction rate constants from JPL06 and IUPAC06, and $\gamma$(HO$_2$→products) from Thornton et al. (2008). Formation of organic nitrates is negligible in the HO$_x$ and HO$_2$ budgets, at least in the model, and is not included in Fig. 5. The CH$_3$O$_2$ concentration is assumed to be 30% of that of HO$_2$ on the basis of the model HO$_2$/CH$_3$O$_2$ ratio. HO$_2$ aerosol uptake is computed using local model values for $\gamma$ and aerosol surface area. O$_2$(1D)+H$_2$O and HCHO photolysis are the major HO$_x$ sources below 4 km. Above that altitude the photolysis of H$_2$O$_2$ becomes dominant, a remarkable feature that has not been reported to our knowledge anywhere else in the troposphere. It reflects the low OH concentrations in Arctic spring and therefore the dominance of photolysis as a H$_2$O$_2$ sink rather than reaction with OH (Fig. 5).
The HO$_2$+HO$_2$ reaction is the principal HO$_x$ sink in the lower troposphere but HO$_2$ uptake by aerosol becomes dominant above 5 km. HO$_x$ sinks from CH$_3$O$_2$+HO$_2$ and OH+HO$_2$ are relatively small. The NO$_x$-based HO$_x$ sinks including HO$_2$+NO$_2$, OH+HNO$_4$, and OH+NO$_2$ are negligibly small because of the low NO$_x$ concentrations, so that gross ozone production is NO$_x$-limited throughout the troposphere (Jaeglé et al., 2001). In contrast, previous aircraft campaigns at northern mid-latitudes (SONEX, INTEX-A) found that the NO$_x$-based reactions dominated the HO$_x$ sink in the upper troposphere, implying NO$_x$-neutral or NO$_x$-saturated conditions for ozone production (Jaeglé et al., 2000; Ren et al., 2008). The observed NO$_x$ concentrations in the upper troposphere in these campaigns (medians of 93 pptv in SONEX, 440 pptv in INTEX-A) are much higher than in ARCTAS (21 pptv), reflecting major sources at northern mid-latitudes from convective injection of pollution and lightning (Jaeglé et al., 1998; Allen et al., 2000; Hudman et al., 2007).

We see from Fig. 5 that HO$_2$ uptake by aerosols is crucial for balancing the HO$_x$ sources with the HO$_x$ sinks independently computed from observations, at least in the upper troposphere. There the main gas-phase sinks (HO$_2$+HO$_2$, CH$_3$O$_2$+HO$_2$, OH+HO$_2$) can balance only 20% of the HO$_x$ source. With HO$_2$ uptake by aerosol included in the budget, the total HO$_x$ sinks balance 50% of the HO$_x$ sources in the lower troposphere (0–3 km) and 70% in the upper troposphere (>6 km). The imbalance in the lower troposphere reflects the high observed HCHO concentrations (Fig. 1), for which we have no explanation. The aerosol sink is ineffective in the lower troposphere because of the relatively high temperatures (average $T=258$ K at 0–2 km, resulting in $\gamma$(HO$_2$)=0.06). Loss of HO$_2$ by uptake by aerosol has a first-order dependence on HO$_x$ concentration, whereas the gas-phase sinks have a quadratic dependence. However, we find that the total HO$_x$ source $P$(HO$_x$) computed from Fig. 5 is strongly correlated in the upper troposphere with both observed [HO$_2$] ($R=0.87$) and [HO$_2$]$^2$ ($R=0.85$), so that it does not test the sink mechanism.

Figure 5 also shows the median vertical profiles of instantaneous HO$_x$ source and sink terms, again computed from the measurements. The main HO$_x$ sources are O(1D)+H$_2$O and HCHO photolysis. The main sinks are HO$_2$ uptake by aerosol and the gas-phase OH+CH$_3$OOH reaction. OH+HOO$_2$ is relatively unimportant due to its much slower rate constant ($1.8\times10^{-12}$ cm$^3$ molecules$^{-1}$ s$^{-1}$, no temperature dependence) compared to OH+CH$_3$OOH ($3.8\times10^{-12}$ exp(200/$T$) cm$^3$ molecules$^{-1}$ s$^{-1}$) as given by JPL06. Such a dominance of the gas-phase HO$_x$ sink by the OH+CH$_3$OOH reaction has not been reported before to our knowledge, except in deep convective outflow where H$_2$O$_2$ has been scavenged but not CH$_3$OOH (Cohan et al., 1999). We attribute it to the low concentrations of NO$_x$ in Arctic spring, suppressing the NO$_x$-based HO$_x$ sinks (see discussion above) and promoting CH$_3$OOH formation.

Figure 5 shows an imbalance between HO$_x$ chemical sources and sinks that reverses sign with altitude. The HO$_2$ sink balances 30% of the source below 3 km, 92% at 3–6 km, and 170% above 6 km. The HO$_2$ lifetime is 2–6 d, sufficiently long that additional terms may be relevant in the HO$_2$ budget including long-range transport, wet and dry deposition, and aqueous-phase oxidation of SO$_2$ by H$_2$O$_2$ in clouds. To consider the effect of these terms, we conducted a HO$_2$ budget analysis in the GEOS-Chem model averaged over the 60–90$^\circ$ N circumpolar Arctic cap. Results are shown in Fig. 6. The budget in the model is balanced by mass conservation; the excess of HO$_2$ sources over HO$_2$ sinks in the tropospheric column reflects accumulation of peroxides over the course of April.

We see from Fig. 6 that influx of peroxides from northern mid-latitudes in the model accounts for 50% of the total HO$_2$ source above 6 km and 20% at 3–6 km. This explains the chemical imbalance in the HO$_2$ budget constrained by
the ARCTAS observations (Fig. 5). Considering the dominant role of H$_2$O$_2$ photolysis as a source of HO$_x$ above 5 km (Fig. 5), this implies a significant contribution of northern mid-latitudes to the HO$_x$ budget of the Arctic free troposphere. Below 3 km, we find in the model that cloud chemistry and deposition of H$_2$O$_2$ together account for 40% of the HO$_x$ sink. This helps but is insufficient to correct the chemical imbalance in the HO$_x$ budget constrained by the observations. As in the case of the HO$_x$ budget, the residual imbalance reflects the high observed HCHO concentrations. Figure 7 gives a summary diagram of the HO$_x$ and HO$_y$ cycling as represented by our model for Arctic spring. Primary sources include the O($^1$D)+H$_2$O reaction within the region (70%) and transport of peroxides from northern mid-latitudes (30%). Photolysis of HCHO produced from oxidation of methane by OH is a major amplifying source of HO$_x$, of comparable magnitude to the primary source from O($^1$D)+H$_2$O. HO$_2$ aerosol uptake accounts for 35% of the HO$_x$ sink. Cycling within the HO$_x$ family (between OH and peroxy radicals) is relatively efficient (chain length=3.4) given the low NO$_x$ concentrations. This is because formation of peroxydes to terminate the chain is slow as a result of the low HO$_x$ concentrations.

6 Implications

The ARCTAS observations show a large missing sink of HO$_x$ and HO$_y$ in Arctic spring relative to current understanding. If our hypothesis that this reflects a fast terminal loss of HO$_2$ to aerosols is correct, then it implies a significant sensitivity of the oxidizing power of the Arctic atmosphere to aerosol perturbations. A measure of this effect is provided by the difference in Fig. 1 between our standard simulation (solid red line) and the gas-only simulation (dashed green line). In the absence of aerosols, OH and HO$_2$ concentrations would increase on average respectively by 32% and 31% in the tropospheric column, the largest effects being in the upper troposphere where uptake by aerosol is particularly efficient (low temperatures). Biomass burning from Siberian wildfires was a major aerosol source to the Arctic in ARCTAS (Warneke et al., 2009), and this aerosol was mainly organic for which we have no information on HO$_2$ uptake. We find in a sensitivity simulation with no biomass burning that OH and HO$_2$ concentrations would increase respectively by 10% and 9% in the tropospheric column.

Uptake of HO$_2$ by aerosol is expected to be particularly efficient as a sink for HO$_x$ in Arctic spring because of the combination of cold temperatures, relatively high aerosol concentrations, and weak UV radiation. On a global scale, however, the OH budget is mainly determined by the tropics and mid-latitudes summer where aerosol uptake would be less important. We find in our model that the global mean tropospheric OH concentration decreases by 3% when we include uptake of HO$_2$ by aerosols as described here.

Laboratory data show a wide range for the reactive uptake coefficient $\gamma$(HO$_2$), as summarized in Fig. 2. Increasing confidence in the role of aerosols for HO$_x$ uptake will require better characterization of $\gamma$(HO$_2$) and its temperature dependence, including in particular for organic aerosol (aqueous and non-aqueous). For the aerosol loadings in Arctic spring, a value $\gamma$(HO$_2$)>0.1 averaged over the aerosol surface area is necessary for uptake to be important.
The HO₂ chemistry in the aerosol phase is another critical issue to resolve. The only product study to our knowledge is that of Loukhovitskaya et al. (2009), who found H₂O₂ to be the main product for solid NaBr surfaces. It is conventionally assumed that uptake by aqueous aerosols would also produce H₂O₂ from the HO₂(aq)+O₂ self-reaction (Thornton et al., 2008) or from catalytic cycles involving transition metal ions (Graedel et al., 1986). We find that an HO₂ uptake mechanism producing H₂O₂ would overestimate the observed H₂O₂ concentrations in ARCTAS, though the mechanism not producing H₂O₂ underestimate the observed H₂O₂ in middle troposphere, suggesting perhaps a contribution from both mechanisms. A mechanism not producing H₂O₂ might involve reaction of HO₂ with acid sulfate to produce peroxymonosulfate (HSO₅₂⁻). Mechanisms and products for HO₂ uptake by different aerosol types need to be studied in the laboratory. Considering that HO₂ uptake by aerosols has opposite effects on H₂O₂ depending on whether or not H₂O₂ is produced as a result of uptake, changes in aerosol types (biomass burning vs. fossil fuel) or aerosol acidity (sulfuric acid vs. ammonium) could have large effects on H₂O₂. This may be relevant to explaining the complex long-term trend of H₂O₂ observed in Greenland ice cores (Möller, 1999).

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