Anthropogenic control over wintertime oxidation of atmospheric pollutants

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Anthropogenic air pollutants such as nitrogen oxides (NO_x = NO + NO_2), sulfur dioxide (SO_2), and volatile organic compounds (VOC), among others, are emitted to the atmosphere throughout the year from energy production and use, transportation, and agriculture. These primary pollutants lead to the formation of secondary pollutants such as fine particulate matter ($PM_{2.5}$) and ozone (O_3) [Seinfeld, 1989; Dabdub et al., 1997; Jacobson et al., 2000; Volkamer et al., 2006;], as well as to acid and nutrient deposition to ecosystems [Schofield, 1976; Irwin et al., 1988; Menz et al., 2004; Greaver et al., 2012;] and perturbations to the abundance and lifetimes of short-lived greenhouse gases [Wang et al., 1976; Fishman et al., 1980; Jacob & Winner, 2009; Ramanathan et al., 2009;]. Free radical oxidation reactions driven by solar radiation govern the atmospheric lifetimes and transformations of most primary pollutants and thus their spatial distributions [Weinstock, 1969; Levy, 1971; Seinfeld, 1989; Collins et al., 2002;]. During winter in the mid and high latitudes, where a large fraction of atmospheric pollutants are emitted globally, such photochemical oxidation is significantly slower [Levy et al., 1985; Klonecki & Levy, 1997; Yienger et al., 1999]. Using observations from a highly instrumented aircraft, we show that multi-phase reactions between gas-phase NO_x reservoirs and aerosol particles, as well as VOC emissions from anthropogenic activities, lead to a suite of atypical radical precursors dominating the oxidizing capacity in polluted winter air, and thus, the distribution and fate of primary pollutants on a regional to global scale.

In the warmer and more photochemically active summer months, the photolysis of ozone (O_3) in the presence of water vapor leads to production of hydroxyl radicals (OH).

$$O_3 + h\nu\ (\lambda < 320\ nm) + H_2O \rightarrow 2OH + O_2 \qquad (1)$$

OH radicals initiate the rapid formation of multiple secondary pollutants such as O_3 and secondary organic aerosols (SOA) during volatile organic compound (VOC) degradation, as well as sulfuric acid and nitric acid (HNO_3) from reaction with sulfur dioxide and nitrogen dioxide (NO_2). During winter, primary radical production via R1 is reduced by more than an order of magnitude due to the combination of reduced sunlight and water vapor [Klonecki & Levy, 1997; Yienger et al., 1999]. Therefore, pollutants, such as nitrogen oxides (NO_x = NO + NO_2), VOC, and SO_2, oxidize more slowly during winter and spread over wider geographic areas than during summer. The overall lower radical production expected during winter suggests a higher sensitivity to the presence of less common radical sources. Yet, few observational constraints of wintertime radical precursors exist on scales suitable to test models of pollutant transport and transformations.

During winter, multiphase processes and direct emissions of photo-labile molecules significantly influence the primary radical budget. For example, at night, nitrogen dioxide (NO_2) reacts with O_3 to generate the nitrate radical (NO_3), which subsequently reacts with NO_2 to form dinitrogen pentoxide (N_2O_5). In winter, N_2O_5 is a major nocturnal reservoir of NO_x radicals and known to react on aerosol particles, clouds, and ground surfaces, but not in the gas-phase. Aerosol particles often have significant liquid water, catalyzing the hydrolysis of N_2O_5 to two HNO_3 molecules, thereby limiting the lifetime of NO_x and impacting $PM_{2.5}$ and acid deposition through subsequent gas-particle partitioning of HNO_3 to form particulate nitrate (pNO_3^-) or deposition of HNO_3 to the ground [Platt and Heintz, 1994; Richards, 1983; Dentener and Crutzen, 1993; Smith et al., 1995; Alexander et al., 2009;]. In particles with sufficient chloride content (pCl^-), N_2O_5 will react predominantly to form nitryl chloride and pNO_3^- [Finlayson-Pitts et al., 1989; Behnke & Zetzsch, 1990; Zetzsch & Behnke, 1992]. During the morning hours, $ClNO_2$ undergoes photolysis recycling NO_x, increasing its lifetime and transport from source regions, while also releasing highly reactive chlorine radicals (Cl), which initiate the oxidation of hydrocarbons as fast or even 10 to 100 times faster than OH [Orlando et al., 2003; Platt & Hönninger, 2003; Simpson et al.,

2015]. N_2O_5 that does not react overnight quickly becomes NO_x during the subsequent day due to NO_3 radical photochemistry.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R2)}$$

$$NO_2 + NO_3 \leftrightharpoons N_2O_5 \quad \text{(R3)}$$

$$N_2O_5 + H_2O\ (\text{het}) \rightarrow 2HNO_3 \quad \text{(R4a)}$$

$$N_2O_5 + Cl^- \rightarrow NO_3^- + ClNO_2 \quad \text{(R4b)}$$

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \quad \text{(R5)}$$

$$Cl + RH \rightarrow HCl + RO \quad \text{(R6)}$$

Utilizing the NSF/NCAR C-130 aircraft during the WINTER campaign, simultaneous airborne observations of all components involved in the conversion of NO_x to N_2O_5 and its corresponding multiphase reactants and products were made (See Figure 1 and supplemental information, SI). Mixing ratios of speciated nitrogen oxides measured by mass spectrometry including $ClNO_2$, N_2O_5, HNO_3, and nitrous acid (HONO), together with NO and NO_2 measured by chemiluminescence (Figure 1, top panels) explain the independently measured sum total reactive nitrogen abundance ($NO_y = NO_x + 2* N_2O_5 + ClNO_2 + HNO_3 + HONO + \ldots$) at all points along the flight track (Figure 1, bottom). Westerly winds export NO_x emissions from the polluted urban corridor of the Northeast U.S. into the marine boundary layer (MBL) over the Atlantic Ocean. Over the course of a winter night, our observations show that ~25-50% of NO_x is converted to N_2O_5, much of which reacts in the MBL to form HNO_3 and $ClNO_2$ (see SI).

Using the suite of *in situ* observations, we can directly assess the importance of each radical source to the oxidative capacity of the wintertime atmosphere (See SI for details). An example set of results from such calculations is shown in Figure 1 (c). We use observed nighttime concentrations of O_3, humidity, $ClNO_2$, formaldehyde (HCHO), and HONO together with modeled photolysis frequencies to calculate the total integrated concentraion of radicals that would be produced by these precursors over the following day. Other radical sources, such as from alkene ozonolysis or dihalogen photolysis were small on a regional basis during WINTER (see SI). While the nocturnal atmosphere near the surface over land is poorly mixed (See SI), vertical profiling provided by the aircraft allowed us to uniquely assess the vertical extent of these radical precursors. As expected, we found that over relatively warmer water in the MBL, air is relatively well mixed up to 800-1500 m altitude (e.g. Figure 2), allowing more straightforward calculations of radical budgets from measured concentrations.

As pollution is transported offshore overnight, and $ClNO_2$ formation continues, we find that $ClNO_2$ photolysis (R5) becomes the single largest source of radical oxidants. The latest pollution intercept occurred before midnight local time, and several more hours of N_2O_5 production and multiphase chemistry could be expected. Estimates of N_2O_5 reactivity on aerosol particles and $ClNO_2$ yield derived from *in situ* observations [McDuffie et al., 2018a; McDuffie et al., 2018b;] suggest $ClNO_2$ concentrations would have continued to increase overnight, accounting for as much as 80% of the daytime radical source the next day.

Other important observed radical sources are O_3 via R1, HCHO via R6 and HONO via R7.

$$HCHO + h\nu\ (\lambda < 324\ \text{nm}) + 2O_2 \rightarrow 2HO_2 + CO \quad \text{(R6)}$$

$$HONO + h\nu\ (\lambda < 578\ \text{nm}) \rightarrow OH + NO \quad \text{(R7)}$$

HCHO photolysis leads to the net formation of two HO_2 radicals, which rapidly cycle to OH in the presence of NO. Annual HCHO sources are dominated by *in situ* VOC oxidation, but during winter, negligible biogenic emissions of isoprene [Goldstein et al., 1998; Luecken et al., 2012;], and overall lower radical concentrations, reduce the secondary production of HCHO. HCHO is directly emitted from a variety of anthropogenic activities, e.g. inefficient combustion and manufacturing processes [Sigsby et al., 1987; Altshuller, 1993; Anderson et al., 1996; Kelly et al., 1999], but with currently uncertain magnitudes and spatial distributions. The GEOS-Chem global transport model underestimates the observed WINTER HCHO by a factor of 2 on average (see SI). Increasing the direct anthropogenic emission of HCHO in the model by a factor of 5 brings the model into good agreement with the observations, with approximately half the HCHO in the model arising from secondary oxidation of anthropogenic VOC and half from direct emissions. Increasing the emissions of anthropogenic VOC that react on an hour timescale to produce HCHO instead of direct emissions of HCHO would also be consistent with the observations, though appropriate observational constraints are lacking. There is strong evidence that emissions of HCHO and related oxygenated VOC from automobiles are significantly higher in the wintertime due to the inefficient combustion associated with cold engine starts [Anderson et al., 1994; Anderson et al., 1996; Li et al., 2010; Clairotte et al., 2013]. Moreover, the observed HCHO is strongly correlated with tracers of fossil fuel and wood combustion (See SI). While smaller than the summertime HCHO sources from biogenic VOC degradation [Fortems-Cheiney et al., 2012; Luecken et al., 2012; Wolfe et al., 2016;], the wintertime anthropogenic emissions of HCHO or its precursors that we infer are very important to the regional source of radicals.

HONO is both directly emitted from combustion [Kirchstetter et al., 1996; Stutz et al., 2002;], and formed *in situ* from multiphase chemistry of NO_2 as well as pNO_3^- photolysis [Kleffmann, 2007; Zhou et al., 2011;]. Figure 1 shows that the measured nighttime HONO concentrations are a small contributor to the primary daytime radical source over the surveyed domain. HONO is more important near the urban areas, very close to the surface (<100 m), and more generally enhanced over land than in the MBL (see SI). Our observations suggest a smaller role for HONO on a regional basis in the daily integrated radical budget than might be inferred from ground-based observations due to the poorly mixed nocturnal atmosphere [Febo et al., 1996; Stutz et al., 2002; Wong et al., 2012]. However, the estimates in Figure 1 neglect a potential source from pNO_3^- photolysis, which we assess below.

The above estimates of daytime radical sources shown in Figure 1 evolve as expected at sunrise as shown in Figure 2. A stalled high-pressure system offshore of New Jersey allowed us a unique opportunity to make multiple transects throughout the morning (Figure 2a) of pollution from the greater New York City area that had aged overnight in the MBL (see SI). As the sun rose during the flight, vertical profiles (Figure 2b) conducted along various segments revealed that the instantaneous radical source from $ClNO_2$ photolysis was 60-80% of the total primary radical source throughout the entire MBL. The importance of $ClNO_2$ as a radical source decreased substantially at altitudes above the MBL, while that of O_3 via R1 increased as expected given the steep gradients in $ClNO_2$ precursors (NO_x and aerosol particles) between the polluted boundary layer and overlying free troposphere. The observed instantaneous production rate of radicals from $ClNO_2$ was a factor of 5 to 10 larger than the other radical sources throughout the morning as the aircraft made multiple intercepts of the pollution plume. HONO photolysis was the next largest instantaneous radical source, in part due to its larger photolysis rate coefficient compared to HCHO. Nighttime N_2O_5 chemistry is a removal mechanism for O_3 (R2-R4) [Platt et al., 1984; Brown et al., 2004] and as such O_3 mixing ratios are often suppressed in NO_x-rich air masses during the night and morning [Stutz et al., 2004], which contributes in part to the negligible instantaneous source of radicals from R1 in the polluted MBL. The aircraft returned to its base (segment E, Figure 2A) by flying above the MBL, where we find that the background

tropospheric source of radicals is dominated by that from O_3 photolysis (R1), consistent with expectations.

We extend this instantaneous observational analysis during this flight using the Framework for 0-D Atmospheric Modeling (F0AM) (Wolfe et al., 2016) , which is based on the master chemical mechanism version 3.3.1 that explicitly tracks over 5800 chemical species in over 17,000 reactions (Bloss et al., 2005; Jenkin et al., 1997, 2003; Saunders et al., 2003) by preforming two simulations; one including and one excluding reactions from chlorine and heterogeneous N_2O_5 formation described in Riedel et al., (2014). Initializing F0AM with WINTER measurements of VOCs and inorganic gas phase species (see SI for details), Figure 3 shows the radical budget occurring the day following our interception of the maximum $ClNO_2$ concentration observed, which occurred on this flight at 6:40am in Figure 2c at point D in Figure 2a. Consistent with our observational analysis, the F0AM predicted instantaneous radical production rate from $ClNO_2$ was a factor of 5 to 12 larger than the other largest radical source throughout the morning, shown in Figure 3. Excluding reactions involving chlorine in F0AM caused an underestimate in the integrated daily radical budget the following day of 1.8 ppbv, or a factor of 3.75. This underestimate occurs primarily from excluding the early morning source of Cl radicals from $ClNO_2$ photolysis, but also from a 114% enhancement (0.62 ppbv) in the integrated daily [HCHO] that occurred because of an increase in VOC oxidation by those Cl radicals (see SI), and an increase in the daily integrated ozone production of 4.7 ppbv, thereby increasing the local source of OH from O_3 photolysis. These results highlight the importance of nocturnal heterogeneous chlorine chemistry in coupling the secondary oxidation of VOCs, NO_y and HO_x cycling, in the overall predicted daily radical budget within the WINTER domain.

We conducted 13 research flights, equally covering daytime and nighttime conditions, over land and the ocean, throughout the eastern U.S. domain (see Figure 1). Applying the above instantaneous radical source analysis to the wider set of flights illustrates the major importance of HCHO and $ClNO_2$ as radical precursors, with both being more important in polluted air, represented by increasing NO_x mixing ratios as shown in Figure 4. These results illustrate the control of wintertime radical sources by anthropogenic emissions of NO_x and VOC, and subsequent multiphase chemistry, with > 70% of the radical source stemming not from the canonical reaction R1, but from $ClNO_2$, HCHO, and HONO photolysis. Daytime observations underestimate the overall contributions of HONO and $ClNO_2$ to the total primary radical source because both species photolyze rapidly and may not be reformed until night. Over land, this effect causes an approximately 10% underestimate of the daily radical source from $ClNO_2$.

More over, recent studies suggest photolysis of pNO_3^- may be an important daytime HONO source, which would not be captured by our strictly observational approach. If daytime production of HONO from pNO_3^- photolysis occurs at the seasonally adjusted rate recently suggested from summertime observations [Ye et al., 2016;], and which our observations do not contradict (see SI), then HONO photolysis integrated over the day would increase the total radical source shown in Figure 4 by ~50% over land, with smaller but non-negligible contributions in the polluted MBL (See SI). Thus, the primary radical budget during winter may well be larger, with even stronger connection to anthropogenic pollution and atypical radical sources than indicated by our conservative estimate shown in Figure 4.

HCHO emissions and the multiphase chemistry of nitrogen oxides that produces $ClNO_2$, pNO_3^-, and HONO, are highly parameterized components of air quality or chemistry climate models, if included at all [Behnke et al., 1997; Perice et al., 1998; Evans & Jacob et al., 2005; Riemer et al., 2003; Anttila et al., 2006; Guenther et al., 2006; Davis et al., 2008; Bertram & Thornton, 2009; Griffiths et al., 2009; Roberts et al., 2009; Vinken et al., 2011; Barkley et al., 2012; Ryder et al.,

2015;]. Incorporating only $ClNO_2$ and HCHO sources consistent with the observations from the WINTER campaign into the GEOS-Chem model of global atmospheric chemistry and transport, we find significant impacts on climate and air quality quantities. For example, $PM_{2.5}$ components, such as SOA and sulfate increase, while nitrate decreases (see SI), and NO_x shifts further into its labile reservoirs, such as peroxy acetyl nitrate (PAN, see Figure 5). These changes are driven by subsequent increased concentrations of oxidant initiators such as HO_x (OH + HO_2) radicals, which increase by 40-80% over the WINTER domain from increased HCHO photolysis and VOC + Cl reactions, with concomitant increases in ozone production (see SI).

Wintertime sulfate is often underestimated by air quality models, while pNO_3^- and nitrate deposition over land have been overestimated [Tesche et al., 2002; Heald et al., 2012; Walker et al., 2012; Gao et al., 2016;]. Additionally, the split between primary and secondary OA remains poorly tested on a regional basis during winter [Fuzzi et al., 2006; Jimenez et al., 2009;]. The increases in regional radical oxidants and changes to NO_x multiphase chemistry implied by our observations reduce such discrepancies and uncertainties. Moreover, these changes halve model underestimates (from 30% to 15% bias) of total peroxy nitrates (such as PAN) measured during WINTER, providing additional support for increased oxidation initiated by atypical radical sources, and increased export of NO_x reservoirs to the global free troposphere.

We have shown that anthropogenic emissions of NO_x and of HCHO and its analogues exert control over the primary source of radical oxidants in polluted air during winter. In the case of HCHO, the dormant wintertime biosphere strongly implies its wintertime sources are dominated by anthropogenic emissions, which are likely enhanced due to inefficient combustion, such as during vehicular cold-starts and residential wood smoke. In the case of NO_x, the natural shift towards nocturnal multi-phase processing and an availability of sea-spray derived particulate chloride allowed the first observational confirmation that its conversion to $ClNO_2$ represents a critically important wintertime radical source throughout the polluted MBL that also serves to enhance [HCHO]. A daytime source of HONO from pNO_3^- photolysis, where the pNO_3^- enhancements stem from multi-phase processing of NO_x emissions would only increase the importance of local and regional anthropogenic emissions over the wintertime radical budget.

The coupling of NO_x emissions, multiphase conversion to pNO_3^- and $ClNO_2$, and subsequent pNO_3^- photolysis to HONO represent a potentially dominant source of radicals in polluted wintertime air. These insights lead to predictions of increased $PM_{2.5}$ and increased export of NO_x to the remote troposphere via PAN, where short-lived greenhouse gases such as O_3 and CH_4 are far more sensitive to its presence [Singh et al., 1981; Roberts et al., 1990]. Other regions of the world, such as China, Europe, and northern India also experience high NO_x, VOC sources from inefficient combustion and reactive chlorine during winter [Sarwar et al., 2014; Lowe et al., 2015; Li et al., 2016;]. Our findings therefore suggest important global scale revisions to our understanding of wintertime pollution transformations, transport and deposition.

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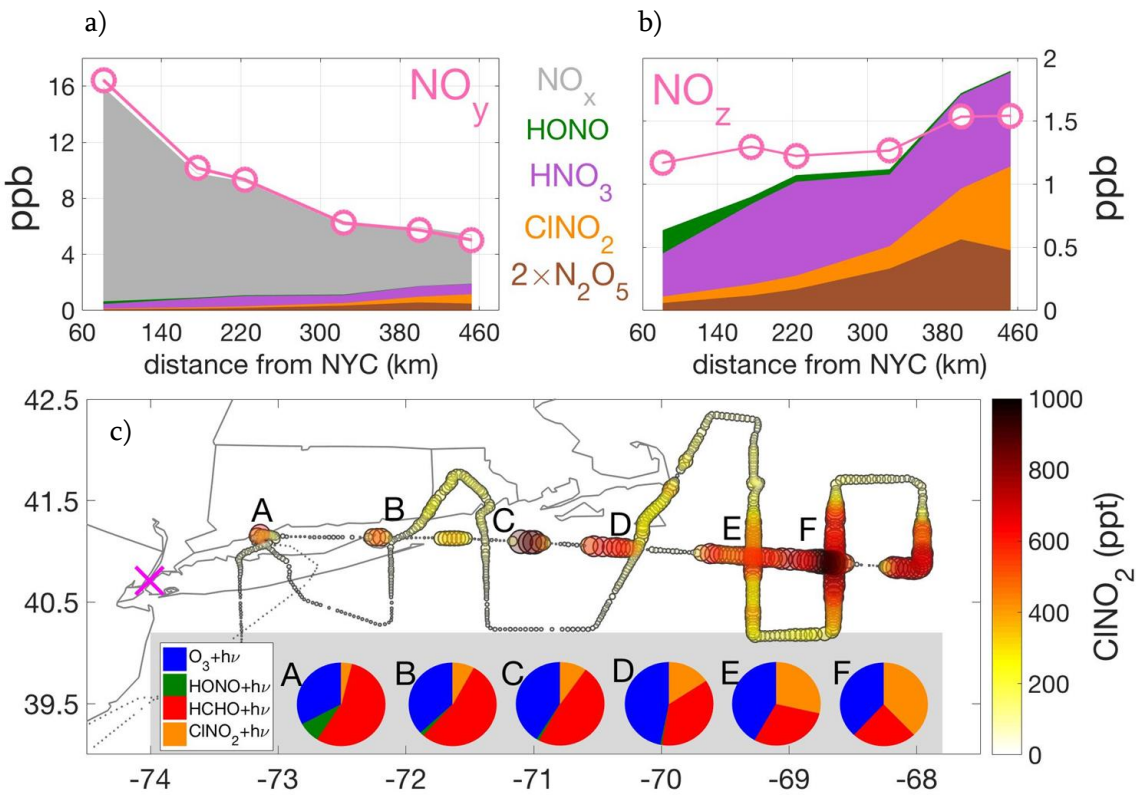

***Figure 1. Top panels**: evolution of nitrogen oxide reservoirs downwind of New York City observed aboard the NSF/NCAR C-130 aircraft during Research Flight 3 (RF; February 7, 2015) of the WINTER campaign. Observations are from below 2 km altitude only, and correspond to 7pm to 11pm local time. NO_y represents the sum of all forms of oxidized nitrogen that can be converted to NO at high temperatures (a) NO_z represents the sum of all oxidized nitrogen species expect for NO_x ($NO + NO_2$) and is derived from the measured $NO_y - NO_x$ (b). The gap between total NO_z and the sum of individual components that occurs near to NYC, while within the total calibration uncertainty of the sum, can likely be explained by a combination of pNO_3^- and peroxynitrates (see SI). **(c)** map of the flight track colored and sized by the measured mixing ratio of $ClNO_2$. The nearly straight trajectory between points A through F consisted of periodic ascents and descents of the aircraft between 500 and 2000 m altitude, profiling the vertical extent of the polluted atmospheric boundary layer. Pie charts show the observationally constrained contributions of different radical precursors to the integrated daytime radical source (see text).*

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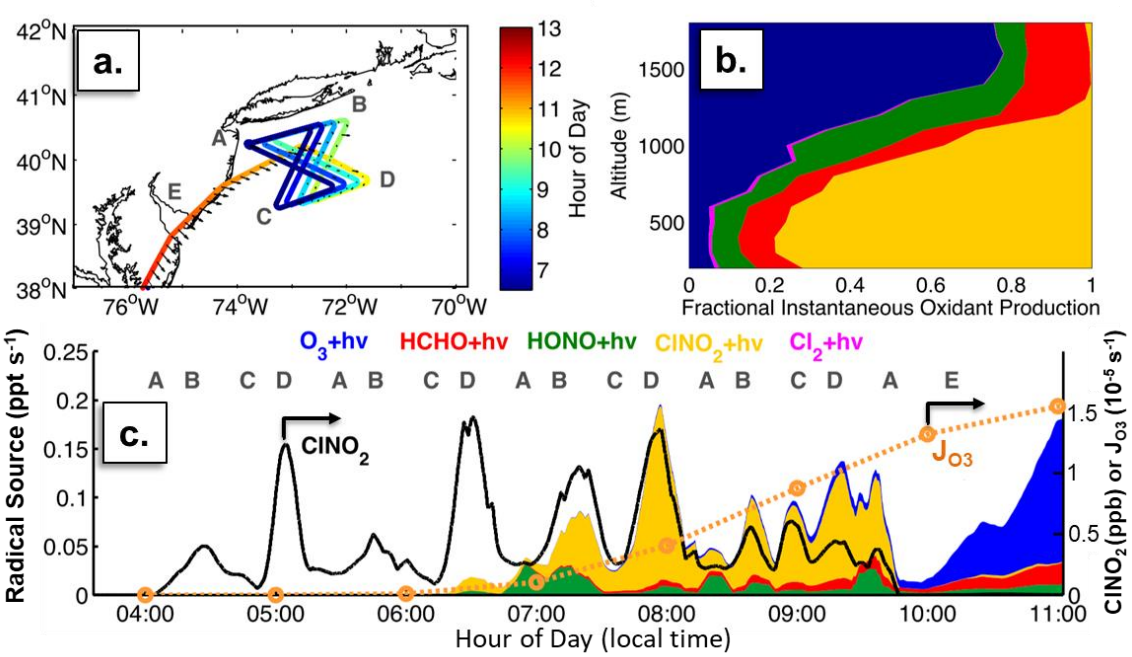

Figure 2. *(**a**) Flight track of the NSF/NCAR C-130 on Research Flight 8 of the WINTER campaign, colored by local time of day. Sunrise occurred at approximately 6:30 AM local time. Only portions with altitudes <2000 m are shown. (**b**) Vertical profiles of the instantaneous radical source calculated from observations of solar radiation and radical precursors. (**c**) Time series of the instantaneous radical source (left axis, stacked color), $ClNO_2$ mixing ratios (right axis, ppb), and the O_3 photolysis frequency (orange circles, right axis, 10^{-5} s^{-1})*

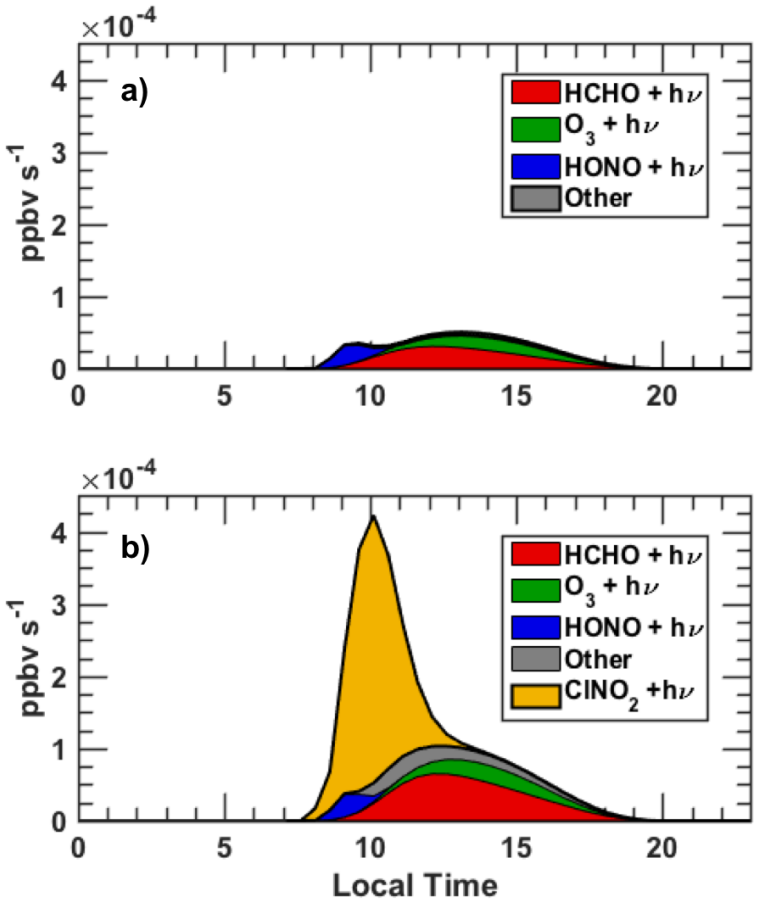

Figure 3. *Summary of daily, net primary radical production rates calculated the day following our interception of the peak $ClNO_2$ concentrations on RF08 using the F0AM box model initialized with WINTER observations without including chlorine reactions (a) and including chlorine reactions (b).*

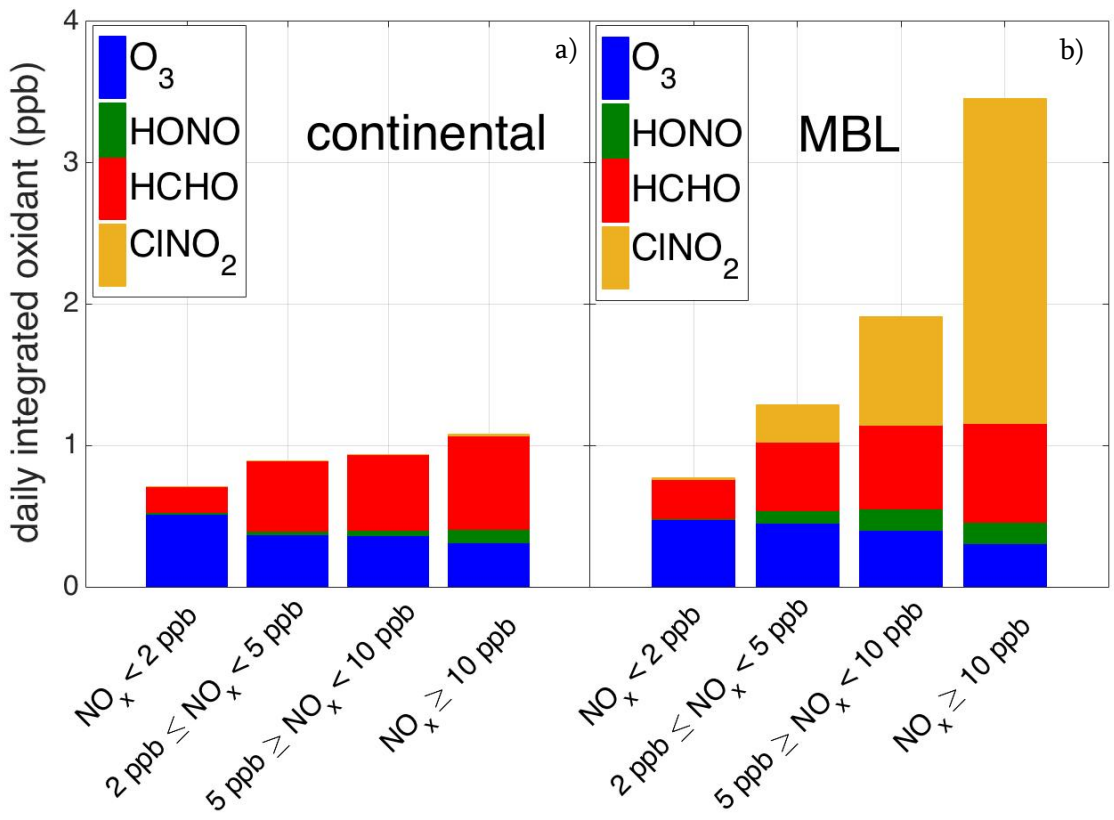

Figure 4. *Summary of daily primary radical source calculated from observations of O_3, H_2O_2, $ClNO_2$, HONO, and HCHO made during the daytime in the continental boundary layer (a), and at night within the MBL (b). Data are binned as a function of observed NO_x mixing ratios with lower values indicating less polluted air and higher values indicating more polluted air. In the left pane, we show only daytime observations over land, as these better reflect a well-mixed polluted boundary layer. For comparison, we show estimates based on nighttime observations within the MBL in the right panel. These two regimes are a fair representation of the typical importance of each radical source over the entire data set. See SI for additional statistics and calculations).*

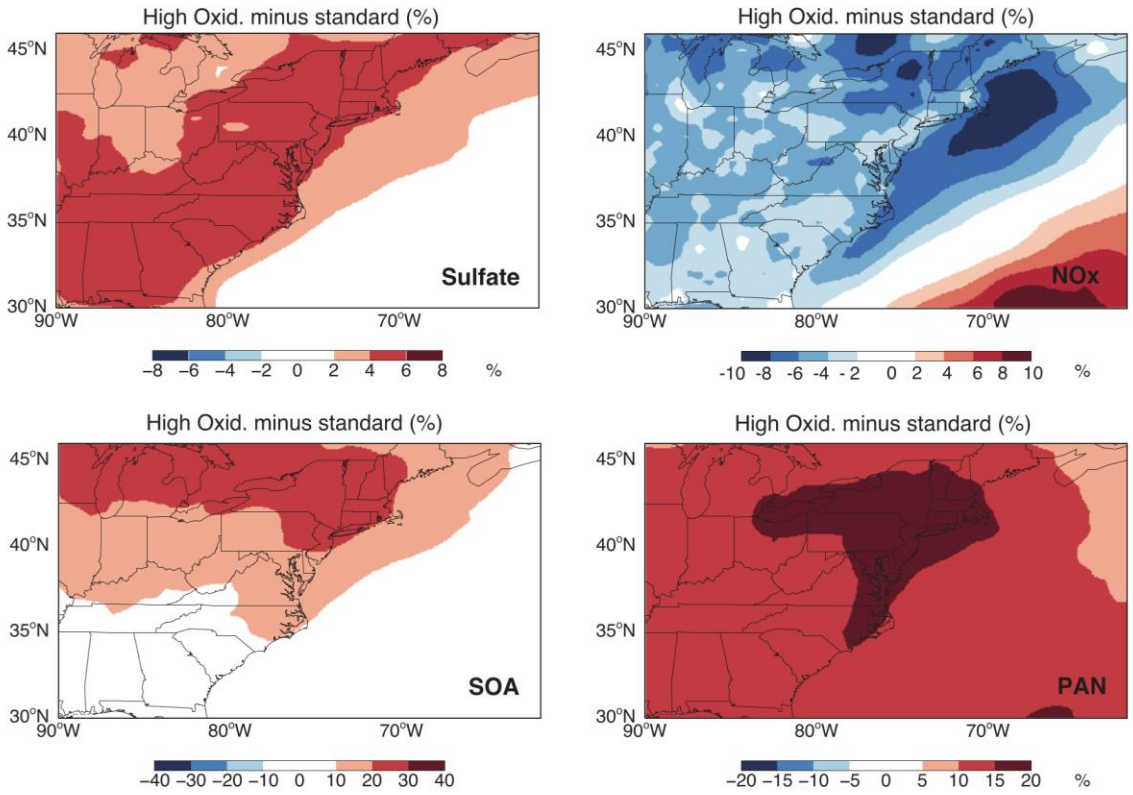

***Figure 5**. Relative changes in GEOS-Chem model predicted sulfate, SOA, NOx and PAN abundances between runs using standard emissions and chemistry, and those using updated emissions of HCHO and $ClNO_2$ chemistry based on the WINTER observations. Enhanced oxidative capacity in the boundary layer from enhanced HCHO (over land) and $ClNO_2$ (in the MBL) leads to increased conversion of SO_2 to sulfate aerosol mass, VOC to secondary organic aerosol mass, and increased conversion of NO_x into reservoirs such as PAN which in turn affects its global distribution.*

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