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## Anthropogenic control over wintertime oxidation of atmospheric pollutants

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### Abstract

During winter in the mid-latitudes, photochemical oxidation is significantly slower than in summer and the main radical oxidants driving formation of secondary pollutants, such as fine particulate matter and ozone, remain uncertain, owing to a lack of observations in this season. Using airborne observations, we quantify the contribution of various oxidants on a regional basis during winter, enabling improved chemical descriptions of wintertime air pollution transformations. We show

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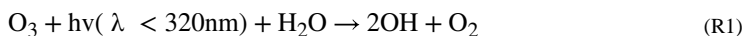
that 25–60% of  $\text{NO}_x$  is converted to  $\text{N}_2\text{O}_5$  via multiphase reactions between gas-phase nitrogen oxide reservoirs and aerosol particles, with ~93% reacting in the marine boundary layer to form  $>2.5$  ppbv  $\text{ClNO}_2$ . This results in  $>70\%$  of the oxidizing capacity of polluted air during winter being controlled, not by typical photochemical reactions, but from these multiphase reactions and emissions of volatile organic compounds, such as HCHO, highlighting the control local anthropogenic emissions have on the oxidizing capacity of the polluted wintertime atmosphere.

## Plain Language Summary

During summer, rapid transformations of primary pollutants, those emitted directly into the atmosphere, into secondary pollutants, such as particulate matter and ozone, are driven by reactions with the hydroxyl radical, formed in the atmosphere when sunlight strikes ozone in the presence of water vapor. During winter, when there is less sunlight and water vapor, production of this radical is lower. Yet, the conversion of primary pollutants into secondary pollutants still occurs rapidly, pointing to a misunderstanding in the chemical processes that drive this conversion during winter. Using aircraft data collected across the northeast US during the winter of 2015, we show that reactions with radicals arising from atypical precursors, such as nitryl chloride, account for more than 70% of the reactions that directly emitted pollutants undergo. We show that during winter, the formation of these radicals are tied to human activities. Our data provides critical constraints for improving the descriptions of chemical processes in air quality models, which will help guide improved air quality policy. Other regions of the world, such as China, Europe, and northern India also experience this seasonal chemical shift in the atmosphere. Our findings, therefore, have global scale implications for understanding wintertime pollution transformations and transport.

## 1. Introduction

Atmospheric primary radicals, formed from the photolysis of closed-shell molecules, initiate and sustain oxidation cycles during air pollution episodes. Understanding sources of these radicals is a key scientific challenge for the design of pollution mitigation strategies because they drive the conversion of primary pollutants into secondary pollutants such as ozone ( $\text{O}_3$ ) and fine particulate matter ( $\text{PM}_{2.5}$ ). In summer, production of hydroxyl radicals (OH) through  $\text{O}_3$  photolysis is often the dominant daily integrated radical source due to high water vapor,  $\text{O}_3$ , and solar radiation.

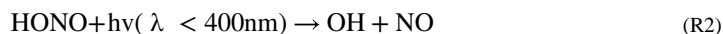


Other sources of hydrogen oxide radicals ( $\text{HO}_x = \text{OH} + \text{HO}_2$ ) can include formaldehyde (HCHO) photolysis, and nitrous acid (HONO) photolysis, but these are usually important only for a portion of the day or close to the ground during summer [Michoud et al 2012; Volkamer et al 2010; Whalley et al., 2018; Young et al., 2014].

During winter, primary radical production via R1 is lower by more than an order of magnitude from reduced sunlight and reduced water vapor [Klonecki & Levy, 1997; Yienger et al., 1999], suggesting a higher sensitivity of oxidation rates to the presence of other less

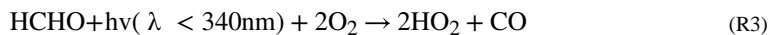
well quantified radical sources. Moreover, colder temperatures and less photochemical oxidation increase the importance of multiphase interactions between trace gases, particulate matter, and cloud and fog droplets, in driving the chemical evolution of primary pollutants. The sources of atypical radical precursors that might drive photochemical oxidation, the multiphase chemical processing of pollutants, and the interplay between them, remain highly uncertain, and indubitably cause some of the problems air quality models have in describing wintertime air pollution [Edwards et al., 2014; Gao et al., 2016; Heald et al., 2012].

HONO photolysis (R2) can be an important OH radical source, even at low light levels typical of winter [Kleffman et al., 2007; VandenBoer et al., 2013; Wong et al., 2012;].



HONO is directly emitted from combustion [Kirchstetter et al., 1996;], and formed *in situ* from the heterogeneous uptake of NO<sub>2</sub> on surfaces [Stutz et al., 2002; Kleffman et al., 2007;]. Daytime HONO concentrations in excess of that expected from these sources are routinely observed [Sorgel et al., 2011; Vander Boer et al., 2013; Wong et al., 2012], leading to numerous *in situ* multiphase production mechanisms being proposed [Kleffmann, 2007; Stemmler et al., 2006; Ye et al., 2016; Zhou et al., 2011]. However, there is not yet consensus on the abundance, production mechanisms, and seasonality of daytime HONO.

Photochemical oxidation of hydrocarbons in the presence of nitrogen oxide radicals (NO<sub>x</sub> = NO + NO<sub>2</sub>) can amplify the primary radical sources by leading to photo-labile intermediates such as HCHO [Levy, 1971]



In the lowest kilometer of the atmosphere, oxidation of the biogenic hydrocarbon, isoprene, is typically the largest regional source of HCHO during summer [Wolfe et al., 2016]. During winter, negligible biogenic isoprene emissions and lower radical concentrations are expected to reduce the production and abundance of HCHO. Thus, the importance of HCHO as a radical source in winter will depend upon direct emissions of HCHO and potential precursors from inefficient combustion, manufacturing processes, and consumer products, all of which remain poorly constrained [Sigsby et al., 1987; Altshuller, 1993; Anderson et al., 1996; Kelly et al., 1999; McDonald et al., 2018].

Coincident with seasonal shifts in photochemistry, multiphase chemical processes that occur in aerosol particles and clouds, are promoted in winter relative to summer [Shah et al., 2018], and can also impact primary radical sources. A prime example is dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), formed from the reaction of NO<sub>2</sub> with O<sub>3</sub> to generate the nitrate radical (NO<sub>3</sub>), which, subsequently reacts with another NO<sub>2</sub> molecule (R4 – R5) [Platt et al., 1984; Brown et al., 2004]. N<sub>2</sub>O<sub>5</sub> hydrolysis on aqueous particles (R6a) is a major sink of NO<sub>x</sub> during winter, which in turn limits daytime radical cycling [Alexander 2009; Jaeglé 2018; Platt and Heintz, 1994; Richards, 1983; Dentener and Crutzen, 1993; Smith et al., 1995; Alexander et al., 2009].

When particles contain chloride,  $\text{N}_2\text{O}_5$  reactions can also form  $\text{ClNO}_2$  [Finlayson-Pitts et al., 1989; Behnke & Zetzsch, 1990; Zetzsch & Behnke, 1992], which undergoes photolysis via R7 during the early morning, releasing  $\text{NO}_x$  and highly reactive chlorine atoms (Cl). Cl atoms initiate the oxidation of various hydrocarbons (RH), in some cases up to 100 times faster than OH [Orlando et al., 2003; Platt & Hönninger, 2003; Simpson et al., 2015].



Resolving whether the multiphase chemistry of  $\text{N}_2\text{O}_5$  is a net sink of radical precursors (via R6a), or source of radical precursors (R6b) during winter is a key challenge. Few observational constraints of these wintertime radical precursors exist to quantify regional wintertime oxidant sources in polluted regions. In this work, we utilize recent observations from the Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) campaign to assess the wintertime primary radical sources in polluted regions of the eastern United States. We find that in polluted air, the regional daily integrated primary radical source is dominated by  $\text{ClNO}_2$ , HCHO, and to a lesser extent HONO.

## 2. Methods

The NSF/NCAR C-130 aircraft was utilized during the WINTER campaign to make airborne observations of many of the above radical precursors as well as related primary and secondary pollutants from February 1 – March 15, 2015. More details on the WINTER campaign instrumentation and results can be found in the Supplemental Information (SI) as well as the WINTER special issue of the Journal of Geophysical Research. Thirteen research flights (Figure S1) were conducted over the eastern U.S., with ~50% of flight hours occurring at night, and more than 80% within 1 km of the surface.

## 3. Analysis

Using the suite of *in situ* observations made during WINTER, we can assess the contribution of each radical source discussed above to the oxidative capacity of the wintertime troposphere. For example, observations of all components involved in the conversion of  $\text{NO}_x$

to  $\text{N}_2\text{O}_5$  and its multiphase reaction products are shown in Figure 1. The observations were made during a flight downwind of New York City, when westerly winds exported  $\text{NO}_x$  emissions from the polluted urban corridor of the Northeast U.S. into the marine boundary layer (MBL) over the Atlantic Ocean. Mixing ratios of  $\text{ClNO}_2$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ , and HONO measured by mass spectrometry, together with NO and  $\text{NO}_2$  measured by chemiluminescence and cavity ring-down spectroscopy (Figure 1, top panels) explain the independently measured sum total of reactive nitrogen oxides ( $\text{NO}_y = \text{NO}_x + 2 * \text{N}_2\text{O}_5 + \text{ClNO}_2 + \text{HNO}_3 + \text{HONO} + \text{alkyl nitrates (ANs)} + \text{peroxy acetyl nitrates (PNs)}$ ) at all points along this flight (Figure 1, bottom). Our observations show that ~25–60% of  $\text{NO}_x$  is converted to  $\text{N}_2\text{O}_5$  on this flight, with ~93% reacting in the MBL to form  $\text{HNO}_3$  and  $\text{ClNO}_2$  [Jaeglé et al., 2018], highlighting the importance of multiphase chemistry under such conditions.

We use these observed nighttime and early morning concentrations of  $\text{O}_3$ ,  $\text{ClNO}_2$ , HCHO, and HONO together with average WINTER measured photolysis frequencies to calculate the total integrated concentration of radicals that would be produced by these precursors over the following day. Other radical sources, such as alkene ozonolysis or dihalogen ( $\text{Cl}_2$ ) photolysis (Haskins et al., 2018;), were < 5% on a regional basis during WINTER (see SI, Figure S6, Figure 2). While the nocturnal atmospheric surface layer is poorly mixed over land, vertical profiling performed by the aircraft allowed us to assess the vertical extent of these radical precursors. We found the MBL to be well mixed up to 800–1500 m altitude (e.g. Figure 2), allowing more straightforward calculations of radical sources from measured concentrations.

As pollution is transported offshore overnight during the flight shown in Figure 1, we find that  $\text{ClNO}_2$  becomes the largest radical reservoir. The direct measurements suggest up to a 38% contribution from  $\text{ClNO}_2$  to the integrated radical production on the following day, with similar contributions from HCHO and  $\text{O}_3$  (R1 and R3), but negligible contributions from HONO. Moreover, this integrated daily radical production calculation (SI Section 3b) is based upon measurements made before local midnight and several more hours of  $\text{ClNO}_2$  production could be expected. Assuming  $\text{N}_2\text{O}_5$  formation continued as observed  $\text{NO}_2$  and  $\text{O}_3$  would suggest, and an  $\text{N}_2\text{O}_5$  reactivity on aerosols from in situ observations [McDuffie et al., 2018a; McDuffie et al., 2018b], then we estimate  $\text{ClNO}_2$  concentrations would increase throughout the night and account for as much as 80% ( $[\text{ClNO}_2] \sim 1500$  pptv) of the integrated daily radical source the next day. This result, while assuming no further formation of  $\text{O}_3$ , HCHO, or HONO, already highlights the important role that anthropogenic  $\text{NO}_x$  emissions have on the wintertime radical sources, given previous estimates of the contribution of  $\text{ClNO}_2$  to the summertime radical budget have been substantially less (8–20%) [Young et al., 2014].

During a second WINTER flight, a stalled high-pressure system offshore of New Jersey (Figure 2a) allowed a unique opportunity to probe the instantaneous morning evolution of pollution from the New York City area that had aged overnight in the MBL (see SI, section 1). As the sun rose, vertical profiles (Figure 2b) made with the aircraft revealed that the instantaneous radical contribution from  $\text{ClNO}_2$  photolysis, calculated as the product of the observed  $\text{ClNO}_2$  concentrations and observed  $\text{ClNO}_2$  photolysis frequencies, was 60–80%

of the total instantaneous radical source (sum of the contributions of O<sub>3</sub>, HONO, HCHO, ClNO<sub>2</sub>, Cl<sub>2</sub> at that time) throughout the entire MBL (SI Section 3a). The importance of ClNO<sub>2</sub> as a radical source decreased substantially at altitudes above the MBL, while that of O<sub>3</sub> via R1 increased as expected, given the steep gradients in ClNO<sub>2</sub> precursors between the polluted boundary layer and free troposphere.

During this flight, HONO photolysis was the next largest instantaneous radical source. Contributions from Cl<sub>2</sub> to the total radical source were low, given small (<15 pptv) observed concentrations [Haskins et al., 2018]. The reactive uptake of ClNO<sub>2</sub> to form Cl<sub>2</sub>, which would amplify the radical source stemming from N<sub>2</sub>O<sub>5</sub> chemistry, was also small on a regional basis [Haskins et al., 2019]. The instantaneous source of radicals from R1 was negligible in the flight shown in Figure 2. O<sub>3</sub> mixing ratios are often relatively suppressed in NO<sub>x</sub>-rich air masses during the night and morning, in part due to nighttime N<sub>2</sub>O<sub>5</sub> chemistry which removes O<sub>3</sub> (R2–R4) [Platt et al., 1984; Brown et al., 2006; Stutz et al., 2004]. The aircraft departed the area (segment E, Figure 2A) flying above the MBL where we find that the background tropospheric source of radicals is dominated by that from O<sub>3</sub> photolysis (R1).

To further evaluate the implications of these results, we explicitly model the full day following the interception of these plumes during this research flight, using a Master Chemical Mechanism based 0-D model [Wolfe et al., 2016]. We perform two simulations, including and excluding reactions from ClNO<sub>2</sub> formation and subsequent reactions of Cl atoms with various VOCs (R8b–R10), using the mechanism described in Riedel et al. (2014) (see SI, Section S4). The model is initialized with WINTER measurements of VOCs and gas phase species including HCHO, HONO, O<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClNO<sub>2</sub> among others (see SI for details). Figure 3 shows the modeled instantaneous radical production occurring the 16 hours following our interception of the maximum ClNO<sub>2</sub> concentration observed on this flight, which occurred at 6:36am, at Location “D” in Figure 2. The selection of point D from Figure 2 to initialize the model provides an upper limit of the importance of ClNO<sub>2</sub> chemistry on radical production. Results from initializing the model on a typical observed plume can be found in the SI.

Consistent with our observational analysis, the model predicts an instantaneous radical production rate from ClNO<sub>2</sub> that is a factor of 5–12 larger than the next largest radical source between 6 am and 11 am (Figure 3). ClNO<sub>2</sub> also dominates the total daily integrated radical source predicted with the model. The simulation including chlorine reactions produced 2.5 ppbv of radicals (Cl+ HO<sub>x</sub>+RO<sub>2</sub>) by the end of the day, which is factor of 3.75 larger than that predicted without chlorine chemistry. The increase in radical production due to inclusion of ClNO<sub>2</sub> chemistry is from the direct production of Cl atoms from ClNO<sub>2</sub> photolysis, a secondary 114% enhancement (0.62 ppbv) in HCHO due to Cl radical initiated VOC oxidation (see SI, section 4), and an increase in daily integrated ozone production of 4.7 ppbv. Initializing the model to produce median ClNO<sub>2</sub> concentrations similarly led to the total radical source being a factor of 3.1 larger than when neglecting Cl radical chemistry. The magnitude of HO<sub>x</sub> enhancement could be different for different locations and time periods, but these results underscore that including Cl-atom chemistry from ClNO<sub>2</sub> is

necessary to adequately represent wintertime oxidation, given the secondary impacts of Cl atoms on HCHO and O<sub>3</sub>.

We apply the above instantaneous radical source analysis to the wider set of flights and integrate these results throughout the day (see SI, section 3b) using predicted photolysis rates and observations of the radical precursors made at night and early morning within 1 km of the surface. Daytime observations underestimate the overall contributions of HONO and ClNO<sub>2</sub> to the total primary radical source because both species photolyze rapidly and may not be reformed until night. The results, shown in Figure 4, illustrate that > 70% of the wintertime radical source in polluted air (represented by increasing NO<sub>x</sub>) stems not from reaction R1 as it would in summer, but from ClNO<sub>2</sub>, HCHO, and HONO photolysis. ClNO<sub>2</sub> and HCHO tend to dominate, but with a strong spatial dependence given the spatial heterogeneity of their formation pathways.

The control of anthropogenic emissions on primary radical sources during winter is evident when considering the contributions of HCHO. Jaeglé et al., (2018) showed that the standard GEOS-Chem model underestimated the observed HCHO during WINTER by a factor of 2 but increasing anthropogenic emissions of HCHO from 10% to 30% of the total HCHO source brought the model into agreement with observations. Increasing emissions of short-lived anthropogenic HCHO precursors, such as ethene and other primary alkenes, followed by their oxidation to form HCHO would also be consistent with the WINTER observations. Oxidation of such alkenes by Cl atoms would enhance HO<sub>x</sub> yields, thereby extending the impact of anthropogenic emissions on the contribution of radical source to the total wintertime radical budget. Ultimately, the resulting modeled wintertime HCHO is primarily from anthropogenic sources, in stark contrast to summer. In the example shown in Figure 1 and reinforced in the overall campaign statistics in Figure 4, HCHO contributes most to the observed radical budget outside of the MBL. Although the total HCHO source we estimate during WINTER is smaller than the isoprene dominated source in summertime [Fortems-Cheiney et al., 2012; Luecken et al., 2012; Wolfe et al., 2016], this result demonstrates the seasonally varying sensitivity of the radical budget to both anthropogenic and biogenic emissions.

The measured nighttime HONO concentrations during WINTER imply it is a small but non negligible contributor to the primary daytime radical source, especially in urban areas close to the surface (<100 m, see SI, section 6), but not in the MBL. For example, HONO contributed a maximum of 8% to the projected daily radical budget on the flight shown in Figure 1, but over land HONO contributed 10–20% to the radical budget at the lowest altitudes surveyed, consistent with its main sources being tied to anthropogenic emissions. Somewhat surprisingly, 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 [Whalley et al., 2018]. Near-source measurements in a poorly mixed nocturnal atmosphere may tend to overestimate the regional impact of this source [Febo et al., 1996; Stutz et al., 2002; Wong et al., 2012].

Recent studies suggest particulate nitrate (pNO<sub>3</sub><sup>-</sup>) photolysis may be an important daytime HONO source [Ye et al., 2016; Romer et al., 2018]. We use early morning observations of



HONO to predict the production of radicals resulting from its photolysis, assuming no daytime production or further emission of HONO in the analysis presented in Figure 4. Therefore, we would under-predict the contribution from HONO to the primary radical sources if photolysis of  $\text{pNO}_3^-$  or other daytime HONO sources [Kleffmann, 2007; Zhou et al., 2011;] are significant. Our simultaneous observations of  $\text{pNO}_3^-$  and HONO suggest a slow daytime production of HONO from  $\text{pNO}_3^-$  photolysis, similar to the rate presented in Romer et al., (2018), which would increase the total radical source shown in Figure 4 by ~4% over land, with smaller contributions in the polluted MBL (SI, Figure S7). During the daytime our measurements of HONO are often at or below our detection limit (30 pptv), thus we can only constrain an upper limit source of daytime HONO (see SI, section 6).

HCHO emissions, the multiphase chemistry of  $\text{NO}_x$ , and aerosol processes that produce and directly affect  $\text{ClNO}_2$ ,  $\text{pNO}_3^-$ , and HONO concentrations, are highly parameterized components of air quality and 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]. Increasing anthropogenic HCHO sources [Jaeglé et al., 2018] and implementing the production of  $\text{ClNO}_2$  [Shah et al., 2018] in the GEOS-Chem model, we find significant impacts on primary and secondary pollutant abundance and air quality metrics relative to the standard model run. For example,  $\text{PM}_{2.5}$  components, such as SOA and sulfate increase by  $0.3 \mu\text{g}/\text{m}^3$  (20–30%) and  $0.12 \mu\text{g}/\text{m}^3$  (2–6%), respectively, while nitrate decreases by up to  $2 \mu\text{g}/\text{m}^3$  (0–5%) [Jaeglé et al., 2018;], and  $\text{NO}_x$  shifts further into its labile reservoirs, such as peroxy acetyl nitrate (PAN, see Figure 5). Given PAN's longer lifetime in winter, this transports  $\text{NO}_x$  further downwind than during summer. These changes are driven by increased concentrations of oxidant initiators such as  $\text{HO}_x$  and  $\text{RO}_2$  radicals, which increase by 40–80% across the WINTER domain from increased HCHO photolysis and  $\text{VOC} + \text{Cl}$  reactions, with concomitant increases in ozone production.

Wintertime sulfate is often underestimated by air quality models, while  $\text{pNO}_3^-$  and nitrate deposition over land have been overestimated [Tesche et al., 2002; Heald et al., 2012; Walker et al., 2012; Gao et al., 2016]. The increases in regional radical oxidants and changes to  $\text{NO}_x$  multiphase chemistry reduce such discrepancies [Jaeglé et al., 2018; Shah et al., 2018] and halve GEOS-Chem underestimates (from 30% to 15% bias) of measured total peroxy nitrates (such as PAN). Recent results show that while models of the WINTER domain predict organic aerosol (OA) from primary sources, most OA sampled is formed secondarily in processes like those that occur during summer [Schroder et al., 2018]. Ultimately, these results provide support for increased oxidation initiated by atypical radical precursors, and increased export of  $\text{NO}_x$  reservoirs to the global free troposphere.

#### 4. Conclusions

We have shown that anthropogenic emissions of  $\text{NO}_x$  and, HCHO and its precursors, exert control over the source of radical oxidants in polluted air during winter. In the case of  $\text{NO}_x$ ,

the natural shift towards nocturnal multi-phase processing and an availability of sea-spray derived particulate chloride allowed the first observational confirmation that conversion of  $\text{NO}_2$  to  $\text{ClNO}_2$  represents a critically important wintertime radical source throughout the polluted MBL with ~25–60% of  $\text{NO}_x$  being converted to  $\text{N}_2\text{O}_5$ , and ~93% reacting in the MBL to form  $\text{HNO}_3$  and  $\text{ClNO}_2$ . In polluted maritime regions, we find that Cl atoms from direct  $\text{ClNO}_2$  photolysis are both the dominant early morning radical source and the dominant integrated daily radical source, and that their presence amplifies the OH source by increasing HCHO formation from VOC + Cl reactions, and increased  $\text{O}_3$  production. HCHO is the largest radical source on a regional basis over land, and the dormant wintertime biosphere implies the HCHO sources are dominated by anthropogenic contributions, either through direct emissions and/or emissions of short-lived precursors.

We find HONO is most important near urban areas close to the surface (<100 m altitude) over land, contributing <8% to the projected daily radical budget within the MBL, which was typically well-mixed from the surface to ~1 km. Our measurements show some support for slower daytime production of HONO from  $\text{pNO}_3^-/\text{pNO}_3^-$  photolysis than reported by Ye et al. (2016) and more broadly consistent with that presented in Romer et al., (2018). Given that measured daytime HONO concentrations were rarely above our detection limit, we conclude that mechanisms controlling HONO's daytime production and potential contribution to primary radicals remain uncertain but smaller on a regional average sense than previous estimates would have suggested.

Ultimately, we show that the dominant sources of radicals in polluted wintertime air arise largely from local and regional anthropogenic emissions, as opposed to background ozone. These insights lead to predictions of increased  $\text{PM}_{2.5}$  and export of  $\text{NO}_x$  to the remote troposphere via PAN, where greenhouse gases such as  $\text{O}_3$  and  $\text{CH}_4$  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  $\text{NO}_x$ , 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 multiphase processes.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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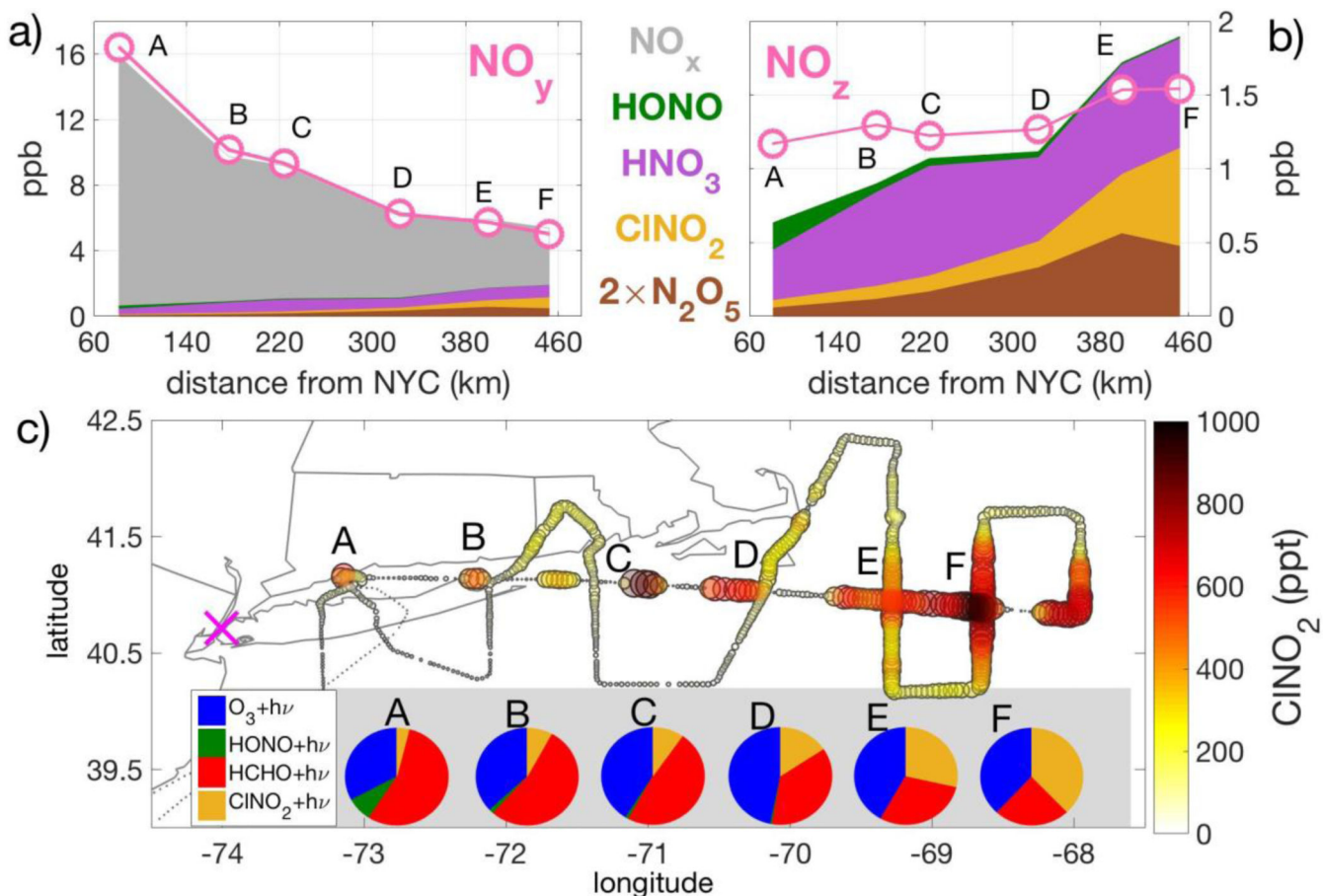
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**Key points:**

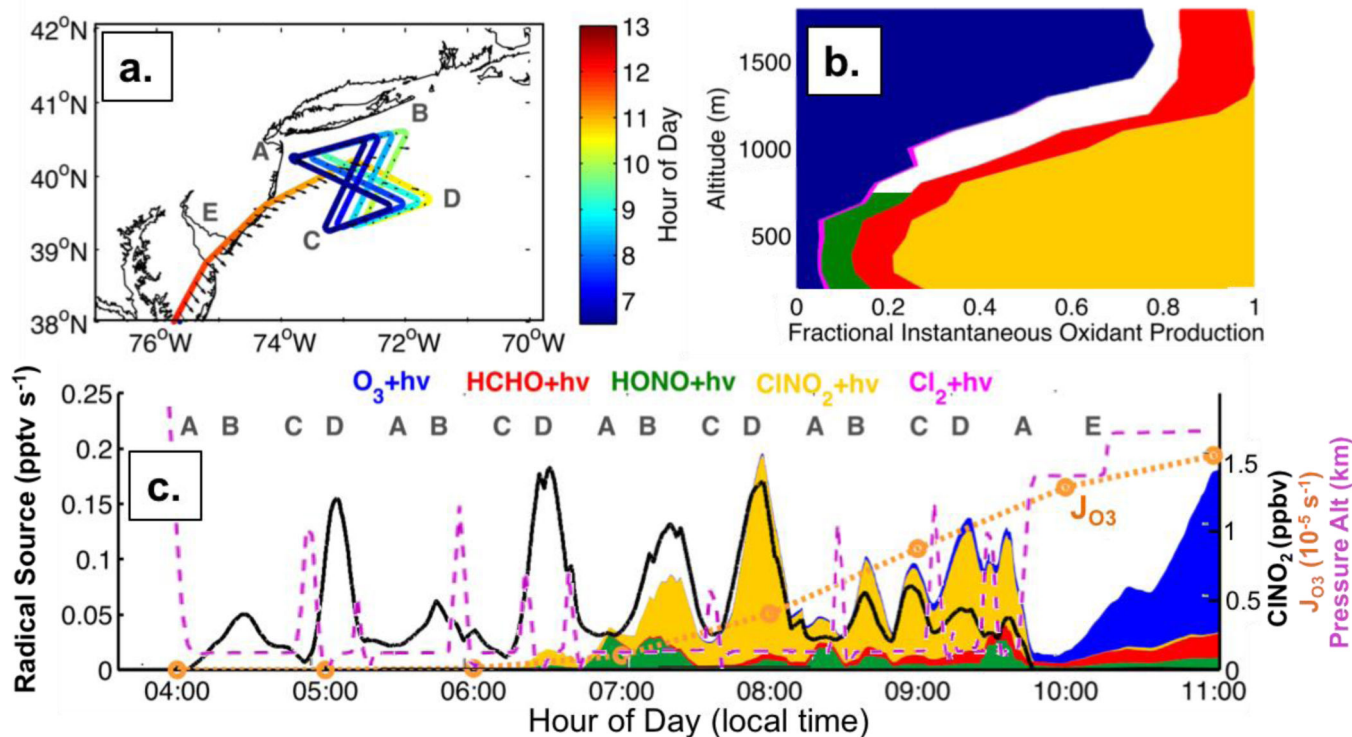
- (1) Observations show atypical radical precursors drive > 70% of atmospheric oxidation in polluted air over the northeast US during winter
- (2) Anthropogenic emissions and multi-phase chemistry largely control the abundance of these atypical radical precursors
- (3) Improved descriptions of these radical sources in air quality models are needed to predict future trajectories in wintertime air pollution





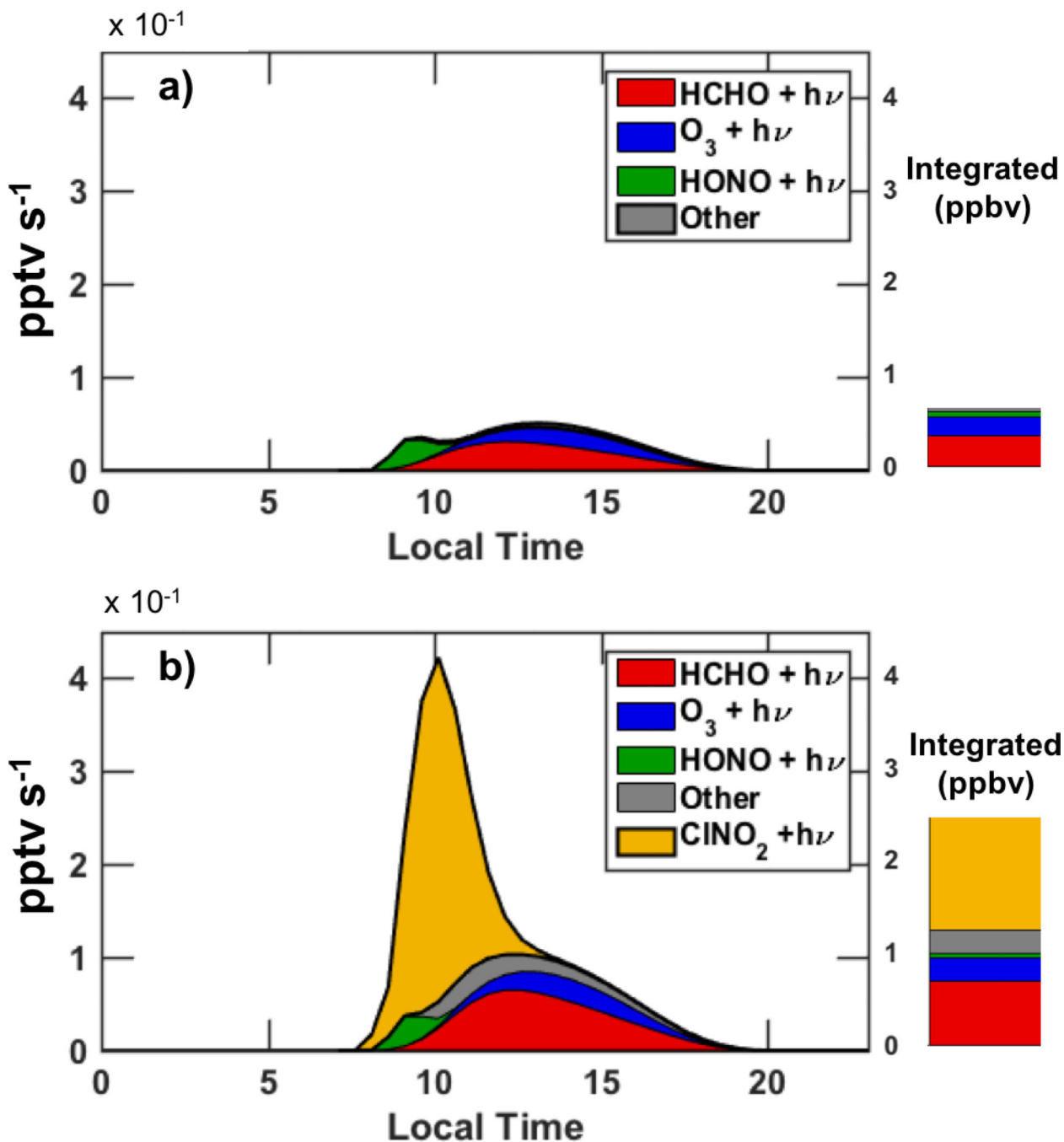
**Figure 1.**

Evolution of nitrogen oxide reservoir species downwind of New York City (purple x) observed during Research Flight 3 of the WINTER campaign. a)  $\text{NO}_y$  represents the sum of all forms of reactive nitrogen oxides that can be converted to NO at high temperatures. b)  $\text{NO}_z$  represents the sum of higher oxides of all reactive nitrogen oxides species excluding  $\text{NO}_x$  ( $=\text{NO}+\text{NO}_2$ ) and is derived from the difference of the measured  $\text{NO}_y$  and  $\text{NO}_x$ . The gap between total  $\text{NO}_z$  ( $=\text{NO}_y-\text{NO}_x$ ) and the sum of the individual components that occurs near NYC is within the total calibration uncertainty of the sum, and can likely be explained by a combination of particle nitrates and gaseous peroxy nitrates (see SI). c) Map of the flight track colored and sized by the measured mixing ratio of  $\text{ClNO}_2$ . The pie charts show the observationally constrained contributions of different radical precursors to the integrated daytime radical source (see text). The six intercepts of the New York City plume, labeled as A–F in (a), (b) and (c), occurred between 7 pm to 11 pm local time, between 250 and 400 m pressure altitude, while the C-130 aircraft was traveling approximately in the north/south direction near the A–F labels in (c). The plume intercept east of label F was excluded because it occurred at a higher altitude (750 m) than the first six.

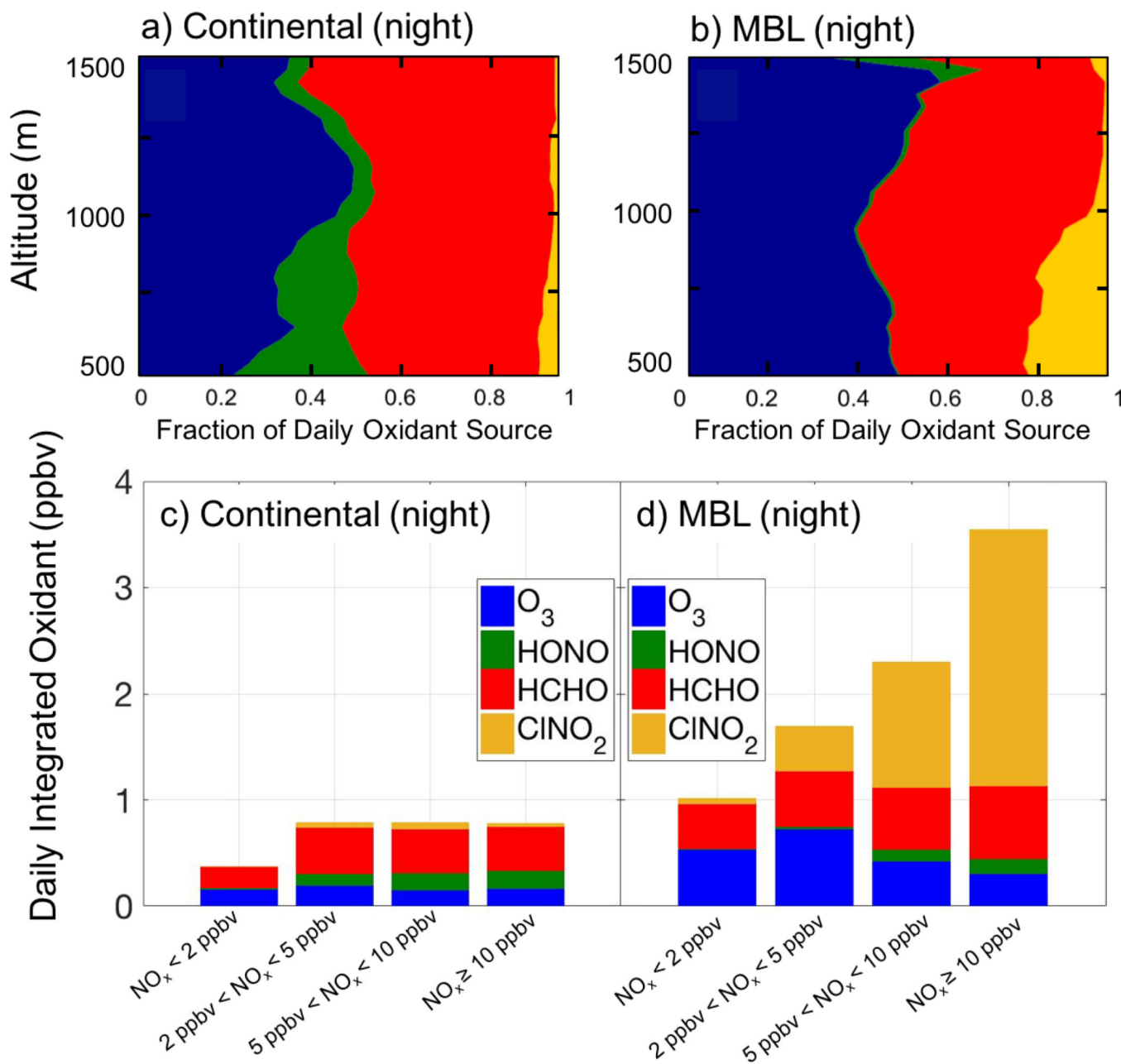


**Figure 2.**

(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. White space indicates HONO measurements at these altitudes were below instrument detection limits. (c) Time series of the instantaneous radical source (left axis, stacked color), ClNO<sub>2</sub> mixing ratios (right axis, ppbv), the O<sub>3</sub> photolysis frequency (orange circles, right axis, 10<sup>-5</sup> s<sup>-1</sup>), and pressure altitude (right axis, km)

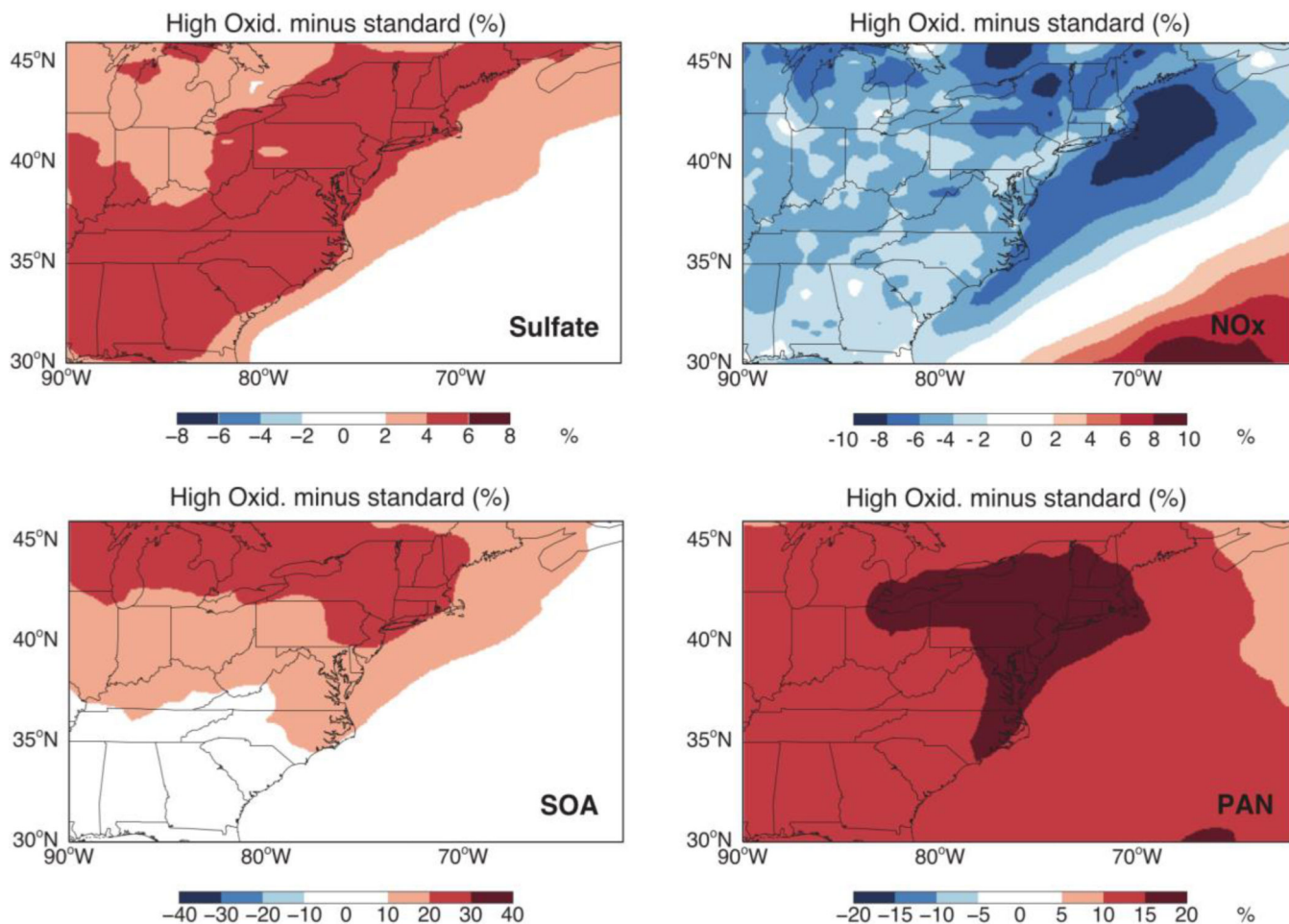


**Figure 3.** Summary of daily, net primary radical production rates calculated the day following our interception of the peak ClNO<sub>2</sub> concentrations on RF08 using the F0AM box model initialized with WINTER observations without including chlorine reactions (a) and including chlorine reactions (b). Bar charts show the integrated daily radical source from each precursor.



**Figure 4.**

Vertical profiles of the daily integrated primary radical sources calculated from observations of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, ClNO<sub>2</sub>, HONO, and HCHO made throughout the campaign in vertical profiling maneuvers during the night below 1.5 km over (a) the continental boundary layer, and (b) within the marine boundary layer (MBL). Averaging over these vertical profiles during the night and binning them as a function of their observed NO<sub>x</sub> mixing ratios with lower values indicating less polluted air and higher values indicating more polluted air, we show the calculated the daily integrated primary radical source from each radical precursor that would result the following day over (c) the continental boundary layer and (d) within the MBL as calculated using the methodology in Section 3b of the SI.



**Figure 5.**

Relative changes in GEOS-Chem model predicted particulate sulfate, SOA, NO<sub>x</sub>, and PAN abundances between runs using standard emissions and chemistry, and those using updated emissions of HCHO and updated ClNO<sub>2</sub> chemistry (described in Jaegle et al., (2018)) based on the WINTER observations. Enhanced oxidative capacity in the boundary layer from enhanced HCHO (over land) and ClNO<sub>2</sub> (in the MBL) leads to increased conversion of SO<sub>2</sub> to sulfate aerosol mass, VOC to secondary organic aerosol mass, and increased conversion of NO<sub>x</sub> into reservoirs such as PAN which in turn affects its global distribution.