Geophysical Research Letters

RESEARCH LETTER
10.1029/2019GL085498

Anthropogenic Control Over Wintertime Oxidation of Atmospheric Pollutants

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Key Points:
- Observations show atypical radical precursors drive >70% of atmospheric oxidation in polluted air over the northeast United States during winter
- Anthropogenic emissions and multiphase chemistry largely control the abundance of these atypical radical precursors
- Improved descriptions of these radical sources in air quality models are needed to predict future trajectories in wintertime air pollution

Supporting Information:
- Supporting Information S1

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Citation:
Haskins, J. D., Lopez-Hilfiker, F. D., Lee, B. H., Shah, V., Wolfe, G. M., DiGangi, J., et al. (2019). Anthropogenic control over wintertime oxidation of atmospheric pollutants. *Geophysical Research Letters*, *46*, 14,826–14,835. https://doi.org/10.1029/2019GL085498

Received 23 SEP 2019
Accepted 11 DEC 2019
Accepted article online 13 DEC 2019
Published online 20 DEC 2019

Abstract During winter in the midlatitudes, 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 that 25–60% of NO_x is converted to N_2O_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 $ClNO_2$. This results in >70% of the oxidizing capacity of polluted air during winter being controlled by multiphase reactions and emissions of volatile organic compounds, such as HCHO, rather than reaction with OH. These findings highlight 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 United States 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 is tied to human activities. Our data provide 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 the sources of these radicals is a key scientific challenge for designing pollution mitigation strategies because they drive conversion of primary pollutants into secondary pollutants such as ozone (O_3) and fine particulate matter ($PM_{2.5}$). In summer, production of hydroxyl radicals (OH) through O_3 photolysis is often the dominant daily integrated primary radical source due to high water vapor, O_3, and solar radiation.

$$O_3 + h\nu\ (\lambda<320\ \text{nm}) + H_2O \rightarrow 2OH + O_2 \quad \text{(R1)}$$

Other smaller summertime sources of hydrogen oxide radicals ($HO_x = OH + HO_2$) can include formaldehyde (HCHO) and nitrous acid (HONO) photolysis (Michoud et al., 2012; Volkamer et al., 2010; Whalley et al., 2018; Young et al., 2014).

During winter, (R1) is slower by more than an order of magnitude due to reduced sunlight and reduced water vapor (Yienger et al., 1999), suggesting greater importance 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, multiphase chemical processing, and the interplay between these processes 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 at low light levels typical of winter (Kleffmann, 2007; VandenBoer et al., 2013; Wong et al., 2012).

$$HONO + h\nu\ (\lambda<400\ \text{nm}) \rightarrow OH + NO \quad \text{(R2)}$$

HONO is directly emitted from combustion (Kirchstetter et al., 1996) and formed in situ from the heterogeneous uptake of NO_2 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; VandenBoer et al., 2013; Wong et al., 2012), leading to numerous in situ multiphase production mechanisms being proposed (Spataro & Ianniello, 2014). 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 ($NO_x = NO + NO_2$) can amplify the primary radical sources by leading to photolabile intermediates such as HCHO (Levy, 1971):

$$HCHO + h\nu\ (\lambda<340\ \text{nm}) + 2O_2 \rightarrow 2HO_2 + CO \quad \text{(R3)}$$

In the lowest kilometer of the atmosphere, oxidation of the biogenic hydrocarbon, isoprene, is typically the largest regional source of HCHO during summer (Wolfe, Kaiser, 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 (Altshuller, 1993; Anderson et al., 1996; Kelly et al., 1999; McDonald et al., 2018; Sigsby et al., 1987).

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). A prime example is dinitrogen pentoxide (N_2O_5), formed from the reaction of NO_2 with O_3 to generate the nitrate radical (NO_3), which, subsequently reacts with another NO_2 molecule, (Platt et al., 1984). N_2O_5 hydrolysis on aqueous particles (R6a) is a major sink of NO_x during winter, which in turn limits daytime radical cycling (Dentener & Crutzen, 1993).

When particles contain chloride, N_2O_5 reactions can also form $ClNO_2$ (Behnke et al., 1997; Finlayson-Pitts et al., 1989), which undergoes photolysis via (R7) during the early morning, releasing 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, (R8) (Orlando et al., 2003).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R4)}$$

$$NO_2 + NO_3 \leftrightharpoons N_2O_5 \quad \text{(R5)}$$

$$N_2O_5 + H_2O\ (\text{het}) \rightarrow 2HNO_3 \quad \text{(R6a)}$$

$$N_2O_5 + Cl^-\ (\text{het}) \rightarrow NO_3^- + ClNO_2 \quad \text{(R6b)}$$

$$ClNO_2 + h\nu \rightarrow Cl + NO_2 \quad \text{(R7)}$$

$$Cl + RH \xrightarrow{+O_2} HCl + RO_2 \quad \text{(R8)}$$

Resolving whether the multiphase chemistry of N_2O_5 is a net sink of radical precursorsvia, or source of radical precursors (R6b) during winter is a key challenge.

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 $ClNO_2$, HCHO, and to a lesser extent HONO.

2. Methods

The National Science Foundation/National Center for Atmospheric Research 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 1 February to 15 March 2015. More details on the WINTER campaign instrumentation and results can be found in the supporting 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 United States, with ~50% of flight hours occurring at night, and more than 80% within 1 km of the surface.

3. Results and 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 NO_x to N_2O_5 and its multiphase reaction products (Figure 1) were made during a flight downwind of New York City, when westerly winds exported urban NO_x emissions into the marine boundary layer (MBL) over the Atlantic Ocean. Mixing ratios of $ClNO_2$, N_2O_5, HNO_3, and HONO measured by mass spectrometry, together with NO and NO_2 measured by chemiluminescence and cavity ring-down spectroscopy (Figure 1, top panels) explain the independently measured sum total of reactive nitrogen oxides ($NO_y = NO_x + 2 * N_2O_5 + ClNO_2 + HNO_3 + HONO +$ alkyl nitrates + peroxy acetyl nitrates, PANs) at all points along this flight (Figure 1, bottom). Our observations show that ~25–60% of NO_x is converted to N_2O_5 on this flight, with ~93% reacting in the MBL to form HNO_3 and $ClNO_2$ (Jaeglé et al., 2018), highlighting the importance of multiphase chemistry under such conditions.

We use the observed nighttime concentrations of O_3, $ClNO_2$, 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 (see SI section S3b). Other radical sources, such as alkene ozonolysis or dihalogen (Cl_2) photolysis (Haskins et al., 2018), were <5% on a regional basis during WINTER (see SI Figure S6 and Figure 2). While the nocturnal 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- to 1,500-m altitude (e.g., Figure 2), allowing more straightforward calculations of radical sources from measured concentrations.

During the flight shown in Figure 1, $ClNO_2$ becomes the largest measured radical reservoir, contributing at least 38% to the calculated next-day integrated radical source, with similar contributions from HCHO and O_3

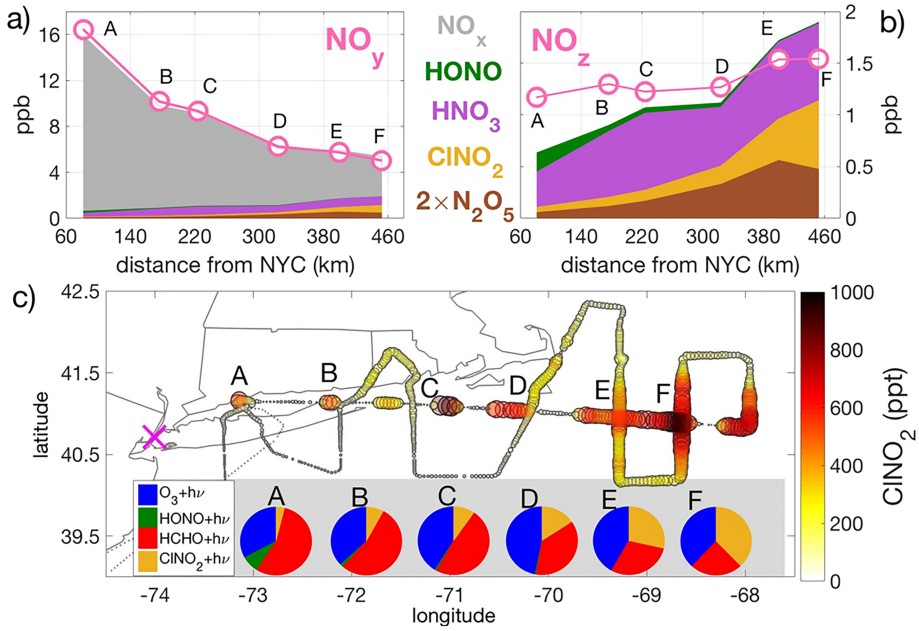

Figure 1. Evolution of nitrogen oxide reservoir species downwind of New York City (purple x) observed during Research Flight 3 of the WINTER campaign. (a) NO_y is the sum of all forms of reactive nitrogen oxides that can be converted to NO at high temperatures. (b) NO_z is the sum of higher oxides of all reactive nitrogen oxides species excluding NO_x ($NO_z = NO_y - NO_x$). The gap between NO_z and the sum of the individual components that occurs near NYC is likely explained by a combination of particle nitrates and gaseous peroxynitrates (see Supporting Information). (c) Map of the flight track colored and sized by the measured mixing ratio of $ClNO_2$. 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)–(c), occurred between 7 p.m. to 11 p.m. local time, between 250- and 400-m pressure altitudes (c). The Plume Intercept F was excluded due to a higher altitude (750 m) than the first six.

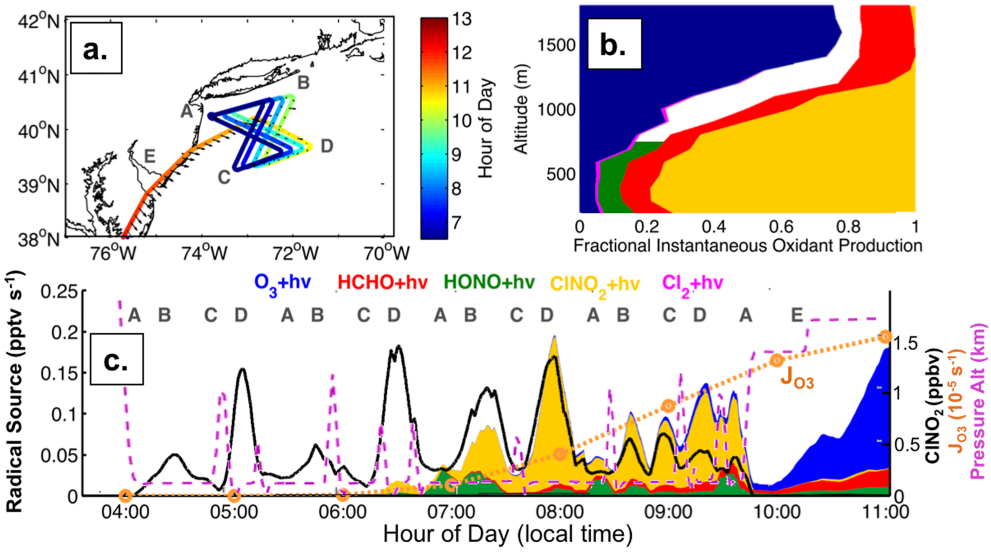

Figure 2. (a) Flight track of the NSF/NCAR C-130 on Research Flight 8 of the WINTER campaign, colored by local time of day. Sunrise occurred at approximately 6:30 a.m. local time. Only portions with altitudes <2,000 m are shown. (b) Vertical profiles of the instantaneous radical source calculated from 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), $ClNO_2$ mixing ratios (right axis, ppbv), the measured O_3 photolysis frequency (orange circles, right axis, 10^{-5} s^{-1}), and pressure altitude (right axis, km)

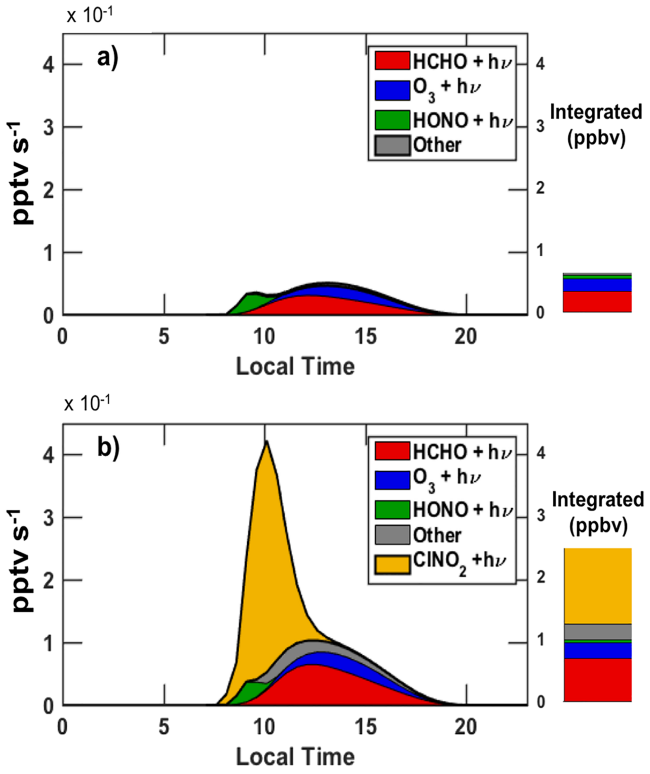

Figure 3. Summary of daily integrated primary radical production rates calculated the day following our interception of the peak $ClNO_2$ concentrations on RF08 using the F0AM box model initialized with WINTER observations without including chlorine reactions (a) and including chlorine reactions (b). Bar charts show the integrated daily radical source from each precursor.

((R1) and (R3)) but negligible contributions from HONO. This integrated radical source calculation is based upon measurements made before local midnight, and several more hours of $ClNO_2$ production could be expected. Assuming N_2O_5 formation continued as observed NO_2 and O_3 would suggest and an N_2O_5 reactivity on aerosols from in situ observations (McDuffie et al., 2018; McDuffie et al., 2018), we estimate $ClNO_2$ concentrations would increase throughout the night and account for as much as 80% ([$ClNO_2$]~1,500 pptv) of the integrated radical source the next day. This result, assuming no further changes to O_3, HCHO, or HONO, highlights the important role of anthropogenic NO_x emissions in wintertime radical sources. Estimates of $ClNO_2$ contributions 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 us to probe the instantaneous morning radical source (see SI) in pollution from the New York City area that had aged overnight in the MBL. As the Sun rose, vertical profiles (Figure 2b) with the aircraft revealed that the observed instantaneous radical source from $ClNO_2$ photolysis, $j_{ClNO2}(t)$ * [$ClNO_2(t)$], was 60–80% of the total instantaneous radical source throughout the entire MBL (SI section S3a).

During this flight, HONO photolysis was the next largest instantaneous radical source. Contributions from Cl_2 were low, given small (<15 pptv) observed concentrations (Haskins et al., 2018). $ClNO_2$ reactive uptake to form Cl_2, which would amplify the radical source stemming from N_2O_5 chemistry, was also small (Haskins et al., 2019). R1 was negligible in the flight shown in Figure 2. O_3 mixing ratios are often suppressed in NO_x-rich air masses during the night and morning, in part due to nighttime N_2O_5 chemistry which removes O_3 ((R2)–(R4)) (Brown et al., 2006). The aircraft departed the area (Segment E, Figure 2a) flying above the MBL where we find that the radical source is dominated by that from O_3 photolysis (R1), as expected, given the steep gradients in $ClNO_2$ between the polluted boundary layer and free troposphere.

To further evaluate the implications of these results, we use a chemically explicit Master Chemical Mechanism based 0-D model (F0AM, Wolfe, Marvin et al., 2016) to simulate radical chemistry during the full day following the interception of these plumes. We perform two simulations, including and excluding reactions of Cl atoms with various volatile organic compounds (VOCs; ((R8)b–R10), using the mechanism described in Riedel et al. (2014) (see SI section S4). The model is initialized with WINTER measurements of VOCs and other gas-phase species including HCHO, HONO, O_3, N_2O_5, and $ClNO_2$ (see Supporting Information for details). Figure 3 shows the modeled instantaneous radical production occurring for 16 hr following our interception of the maximum $ClNO_2$ concentration (6:36 a.m., Location "D," Figure 2). We also initialized the model with median $ClNO_2$ concentration from all intercepts in this flight, results are briefly discussed below and shown in the Supporting Information.

Consistent with our above observational analysis, the model predicts an instantaneous radical production rate from $ClNO_2$ that is a factor of 5–12 larger than the next largest radical source between 6 a.m. and 11 a.m. (Figure 3). $ClNO_2$ also dominates the total daily integrated radical source predicted with the model. The simulation including chlorine chemistry produced 2.5 ppbv of radicals (Cl + HO_x + RO_2) by day's end, which is a factor of 3.75 larger than that predicted without chlorine chemistry. The increase in radical production stems from Cl radicals from $ClNO_2$ photolysis, a secondary 114% enhancement (0.62 ppbv) in HCHO due to Cl radical initiated VOC oxidation (see SI section S4) and an increase in ozone production. Using median $ClNO_2$ concentrations similarly led to the total radical source being a factor of 3.1 larger than when neglecting Cl radical chemistry. The magnitude of the HO_x enhancement could be different for

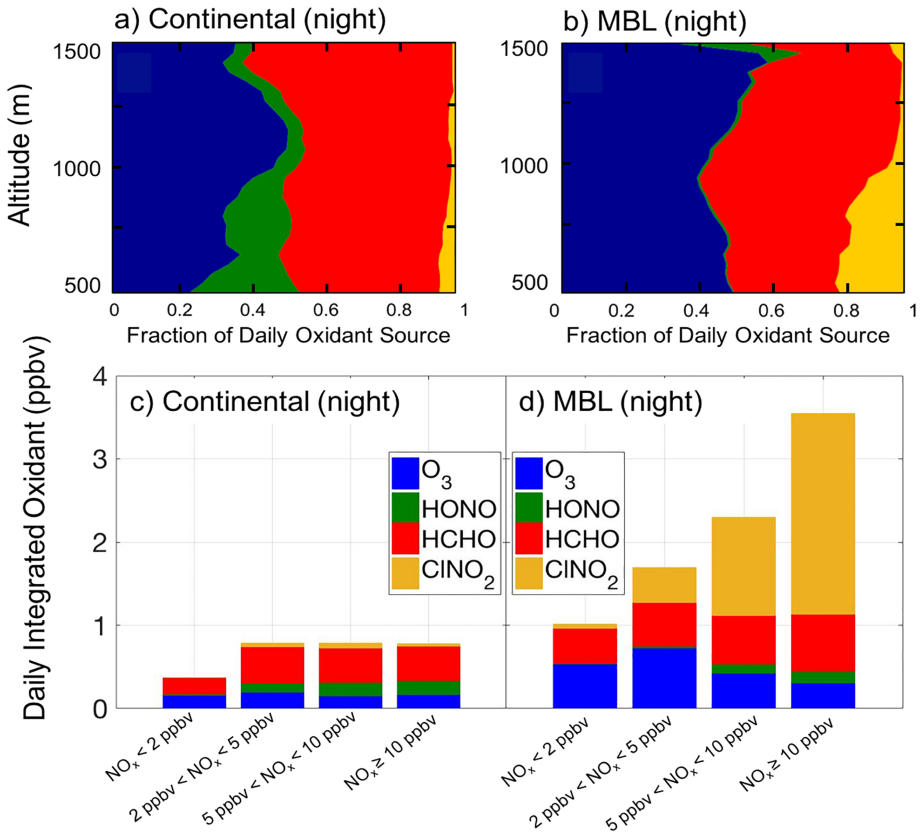

Figure 4. Vertical profiles of the daily integrated primary radical sources calculated from observations of O_3, H_2O, $ClNO_2$, HONO, and HCHO made throughout the campaign in vertical profiling maneuvers during the night below 1.5 km over (a) the continental boundary layer and (b) within the marine boundary layer (MBL). Averaging over these vertical profiles during the night and binning them as a function of their observed NO_x mixing ratios, 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 S3b of the SI.

different locations and time periods, especially with a different mix of VOC, but these results underscore that including Cl-atom chemistry from $ClNO_2$ is necessary to represent wintertime oxidation, given the secondary impacts of Cl atoms on HCHO and O_3.

We apply the above daily integrated radical source analysis to the wider set of flights (see SI section S3b) 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 $ClNO_2$ 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_x) stems not from reaction (R1) as it would in summer, but from $ClNO_2$, HCHO, and HONO photolysis. $ClNO_2$ and HCHO tend to dominate, but with a strong spatial (vertical and horizontal) dependence reflecting distribution of emission sources, relative lifetimes, and mixing.

The control of local and regional anthropogenic emissions on primary radical sources during winter is evident when considering the contributions of HCHO. HCHO contributes most to the observed radical budget outside of the MBL (Figures 1 and 4). Jaeglé et al. (2018) showed that the standard GEOS-Chem model underestimated 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. 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. The extent to which measured alkenes explain the HCHO should be evaluated. Ultimately, the resulting modeled wintertime HCHO

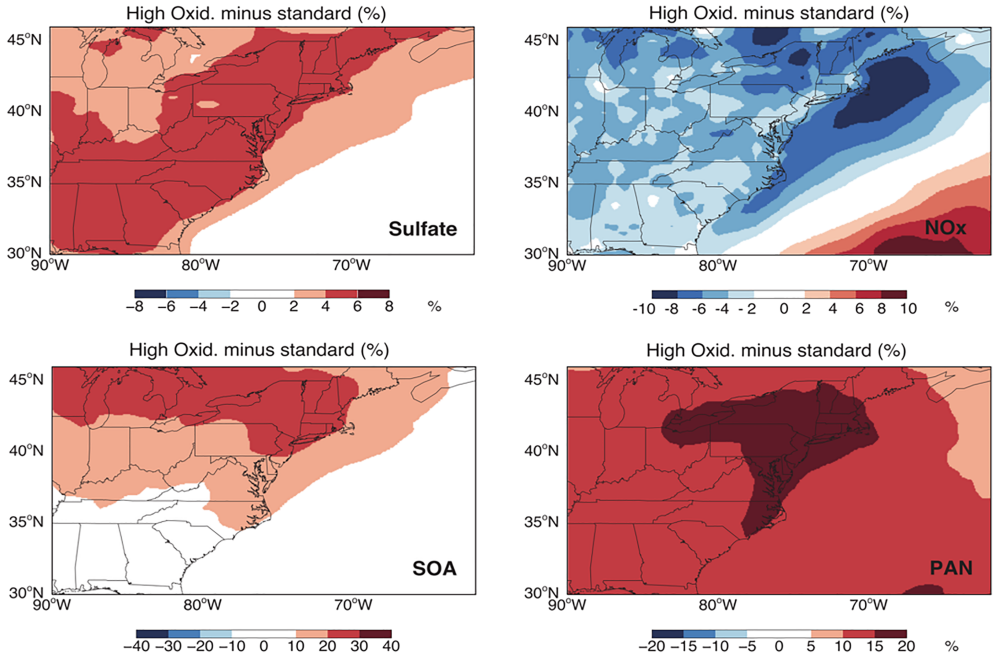

Figure 5. Relative changes in GEOS-Chem model predicted particulate sulfate, SOA, NOx, and PAN abundances between runs using standard emissions and chemistry, and those using updated emissions of HCHO and updated $ClNO_2$ chemistry (described in Jaeglé et al., 2018) based on the WINTER observations. 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.

is primarily from anthropogenic sources, in stark contrast to summer. Although smaller than the isoprene dominated source in summertime (Fortems-Cheiney et al., 2012; Luecken et al., 2012; Wolfe et al., 2016), the total HCHO source we estimate during WINTER demonstrates the seasonally varying sensitivity of the radical budget to both anthropogenic and biogenic VOC emissions.

The measured nighttime HONO concentrations during WINTER imply it is a small but nonnegligible contributor to the primary daytime radical source, especially in urban areas close to the surface (<100 m, see SI section S6), 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_3^-) photolysis may be an important daytime HONO source, but the rate remains debated (Romer et al., 2018; Ye et al., 2016). 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 underpredict the contribution from HONO to the primary radical sources if photolysis of pNO_3^- or other daytime HONO sources are significant. Our simultaneous observations of pNO_3^- and HONO suggest a slow daytime production of HONO from 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). Daytime HONO concentrations were often at or below our detection limit (30 pptv); thus, we can only constrain an upper limit source of daytime HONO (see SI section S6).

HCHO emissions, the multiphase chemistry of NO_x, and aerosol processes that produce and directly affect $ClNO_2$, pNO_3^-, and HONO concentrations, are highly parameterized components of air quality and chemistry-climate models, if included at all (Evans & Jacob, 2005; Riemer et al., 2003; Bertram &

Thornton, 2009). Increasing anthropogenic HCHO sources (Jaeglé et al., 2018) and implementing the production of $ClNO_2$ (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, $PM_{2.5}$ components, such as secondary organic aerosol and sulfate increase by 0.3 $\mu g/m^3$ (20–30%) and 0.12 $\mu g/m^3$ (2–6%), respectively, while nitrate decreases by up to 0.25 $\mu g/m^3$ (0–5%) (Jaeglé et al., 2018), and NO_x shifts further into its labile reservoirs, such as PAN (see Figure 5). Given PAN's longer lifetime in winter, this transports NO_x further downwind than during summer. These changes are driven by 40–80% increases in HO_x and RO_2 radical concentrations across the WINTER domain from increased HCHO photolysis and VOC + Cl reactions, with concomitant increases in ozone production.

Wintertime sulfate is often underestimated by air quality models, while pNO_3^- and nitrate deposition over land have been overestimated (Gao et al., 2016; Heald et al., 2012; Tesche et al., 2006; Walker et al., 2012). The increases in regional radical sources and changes to NO_x multiphase chemistry we suggest reduce such discrepancies (Jaeglé et al., 2018; Shah et al., 2018) and also 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 from primary sources, most organic aerosol sampled is formed secondarily in processes like those that occur during summer (Schroder et al., 2018; Sullivan et al., 2019). Ultimately, our results provide support for increased oxidation initiated by atypical radical precursors, and increased export of NO_x reservoirs to the global free troposphere.

4. Conclusions

We have shown that anthropogenic emissions of NO_x, and HCHO and its precursors, exert control over radical sources in polluted air during winter. We provide novel and unique observational confirmation that conversion of NO_2 to $ClNO_2$ represents a critically important wintertime radical source throughout the polluted MBL. In polluted maritime regions, we find that Cl atoms from direct $ClNO_2$ 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 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 local or regional anthropogenic contributions, either through direct emissions and/or emissions of short-lived precursors, such as primary alkenes.

As the HCHO source evaluation implies, it is possible some reactive VOC, such as alkenes, went unmeasured during the WINTER campaign. The measured suite of alkenes presented a negligible daily integrated source of OH via ozonolysis (see SI Figure S6). However, oxidation of unmeasured alkenes by Cl atoms and ozone would further enhance HO_x production compared to our predictions herein, thereby reinforcing our conclusion that regional anthropogenic emissions control the wintertime radical budget. Our results therefore motivate further work to more broadly explore the types of VOC and associated Cl, OH, O_3, and NO_3 reactivity present in polluted wintertime environments.

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 pNO_3^- photolysis than reported by Ye et al. (2016) and more broadly consistent with that presented in Romer et al. (2018). We thus conclude that daytime HONO production and contribution to primary radicals remain uncertain, but is likely smaller than previous estimates would have suggested.

The dominant sources of these less commonly considered radical precursors in polluted wintertime air arise largely from local and regional anthropogenic emissions, as opposed to background ozone. Incorporating these sources into a chemical transport model increased predicted $PM_{2.5}$ and export of NO_x to the remote troposphere via PAN, where greenhouse gases such as O_3 and CH_4 are far more sensitive to its presence (Hudman et al., 2004). Other regions of the world, such as China, Europe, and northern India also experience elevated VOC concentrations from inefficient combustion and high NO_x during winter which may mix with reactive chlorine, especially near coasts or chlorine emissions from coal combustion (Li et al., 2016; Lowe et al., 2015; Sarwar et al., 2014). Our findings therefore suggest important global-scale revisions to our understanding of wintertime pollution transformations, transport, and multiphase processes.

Acknowledgments

This work was supported by the National Science Foundation AGS 1360745 and AGS-1822664 and NASA NNX15AT96G. The WINTER data are available online (http://data.eol.ucar.edu). The Framework of 0-D Atmospheric modeling employed in this work can be found here (https://sites.google.com/site/wolfegm/models).

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