WINTERTIME INVESTIGATION OF TRANSPORT, EMISSIONS, AND REACTIVITY

AN NSF/NOAA AIRCRAFT INVESTIGATION

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Wintertime INvestigation of Transport, Emissions, and Reactivity (WINTER): A C-130 Aircraft Investigation

1. Introduction

Anthropogenic pollutants are emitted to the atmosphere throughout the year with a varying degree of seasonality. For example, emissions of carbon dioxide from fossil fuel combustion in industrialized nations are modestly larger in winter [*Blasing et al.*, 2005], while other emissions, such as those associated with agriculture, are markedly stronger in summer. Atmospheric chemical transformations, which play a large role in driving the associated environmental impacts, have strong seasonal dependencies. In the warmer and more photochemically active summer months, strong oxidant formation leads to the rapid production of multiple secondary pollutants such as ozone and organic aerosol. In winter, reactive primary pollutants, such as nitrogen oxides ($NO_x = NO + NO_2$), volatile organic compounds (VOC), sulfur dioxide (SO_2), etc., oxidize far more slowly and consequently spread over wider geographic areas downwind of sources. This distribution, in combination with reduced sunlight and colder temperatures, changes the overall chemical state of the atmosphere (e.g., [*Yienger et al.*, 1999]). Multiphase processes involving interactions between the gas and aerosol particles or ground surfaces are important to oxidative processing in winter but are far more difficult to parameterize relative to gas-phase processes. Consequently, the rates at which primary pollutants are oxidized during winter are not as well understood, leading to uncertainty in the impacts of these emissions on air quality and climate.

The large majority of field intensives in polluted regions have focused primarily on understanding emissions, transformation and transport under warmer summertime conditions. This emphasis has been largely driven by the considerations above, especially with regard to regional photochemical ozone and secondary organic aerosol production, which is most acute in summer months. However, there are a number of outstanding scientific questions that can only be addressed by a wintertime study examining emissions, gas-phase transformation processes, and secondary aerosol mass formation, including their geographic distributions and export to remote regions. We therefore propose a wintertime aircraft-based field intensive using the NSF C-130 in conjunction with a ground-based field intensive at an instrumented tower site to investigate these topics over the northeastern United Sates (NE US).
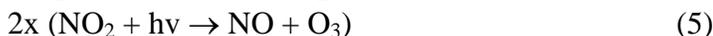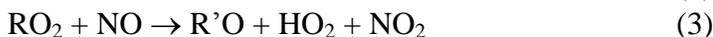
2. Scientific Questions

2.1 Goal 1: Transformations of Wintertime Emissions

> **How does multiphase reactive nitrogen chemistry affect oxidant availability, ozone production, reactive halogen cycling and the export of pollutants during winter?**
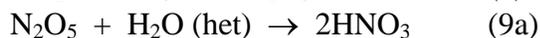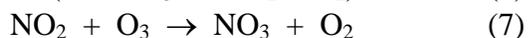
During summer, the ample supply of both solar actinic radiation and water vapor under warm, sunlit conditions provides a strong source for hydroxyl radicals, OH, the most important atmospheric oxidant [*Levy*, 1971].

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

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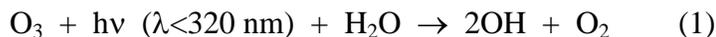
Concurrent oxidation of NO_x and VOC under these conditions occurs rapidly, and leads to the well-known phenomenon of photochemical ozone production in near source regions. Oxidation of a hydrocarbon (RH) to an organic peroxy radical (RO_2) in the presence of NO_x and sunlight leads to the net production of two O_3 and an oxidized VOC (R'O), which can continue through the cycle.

$$OH + RH \rightarrow RO_2 + H_2O \qquad (2)$$
$$RO_2 + NO \rightarrow R'O + HO_2 + NO_2 \qquad (3)$$
$$HO_2 + NO \rightarrow OH + NO_2 \qquad (4)$$
$$2x\ (NO_2 + hv \rightarrow NO + O_3) \qquad (5)$$

During winter, the primary production of OH from ozone photolysis is reduced by more than an order of magnitude, leading to inefficient daytime oxidation of both NO_x and VOC. Wintertime NO_x emissions under these conditions can lead to net destruction of ozone in near source regions via a set of dark reactions involving formation and loss of N_2O_5.

$$2x\ (NO + O_3 \rightarrow NO_2 + O_2) \qquad (6)$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (7)$$
$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (8)$$
$$N_2O_5 + H_2O\ (het) \rightarrow 2HNO_3 \qquad (9a)$$

Results from the NARE 96 campaign [*Parrish et al.*, 1999], as well as analysis of the relationships between ozone and CO at marine sites downwind of the U.S. East Coast [*Parrish et al.*, 1998], are consistent with this mechanism. The longer photochemical lifetime of NO_x in winter compared to summer, however, leads to a much broader background level of NO_x that has been suggested to shift the balance of ozone production and destruction to a net ozone producing

Figure 1. *The fraction of total nitrate ($HNO_3 + NO_3^-$) formed over the U.S. from heterogeneous hydrolysis of N_2O_5 as predicted by the GEOS-Chem model for winter (W) and summer (Su).*

regime through large areas of the troposphere [*Yienger et al.*, 1999]. The balance between near-source ozone destruction and widespread ozone production resulting from wintertime anthropogenic emissions remains unclear but is critical to the understanding of seasonal and long-term trends in tropospheric ozone [*Cooper et al.*, 2010; *Cooper et al.*, 2012; *Mickley et al.*, 2001; *Parrish et al.*, 2012; 2013; *Shindell et al.*, 2006].
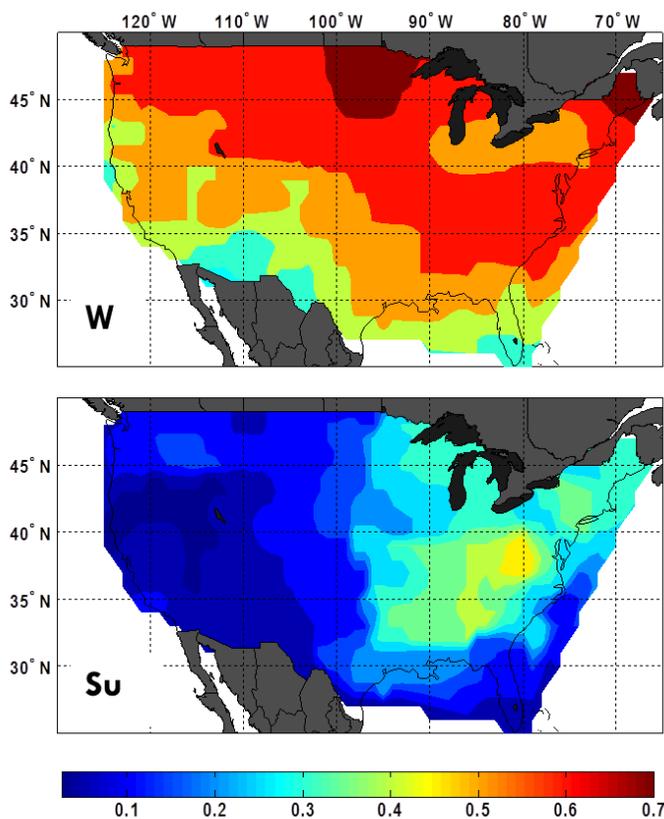
The balance between ozone destruction and production in high NO_x regions depends linearly on the primary radical (HO_x = OH + HO_2) production rate [*Kleinman*, 2005; *Thornton et al.*, 2002]. Model to measurement comparisons of HO_x in the Northeast between summer and winter show that models can adequately represent OH levels in polluted regions in summer but significantly underestimate them (factor of 5) during winter [*Cai et al.*, 2008; *Ren and Chen*, 2005]. Although there are relatively few measurements of radical species and their precursors available for model evaluation, such comparisons suggest a general lack of understanding of wintertime oxidant and radical sources, which in turn creates uncertainty in model predictions of ozone production rates, and the conversion rates of NO_x to inorganic and organic nitrates, SO_2 to sulfate, and VOC to oxidized low volatility compounds. Such errors then lead to uncertainty in the predictions of the net export of these species to more remote regions.

There are several key mechanistic uncertainties related to these issues. The first is the fate of N_2O_5, which either can be lost via reaction with aerosols, deposit to the surface, or decompose to reform NO_x. The relative importance of these paths depends primarily upon the efficiency of N_2O_5 reactive uptake to aerosols and clouds in the winter season, for which there is little, published field data. Summertime aircraft intensives and ground-based measurements have identified large variability in the rate of this process [*Bertram et al.*, 2009; *Brown et al.*, 2006; *Riedel et al.*, 2012b]; however the fate of N_2O_5 is far more important to its ultimate impacts on NO_x and O_3 in winter than summer [*Alexander et al.*, 2009a; *Davis et al.*, 2008; *Thornton et al.*, 2010]. For example, GEOS-Chem model predictions suggest ~ 50-70% of NO_x over the NE US is converted to HNO_3 via N_2O_5 hydrolysis in the winter, compared to only 30% in the summer [*Alexander et al.*, 2009a].

Figure 2. *Predicted annual production rate of $ClNO_2$ is shown for the continental U.S. Color scale is logarithmic in units of gCl per 1^ox1^o grid cell per year. Adapted from Thornton et al. [2010]*

Related to these questions is the wintertime production of $ClNO_2$, a photolabile halogen species that results from reaction of N_2O_5 with chloride containing aerosol.
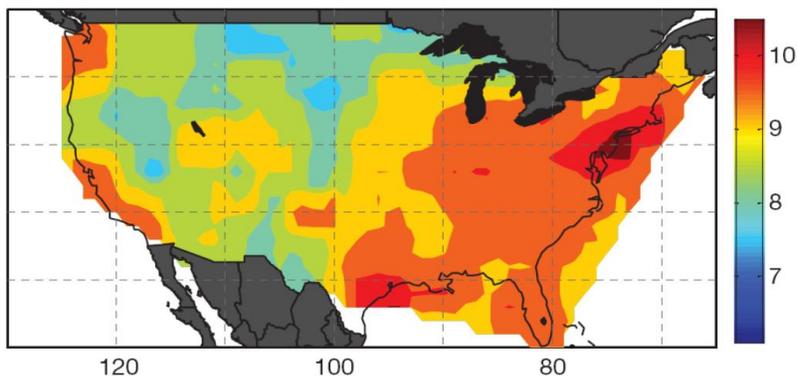
$$N_2O_5 \text{ (g)} + Cl^- \text{ (aq)} \rightarrow NO_3^- \text{ (aq)} + ClNO_2 \text{ (g)} \qquad (9b)$$

Recent wintertime field and modeling studies of this compound suggest that it is likely most prevalent in winter, particularly in the NE US [*Kercher et al.*, 2009; *Thornton et al.*, 2010] (see Figure 2). Because $ClNO_2$ undergoes photolysis during morning hours, its production contributes to daytime radical formation, thereby influencing the balance of ozone production and destruction from nitrogen oxide emissions.

$$ClNO_2 + h\nu \rightarrow Cl + NO_2$$
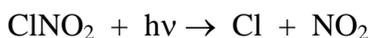
$ClNO_2$ in fact may be a significant contributor to radical production, especially during winter. For example, results from the CalNex campaign in the Los Angeles basin suggest that $ClNO_2$ contributed ~10% to the primary daytime radical source [*Young et al.*, 2012] during late spring / early summer conditions. During winter, the relative contribution is anticipated to be much larger. As shown in Figure 3, $ClNO_2$ abundances in the New York City plume during winter, likely similar to the 0.5 to 4 ppbv measured in Los Angeles [*Kercher et al.*, 2009; *Riedel et al.*, 2012a; *Young et al.*, 2012], could exceed that from ozone photolysis (reaction 1 above) by a factor of 3, due in large part to a lower concentration of water vapor for reaction with $O(^1D)$.

$ClNO_2$ formation also directly and indirectly impacts the lifetime and export of NO_x with consequences for the downwind HO_x abundance and partitioning of total reactive nitrogen, NO_y ($NO_y = NO_x + NO_3 + N_2O_5 + ClNO_2$ + acyl peroxy nitrates + alkyl nitrates + HNO_3). $ClNO_2$ is relatively unreactive at night, and thereby acts to transport NO_x throughout the night and early morning. The subsequent photolysis of $ClNO_2$ after sunrise is then a net NO_x source in rural or remote regions. The simultaneous pulse of Cl-atoms can also affect NO_y partitioning by enhancing the net formation of acyl peroxy nitrates such as PAN. Consistent with this idea are recent global modeling simulations using the

Figure 3. *Example MCM box model calculations of the radical production rate from $ClNO_2$ and ozone photolysis for two cases of LA in June and NY City in February. For simplicity, the only differences between the two cases are the seasonal and latitude dependent photolysis frequencies, temperature, and water vapor mixing ratios. Otherwise, NO_x, O_3 and VOC are assumed to be similar.*

Community Atmosphere Model (CAM) with comprehensive gas and multiphase halogen chemistry [*Long et al.*, 2013]. The model predicts higher NO_x abundance, with enhancements exceeding 100% especially downwind of polluted coastal regions, when comparing simulations with fully coupled halogen chemistry to those without. Figure 4 shows the annual mean perturbations to NO_x in the planetary boundary layer due to the incorporation of halogen chemistry. The enhanced NO_x downwind of the eastern US and northern Europe is driven primarily by $ClNO_2$ formation and processing.
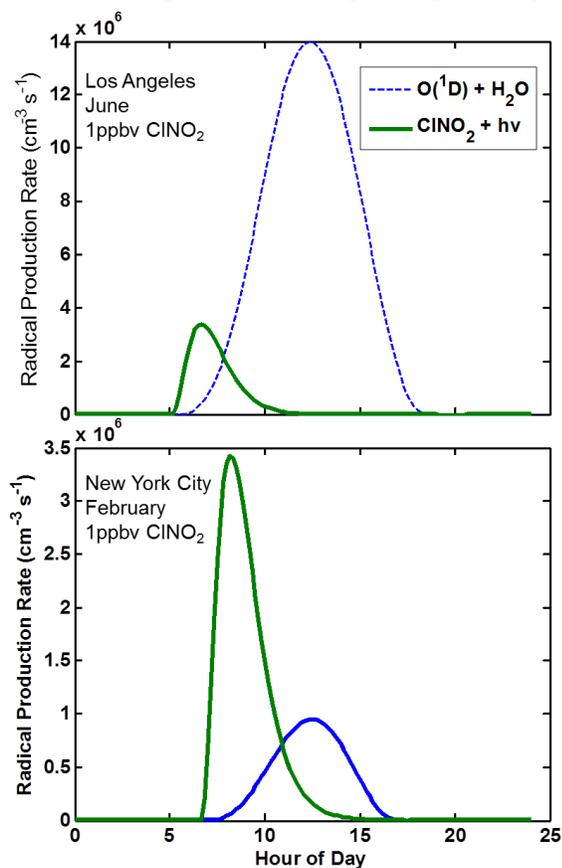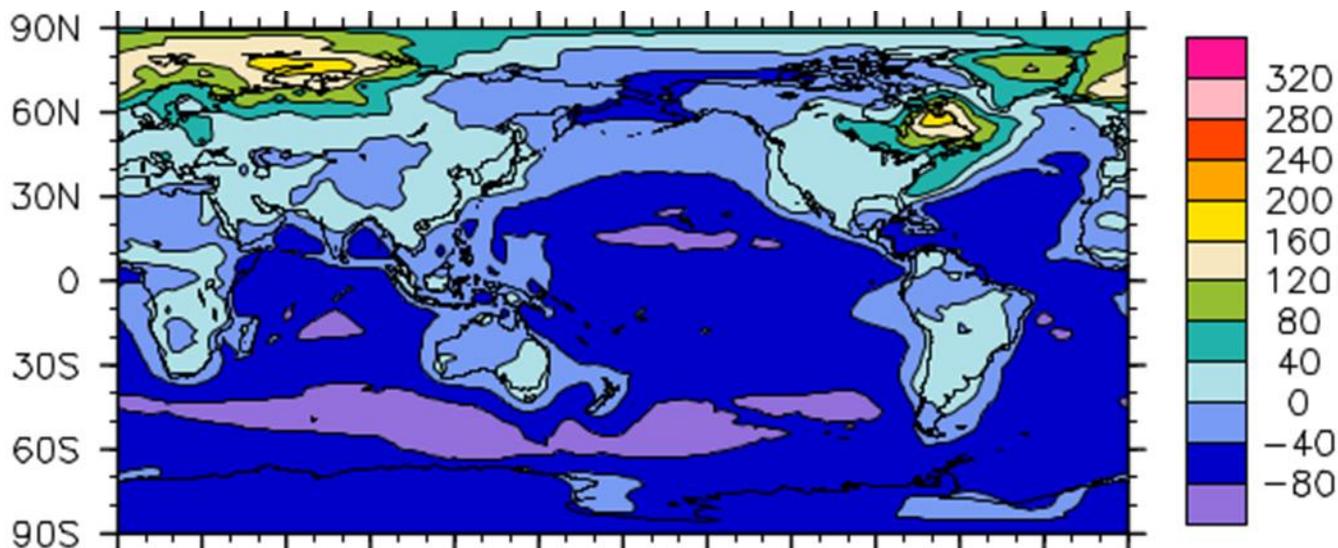
Figure 4. *CAM simulations of the annual mean perturbation to NO_x abundance in the planetary boundary layer resulting from incorporation of full halogen chemistry [Long et al., 2013].*

Nitrous acid, HONO, is another radical precursor species thought to arise principally from multiphase reactions of NO_x. Field observations have shown that HONO is ubiquitously present in continental near-surface air impacted by NO_x, and is especially enhanced in the nocturnal boundary layer of urban regions [*Platt et al.*, 1980]. Vertical profile measurements, mostly from ground-based platforms, show HONO concentrations decrease strongly with height above ground during stable conditions [*Stutz et al.*, 2002; *Wong et al.*, 2012], consistent with an important HONO source at the ground. At night, dark reactions of NO_2 on ground surfaces and direct emissions from combustion, are thought to contribute to the HONO source in urban regions [*Stutz et al.*, 2002]. However, the molecular mechanisms of the dark heterogeneous conversion of NO_2 to HONO remain uncertain and thus HONO formation is difficult to accurately incorporate into models [*Elshorbany et al.*, 2012]. In addition, several daytime sources of HONO involving photochemistry on surfaces or release from soils have been proposed to explain lower but potentially more important daytime HONO concentrations measured in polluted and rural regions [*Stemmler et al.*, 2006; *Su et al.*, 2011; *Wong et al.*, 2012]. The abundance, production mechanism and seasonality of HONO observed during daytime are topics of intense current debate [*Oswald et al.*, 2013; *Sorgel et al.*, 2011; *VandenBoer et al.*, 2013].

During the day, HONO undergoes photolysis to yield OH and NO, potentially contributing significantly to the radical budget, especially in the morning.

$$HONO + h\nu \rightarrow OH + NO \quad (9)$$

Ground-based measurements suggest that HONO can contribute up to 30% to the daytime OH production during summer, and a recent global modeling study suggests HONO is the dominant wintertime OH source over the NE US, by factors of 2 or more, within the lowest model level (30m above ground) [*Alicke et al.*, 2002; *Elshorbany et al.*, 2012; *Sorgel et al.*, 2011].

There are few simultaneous aircraft measurements of HONO and $ClNO_2$, and none to our knowledge in winter that would allow analysis of their spatial distributions or impact on wintertime oxidant formation. During CalNex, a summer time campaign, the NOAA P-3 aircraft provided the first insights into the typical vertical profile of $ClNO_2$ over the LA basin. Together with vertical gradients in HONO measured by the UCLA multiple long-path Differential Optical Absorption Spectrometer (DOAS) instrument, *Young, et al* [2012] recently showed that on a column total basis, $ClNO_2$ was a much more important radical source than HONO produced at night, even though at surface level $ClNO_2$ and HONO had similar nighttime mixing ratios. Although there was considerable variability with height on individual profiles, in an average sense, $ClNO_2$ showed little variation with height through the residual boundary layer, while HONO had a maximum near surface and fell exponentially with height above surface level

(Figure 5). $ClNO_2$ production is driven mainly by the reaction of N_2O_5 and aerosol particles, which tend to be distributed through the boundary layer, while, as noted above, HONO production appears to be produced primarily on ground surfaces. The generally stratified nocturnal atmosphere then restricts the importance of HONO to the near surface layers, at least in this example. Daytime observations of HONO during CalNex (not shown) suggested it to be a large contribution to radical production, at least at surface level.

During the 2013 Southeast Atmosphere Studies (SAS) campaigns, which included both the NOAA P-3 aircraft (SENEX) and the NSF C-130 (NOMADSS), both $ClNO_2$ and HONO were major foci of aircraft measurements. While results of these studies will soon be forthcoming, their focus was also on photochemically active, summertime conditions in a biogenic rich area. These data will provide an important contrast to the measurements proposed here.

Two recent wintertime field campaigns in continental regions support this overall picture of the role of unconventional radical sources in winter.
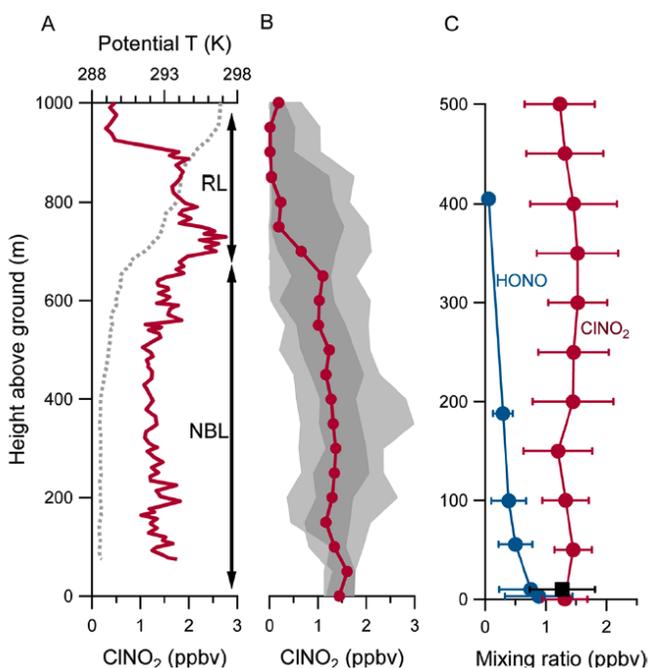

Figure 5. *$ClNO_2$ and HONO mixing ratios as a function of height above ground surface in the Los Angeles basin during the CalNex 2010 campaign. **A.** Example vertical profile of $ClNO_2$ and potential temperature from the NOAA P-3 aircraft. **B.** Median (circles), 25th and 75th percentiles (dark shade) and 10th and 90th percentiles (light shade) from 21 nighttime profiles across the L.A. basin. **C.** Comparison of average $ClNO_2$ from P-3 profiles to average HONO from a multiple long-path DOAS instrument over the range 0-500 m. The DOAS was located in Pasadena, CA, while the $ClNO_2$ profiles were distributed throughout the L.A. Basin.*

The NACHTT (Nitrogen, Aerosol Composition and

Halogens on a Tall Tower) campaign took place at a suburban site near Denver, CO in February – March 2011 and included vertically resolved measurements of NO_x, O_3, N_2O_5, $ClNO_2$, HONO, aerosol size distributions and composition [*Brown et al.*, 2013]. Measurements indicate that $ClNO_2$ and HONO originate from distinct sources, with $ClNO_2$ often associated with pollution plumes aloft [*Riedel et al.*, 2013] and HONO typically associated with shallow layers near the ground surface [*VandenBoer et al.*, 2013]. A radical budget analysis showed HONO to be by far the dominant source of primary radicals in near-surface air. The UBWOS (Uintah Basin Winter Ozone Studies) took place in a remote area of northeast Utah with the goal of determining the cause of recently observed high ozone events associated with oil and gas producing regions in the western U.S. The studies included measurements of HONO, $ClNO_2$ and their precursors. Although vertically resolved measurements are not available, the results for the first study, which occurred in 2012 during a winter without high ozone events, showed that both HONO and $ClNO_2$ were much larger primary radical sources than $O(^1D)$ + H_2O, and that these radical sources together with formaldehyde photolysis were the critical difference between ozone production and destruction due to NO_x emissions in winter. With these radical sources included, a box model could quantitatively reproduce the observed ozone production of ~12 ppbv day^{-1}; without these sources, the same model predicted total destruction of ozone due to NO_x emissions in this basin [*Edwards et al.*, 2013]. This result demands further investigation of the influence of these radical sources on wintertime ozone budgets in other regions.

Results from these limited field studies suggest that nighttime production and daytime photolysis of $ClNO_2$ and HONO together represent a potentially dominant source of primary radicals to initiate oxidative processes in polluted air masses in winter. However, there is simply no data available to assess the ubiquity of these radical sources in different environments, nor what their relative or absolute magnitudes are in some of the most polluted air sheds in North America. We hypothesize that the influence of these sources could be large during regional transport (and export) of the pollution plumes from the Eastern U.S. seaboard. However, their interplay is not clear and would be impossible to model in the absence of measurements. For example, during export of pollution plumes from the coast, HONO production is likely to decrease in importance in the absence of a land surface for efficient heterogeneous uptake of NO_2. Conversely, production of $ClNO_2$ may increase in importance due to the greater surface area of Cl^--containing marine aerosol over the coastal ocean. The altitude and depth of plume advection, the overall composition of the gas and aerosol species in these plumes, the plume sources (e.g., urban vs. power plant) and the dilution rates and transport patterns will strongly influence these effects.

As illustrated above, the stratified nocturnal atmosphere is a major factor influencing the potential importance of the two radical sources $ClNO_2$ and HONO. More generally, we expect substantial horizontal and vertical variability in the dominant radical sources and oxidation pathways active during winter. The relevant scales of variability could be tens of meters in the vertical at night and a few kilometers in the horizontal. Such spatial heterogeneity confounds the representativeness of ground based measurements. Hence the need for a wintertime aircraft mission to evaluate the key chemical processes and transport pathways on the spatial scales typical of regional and global models.

Recent advances in aircraft-deployable instruments now allow investigation of the processes described above at an unprecedented level of detail and accuracy. Techniques now available include high-time-resolution measurements of the key NO_x and halogen species such as N_2O_5, $ClNO_2$, Cl_2, HONO and related precursor trace gases and aerosol composition. **There have been no prior wintertime aircraft studies of N_2O_5, $ClNO_2$, and HONO.**

2.2 Goal 2: Wintertime aerosol formation mechanisms

> **How do differences in temperature, oxidants, biogenic emissions, and boundary layer dynamics between winter and summer impact secondary aerosol formation?**

Formation and growth of aerosols from gas-phase precursors is an important problem with significant uncertainties that limit our understanding of the impacts of short-lived species on air quality and climate [*Shindell et al.*, 2009]. The transformation processes that lead to secondary aerosol include oxidation of sulfur, reactive nitrogen and VOC emissions, and as such are driven by the availability of oxidants and, thus, dependent on the processes summarized above. Furthermore, the equilibrium partitioning of semi-volatile species, such as ammonia, nitric acid, and organic compounds, with aerosols is strongly temperature dependent. This temperature dependence should lead to significant seasonal shifts in the rates and mechanisms of secondary aerosol formation with consequential changes in the dominant aerosol components in polluted regions. These seasonal shifts in kinetics and thermodynamics provide an opportunity to directly test model sensitivities to specific processes or meteorological conditions.

The partitioning of semi-volatiles between gas and particle phases is a function of the absolute mass concentrations and chemical compositions of each component, temperature, and relative humidity. These characteristics of the multiphase system are subject to boundary layer dynamics, with potentially highly localized features and synoptic meteorology. Therefore, to quantitatively test model predictions of wintertime aerosol mass concentrations, composition, and transport, an aircraft study is critical to provide the data over large enough spatial scales to separately examine whether model-measurement errors arise from inadequate model resolution or dynamics, or from
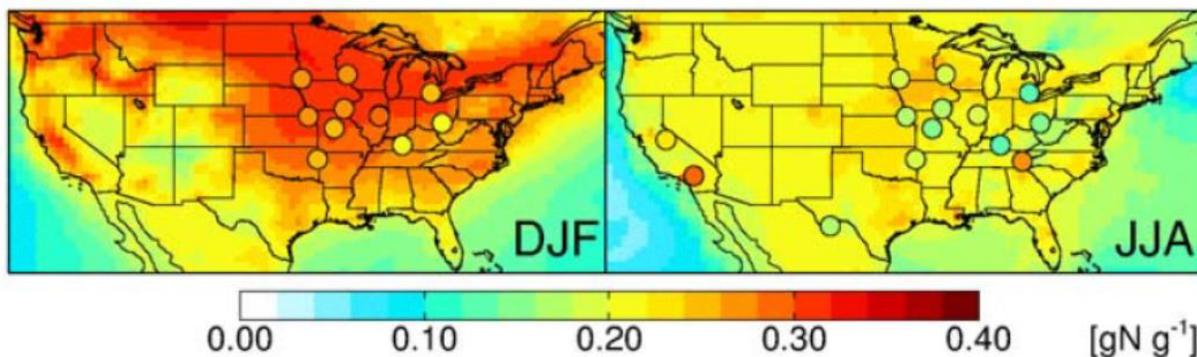
Figure 6. The fraction of inorganic nitrogen in mean surface fine particulate matter mass during winter (left) and summer (right). Measurements from the Midwest Ammonia Monitoring Project (dots) are overlaid on Geos-Chem output. Taken from Heald et al. [2012].

incomplete chemical mechanisms or aerosol thermodynamics. Moreover, in wintertime, strong

gradients and substantial day-to-day variation develop in meteorological parameters associated with variability in the position of the polar jet. Surface air temperature can increase by more than 10 C from New York to central Georgia, often with much of that change occurring in a very narrow band dictated by the location of the polar front. An aircraft equipped to study oxidant and inorganic aerosol precursors together with aerosol composition could therefore provide new insights into the sources and persistence of wintertime aerosol across a wide range of this parameter space.

The uncertainties in the chemical transformations discussed in the preceding section have a direct impact on our quantitative descriptions of aerosol formation in winter. Nitric acid is a highly volatile species whose partitioning with the aerosol phase is strongly dependent on both temperature and aerosol acidity. Nitrate is a dominant component of inorganic aerosol in the Western U.S. but far less prevalent in the Eastern U.S., except in winter, when it can drive exceedences of National Ambient Air Quality Standards for particulate matter [*Katzman et al.*, 2010]. Recent model predictions suggest nitrate contributes ~30% of particulate mass during winter (see Figure 6) [*Appel et al.*, 2008; *Heald et al.*, 2012].

In spite of this important contribution to particle mass, percent deviations between modeled and measured concentrations of particulate NO_3^- reach 100% over the eastern U.S. during winter due to multiple factors. Understanding of wintertime nitrate aerosol formation is limited in part by uncertainty in the multiphase chemistry of N_2O_5 discussed above, specifically, the heterogeneous reaction rate and the relative importance of the $ClNO_2$ formation channel [*Heald et al.*, 2012; *Mathur et al.*, 2008; *Sarwar et al.*, 2012; *Zhang et al.*, 2012]. An important, but poorly constrained coupling in this regard is the inhibition of N_2O_5 reactive uptake by aerosol nitrate [*Bertram and Thornton*, 2009; *Wahner et al.*, 1998]. The so-called "nitrate effect" is essentially a suppression of the N_2O_5 reaction rate by the build-up of reaction products. Because daytime HNO_3 formation by $OH + NO_2$ is small due to low oxidant production, the nitrate effect in N_2O_5 hydrolysis implies wintertime nitrate formation is potentially a self-limiting system. Furthermore, because inorganic nitrate aerosol formation and associated phase partitioning with gaseous HNO_3 are strongly pH dependent, these processes are directly coupled with the availability of ammonia (NH_3), SO_2 and its reaction products (sulfuric acid and particle sulfate), all of which are vary seasonally and spatially. This chemical system will also evolve over time in response to relative differences in the projected future emission trends for NH_3 and SO_2 [*Heald et al.*, 2012; *Pinder et al.*, 2008]. $ClNO_2$ formation can lower the absolute local abundance of HNO_3 available for ammonium nitrate aerosol, and thereby offer another potential explanation for model overestimates in the NE U.S. [*Appel et al.*, 2008; *Heald et al.*, 2012; *Zhang et al.*, 2012]. Thus, ammonia emissions and abundance, chloride availability, and sulfur emissions and oxidation are critical to understanding the production and processing of nitrate aerosol and its associated impacts on air quality and radiative forcing. Furthermore, because all of these processes are temperature dependent and vary with height [*Neuman et al.*, 2003], the current lack of aircraft data is a critical limitation in understanding the interplay between these gas and aerosol species.

Sulfate is often a principal component of aerosol in polluted regions, particularly in the Northeast U.S., which lies downwind of the large SO_2 source region associated with coal-fired electric power generation in the Ohio River Valley. H_2SO_4, the end product of photochemical SO_2

oxidation, is a critical driver of both new particle formation and particle growth. The competition between local conversion of sulfur emissions to aerosol sulfate and the export of SO_2 to the free troposphere therefore has important implications for aerosol direct and indirect radiative forcings [*Shindell et al.*, 2009]. Photochemical oxidation of SO_2 in the gas phase occurs more slowly in winter, and the dominant sulfate formation mechanism has been suggested to shift toward aqueous phase S(IV) oxidation by H_2O_2, O_3, and transition metals primarily in cloud droplets [*Alexander et al.*, 2009b]. Global models generally overpredict SO_2 and underpredict sulfate, due in part, to uncertainty in the treatment of these oxidants [*Berglen et al.*, 2004]. Such biases subsequently impact aerosol thermodynamic calculations of water content and acidity, predictions of the aerosol nitrate burden and the reactive uptake rate of N_2O_5 to aerosols.
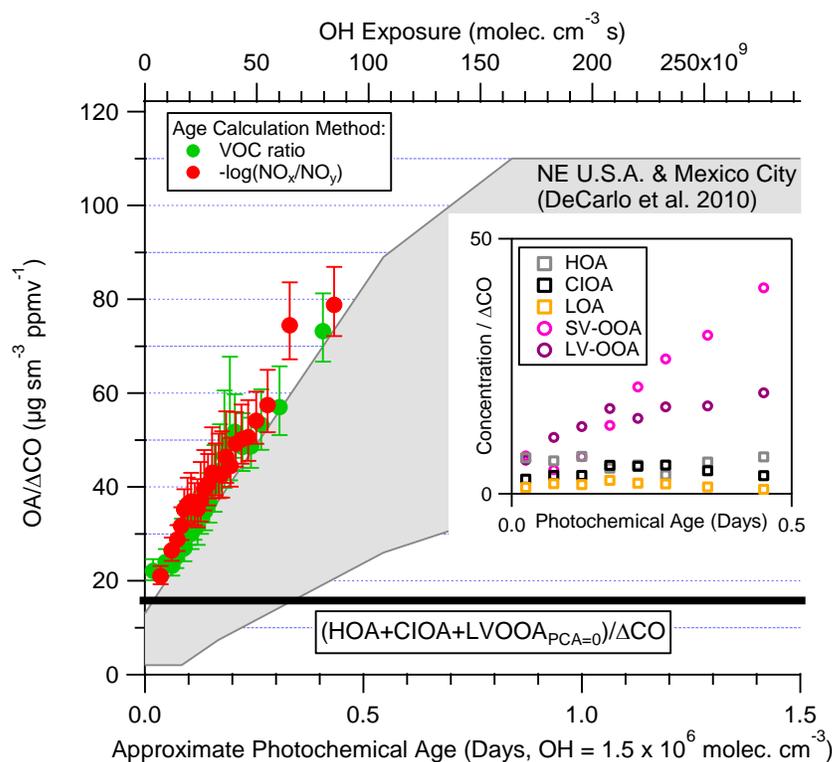

Figure 7: *The evolution of OA/ΔCO versus photochemical age for Pasadena during CalNex. The measured ratios are averaged into 25 bins according to photochemical age. The enhanced CO (ΔCO) is the ambient CO minus the estimated background CO (105 ppb). The standard error of OA/ΔCO is smaller than the size of the data point, and therefore is not plotted. Instead error bars representing the uncertainty in the ratio due to an uncertainty of ±20 ppbv in background CO are shown. Photochemical age is determined by two methods: (1) following Parrish et al. [2007] and using the ratio of 1,2,4-trimethylbenzene to benzene (green); (2) following Kleinman et al. [2008] and defining the photochemical age as –log₁₀(NOₓ/NOᵧ) (red). All photochemical ages have been standardized to an OH radical concentration 1.5 x 10⁶ molec. cm⁻³, and the corresponding OH exposure is shown on the top axis. The gray region is adapted from DeCarlo et al. [2010] and represents the evolution of OA/ΔCO observed in the northeastern United States and the Mexico City areas during summer. The black horizontal line is the ratio of (HOA + CIOA + 'background LVOOA') to ΔCO. (**Inset**) Evolution of the PMF component concentrations normalized to ΔCO versus photochemical age. Data is binned according to photochemical age.*

Secondary organic aerosol (SOA) is a topic of intense recent interest (e.g., [*Jimenez et al.*, 2009]) as its mass contribution is typically of comparable magnitude to that of aerosol sulfate [*Zhang et al.*, 2007]. As with secondary nitrate and sulfate aerosol, SOA formation is a function of both oxidant availability and thermodynamic partitioning of semi-volatile species to the aerosol phase and, consequently, the nature of primary production pathways differs during winter and summer. The lack of strong biogenic VOC emissions in winter removes one of the primary VOC sources thought to contribute to SOA. The equilibrium repartitioning of primary organic aerosol (POA) components into the gas phase and subsequent oxidation to form SOA should also be slower [*Robinson et al.*, 2007]. As such, wintertime organic aerosol may have a larger contribution from anthropogenic POA emission sources, such as agricultural burning and bio and fossil fuel use, with potentially different optical and hygroscopic properties than that of summertime organic aerosol. Moreover, the properties and timescales of SOA formation may be significantly different in winter compared to summer due to the expected lower abundance of oxidants (see, e.g. Figure 7). Interestingly, organic aerosol observations from surface sites show comparable loading in winter vs. summer, and several models fail to reproduce wintertime observations [*Carlton et al.*, 2010; *Mathur et al.*, 2008; *Shrivastava et al.*, 2008] Such findings suggest problems in the model representations of winter-to-summer changes in continental boundary layer dynamics, emissions and processing of organic aerosol precursors, or some combination of all three [*Mathur et al.*, 2008]. To our knowledge, there have been no aircraft intensives aimed at understanding wintertime organic aerosol in or downwind of urban locations in the continental US.

2.3 Goal 3: Wintertime emissions

> **How large are the changes in emissions from combustion and agricultural sources between winter and summer, and how do these differences affect distribution and processing of pollutants?**

While anthropogenic emissions of several species important for air quality and climate may have a modest seasonality on a national scale, seasonal changes across source types may differ significantly and vary regionally. Moreover, emissions of key pollutants such as NO_x and SO_2 from fixed point sources (mainly power plants) in the Northeast U.S. have fallen dramatically, by 30 – 50% over the past decade (**Figure 8**). Satellite observations and CEMS data suggest NO_x emissions have continued to decrease even during winter over larger regions of the U.S.[*Russell et al.*, 2012]
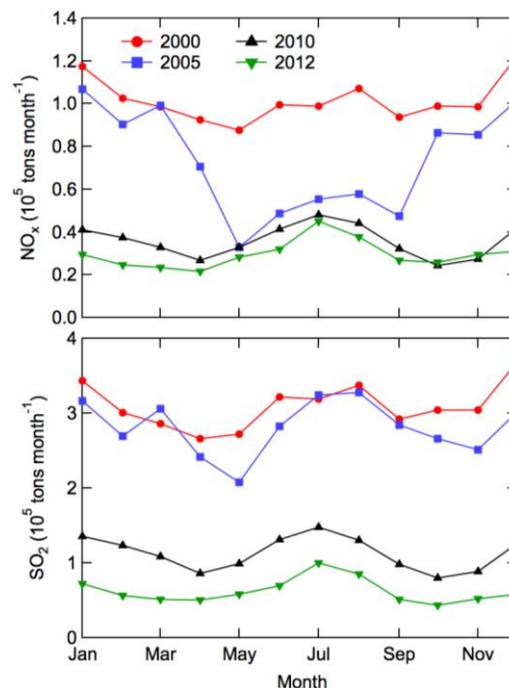
Figure 8. CEMS NO_x (Top) and SO_2 (Bottom) emissions from Northeast U.S. fixed location point sources (mainly power plants) for select years.

In the recent past, the increased need for home heating in winter months leads to 8 to 20% larger CO_2 emissions nationally relative to summer [*Blasing et al.*, 2005; *Levin et al.*, 2003], and likely changes the mix of emission sources of other species including NO_x and carbon monoxide (CO).

While the change in total fossil fuel combustion emissions of CO_2 between summer and winter is modest, the reduction in the biogenic uptake of CO_2 leads to a larger net input of CO_2 and enables a more straightforward interpretation of anthropogenic CO_2 fluxes. Thus, absolute CO_2 emissions from urban centers are more easily and accurately characterized from downwind aircraft transects in winter, and CO_2 consequently serves as a useful tracer for combustion emissions during this season.

Agricultural emissions of NH_3 show a pronounced seasonal cycle, with large decreases in wintertime due to the temperature dependence of its volatility and reduced fertilizer use [*Gilliland et al.*, 2003; *Heald et al.*, 2012; *Pinder et al.*, 2006]. Total NH_3 emissions across the U.S. are lowest during January and February, and increase by factors of 3 to 5 during spring through summer. Nevertheless, violations of the particulate matter ambient air quality standards in winter are associated with high loading of ammonium nitrate aerosol. Changes in ammonia emissions and atmospheric loadings influence the formation of secondary aerosol via its interaction with both HNO_3 and H_2SO_4 as described above. A payload aiming to test wintertime nitrate formation pathways would also provide useful top-down constraints for modeled NH_3 emission rates over broad geographical areas.

Emissions of soluble chloride in any season remain highly uncertain, especially inland of coastal regions. Coal combustion [*McCulloch et al.*, 1999], water cooling activities associated with power plants [*Chang et al.*, 2002], and biomass burning (e.g., [*Keene et al.*, 2006]) are all potentially important regional sources. In much of the eastern US, the annual average ratio of Cl/Na in precipitation is 50-100% higher than that expected from sea spray alone, consistent with the existence of other chloride sources (see **Figure 9**). To our knowledge, state-of-the-art measurements of chloride emissions from power plants or other combustion sources have not been conducted in the U.S. Inaccurate or incomplete chloride emission inventories will cause significant uncertainty in model predictions of the importance of inland $ClNO_2$ formation.

Figure 9. Annual mean (1996–2010) wet deposition of chloride (mg/yr, top) and the mole ratio of chloride to sodium (bottom) measured in precipitation by the National Atmospheric Deposition Program (NADP); ratios >1.2 are higher than that in seawater.

In addition to addressing a lack of information on wintertime emissions, a winter time study would broadly improve our understanding of emissions of a host of short lived pollutants from urban and industrial sources. For example, anthropogenic sources dominate the emissions of volatile organic compounds (VOCs) in winter, especially in the NE
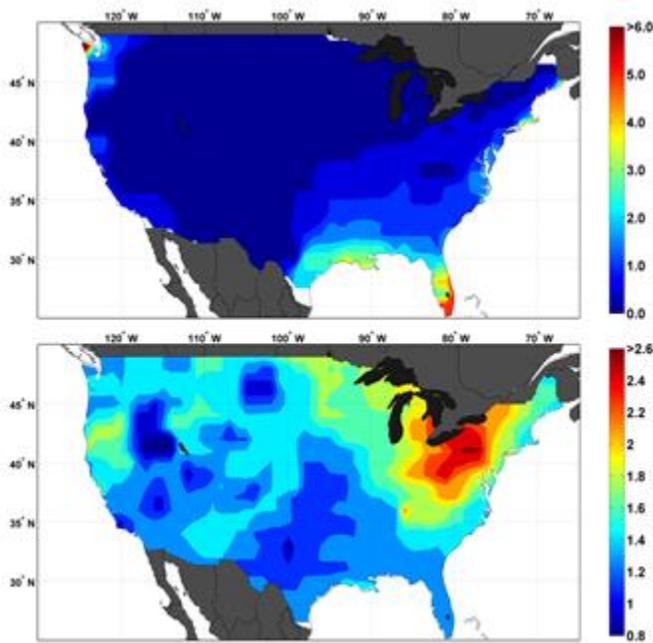
US, thereby facilitating the distinction between anthropogenic and biogenic emissions. Oxidation rates are also normally slower for all VOC types, such that near-source downwind aircraft transects are less likely to be influenced by chemical processing and more likely to reflect emissions. The lack of strong CO_2 uptake to the biosphere allows its use as a direct tracer of combustion. Emission factors relative to fuel use can then be determined for a wide variety of short-lived pollutants more reliably than in summer. Examples include black carbon, SO_2, NO_x, and carbon monoxide (CO) among others.

Wintertime transport of such emissions is distinct from summer in that local convection is minimal, while horizontal advection can be relatively more important with vertical exchange and long-range transport driven by frontal passages. Temperature inversions, which can persist well into the day during winter, can confine pollutants into shallow layers with higher concentrations. The extent to which net transport of pollutants from source regions to the rural and remote atmosphere is influenced by chemical processing and physical processing under these higher concentration and suppressed vertical ventalation conditions remains poorly characterized with *in situ* observations.

3. Experimental Design

To address the above issues, we proposed to conduct a coordinated aircraft and ground-based experiment in the northeastern U.S. during winter. The aircraft component will generate a comprehensive suite of multiphase observations over broad spatial and altitudinal scales. These measurements will be complemented with high-resolution tower-based observations of reactive species within the nocturnal boundary layer including HONO (much of which is produced at or near the ground surface) and key aspects of aerosol composition that cannot be quantified from aircraft using current techniques.

3.1 NSF C-130 Deployment

The suite of instruments summarized in Table 1 would be mounted on the NCAR C-130, which would be deployed at a central location in the Northeast U.S. Past field campaigns with similar aircraft have successfully operated out of airfields in New Jersey (WATOX '86), Rhode Island (NARE 96), and New Hampshire (ICARTT 2004), all of which would be suitable for the WINTER study. The U.S. DOE G-1 aircraft recently operated a wintertime experiment out of Hyannis, MA in January 2013. A six week study would be sufficient time to generate the required data. The best timing would be mid-winter when wintertime atmospheric chemical mechanisms
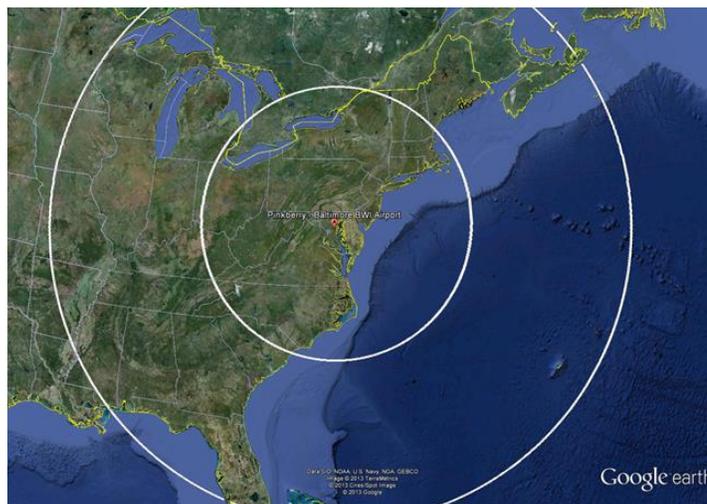

Figure 10. Map indicating the range of the C-130 aircraft for intensive research flights (inner circle) and those combining high altitude transit with low altitude cruising (outer circle).

dominate. Operation into late winter would provide information on the transition from winter to

springtime conditions. We therefore propose the study take place between January and March and as early as 2015.

C-130 flights originating from a location in the urban corridor of the Northeast U.S. could sample and follow pollution plumes from various sources over land and ocean, provide vertical profiles of boundary layer structure and composition, survey emissions upwind of the region, including power plants in the Ohio River Valley, measure export of pollutants from the region, and contrast the composition of the relatively clean and versus moderately to heavily polluted troposphere. A 4-6 week intensive measurement period would allow 12-20 research flights, which could be divided approximately equally between daytime and nighttime operation, with an emphasis on capturing transition periods from night into day or day into night.

3.1.1 Flight Planning and Wintertime Logistics

Figure 10 illustrates typical ranges of research flights utilizing the C-130 aircraft, assuming, for illustrative purposes, that the aircraft is based near Baltimore, MD. The C-130 has a maximum endurance of 10 hours and a range of 2490 nautical miles. Research maneuvers, such as vertical profiles, together with reserve fuel requirements, weather, and airspace restrictions ultimately reduce these such that the actual range and duration will depend on the day's flight plan and weather conditions. The ranges indicated in **Figure 10** are therefore approximate and mainly demonstrate the full extent of possibilities with the C-130. The inner circle indicates the range for a fairly intensive roundtrip research flight that starts with a fully loaded aircraft and dedicating 5 hours of research time to nearly continuous vertical profiling between the ground and 2500 ft asl with transects upwind and downwind of specific sources. Equally possible within this range is a transit at altitude to a location approximately on the perimeter of the inner circle, followed by 3 hours of intensive maneuvers with a direct return to base. The outer circle indicates the range for a research flight that includes a transit at 15000 ft asl to approximately the perimeter of the inner circle followed by a cruise at 1000 ft asl. A range between these two circles is more likely given fuel reserve requirements as the distance from alternate landing sites increases and maneuvers in addition to a constant low altitude cruise will be desired. A combination of such approaches would allow characterization of specific source

Figure 11. Example flight patterns for WINTER.

plumes, either from power plants or urban regions, contrast regional variations (coastal versus inland), and sample polluted continental outflow significantly offshore.

Our approach to flight planning will be based in part on plans used in previous aircraft campaigns that took place in the Northeastern U.S. (NARE, ICARTT, and NEAQS) and successfully sampled power plant plumes, urban air at night, and pollution outflow over the N. Atlantic (e.g., http://www.esrl.noaa.gov/csd/projects/2004/). We aim to characterize some of the same urban regions and point sources in order to provide direct comparisons in terms of seasonality of emissions and processing, and within the context of longer-term trends in

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emissions. The operations base will be shifted south in WINTER (to NASA Langley in Hampton, VA instead of Portsmouth, NH) to allow more frequent sampling of the mid-Atlantic region and occasional access to the Southeast. Moreover, a greater number of nighttime flights are planned for WINTER than were conducted during the previous campaigns.

Shallow boundary layers at night, and even well into daytime during winter, will provide a special challenge to flight planning and characterizing polluted regions [*Bakwin et al.*, 1998; *Holzworth*, 1967; *McGrath-Spangler and Denning*, 2013; *Seidel et al.*, 2012]. ***Missed approaches at airports, and low altitude runs in the marine boundary layer (MBL) have successfully sampled confined pollution and its outflow in past campaigns, and will be used in WINTER***. The MBL can be deeper than over land during winter [*McGrath-Spangler and Denning*, 2013], facilitating sampling of pollution outflow from N. America. Lower altitudes will be further characterized by independently-funded flights with a light aircraft operated by the University of Maryland (see below). In the months prior to deployment, we will work with RAF personnel to develop feasible low altitude flight plans near key urban areas and downwind of point sources.

Figure 11 depicts four example flight paths. These flight paths are largely derived from NOAA P-3 flights during the 2004 NEAQS campaign. Each path includes several modules that illustrate the types of objectives of interest and range of the operations area:
- **Constant altitude source plume crossings and Lagrangian sampling, at low altitude ~ 500 m.**

- **Missed approaches: specifically for nighttime flights or times when the mixed layer depth is shallow, use local airports in and downwind of major metropolitan areas to characterize vertical extent of nocturnal chemistry down to the surface.**

- **Stair step and spirals to assess vertical profiles of pollutants, boundary layer - free troposphere exchange, and when possible, the role of cloud processing.**

Most flights would be more focused on specific objectives than implied by these patterns alone. The magenta path exploits the full range of the C-130, to characterize the Atlanta, GA region which will not be a frequent target area, but is an important one to characterize nonetheless given recent summertime campaigns in that region and its position in a distinctly milder climate zone in winter compared to the Northeast U.S. The yellow path shows a flight or flights that could survey power plants in the Ohio River Valley and the New York City (NYC) plume; the inset shows the aircraft altitude profile for this path (ranging between 0 − 3000 m). An alternative flight could focus entirely on the NYC plume, i.e. continuing the zig-zag pattern further off-shore (assuming southwesterly flow). From this broad set of objectives, actual flight plans will be developed using custom weather forecasts and chemical forecasts from the GEOS-Chem chemical transport model.

3.1.2. Aircraft Payload
Table 1 summarizes the key set of instrumentation that will be supplied by request, by the PIs, or by collaborators. Instruments are prioritized as follows. Priority 1 instruments are required to address the scientific questions outlined above. Priority 2 instruments would be needed to carry out a more comprehensive evaluation of associated emissions. Priority 3 instruments could be used to address important but somewhat more peripheral scientific issues and would be included

as interest and resources allow. All priority 1 instruments have flight experience either on the C-130, the NASA DC-8, and/or the NOAA P-3, and the capabilities of each have generally been described in the literature [*Bertram et al.*, 2011; *DeCarlo et al.*, 2006; *Dube et al.*, 2006; *Kercher et al.*, 2009; *Lee et al.*, 2003; *Orsini et al.*, 2003; *Perring et al.*, 2013; *Thornton et al.*, 2000; *Wagner et al.*, 2011; *Washenfelder et al.*, 2008; *Washenfelder et al.*, 2011; *Yatavelli et al.*, 2012; *Young et al.*, 2012]. The Iodide HR-ToF-CIMS, recently flown by UW on the NOAA P-3, successfully recorded data for 100% of all research flights, and preliminary data continues to be uploaded to the data archive. Its performance metrics, in terms of sensitivity and detection limits, will be detailed in a forthcoming manuscript, and are as good or better than the CIMS used previously by the PI [*Kercher et al.*, 2009; *Riedel et al.*, 2012a; *Riedel et al.*, 2013; *Thornton et al.*, 2010]. Acetate chemical ionization [*Bertram et al.*, 2011; *Veres et al.*, 2008; *Yatavelli et al.*, 2012] will be employed on a mass spectrometer identical to the Iodide HR-ToF-CIMS discussed above.

Together, the suite of instrumentation we will deploy and source regions we will target, will allow us to address the specific goals summarized above while allowing investigation of new or unexpected avenues in the seasonality of emissions, chemical processing and transport mechanisms. There is an intentional degree of redundancy between the chemical species targeted by any one instrument. Duplication of key measurements ensures the most comprehensive data coverage possible and allows for intercomparisons that reduce the likelihood of artifacts for newer, less well-characterized measurements (e.g. HONO). NH_3 measurements are challenging, especially from aircraft. Los Gatos Research (LGR Inc) has indicated it may provide an NH_3 instrument, among others, and help deploy it at no cost should such a campaign go forward. The instrument has flight experience on the DOE G-1 aircraft,[*Leen et al.*, 2013] and together with the AMS and PiLS measurements will provide a useful constraint on total ammonia.

Table 1. Instruments to be deployed on the C-130 aircraft.

Measurement	Technique	Flight Ready	Requested / Supplied	Priority	Science Goal
NO, NO_2, total alkyl and peroxy nitrates, HNO_3	UCB TD-LIF[*Perring et al.*, 2013; *Thornton et al.*, 2002]	Y	S	1	1, 2, 3
NO_3, N_2O_5, O_3	NOAA CaRDS	Y*	S	1	1, 2, 3
$ClNO_2$, Cl_2, N_2O_5, hydroxynitrates, HNO_3	UW HR-ToF-CIMS (Iodide)[*Kercher et al.*, 2009; *Lee et al.*, 2013]	Y*	S	1	1, 2, 3
Inorganic Acids (HONO, HNCO, HCl, HNO_3, others)	UW HR-ToF-CIMS (Acetate)[*Lee et al.*, 2013; *Yatavelli et al.*, 2012]	Y**	S	1	1, 2, 3
HONO	ACES (NOAA)[*Washenfelder et al.*, 2008;	Y	S	1	1

	Young et al., 2012]				
SO$_2$	UV Fluorescence	Y	S	1	2, 3
CO$_2$/CH$_4$/CO/O3	NCAR CARI	Y	R	1	1, 2, 3
NO	NCAR CARI	Y	R	2	1, 3
Rapid response VOC	NCAR TOGA	Y	R	1	2, 3
Whole Air Sampler (VOC)	NCAR WAS	Y	R	2	1, 2, 3
Aerosol and cloud size distribution	UHSAS and FSSP	Y	R	1	1, 2, 3
Aerosol composition (non-refractory organic, sulfate, nitrate)	NCAR ToF-AMS led by CU Boulder	Y***	R	1	1, 2, 3
Aerosol composition (water-soluble, e.g. Cl$^-$, NO$_3^-$, NH$_4^+$, Na$^+$)	Georgia Tech PiLS[*Lee et al.*, 2003; *Orsini et al.*, 2003]	Y	S	1	1, 2, 3
NH$_3$	ICOS (LGR Inc)	Y	S	2	1, 2, 3
Formaldehyde (HCHO)	ISAF (LIF)	Y	S	2	1, 2, 3
Actinic Flux	Spectroradiometer	Y	R	2	1, 2
Black carbon mass	SP2	Y	N/A	3	2,3
OH, HO$_2$, and RO$_2$	CIMS or LIF	Y	N/A	3	1, 2
Aerosol extinction	Cavity ring down	Y	N/A	3	2, 3
Aerosol absorption	Photoacoustic	Y	N/A	3	2, 3

3.2. Small Aircraft Sampling

Several key issues relevant to addressing the primary goals outlined above cannot be adequately evaluated with the C-130 aircraft observations alone. Air traffic and other restrictions of C-130 operations will limit our ability to fully characterize near surface pollution. As such, WINTER activities will be augmented by coordinated measurements from a light aircraft operated by the University of Maryland. Vertical profiles of NO, NO$_2$, NO$_y$, O$_3$, CO, CH$_4$, CO$_2$, and related meteorological conditions near the Langely base of operations will facilitate interpretation of near-surface measurements in the context of the deeper boundary layer. Ongoing soundings and remote sensing of aerosol and cloud properties at NASA Langley, Howard University's Beltsville, MD site, and elsewhere will also be useful in this regard.

3.3. Regional Modeling for Planning and Analysis

As noted in the introduction, there are few if any field campaigns over the NE U.S. that provide an adequate test of the emissions and chemical mechanisms expected to be important in wintertime. A key outcome of the WINTER study will be to improve the accuracy of wintertime processes in regional and global chemical transport and chemistry-climate models. This goal will be achieved by providing a state-of-the-art measurement suite over a reasonably large geographical source region that can be used to test and improve models, while also involving current models during the study in forecast mode to plan and execute flight missions. We envision utilizing both high resolution chemical transport models driven in part by input from global models, such as GEOS-Chem operated in nested-grid mode, WRF-Chem, and other platforms.

A primary tool for flight plan development will be the GEOS-Chem nested grid aerosol-oxidant simulation driven by GEOS-5 meteorological fields from NASA's Global Modeling and Assimilation Office (GMAO) at a horizontal resolution of 1/2º latitude by 2/3º longitude over N. America.[*van Donkelaar et al.*, 2012] We will conduct hindcast simulations for 5 winters with up-to-date emissions inventories from the EPA and NOAA collaborators (see, e.g. Figure 6). These simulations will be used prior to the campaign to develop specific flight patterns. During the mission, the forecasting team will use 5-day GEOS-5 chemical forecasts of CO, CO_2, SO_2, O_3, and aerosols from GMAO at 0.25° resolution for daily flight planning. The GEOS-Chem simulation will be run in near-real time (NRT) mode using GEOS-5 real-time analysis, with results available 2-3 days after the flights to rapidly compare with observations for assessing how the flights are meeting mission goals.

After the mission, both observational analyses and modeling activities at regional and global scales will occur with the aim of addressing the science questions outlined above. Nested-grid simulations with the GEOS-Chem aerosol-oxidant model over N. America will be conducted and evaluated against the ensemble of aircraft and ground-based observations collected during WINTER to address the impact of HONO and $ClNO_2$ on O_3 production and oxidation rates, the relative importance of secondary aerosol formation pathways, and the accuracy of bottom-up anthropogenic emission inventories for the NE U.S. The GEOS-Chem model will be used to construct budgets for NO_x, SO_2, VOCs and O_3 over the WINTER region and assess the export efficiencies of these species. These wintertime budgets will be contrasted to summertime budgets for the same region, and then also compared to those of other polluted regions across the globe.

4. Broader Impacts
Wintertime processes are poorly sampled, and thereby a campaign as proposed herein would fill a major gap in current understanding that impacts broad areas of Earth system science. Findings from such a campaign will aid the development and optimization of Earth system models and address current scientific issues relevant to air quality and climate. By addressing the paucity of data on primary pollutant emissions and distributions during winter, it would provide important constraints on the causes of degraded surface air quality in winter, potential nitrogen and acid deposition to ecosystems, such as the sensitive Chesapeake Bay, export of pollution across national boundaries, and the contribution of anthropogenic emissions to changes in the global tropospheric O_3 background and thus oxidizing capacity. These issues are potentially important to governmental and non-governmental environmental organizations at the local, state, and federal levels with international dimensions as well. Broad dissemination of the results in open-access and high quality peer-reviewed journals will make results from this study available to stakeholders for use as objective and independent observational metrics.

This project will involve the training of several graduate and undergraduate students from multiple institutions in state-of-the-art measurement techniques and atmospheric science. We would also request NCAR EOL to assist in planning and conducting outreach activities to local K-12 and the general public oriented around the uniquely inspiring activities associated with use of the C-130 aircraft for scientific missions. These activities would include visits to the aircraft by local K-12 students near the operations base and a general "media day", where local media outlets visit the aircraft for a press conference. Coupled with the "media day," we would utilize social media outlets to reach a broader audience than the local media outlets alone.

5. Appendix – Acronyms/Abbreviations Used

AMS	Aerosol Mass Spectrometer
CAM	Community Atmosphere Model
CIMS	Chemical Ionization Mass Spectrometry
CMAQ	Community Model for Air Quality
DOAS	Differential Optical Absorption Spectroscopy
DJF	December January February
GEOS	Global Earth Observing System
IC	Ion Chromatography
JJA	June July August
MC	Mist Chamber
MCM	Master Chemical Mechanism
NADP	National Atmospheric Deposition Program
PiLS	Particle into Liquid Sampler
POA	Primary Organic Aerosol
PTRMS	Proton Transfer Reaction Mass Spectrometry
SOA	Secondary Organic Aerosol
SP2	Single Particle Soot Photometer
TDLAS	Tunable Diode Laser Absorption Spectroscopy
TD-LIF	Thermal Dissociation Laser Induced Fluorescence
UHSAS	Ultra-High Sensitivity Aerosol Spectrometer
UV	Ultraviolet
VOC	Volatile Organic Compounds
VUV	Vacuum Ultraviolet
WRF	Weather Research Forecasting

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