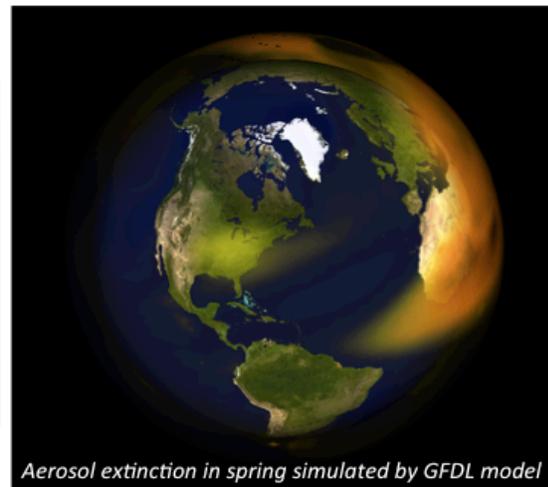


Southeast Nexus (SENEX)

Studying the Interactions Between Natural and Anthropogenic Emissions at the Nexus of Air Quality and Climate Change



**A NOAA Field Study in the Southeast U.S.
in Summer 2013**

Introduction

Earth's climate is changing as a result of the radiative forcing exerted by several different greenhouse gases and aerosol species (1). Greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and tropospheric ozone (O_3) warm the climate through the absorption of radiation. Aerosols affect climate both directly through the scattering and absorption of radiation, and indirectly through the nucleation of cloud droplets. The net effect of anthropogenic aerosol is estimated by IPCC and other studies to cool the surface climate, and as a result aerosols may have masked as much as 50% of the warming due to greenhouse gases (2). Climate forcing agents such as ozone and aerosols are also air pollutants, making air quality and climate two issues that are intimately coupled. To develop effective policies, research at the nexus of air quality and climate is urgently needed to guarantee that improvements in air quality are not achieved at a cost to climate, and vice versa.

NOAA has one of the world's leading research programs to improve our understanding of the most important climate forcing agents. The program includes the monitoring of abundances, and the quantification of emissions, the chemical formation of agents such as ozone and aerosols, and the characterization of their climate-relevant properties. NOAA's research program also includes the development of a Global Climate Model (GCM) that combines our understanding of all relevant processes to calculate and predict atmospheric abundances of the climate forcing agents and their impacts on climate and air quality. With this combination of measurement and modeling capabilities, NOAA is poised to make major advances in our understanding of key interactions among climate and air quality, and of the relative importance of natural processes versus human activities in controlling the atmospheric distribution of climate forcing agents.

In the last decade, NOAA has conducted intensive field studies focused on various aspects of the interactions between climate and air quality in the Northeast U.S. (2002, 2004), Texas (2000, 2006), Alaska (2008) and California (2002, 2010) (3-5). These regions differ in their atmospheric emissions and composition, and the processes that control these. For example, Figure 1 shows the average distribution of ammonium sulfate and organics, two of the main aerosol species, across the U.S. Through the synergy of these targeted field studies, many general insights into the sources and climate impacts of anthropogenic emissions have emerged.

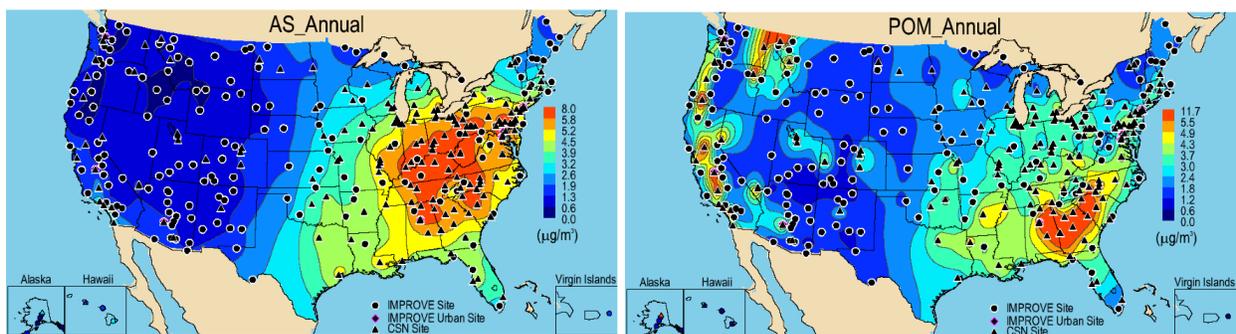


Figure 1: Annual average mass loadings of ammonium sulfate (left) and organic aerosol (right) from IMPROVE and CSN network measurements during 2005-2008 (6). Ammonium sulfate concentrations are highest in the East where many coal-fired power plants are located. Organic aerosol is high along the Pacific coast and in the Southeast.

Here, we propose to do an intensive field study in the Southeast U.S., a region with significant anthropogenic emissions, meteorological conditions that are conducive to active

photochemistry and where natural hydrocarbon emissions are the highest in the Nation. As a result, the atmospheric abundances of many climate forcing agents and air pollutants are high in the Southeast (Fig. 1). However, the extent to which these abundances are controlled by natural vs. anthropogenic emissions is very poorly understood. For aerosols in particular, the climate radiative forcing, defined as the change in net irradiance at the tropopause between present and pre-industrial, is therefore very uncertain. In addition, the Southeast U.S. has not warmed like other parts of the U.S. in response to global climate change (7, 8), and the temperature anomaly has been suggested to be related to aerosols derived from a combination of anthropogenic and biogenic precursors (9, 10).

The Southeast U.S. is chosen here as an (easily accessible) example region of the atmosphere where the interplay between anthropogenic and biogenic emissions to form climate-forcing agents is particularly important. It should be noted that the results of this study will be relevant for many regions of the atmosphere. While the field intensive necessarily has a regional focus, the study is fully intended to advance our description of the global distribution of climate forcing agents and their climate-relevant properties.

The field intensive in the Southeast will build on and extend the Southern Oxidants Study (SOS) that was conducted by NOAA and partners in the Southeast in the 90s. While SOS primarily focused on tropospheric ozone formation, advances in instrumentation warrant a re-examination of this region of the atmosphere with an added focus on aerosols and their climate-relevant properties. Such a study is timely now for several different reasons. First, NOAA can partner with a group of colleagues from academia and other agencies in the so-called Southern Oxidants and Aerosol Study (SOAS), which has the same objectives. Anthropogenic emissions have strongly decreased since the 90s and studying their effects on pollutants will give new and unique insights into their chemical formation.

Scientific Background

Sulfate Aerosol

Two of the main aerosol species over the U.S. are sulfate and organics; average distributions of these species are shown in Figure 1. Sulfate is formed from sulfur dioxide (SO_2) primarily emitted from coal combustion, and is highest in the Eastern U.S. where many large coal-fired power plants are located. The formation of sulfate from SO_2 occurs either in the gas phase or by in-cloud oxidation. The latter process is more rapid, but occurs only in cloudy atmospheres. The relative importance of gas-phase and in-cloud oxidation formation of sulfate is not well understood. For example, a comparison between seven air quality forecast models revealed that models that include in-cloud oxidation generally over-predict sulfate mass loadings, whereas models that do not include in-cloud oxidation generally under-predict sulfate mass loadings (11). Similar difficulties to model sulfate accurately have been reported for global models, which can calculate similar amounts of sulfate deposition despite large differences in conversion rate and residence time (12). Gas-phase processes also determine new particle formation and number concentrations, which are particularly important to describe the indirect effect of aerosol on climate (13). Deposition, the scattering of radiation as a function of humidity, and cloud nucleation are the other key process that determine the climate impact of sulfate. Deposition in particular is very poorly constrained by field data. Aircraft data are important to constrain

models of atmospheric sulfate, because many of the differences stem from vertical mixing and cloud parameterizations.

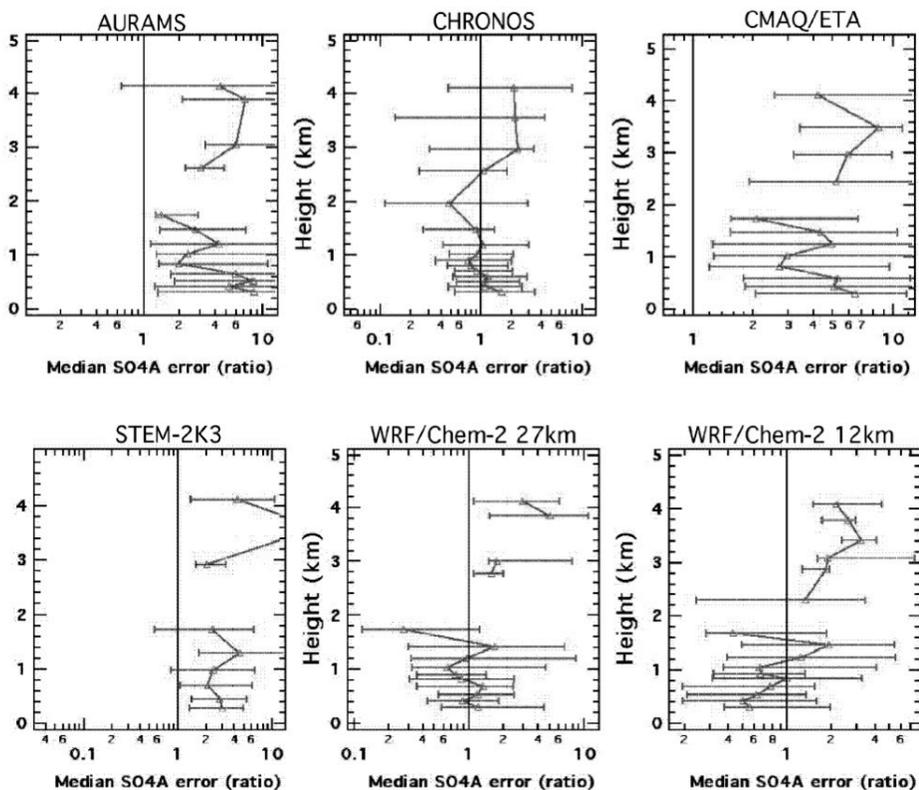


Figure 2: Vertical profiles of median model/observed ratios of PM_{2.5} sulfate for data obtained during the 2004 NOAA study in the Northeastern U.S. Models that included cloud oxidation (AURAMS, CMAQ/ETA and STEM-2K3) overestimated sulfate at all flight altitudes (11).

Organic Aerosol

Organic aerosols are directly emitted from biomass burning and internal combustion sources (primary organic aerosol or POA), and another large fraction is formed in the atmosphere from various natural and anthropogenic precursor gases (secondary organic aerosol or SOA). As the total emissions of natural precursors are much higher than those of anthropogenic precursors, most models attribute a large fraction of organic aerosol to natural sources (14). Moreover, as natural emissions of precursors are temperature dependent, some models indicate that the organic fraction may increase in a future warmer climate (15), although feedbacks from land-use change and higher carbon dioxide are important to consider (16). In contrast with the above, measurements in tropical forests, where natural emissions are the highest, do not show a high mass of organic aerosol (17). Organic aerosol mass tends to be highest in polluted areas: in the U.S., the highest concentrations are found in California and the Southeast (Fig. 1). Several studies have shown that the organic aerosol mass loadings in polluted air cannot be explained through formation from measured anthropogenic precursors (18). Also, radiocarbon dating studies generally attribute the dominant fraction of organic carbon aerosol to modern sources of carbon (19). To reconcile these findings, it has been proposed that anthropogenic emissions may exert a significant control on the formation of organic aerosol from natural precursors (20). The

nature of this control is unknown; the role of pre-existing aerosol, nitrogen oxides (NO_x) and the formation of organosulfates have all received attention (21, 22). Various other mechanisms for organic aerosol formation have also been studied, including nighttime (23) and aqueous-phase processing (24). Field studies are urgently needed to quantify the net effects of all of these mechanisms on aerosol formation.

Due to the uncertainties in the source attribution of organic aerosol, its climate forcing is poorly known. As an example, Figure 3 shows the direct radiative forcing due to increases in secondary organic aerosol according to two scenarios that vary in the type of aerosol to which the organics can partition (25). The radiative forcing is very uncertain in a region such as the Southeast U.S., where both natural and anthropogenic precursor emissions are high. In addition, the radiative properties of organic aerosol depend strongly on its chemical composition, water uptake and cloud nucleating properties, which all need to be further constrained by field observations.

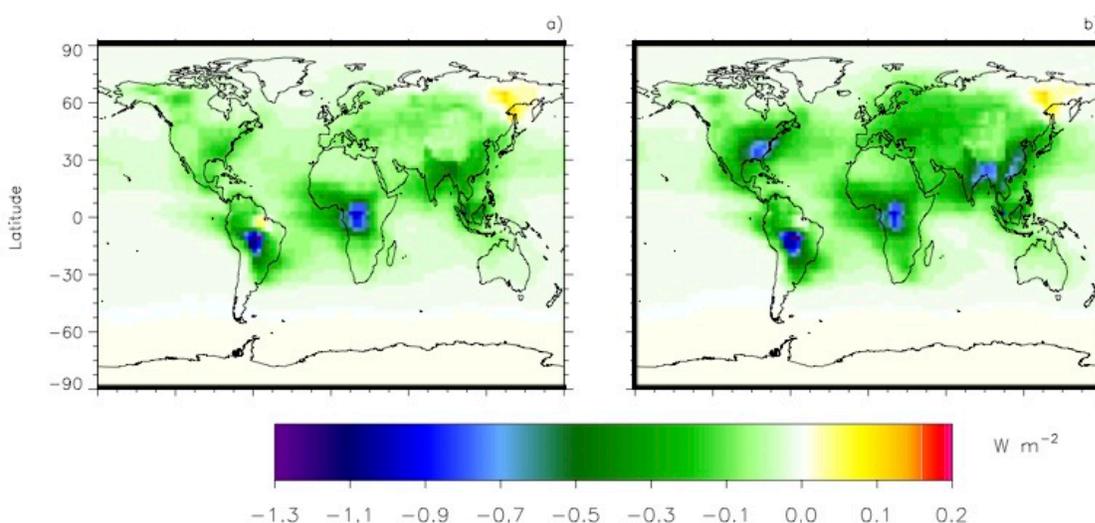


Figure 3: Modeled direct radiative forcing due to increases in secondary organic aerosol (SOA) between pre-industrial times and the present. Left panel: SOA is allowed to partition to primary organic aerosol (POA) from all sources. Right panel: SOA is allowed to partition to POA **and** ammonium sulfate (25). The Southeast U.S. shows a large sensitivity to the assumed partitioning.

Tropospheric Ozone

Another challenge is the understanding of ozone chemistry in the presence of isoprene and NO_x . A large overestimate of ozone over the Southeast U.S. in summer (Fig. 4) has been a long-standing problem in global and regional air quality models (26, 27), reflecting a gap in our current understanding of isoprene- NO_x -ozone chemistry. This incomplete understanding results in large uncertainties in predictions of future air quality in response to changes in natural and anthropogenic activities. Two possible controls on ozone production over the southeast U.S. have been identified recently as a result of progress in laboratory and field measurements:

(1) The **yield and fate of isoprene nitrates** formed in the oxidation of isoprene. Different treatment of isoprene nitrates causes large variations of global and regional ozone budget among different models (28-32). These nitrates represent an important terminal sink of NO_x if they are not recycled, but analyses of field observations suggest at least partial recycling (28-30).

(2) **The role of nighttime chemistry.** While a significant fraction of NO_x emissions occur at night (33), the amount of NO_x from nighttime emissions that is carried over to daytime (when it can contribute to ozone production) is largely dependent on nighttime processes involving NO_3 and N_2O_5 . Recent progresses in laboratory and field experiments have suggested large errors in the representation of these processes in current models, including the uptake coefficient of N_2O_5 and NO_3 (34, 35), the yield and fate of organic nitrates from isoprene+ NO_3 (36, 37) and terpenes+ NO_3 reactions (38, 39).

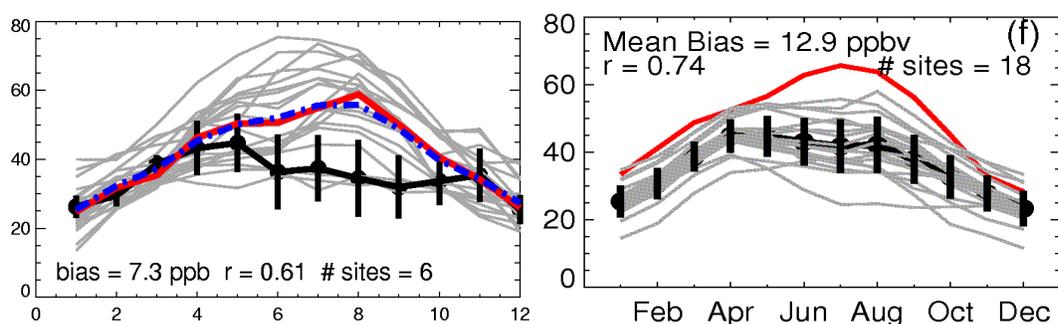


Figure 4: Monthly mean surface O_3 concentrations (ppb) over Southeast US. Left: Observed values from CASTNET sites (black circles) vs. multiple model mean (blue dot dashed lines) and median (red solid lines) for the year 2001, gray lines represent individual models. Right: Multiyear mean of observed values from CASTNET sites (black circles) vs. AM3 simulations (red solid line) over 1981-2000, gray lines represent individual sites.

Improving the representation of isoprene and terpene oxidation mechanisms in models will potentially have several benefits. It will improve our understanding of the response to changes in climate of surface ozone and aerosols in regions that are influenced by anthropogenic and biogenic emissions, with the Southeast U.S. as an example (28, 40, 41). Furthermore, improving our understanding of isoprene chemistry under various NO_x levels will (i) improve the estimates of global isoprene emissions from satellite observations of formaldehyde, one of the isoprene oxidation products (42-46), (ii) improve the description of the transport and global distribution of nitrogen oxides, which is essential to understand global oxidant levels and methane lifetime, and (iii) improve the representation of SOA precursors such glyoxal in global models.

NOAA Study in the Southeast U.S. in Summer 2013

The Southeast is of significant interest to study many of the processes outlined above. Natural emissions of precursor gases such as isoprene and monoterpenes are the highest in the U.S. and rival those found in tropical forests. The region has high humidity and the cloud processes that form sulfate and organics are expected to be important. In addition, anthropogenic emissions are significant in the Southeast and photochemistry is rapid. Both sulfate and organic aerosol are high in the region (Fig. 1) and their radiative influence is increased through hygroscopic growth under the high-humidity conditions, allowing them to exert a potentially strong but highly uncertain radiative forcing of climate (Fig. 3). Evidence from molecular tracers (47) and radiocarbon dating (19) has indicated the presence of oxidation products from natural hydrocarbons in the aerosol. A strong seasonal variation in aerosol optical depths was attributed

to aerosol formation from natural precursors (48). Surface monitoring networks (IMPROVE, STN), however, attribute this seasonal variation to changes in sulfate (49).

We propose here to conduct an airborne study in the Southeast U.S. in 2013 to quantify the emissions of greenhouse gases and aerosol, and to investigate the roles played by anthropogenic and natural emissions in the formation of ozone and aerosol in the atmosphere. The climate relevant properties of the resulting aerosol mixture will be quantified. The study will take place in summer because the temperature-dependent biogenic emissions and sulfate concentrations are largest in the summer.

The major questions that we propose to address and the payoff of those studies are listed in the next section. The airborne study proposed here is timely and apt for several reasons:

1. A study in the Southeast provides a logical next step in NOAA's field missions, as it targets the region where natural precursor emissions are highest in the U.S. The quantification of natural and anthropogenic sources of aerosol and ozone in the Southeast is also strongly tied to the theme of air-quality-climate interactions that NOAA focused on during the CalNex study in California in 2010.
2. New measurement methods have been developed in recent years. For example, measurements of organic aerosol (20, 50) and reaction intermediates, such as glyoxal (51), organosulfates (21), and acids (52, 53) as well as nighttime chemical species (NO_3 , N_2O_5 and ClNO_2) are now possible. Making these measurements from a research aircraft will give more detailed insights into the formation mechanisms of ozone and aerosol, and allow for evaluation and improvement of the mechanisms used in models.
3. The last detailed airborne measurements in the Southeast were made during the Southern Oxidant Studies (SOS) in the 90s (54), before these new methods were available. The earlier studies were focused on ozone and helped to understand the important role that natural emissions play in photochemical ozone formation. Important reductions in anthropogenic emissions have taken place since the 90s, affecting both ozone and aerosol concentrations. A new study will help elucidate trends and changes brought forth by various human actions in a very rapidly changing region of the country.
4. The development of a new chemistry-climate model (AM3) has recently been completed at GFDL, including oxidation mechanisms for biogenic hydrocarbons leading to the production of ozone and SOA. New studies have indicated a key role of isoprene nitrates in controlling production of ozone and SOA. This field campaign can provide a wealth of new atmospheric data for evaluating and improving AM3, reducing the uncertainties in its projections of future changes in regional air quality and climate and possibly helping to address the long-standing overestimate of ozone concentrations over the southeast in models.
5. NOAA's research interests in the Southeast overlap significantly with those from colleagues at other agencies (EPA, NCAR, NASA, DOE) and in academia, who are planning for a parallel study in the Southeast in 2013. These partners are planning for surface measurements at a forest site and for airborne flux measurements of natural hydrocarbons. Collaboration with these partners will greatly enhance the impact of the study proposed here.

6. The “role of aerosols in regional climate” was recently identified as an important crosscutting research challenge for NOAA in the report “Toward Understanding and Predicting Regional Climate Variations and Change”, which was put together after the NOAA Science Challenge Workshop in September 2011 (www.nrc.noaa.gov/plans_docs/Climate_Science_Workshop_White_Paper.v4_Final.pdf). The lack of warming in the central and southern U.S., in stark contrast with simulations used for the IPCC Fourth Assessment Report, is mentioned as a particular issue to be resolved.

Southeast Field Study: Specific Science Questions

1. What are the emissions of aerosol, aerosol precursors and greenhouse gases in the SE U.S.?

- How well do inventories represent the urban emissions of organic aerosol, black carbon NO_x, volatile organic compounds (VOCs), SO₂ and greenhouse gases?
- How well do inventories represent the emissions of aerosol precursors from point sources, such as coal-fired power plants?
- How well do inventories represent biogenic VOC emissions?
- How significant are the emissions from biomass burning?

Approach: To answer these questions, the NOAA WP-3D will make flight legs downwind from urban and point sources of trace gases and aerosol, and measure the mixing ratios of biogenic VOCs during regional surveys.

2. What is the composition and distribution of aerosol in the SE U.S.?

- What is the relative importance of sulfate, organics and other chemical components?
- How does this change with altitude?

Approach: Average mass loadings of aerosol will be determined from flights in specific regions and under specific meteorological conditions (pre- and post-frontal), and compared to models.

3. What are the formation mechanisms of secondary species (ozone, sulfate and organics) in the SE U.S.?

- What do the vertical profiles of sulfate and of organic aerosol reveal about their respective sources?
- How do biogenic emissions affect ozone production by modifying the processing and export efficiency of NO_x emissions through organic nitrates? What is the role of terpenes in global oxidation?
- How important is organic aerosol and ozone formation from nighttime oxidation of biogenic VOCs?
- How important is the formation of sulfate and organics from aqueous-phase processes?

Approach: What are the significant precursors of organic aerosol? What role do anthropogenic emissions play in the formation of organic aerosol from biogenic precursors? To answer these questions, the NOAA WP-3D will follow air masses from different sources (urban, power plants, forests) as they are processed during the day, at night, with and without the presence of biogenic emissions, and through cumulus and shallow convective clouds,

4. Which deposition processes are critical for determining atmospheric concentrations of aerosol, ozone and NO_y?

- What deposition processes (dry, and in-cloud or below-cloud wet deposition) are controlling aerosol lifetimes?
- What techniques and instrumentation can be deployed in SOAS to quantify aerosol, ozone and NO_y deposition?

Approach: The rate at which species are lost by deposition can be estimated using measurements of different hydrocarbon species, which are removed at different rates based on their reactivity with hydroxyl radicals.

5. What are the climate-relevant properties of aerosol in the SE U.S.?

- What are the extinction, absorption and CCN properties of aerosol from primary and secondary sources? How do these depend on the high humidity in the SE U.S.
- What fraction of the organic aerosol is natural versus controlled by anthropogenic emissions?
- How will this change in the future as a result of warming and changes in anthropogenic emissions?
- Given that black carbon is co-emitted with other species, will controlling specific BC sources have a net warming or cooling effect?

Approach: Aerosol extinction, absorption and cloud nucleating properties will be measured from the aircraft for different aerosol types. Correlating the variability in aerosol with inert tracers for different emission sources, e.g. carbon monoxide (CO) for urban emissions, acetonitrile for biomass burning emissions, will help to describe the fraction of aerosol that is controlled by anthropogenic emissions.

The NOAA WP-3D Research Aircraft and its Proposed Payload

Access to the NOAA WP-3D research aircraft is essential to answer all the science questions described in the previous section. The ability of the aircraft (i) to sample air masses that contain a different mixture of emissions (urban, power plant, forest), (ii) to follow these air masses as they are transported and chemically transformed in the atmosphere, and (iii) to measure the vertical distribution of trace gases and aerosol in the atmosphere, is unique and cannot be obtained with any other platform.

The proposed payload for the Southeast mission is described in Table 1. The aircraft cannot physically accommodate all of these instruments; final choices will depend on instrument availability, investigator interest, and funding.

Parameter	Method	Priority
<i>Gas Phase</i>		
Carbon dioxide (CO ₂) and methane (CH ₄)	Infrared laser absorption	1
Carbon monoxide (CO)	VUV fluorescence	1
Nitrogen oxides (NO, NO ₂ , NO _y)	O ₃ chemiluminescence	1

Ozone (O ₃)	NO chemiluminescence	1
NO ₃ , N ₂ O ₅	Cavity ring-down absorption	1
Sulfur dioxide (SO ₂)	Pulsed UV fluorescence	1
Non-methane hydrocarbons	Whole air sampler (WAS) & post-flight gas chromatographic analysis	1
Oxygenated hydrocarbons including formaldehyde (HCHO)	Proton-transfer-reaction mass spectrometry (PTR-MS)	1
Glyoxal (CHOCHO)	Laser-induced phosphorescence (LIP)	1
Peroxides, epoxides, acids	CF ₃ O ⁻ chemical ionization mass spectrometry (CIMS)	
Organic and inorganic acids, including formic, nitric, nitrous and isocyanic acid (HCOOH, HNO ₃ , HONO, HNCO)	Acetate (CH ₃ COO ⁻) ion CIMS	1
Peroxyacyl nitrates (PANs)	I ⁻ CIMS	2
Nitric acid (HNO ₃)	SiF ₅ ⁻ CIMS	2
Ammonia (NH ₃)	H ⁺ (CH ₃ COCH ₃) ₂ CIMS	2
<i>Aerosol Phase</i>		
Size-resolved non-refractory aerosol composition	Compact time-of-flight aerosol mass spectrometry (AMS)	1
Bulk aerosol composition, including organic acids	Particle-in-liquid sampler (PiLS) & ion chromatography (IC)	1
Single particle composition	Particle analysis by laser mass spectrometry (PALMS)	1
Single particle black carbon	Single particle soot photometer (SP2)	1
Aerosol number, surface and volume distribution	Ultra high sensitivity aerosol spectrometer (UHSAS), condensation particle counters (CPC), optical particle counters (OPC)	1
Aerosol extinction, f(RH)	Cavity ring-down spectrometer	1
Aerosol absorption	Laser photo-acoustic spectrometer	1
Filter-based aerosol absorption	Particle soot absorption photometer	1
Cloud condensation nuclei concentration	CCN counter	2
<i>Other</i>		
Cloud probes	Various Droplet Measurement Technologies (DMT) probes	1
Meteorological parameters	Various sensors	1

Table 1: Proposed payload of the NOAA WP-3D research aircraft during the proposed field mission in the Southeast U.S. in summer 2013.

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