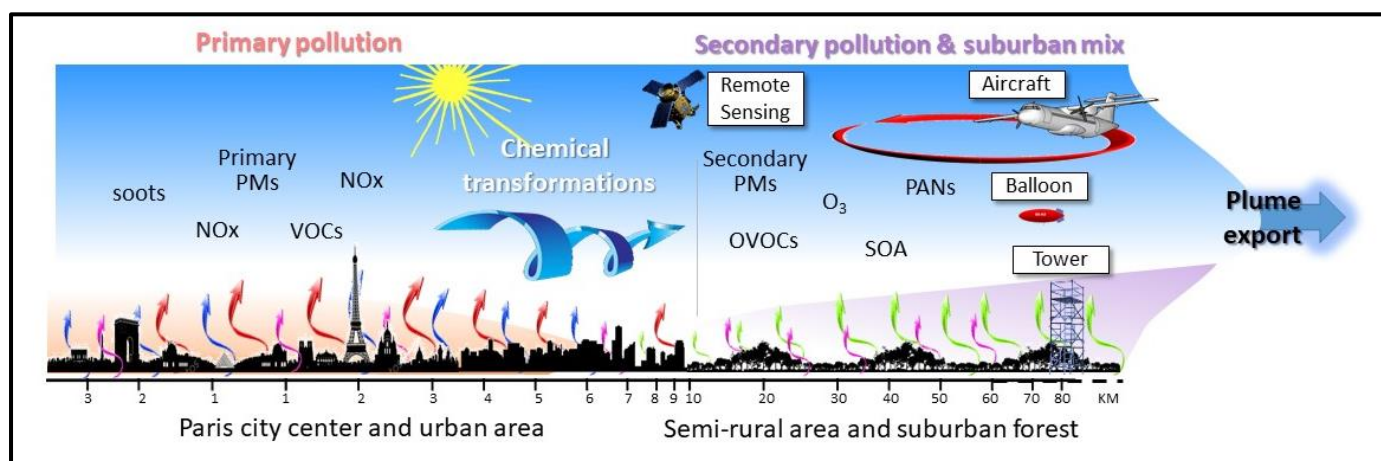


ACROSS: A mission to explore the atmospheric transformation of chemical compounds in mixed anthropogenic-biogenic environments



By

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and

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Executive Summary

Humans have recognized for a long time that their air can become contaminated through natural and non-natural events. The problem became particularly apparent as people moved into large cities where the high population densities exacerbated the pollution associated with home heating and industry. Awareness became particularly acute when thousands of people died during severe episodes.

In recent decades, significant progress has been made in understanding the causes and impacts of urban air pollution, generally leading to improved air quality through enhanced knowledge and regulatory action. While significant numbers of people still die prematurely each year from air pollution, progress continues to be made. Scientific investigation has exposed the processes by which primary pollutants, such as oxides of nitrogen and volatile organic compounds, are processed in the atmosphere, leading to their oxidation and ultimate removal, while at the same time producing secondary species such as ozone and organic aerosols. Both primary and secondary species can be toxic for humans, animals and plants.

Recent research has uncovered the complex chemistry of natural organic compounds released from trees and other plants. Because of the chemical structures of these compounds, they react differently than organic substances typically found in urban environments. At present, it is not clear if the mixing of biogenic organic compounds with urban makes air quality better or worse. In the end, the answer may be quite complex. The ACROSS (**A**tmospheric **C**hemist**Ry** **O**f the **S**uburban fore**S**t) project focuses on scientific research to understand the detailed chemistry and physics of urban air mixed with biogenic emissions with the goals to increase detailed understanding of the chemical processes and to use this knowledge to improve the performance of air quality models. Enhanced knowledge and improved models will allow society to develop better strategies to improve air quality and save lives.

The central component of ACROSS is a comprehensive summertime field study with many instruments for the measurement of primary and secondary constituents. Measurements will be made from research aircraft, a tower located in a forest, tethered balloons and/or drones, and mobile platforms. Observations from the field study will be analyzed in a variety of ways involving statistical approaches and comparisons with different types of numerical models. The results of the campaign will be widely disseminated through presentations and peer-reviewed publications. Significant broader impacts are expected including training of students, public outreach, and providing useful information to policymakers. The ACROSS observations are expected to provide a unique dataset that will improve understanding of fundamental processes and that can be used to improve model representations of processes that are operative in these environments.

Overview

Chemical compounds that are released into the atmosphere undergo a variety of multi-phase chemical and physical processes leading to their transformation into many products. These substances can negatively affect air quality and thus human and ecosystem health. It is critically important to understand the factors that control the complex interactions between dynamics and chemistry at a variety of scales.

Direct observations of key primary and secondary species are critical to advancing knowledge of atmospheric chemical and physical processes. It is also beneficial to make measurements from a variety of platforms because this allows better assessment of the spatial and temporal variability of target species. Numerical models can be used to forecast atmospheric conditions and to assess differences between predicted and observed quantities.

Enhanced understanding of atmospheric transformation processes leads to improved representation in numerical models, which helps advance high-quality predictions of the abundance of species and allows accurate testing of mechanisms with the goal to use such information to improve air quality. ACROSS (**A**tmospheric **C**hemist**R**y **O**f the **S**uburban fore**S**t) is a project designed to improve understanding of atmospheric oxidation through a carefully planned observational field campaign and subsequent analysis of the data. The project also includes implementation of well-conceived, complementary laboratory studies and the testing of representations of chemical and physical processes within numerical models.

This document provides background and presents a general framework for conducting the ACROSS study. Analyses of available data are used to constrain the observational philosophy. Potential observational platforms are identified that could stage the instrumentation needed to address ACROSS goals.

Why is Now the Time to Study Paris Air Quality?

Why Study Paris Air Quality?

Since the early work on atmospheric composition of Menard, Toupance, Perros and Carlier (e.g. Benarie et al, 1979, Kalabokas et al, 1988, Tsalkani et al, 1991), two large campaigns focused on air quality – ESQUIF (1998-2000) and MEGAPOLI (2009-2010) – have taken place in the greater Paris area.

The ESQUIF study (**E**tude et **S**imulation de la **Q**ualite de l'**a**ir Ile de **F**rance) was conducted from a variety of platforms with goals to improve understanding of urban chemistry and dynamics, and to improve and validate air quality models (Menut et al., 2000). Ground-based observations included atmospheric physical state, aerosol physical properties, and gas phase compounds. Measurements were conducted aboard five aircraft that included several important components of urban air. Models were employed to conduct forecasts and to analyze the observations. It was found that pollution episodes in the Paris area are the result of local production with meteorological conditions of weak winds and high temperatures. These episodes can occur with deep or shallow boundary layer heights and do not necessarily require strong temperature inversions.

The MEGAPOLI (**M**egacities: **E**missions, urban, regional and **G**lobal **A**tmospheric **P**OLLution and climate effects, and **I**ntegrated tools for assessment and mitigation) study involved ground- and aircraft-based observations designed to improve understanding of organic aerosol formation in the processing of Paris emissions (Baklanov et al., 2010; Beekmann et al., 2015; Freney et al., 2014; MEGAPOLI, 2009-2010). This project sought to assess impacts of megacities on local, regional and global air quality, to quantify feedbacks between air quality and local, regional, and global climate, and to develop improved predictive tools for urban air quality. Observations that were conducted at surface sites included important gas-phase species and aerosol properties. Also, the ATR-42 from the French research aircraft fleet was equipped with instruments for the measurement of many of the same quantities as made at the ground sites. Data from these studies were used to assess the performance of models, constrain urban emission inventories, and develop budgets for HO_x radicals (Michoud et al., 2012) and O₃ as presented in more than 80 scientific papers. Aerosol mass concentrations and organic aerosol fractions were found to be enhanced by air masses that spent longer time over land. The amount of organic aerosol was found to increase with photochemical age consistent with the conclusion that it was the result of secondary organic aerosol formation. Modeled HO_x radicals agreed well with observations within their uncertainties, but necessarily included estimation of some controlling species because of lack of measurements.

While these studies led to improved understanding of atmospheric physical and chemical processes for Paris urban outflow, many questions remain related to the oxidation of organic compounds, the formation of secondary organic aerosol, and the budgets of HO_x radicals. Advances in measurement capabilities for gas- and condensed-phase oxygenated organic compounds and in development of detailed mechanisms describing the degradation of organic compounds allow more detailed scientific inquiry into these topics.

Why a Study of Air Quality Now?

In the last decade or so, analytical techniques based on mass spectrometry as applied to atmospheric measurements of radicals and organic compounds have advanced (e.g. Albrecht et al., 2019; Mattila et al., 2018; Riva et al., 2019). These have led to quantification of a wide variety of species through semi-direct and indirect chemical and ionization processes. Such measurements have revealed interesting chemical processes, such as the autooxidation of large organic peroxy radicals, for example (Zhao et al., 2018). Optical techniques based on cavities have also led to observations of atmospheric species such as NO₃, NO₂, NO, and glyoxal (Li et al., 2019; Liang et al., 2019, Wang and Lu, 2019).

Aerosol size measurements have improved with current capability to as small as one nanometer diameter (Biswas et al., 2018; Surawski et al., 2017), allowing better connection between relevant gas-phase species and freshly nucleated particles containing only a few molecules. Aerosol composition can also be measured with greater specificity (DeCarlo et al., 2006; Zuth et al., 2018). Given the importance of organic compounds within the aerosol phase, such measurements are critical to illuminating the pathways by which emitted species are transformed and eventually removed from the atmosphere.

Theoretical, field, and laboratory studies have improved understanding of the processes leading to formation and growth of secondary organic aerosol (e.g. Bianchi et al., 2019;

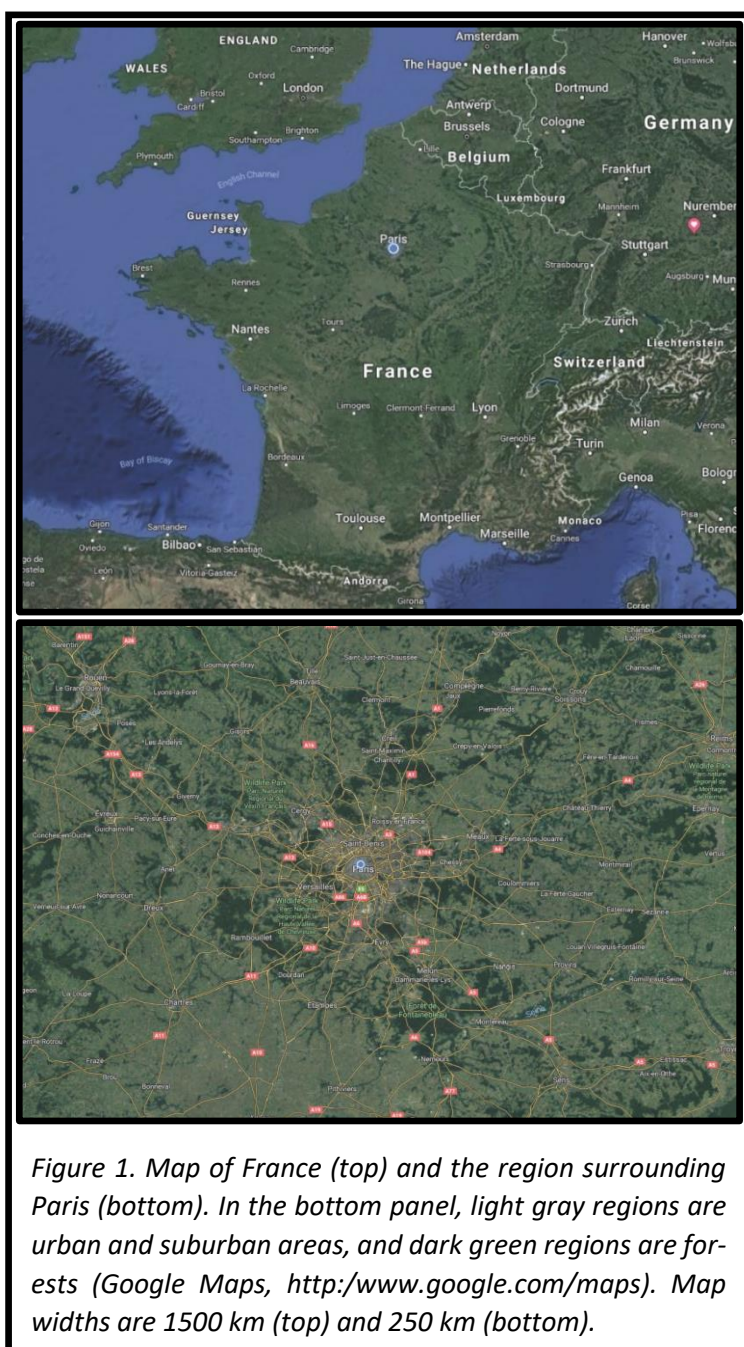
Daellenbach et al., 2019; Gentner et al., 2017). Testing such information under atmospheric conditions allows tests of explicit mechanisms and can eventually lead to improved condensed mechanisms for use in chemical transport models.

Application of multiple platforms to an atmospheric observational study allows assessment of processes on a variety of scales. Tower-based observations can be used to study scales from leaf-level to several kilometers. Aircraft observations can integrate over tens to hundreds of kilometers while also studying very local impacts of fast photochemistry. Balloons and drones can observe at intermediate scales. Mobile platforms measure at local scales, but at a variety of locations.

In many cities, air quality networks are having difficulty predicting ozone and fine particles simultaneously. This could

be the result of the over-parameterization of operational air quality models that may not be capable of simulating the atmosphere with changing environments. In Paris, like elsewhere, new comprehensive datasets for particle abundance and properties and for oxidants are hence needed to support the efforts to improve model representations of chemical mechanisms.

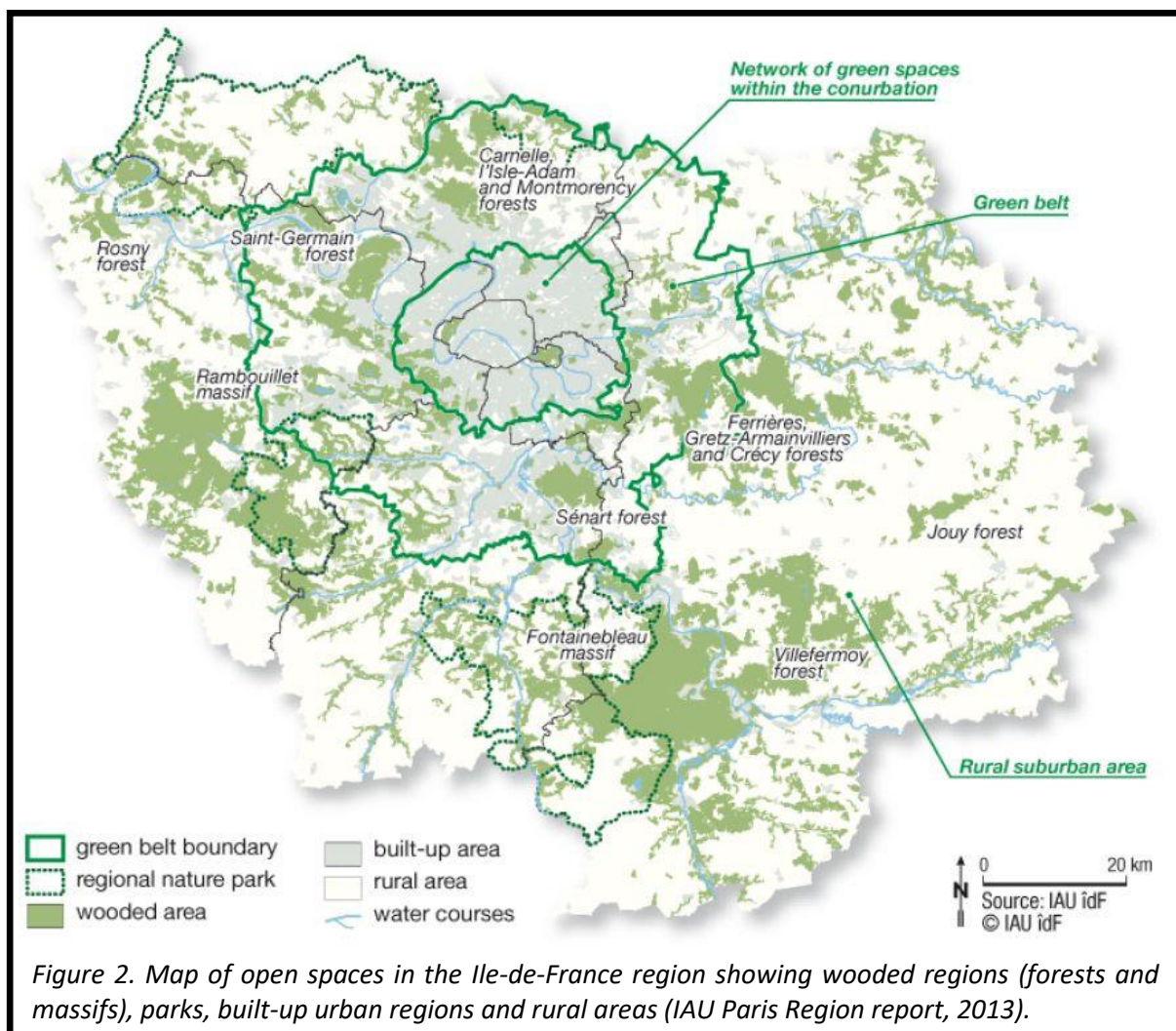
Paris is relatively unique in that it is located some distance from other major urban centers. Brussels is the closest city with a population over 1 million (264 km, pop 2.1 million). London is the closest megacity (344 km, pop 14.7 million). There are several cities, mostly in the Netherlands and Germany, with populations of 1.4 to 5.7 million at distances of 370 to 500 km. Transport times to Paris from these cities is 1 to 2 days with 10 km/hr wind speed. The nearby topography is relatively flat with the Seine and Marne valleys at elevations from 25 to 35 m and nearby higher elevations up to 150 m.



While there have been many studies of megacity air quality in the last one or two decades, including ESQUIF and MEGAPOLI discussed earlier, but also studies in other locations (SOAS, southeast US; GOAmazon, Brazil; KORUS, south Korea; BERLIOZ, Berlin), Paris is a perfect situation, as described later, for a well-planned study with state-of-the-art observations to advance knowledge on atmospheric composition and air quality, particularly as it related to the study of mixed urban and biogenically-influenced air masses.

Geography & Meteorology of Paris Region

Paris is the capital and most populous city in France. It is situated in the north-central part of the country centered at 48.8647° N and 2.3490° E. Figure 1 (top) shows a map of France and surrounding countries, and Figure 1 (bottom) displays the region around Paris. Paris sits at a low elevation (25-35 m) with nearby hills reaching up to a maximum of 122 m (Montmartre) with higher elevations to the east and southwest (up to about 150 m). The city is in a basin formed by the Seine River and its tributaries. The bottom panel of Figure 1 shows that the forested regions near Paris are abundant and nearly surround the metropolitan region. This is shown more clearly in Figure 2, in which parks, wooded areas, urban, and rural areas are depicted in the Ile-de-France region. Areas of interest that may emit significant amounts of biogenic VOCs include the Rambouillet massif (with the Haute Vallée de



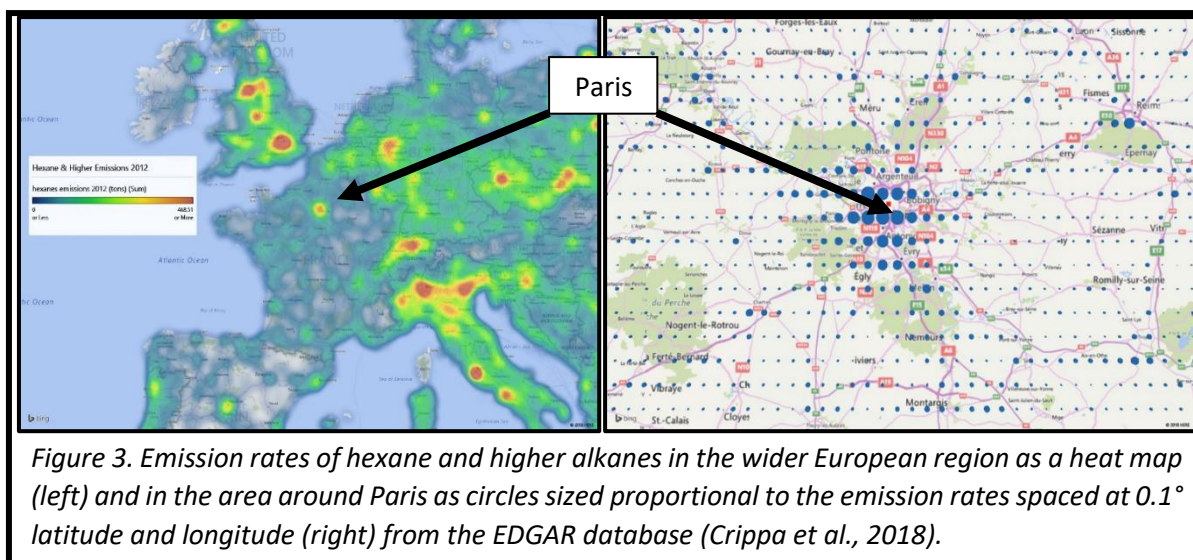


Figure 3. Emission rates of hexane and higher alkanes in the wider European region as a heat map (left) and in the area around Paris as circles sized proportional to the emission rates spaced at 0.1° latitude and longitude (right) from the EDGAR database (Crippa et al., 2018).

Chevreuse Regional Natural Park), Fontainebleau massif, Villeferney forest, Jouy forest, Ferrières, Gretz-Armainvilliers, and Crécy forests, Sénart forest, Carnelle, l'Isle-Adam, and Montmorency forests, Rosny forest, and the Saint Germain forest, in addition to forested areas within the Paris metropolitan region (e.g. Bois de Vincennes, Bois de Boulogne).

The climate of Paris (Climate-Data.org, <https://en.climate-data.org/europe/france/ile-de-france/paris-44/>, 1982-2012) is temperate with cool winters and warm summers, usually being influenced by the north Atlantic waters that are warmed by the Gulf Stream and the North Atlantic Current. Monthly average high temperatures are 16° C, 20° C, 23° C, 25° C, 24° C, and 21° C for April through September. Annual precipitation is about 65 cm, averaging about 25 mm/month in April and May, decreasing to 21-22 mm/month in July and August, and 16 mm/month in September. There is an average of 10 to 14 days per month with some rain between April and September. During April, there is an average of 5 hours of sunshine per day. In May and June, the average is 6 hours, while July, August, and September average 8 hours.

The Paris metropolitan source region (*unité urbaine de Paris*) is approximately circular with a diameter of about 60 km, an area of 2,845 km² and a population of about 10.7 million. A larger region that includes surrounding suburbs (*aire urbaine métropolitaine de Paris*) has a diameter of about 150 km, an area of 17,175 km², and a population of about 12.5 million (INSEE, <https://www.insee.fr/fr/statistiques/1280952>). As an indication of the urban emission region, the sum of emissions of hexane and higher alkanes taken from the EDGAR emissions database (Crippa et al., 2018) are shown in Figure 3 over much of the European continent (left) and the Paris region (right). The latter shows a core source region that is about 30 km in diameter.

Brief History of Advances in Understanding Air Quality

Throughout their existence, humans have worked in various ways to produce energy for heating, cooking, transportation and fabrication. The side effect of these activities has been to pollute the environment. Early on, the main issue was smoke from combustion (first from wood), which became particularly a problem as cities grew to large sizes. This was

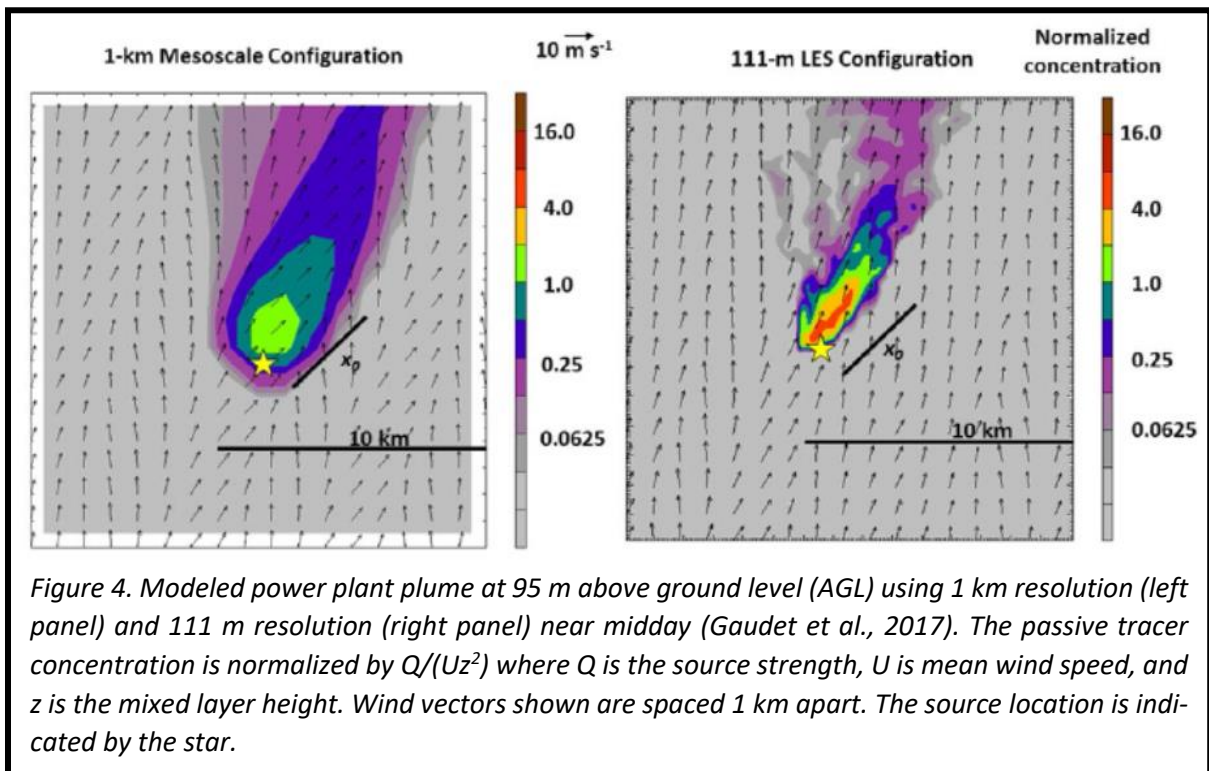
followed by increased substitution of wood by coal. When combined with unfavorable meteorological conditions (e.g. temperature inversions, weak winds), the problem was exacerbated. By the end of the 16th century, the problems of urban air pollution were well documented. The effects of smoke on blocking sunlight were commonly noted. Even before causes of disease were well-understood, it was recognized that coal smoke negatively impacted breathing. Many deaths were attributed to air pollution in the 19th and 20th centuries (e.g. Beach and Hanlon, 2018; Hanlon, 2015; Stradling and Thorsheim, 1999) which continues to the present (World Health Organization Technical Report, 2013). As emissions from coal burning were addressed, first through increasing heights of chimneys (e.g. Douet, 1988) and later through physical removal of particles (Slack and Falkenberry, 1970), negative impacts of other emissions were noted, such as sulfur emanating from copper smelters and other industrial activities. In the mid-twentieth century, it was recognized that Los Angeles smog was formed from the interaction of sunlight with hydrocarbons and oxides of nitrogen (Haagen-Smit, 1952) producing secondary products such as ozone, aerosols, organic acids, and peroxides. Studies since have revealed the details of this chemistry (e.g. summarized in Brasseur et al., 1999; Seinfeld and Pandis, 2016) and the deleterious effects of pollutants on human health (such as lung development in children) and ecosystems (such as crop yields) (e.g. Cohen et al., 2017; Fleming et al., 2018; Gakidou et al., 2017).

In the 1600s, scientists suggested that industries be moved out of cities to improve urban air pollution. In the 1700s and early 1800s, air pollution problems were settled mostly by litigation rather than regulation. In the 19th century, some government regulations were introduced, mostly to control smoke. Early in the 20th century, rules were implemented with the goal to reduce smoke emissions from industrial activities, but the problem of pollution from domestic sources was not yet being addressed. The earliest regulations were at local levels, but significant smog episodes in the 1940s and 1950s led to federal action in the form of Clean Air Acts (UK and US). These had dramatic effects on eliminating the severe problems of previous decades. Gradually standards were developed for specific compounds and types of particulate matter.

Technological solutions for controlling emissions have been developed to address specific problems, such as sulfur from power plants and organic carbon compounds from vehicles. Such technology has led to steady improvement in amounts of primary and secondary species in urban areas. Despite these advances, poor air quality remains a problem in some developed cities and in urban and rural regions of many in developing countries. Indeed, even as emissions of precursors has been reduced through regulation, the concentrations of secondary species such as ozone have increased.

Factors Influencing Atmospheric Composition

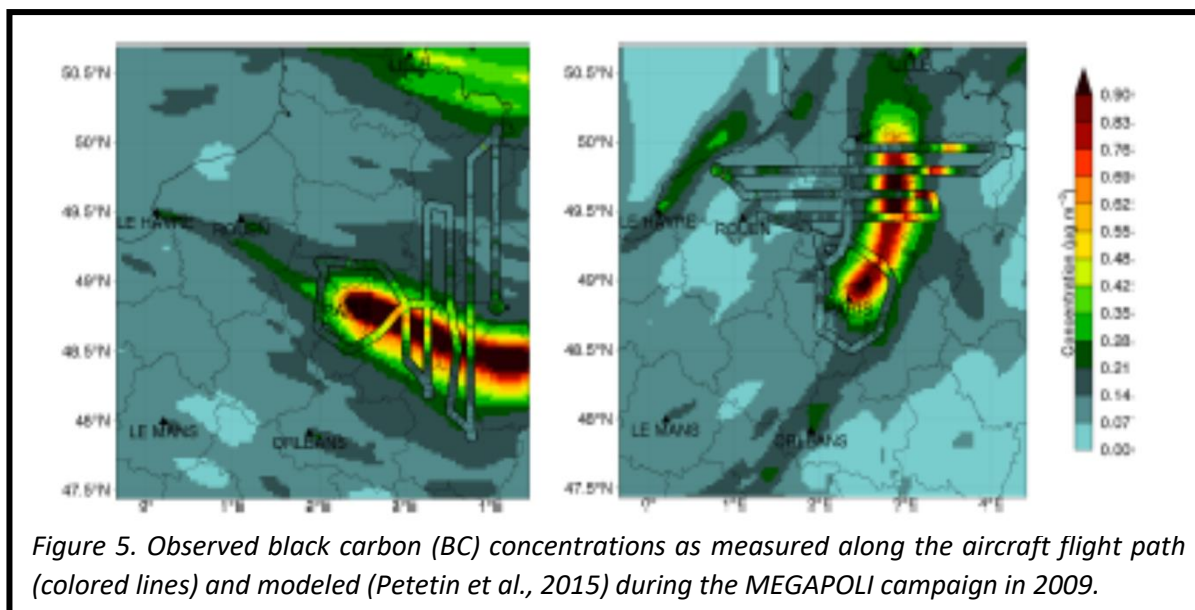
The composition of the atmosphere evolves with location and time due to emissions of primary species and the interaction of atmospheric chemical and physical processes that lead to production of secondary components. The following sections discuss processes contributing to atmospheric composition in various environments.



Urban Plumes

When they are sufficiently dense and when they are located within regions of lower emissions, urban emissions can form a plume similar to that expected from a large point source. Emissions of gases and particles from urban regions travel horizontally with the wind and slowly mix with background air that distributes components throughout the boundary layer. Viewed at relatively low resolution, of order the dimension of the source region, an urban plume appears to emanate from a homogeneous area source whose emissions form a gaussian plume moving downwind, dispersing in the horizontal and vertical directions, undergoing dilution, and experiencing chemical transformations. At higher resolution, the inhomogeneity of the individual urban sources (e.g. industrial plants and highways) becomes evident, and the plume can show ragged structure as it interacts with the turbulent structure of the atmosphere. Figure 4 shows some of these phenomena at a single altitude for a simulated power plant plume at two resolutions (Gaudet et al., 2017). Many such point sources and area sources combine to form an urban plume, resulting in a complex mixture. Figure 5 depicts model and aircraft measurements of black carbon for the Paris plume during the MEGAPOLI campaign in 2009. The model resolution is 3 km, and the measurements of black carbon have an effective horizontal resolution of 6 km (sample integration 60 secs, aircraft speed 100 m/sec) (Lamorte et al., 2016; Petetin et al., 2015; SAFIRE, www.safire.fr) These resolutions are sufficient to capture much of the horizontal detail of the Paris urban plume (about 30-60 km horizontal diameter). In comparing observations and models, one can see that chemical transport models are not always successful in their representations of the location of urban plumes and the range of concentrations.

Knowledge of the vertical extent of the Paris plume is also important. Emitted substances are expected to be initially found near the surface where most emissions occur, eventually spreading throughout the planetary boundary layer. This layer is generally, although



not necessarily well-mixed, has a depth that can vary depending on wind speed, surface heat balance, free atmosphere density, and vertical wind shear. Typical Paris spring and summer boundary layers range from very shallow values at night (100 m or less) up to 2500 m during late afternoon (e.g. de Bruine et al., 2017). Regional models historically have had insufficient resolution to quantify structure within the boundary layer, but this has improved over time.

Anthropogenic Emissions

Human activities involved in transportation, energy production (electricity and heating), industrial processes, and other activities using volatile chemical products (pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products) lead to emission of many individual compounds. These include the volatile organic compound (VOC) classes of alkanes, alkenes, aromatics, and oxygenated compounds. In addition, inorganic compounds are emitted that include carbon monoxide, carbon dioxide, oxides of nitrogen (nitric oxide and nitrogen dioxide) and other oxidized and reduced nitrogen compounds (e.g. ammonia and nitrous oxide), and sulfur dioxide. Primary aerosols are also emitted that contain heavy metals, elemental carbon, and low volatility organic compounds. The emission trends of these species reflect changes in population, transportation, energy usage by various sectors, and industrial processes, as well implementation of regulations to limit emissions.

For the years 1995, 2005 and 2015, France had annual anthropogenic NO_x emissions of 1.61, 1.24, and 0.88 Tg-y⁻¹ (Crippa et al., 2018; OECD, https://stats.oecd.org/Index.aspx?DataSetCode=AIR_EMISSIONS#). The United States emitted 21.1, 18.0, and 11.7 Tg-y⁻¹ for those same years (Crippa et al., 2018; EPA, <https://aqs.epa.gov/>; OECD). China, on the other hand, had emissions of 11.6, 20.4, and 26.9 Tg-y⁻¹ (Azimi et al., 2018; Crippa et al., 2018; Li et al., 2017; Zhao et al., 2013). Global anthropogenic NO_x emissions for the same three years are estimated at 94, 108, and 131 Tg-y⁻¹ (Crippa et al., 2018). Anthropogenic non-methane volatile organic compound (NMVOC) emissions have similar trends. The emissions for France in 1995, 2005 and 2015 were 1.85, 1.24, and 0.82 Tg-y⁻¹ (Crippa et al., 2018; OECD). For the United States, the values were 19.7, 14.8, and 13.0 Tg-y⁻¹ for the same years (Crippa et al., 2018; EPA; OECD). China had NMVOC emissions of 18.2, 22.5, and 32.3 Tg-y⁻¹ (Crippa et al., 2018; Li et

al., 2017), and global anthropogenic NMVOC emissions (including distribution leaks) were 191, 204, and 238 Tg-y⁻¹ for the same years (Crippa et al., 2018).

The trends in decreasing anthropogenic emissions in the United States and Europe are testimony to the success of regulations. Reduced emissions are also reflected in temporal changes in urban atmospheric composition (e.g. Crippa et al., 2018; Monks et al., 2015; Simon et al., 2015). Trends in global emissions are opposite due to increases in developing regions such as China, India and Africa.

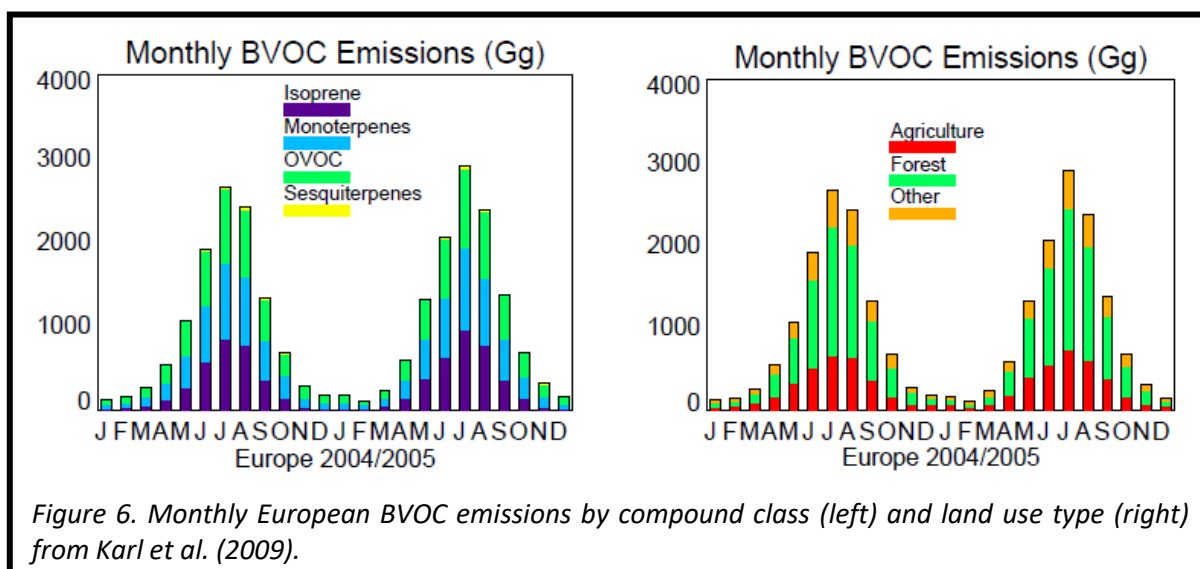
Biogenic Emissions

The biosphere emits a large variety of compounds into the atmosphere from the growth and burning of flora. These include emission of many hydrocarbons including alkanes, alkenes, alcohols, aldehydes, ketones, acids, and organic sulfur compounds (Guenther et al., 2012; Messina et al., 2016). Inorganic compounds including carbon monoxide, carbon dioxide, oxides of nitrogen, sulfur dioxide, and halogens are also emitted. Particles contain substances from wildfires (e.g. elemental carbon, organic compounds, sulfur compounds), those from soil due to mobilization of mineral dust containing mainly oxides and carbonates of common crustal elements, and sea salt containing mostly sodium chloride, but also other inorganic halogen compounds, sulfates, metal ions, and organic compounds. Emissions change in response to several factors including temperature, and to environmental factors such as available photosynthetic active radiation, temperature, leaf area, CO₂, soil moisture and other influences such as land use (Crippa et al., 2018; Guenther et al., 2012; Karl et al., 2009). Many substances undergo two-way exchange (emission and deposition) between the surface and the atmosphere.

Models have been developed that describe the emissions of several important atmospheric components from the biosphere (Bauwens et al., 2017; Guenther et al., 2012; Karl et al., 2009; Messina et al., 2016). These inventories are designed to quantitatively account for the factors that control the release and/or uptake of chemical species and thus to define temporally and spatially dependent speciated exchange rates.

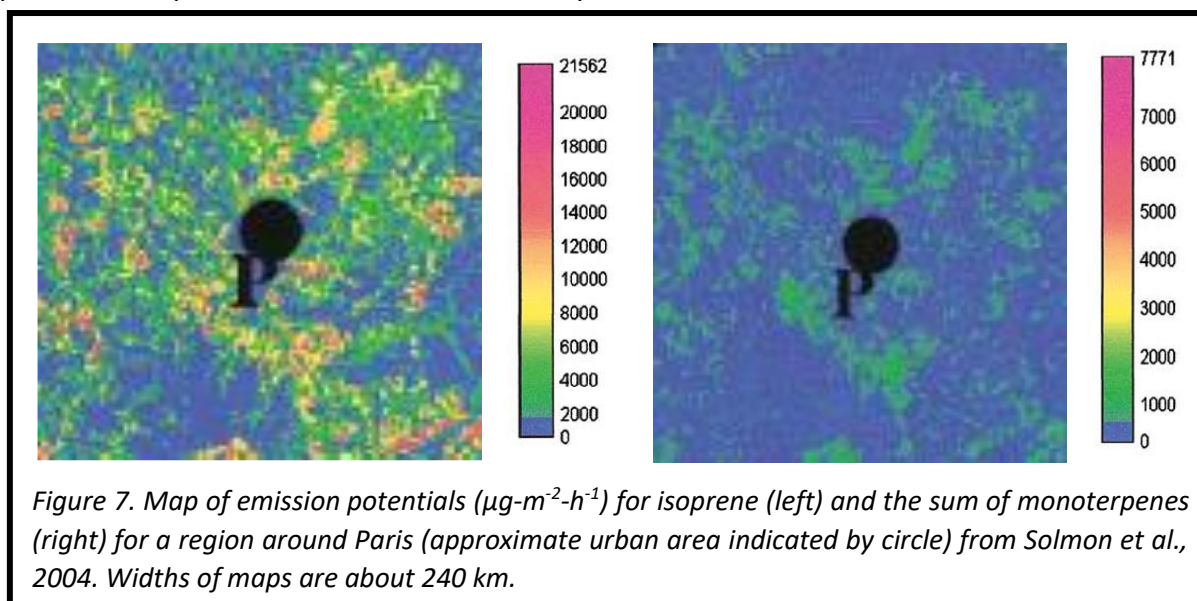
Isoprene (C₅H₈) annual emission rates in France are estimated at 478 Gg y⁻¹ for 2015 (Bauwens et al., 2017). Global emissions for 2015 are estimated in two recent studies at 530 Tg y⁻¹ for isoprene, in the range of 130 to 170 Tg y⁻¹ for the sum of mono- and sesquiterpenes (C₁₀ and C₁₅ compounds), about 160 Gg y⁻¹ for oxygenated VOCs, and totaling about 1000 Tg y⁻¹ (e.g. Guenther et al., 2012; Messina et al., 2016). The range of global emission values reported in the literature for BVOCs is large (isoprene 290-680 Tg y⁻¹, terpenes 47-188 Tg y⁻¹, and oxygenated compounds 107-205 Tg y⁻¹; from an analysis by Messina et al., 2016) indicating more work is needed to validate emission estimates. For comparison, see annual total anthropogenic NMVOC emissions discussed earlier. Biogenic VOC emissions have been estimated through model simulations to have increased slightly over the period 1979-2014, with isoprene increasing 0.76% y⁻¹ globally and 0.68% y⁻¹ in France (Bauwens et al., 2017).

Biogenic and anthropogenic emissions do have different spatial and temporal patterns, but it is expected that the global importance of biogenic NMVOCs from the consistent reduction in anthropogenic NMVOC emissions in developed countries systematically



increases the importance of isoprene and terpenes in atmospheric chemical processes. This could change the timing, abundance, location, and the identity of secondary photochemical products. Note that the global increase in anthropogenic NMVOC emissions, which is currently driven by the large increases in developing countries, implies that these locations have a different trend in the relative role of biogenic versus anthropogenic VOCs.

The factors mentioned earlier that affect emissions of VOCs and other compounds from the biosphere lead to temporal and spatial variations in emission rates. Karl et al. (2009) assessed the emissions of BVOCs over the whole of Europe and provided monthly emission amounts for classes of BVOCs (Figure 6, left) and for land use types (Figure 6, right) for the years 2004 and 2005. These calculations indicate peak emissions in July, with emissions slightly lower in June and August. Isoprene, the sum of monoterpenes, and the sum of OVOCs each contribute about one-third of the emission mass. Note that in the small contributions of sesquiterpenes in this analysis does not mean they are unimportant. Many compounds in this class are highly reactive and difficult to measure (Pollmann et al., 2005). They also tend to have large secondary organic aerosol (SOA) yields that further increases their potential importance despite low emission rates. In July, forest emissions are about 58% of the total,



agriculture contributes about 23%, and the remaining from other land use categories. These statistics do not necessarily apply to the region around Paris. Studies have indicated dominance of isoprene in BVOC emissions in the Paris area (Karl et al., 2009; Solmon et al., 2004) as shown in Figure 7.

Nitric oxide (NO) can be emitted by agricultural and other soils (e.g. Laville et al., 2009). Depending on the proximity to emissions of NO_x from fossil fuel combustion, biogenic sources of reactive nitrogen might not be significant. The forest canopy can also serve as a sink for atmospheric NO_x via chemical oxidation (Min et al., 2014). There have been reports of HONO (nitrous acid) emissions from soils due to bacterial activity (e.g. Oswald et al., 2013).

Tropospheric Chemistry

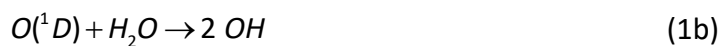
Tropospheric components can react with several oxidants: hydroxyl radicals (OH), nitrate radicals (NO₃), chlorine atoms (Cl), stabilized Criegee intermediates (sCIs) and ozone (O₃). Ground-state and excited state oxygen atoms (O(³P), O(¹D)) are present in the troposphere, but do not directly function as oxidants of important trace gases, rather they form O₃ and OH from reaction with O₂ and water vapor, respectively. All the oxidants can be operative depending on the time of day, the reaction partner, and the values for their reaction rate coefficients. As molecules are processed by the atmosphere, HO_x free radicals are produced (HO₂, RO₂, RO, OH). The chemical pathways for a given radical can involve radical-radical, radical-NO_x, and unimolecular processes. Different products are formed depending on which pathways are dominant (e.g. Seinfeld and Pandis, 2016; Stockwell et al., 2012; Wennberg et al., 2018). Some reactions are radical propagating (leading to radicals as products), while others are terminating (leading to radical reservoirs or long-lived products). In the sections that follow, the chemistry is discussed as related to each oxidant.

Hydroxyl Radicals (OH)

Hydroxyl radicals are produced in the troposphere from several photolysis and thermal reactions. In the remote atmosphere, the primary source of OH is from the photolysis of O₃ in the ultraviolet spectral region.



The electronically excited oxygen atom may be quenched to the ground state by collision with atmospheric components including nitrogen and oxygen. When it reacts with water vapor, two OH radicals are formed.



Other photolysis processes can contribute to the production of OH. These include photolysis of hydrogen peroxide (H₂O₂), nitrous acid (HONO).



Hydroperoxyl radicals (HO₂) react with NO to produce OH (reaction 2c below).

When OH reacts by abstraction of a hydrogen atom, an organic peroxy radical is formed.

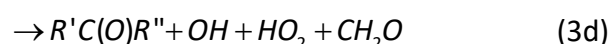


HO₂ radicals, which have chemistry like RO₂, are formed from a variety of processes involving OH, from photolysis (e.g. OH+CO, OH+CH₂O, CH₂O+hν), and from reaction of RO₂ radicals. Both RO₂ and HO₂ radicals react readily with NO:

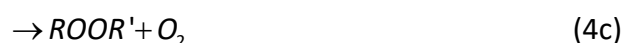


Alkoxy radicals (RO) from reaction 2a react with O₂, isomerize, or decompose to form other peroxy radicals or HO₂ (e.g. Carter et al., 1976) also producing a variety of other products. Alkyl nitrates are formed in minor channels (reaction 2b) that depend on the size of the R group and ambient temperature and pressure (e.g. Atkinson, 1997; Lightfoot et al., 1992; Zhang et al., 2004). Depending on their structure, organic peroxy radicals can isomerize (similar to alkoxy radicals) followed by addition of molecular oxygen that repeats in an autoxidation process leading to highly oxidized molecules (HOMs) defined as those having an O:C ratio of 0.7 or greater (Bianchi et al., 2019). HOMs often have low saturation vapor concentrations (C*) and can contribute significantly to new particle formation and to particle growth (Bianchi et al., 2019; Crouse et al., 2013; Praske et al., 2018; Pye et al., 2019).

Organic peroxy radicals also react with HO₂:



When reacting with HO₂, most alkyl RO₂ radicals form ROOH (reaction 3a), while acyl peroxy radicals (RC(O)O₂) branch to ROOH, OH, and O₃ (reactions 3a, 3b, 3c). Dienes (such as isoprene) react to primarily give ROOH (reaction 3a) but have a minor pathway to OH and HO₂ (reaction 3d). Peroxy radicals also react in self-reaction (with the same type of peroxy radical) and cross reaction (with a different type):

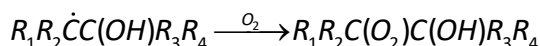
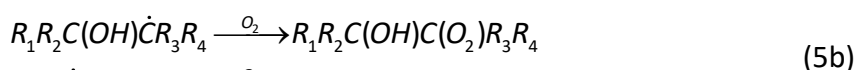
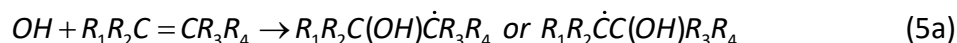


Most peroxy radicals branch between channels 4a and 4b (radical and molecular, respectively), while 4c does not seem to be operative with small peroxy radicals. RO₂ formed from monoterpenes, though, seem to form peroxide “dimers” readily (e.g. Zhao et al., 2018)

which, because of their low saturation vapor concentrations, can contribute significantly to SOA formation.

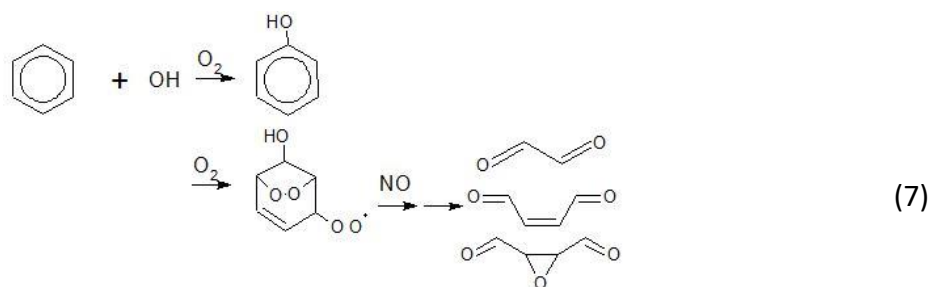
Peroxy radicals react with NO_2 in association reactions that lead to peroxy nitrates. This is well-known in the reaction of acyl peroxy radicals to form PAN and related compounds, but the reaction has been demonstrated for HO_2 and many RO_2 radicals and is likely operative for all RO_2 . There is a wide range of thermal stabilities for the peroxy nitrate products.

The oxidation of alkenes, like alkanes, can be initiated by reaction with OH leading to hydroxy-peroxy radicals.



Such chemistry is operative in the oxidation of BVOCs as many are unsaturated.

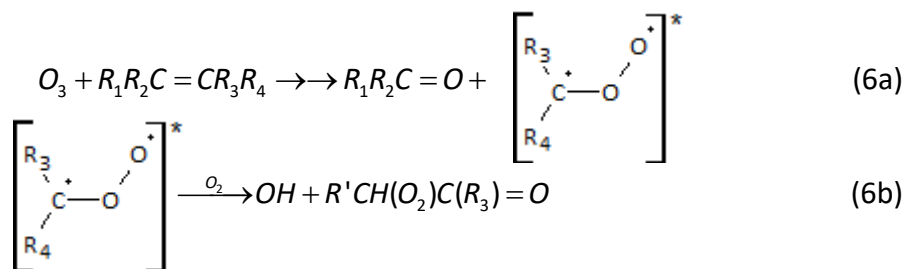
Aromatic compound oxidation can be initiated by OH radicals through reaction with a side chain (as above for alkanes or alkenes) or with the ring in pathways that produce a variety of products (e.g. Wang et al., 2017). As an example, when benzene reacts with OH, phenol, peroxides, nitrates, and ring-opening products are produced, many of which can be incorporated into aerosols.



Ozone (O_3)

Ozone is present in the troposphere because of transport from the stratosphere and due to in situ production. Ozone is produced when NO_2 is photolyzed followed by oxidation of NO by peroxy radicals (reactions 2a and 2c). Since the latter is usually the rate limiting step, then the gross rate of ozone production is simply the rate of NO oxidation by peroxy radicals. As an example, Thornton et al., 2002 used data collected near Nashville, and derived a midday average gross ozone production rate ($P(\text{O}_3)$) of about $5 \text{ pptv}\cdot\text{s}^{-1}$ or $18 \text{ ppbv}\cdot\text{hr}^{-1}$. Ozone is destroyed through photolysis to $\text{O}(^1\text{D})$ (reaction 1a) followed by reaction with water vapor (reaction 1b) and by reactions with OH and HO_2 . The net ozone tendency (production minus loss) depends on NO concentrations and varies from net loss in remote environments to net production in continental rural and urban locations.

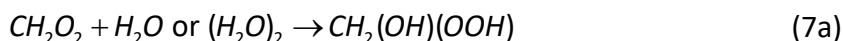
Under tropospheric conditions, alkanes do not react with ozone at a significant rate. Reaction of alkenes with O_3 leads to formation of carbonyl compounds and energetic Criegee intermediates. The latter can decompose or be stabilized and undergo further reaction with atmospheric components. Decomposition leads to OH and a carbonyl-substituted peroxy radical (only one isomer of carbonyl and peroxy radical shown).



Stabilized Criegee intermediates (sCI)

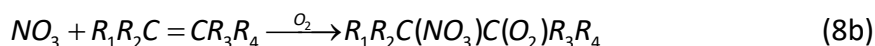
Stabilized Criegee intermediates (sCIs) are produced in the oxidation of alkenes by O_3 , as discussed above. They have reactivities that depend on their structures. One factor is possible syn- or anti- conformers possible depending on the structure of the organic group. sCIs can react with water vapor (including the water dimer), SO_2 , carbonyl compounds, alkenes, NO_2 , and organic acids (Khan et al., 2018 and references therein). They can also rearrange through hydrogen shift and ring closure reactions (Lester and Klippenstein, 2018 and references therein).

When the 1-carbon sCI (formed in the ozonolysis of 1-alkenes including isoprene) reacts with the water monomer or dimer, the following pathways are possible. The product distribution favors channel 7a leading to hydroxymethyl hydroperoxide for reaction with the monomer, and channel 7c for reaction with the dimer (Nguyen et al., 2016)



Nitrate radicals (NO_3)

Nitrate radicals (NO_3) are formed from the reaction between NO_2 and O_3 . They are formed day and night, but their concentrations are reduced during daytime because of their rapid photolysis and reaction with NO . They react with alkenes through addition to the double bond, and with aldehydes by abstraction.



Further reaction of organic nitrate peroxy radicals (reaction 8b) can lead to organic nitrate alcohols, organic nitrate carbonyls, and organic nitrate hydroperoxides (e.g. Yeh et al., 2015).

NO_3 radicals can produce dinitrogen peroxide (N_2O_5) by their association with NO_2 . N_2O_5 is thermally unstable and decomposes at a rate that is highly temperature dependent (e.g. Cantrell et al., 1993; Ide et al., 2008).

Chlorine atoms (Cl)

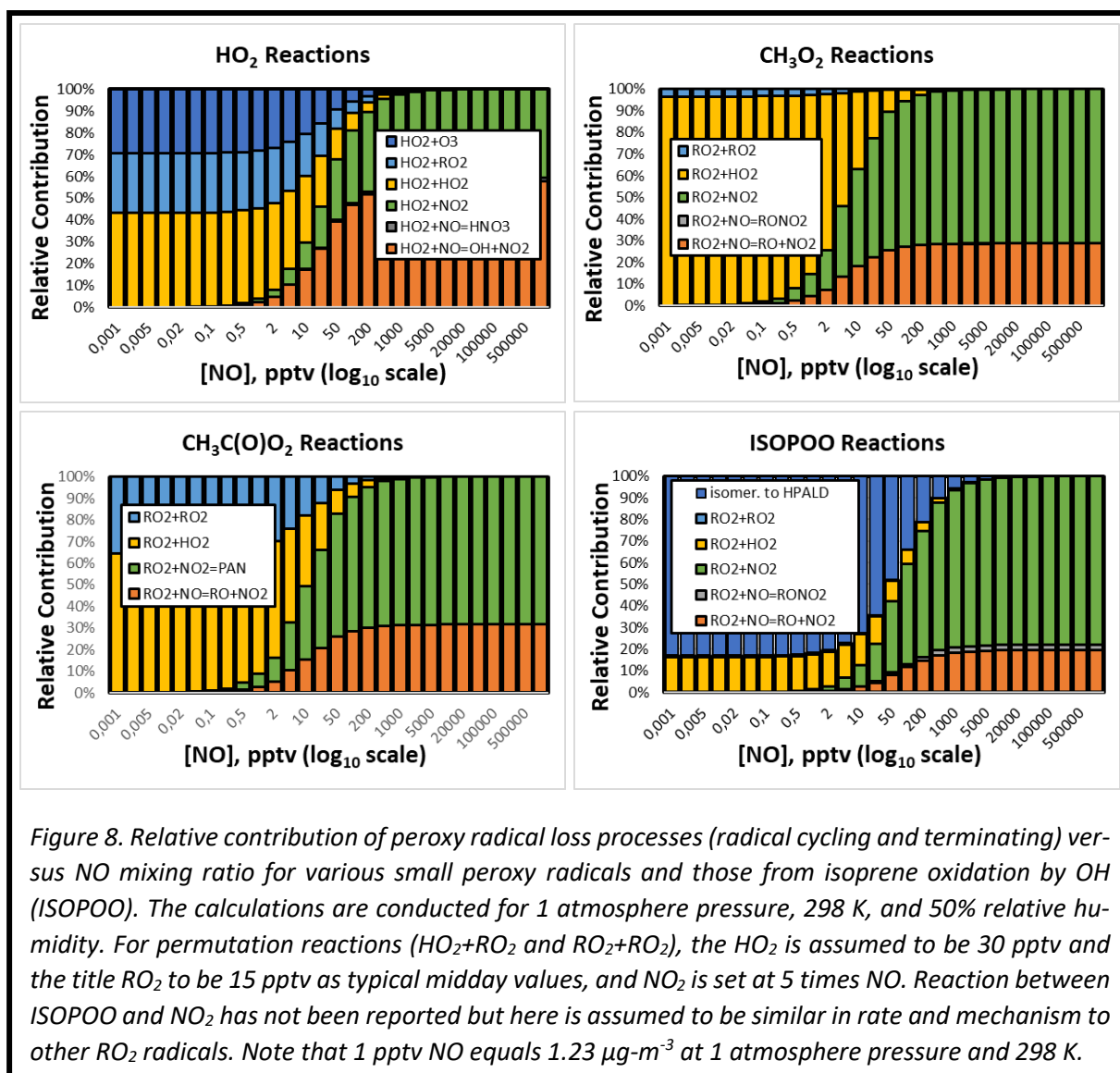
Chlorine atoms are produced in the photolysis of inorganic chlorine compounds such as $ClNO_2$ and Cl_2 , which are formed in heterogeneous reactions between N_2O_5 or $ClONO_2$ and

sea salt. They are also formed in acid displacement reactions between acids and sea salt, and from the reaction of OH with HCl (Wang et al., 2019b)

Chlorine atoms react like OH (abstract from alkanes and add to alkenes) but are less selective in which hydrogen atoms are abstracted, potentially leading to different product distributions. Peroxy radicals formed from oxidation initiated by chlorine atoms react like those formed from other oxidants and can, depending on their structures, also undergo autoxidation.

Implications

Tropospheric chemistry, through the action of various oxidants, produces secondary products such as O₃, oxygenated VOCs (OVOCs) and SOA (e.g. Curci et al., 2009; Pandis et al., 1992; Sicard et al., 2016; van Dingenen et al., 2004; Zong et al., 2018). As oxidation of VOCs takes place, products of the reactions are VOCs that contain more oxygen (increase in O:C ratio and decrease in H:C ratio) and those that undergo fragmentation (C-C bond cleavage). In addition to being chemically reactive, many OVOCs are readily photolyzed, sometimes to produce additional free radicals (e.g. Bouzidi et al., 2014). Also, as VOCs become more



oxidized, their volatility is reduced, and they can contribute to NPF and particle growth (e.g. Bianchi et al., 2019; Grosjean and Seinfeld, 1989; Heisler and Friedlander, 1977; Kerminen et al., 2018; McMurry and Grosjean, 1985; Ziemann and Atkinson, 2012).

Using known rate coefficients for the chemical reactions discussed earlier, the relative roles of peroxy radical-NO_x reactions versus peroxy radical self and cross reactions as a function of NO for various representative peroxy radicals are shown (Figure 8). It can be seen that for small peroxy radicals at NO levels less than about 10-30 pptv, radical permutation reactions dominate, while reactions with NO_x dominate at higher NO amounts. Interestingly, the transition from low-NO to high-NO chemistry for isoprene-derived peroxy radicals is calculated to occur around 50 to 100 pptv. Thus, urban atmospheres are represented by the dominate processes at high NO values (daytime NO values 10 to 100s $\mu\text{g}\cdot\text{m}^{-3}$), whereas remote atmospheres undergo processes at low NO amounts (1 to 10 $\text{ng}\cdot\text{m}^{-3}$). Continental rural atmospheres are represented by intermediate NO conditions (50 to 500 $\text{ng}\cdot\text{m}^{-3}$).

Table 1. Summary of literature-reported impacts of various parameters on SOA yields (at $C_{\text{OA}} = 10 \mu\text{g}\cdot\text{m}^{-3}$) for α -pinene. Symbols indicate positive (+) or negative (-) correlation between organic aerosol yield and the parameter.

| Reference | SOA yield | Oxidant | NO _x | VOC | VOC/ NO _x | HO ₂ / RO ₂ | OH | UV |
|-------------------------|-----------|-------------------------|-----------------|-----|-------------------------|--------------------------------------|----|----|
| Eddingsaas et al., 2012 | 0.07-0.37 | OH | - | | | | | |
| Han et al., 2016 | 0.04-0.35 | OH | - | | | | | |
| Henry & Donahue, 2011 | 0.15 | O ₃ | | | | + | | |
| Henry et al., 2012 | 0.17 | OH | | | | | + | |
| Henry et al., 2012 | 0.08 | O ₃ , OH | | | | | | |
| Lane et al., 2008 | 0.06 | OH | - | | + | | | |
| Ng et al., 2007 | 0.07-0.46 | OH | - | | | | | |
| Presto et al., 2005 | 0.0-0.3 | O ₃ | - | + | + | | | - |
| Stirnweis et al., 2017 | 0.05-0.11 | O ₃ , OH | - | | | | | |
| Zhao et al., 2018 | 0.02-0.10 | OH | - | | | | | |
| Zhao et al., 2018 | 0.10-0.13 | OH (w/SO ₂) | ~0 | | | | | |

What impact do NO_x levels have on yields of secondary organic aerosols and rates of new particle formation (NPF) from organic compounds? Current evidence indicates that SOA formation is suppressed at high NO_x, but there is evidence that at least part of this may be an indirect effect due to changes in OH levels (Zhao et al., 2018). There are also interesting effects of SO₂ amount, temperature, relative humidity, ultraviolet (UV) light, oxidant type, and ratios of peroxy radicals. Representative reports of SOA yields from the oxidation of α -pinene are summarized in Table 1. Such studies have been conducted for several anthropogenic and biogenic hydrocarbons including isoprene (Fry et al., 2018; Song et al., 2018), other monoterpenes (Ng et al., 2007; Sarrafzadeh et al., 2016; Zhao et al., 2015, 2018), aromatics (Izumi and Fukuyama, 1990), alkanes (Aimanant and Ziemann, 2013; Li et al., 2019), alkenes (Liu et al., 2017, 2019), aldehydes (Chacon-Madrid et al., 2010; Chan et al., 2010), and other compounds (Algrim and Ziemann, 2016, 2019). Also, Wildt et al. (2014) and Zhao et al. (2018) report that NPF from monoterpenes is inhibited by the presence of NO_x due to reaction of peroxy radicals with NO, consistent with the observations in other studies of reduction in SOA yields with

increasing NO_x. McFiggans et al. (2019) have reported that monoterpene aerosol yields are reduced by increases in isoprene, carbon monoxide and methane.

Paris Air Composition – Current State and Recent Trends

The composition of air within the Paris metropolitan area and the surrounding region has been monitored for some time. This includes roadside measurements as well as observations of the more general composition. Figure 9 shows trends in one-year average concentrations of several key primary and secondary compounds from several roadside monitoring stations within Paris (Airparif, 2018). For comparison, data for roadside stations (one per city) in Denver, New York, and Los Angeles are shown (EPA, <https://ags.epa.gov>). In the past decade, the overall trends of most of the species shown are negative, except for O₃. These are continuations of earlier trends. For example, the annual average roadside concentration of CO for Paris was 18 mg·m⁻³ in 1998; the value decreased systematically from 1998 to 2008.

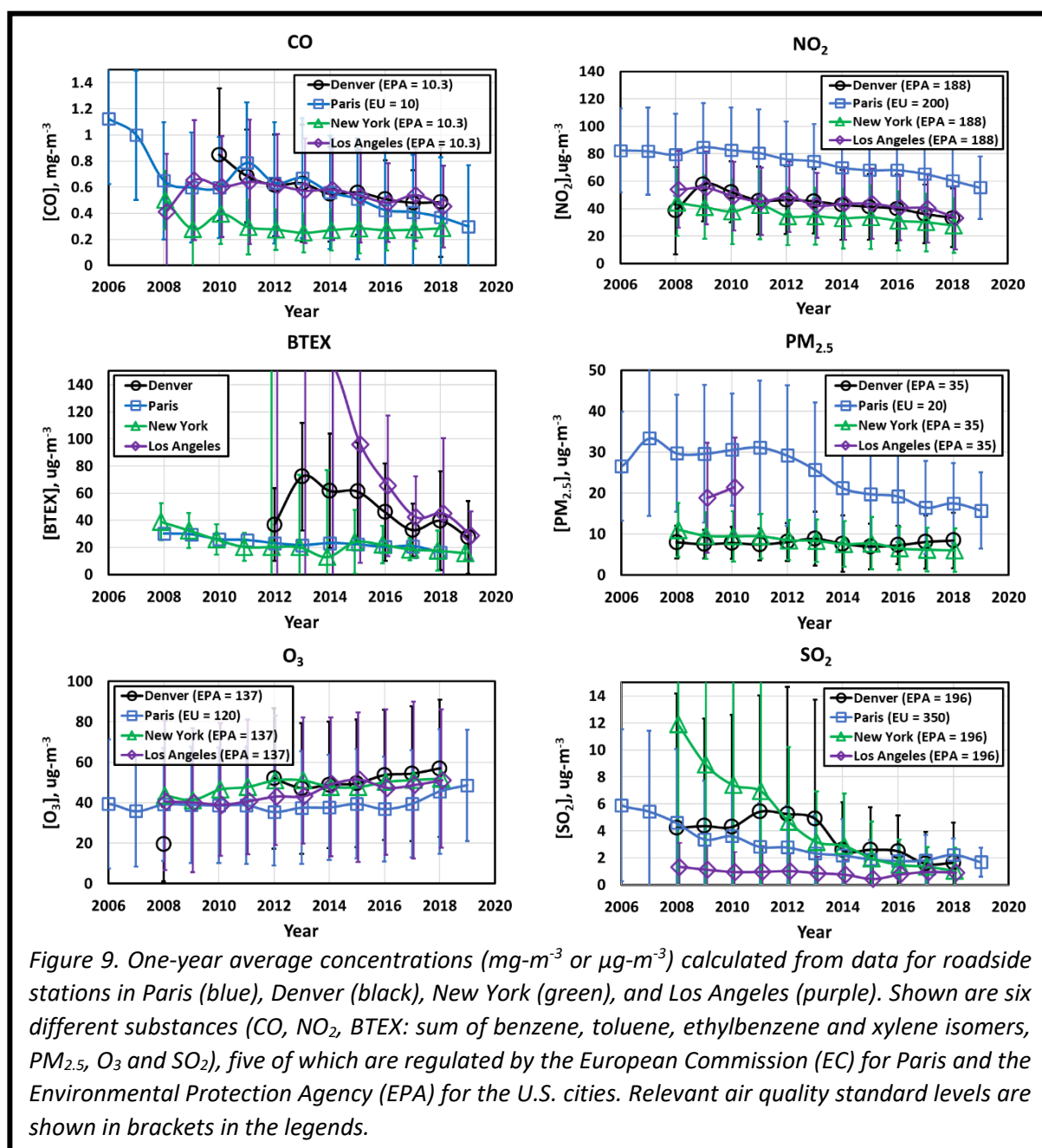
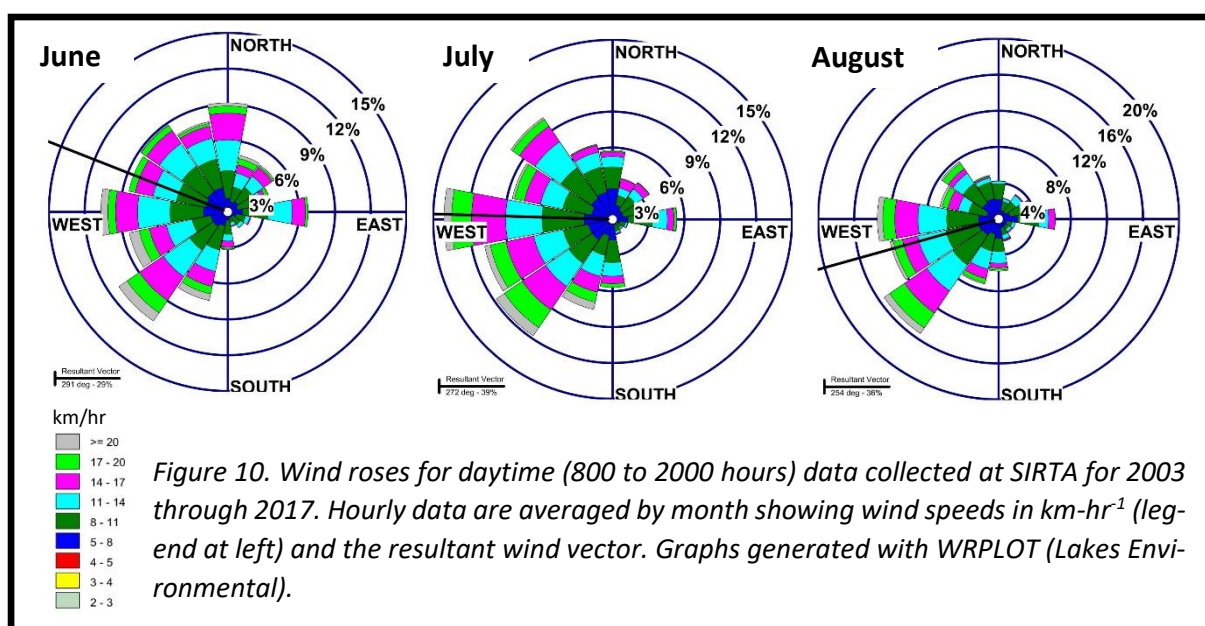


Figure 9. One-year average concentrations (mg·m⁻³ or µg·m⁻³) calculated from data for roadside stations in Paris (blue), Denver (black), New York (green), and Los Angeles (purple). Shown are six different substances (CO, NO₂, BTEX: sum of benzene, toluene, ethylbenzene and xylene isomers, PM_{2.5}, O₃ and SO₂), five of which are regulated by the European Commission (EC) for Paris and the Environmental Protection Agency (EPA) for the U.S. cities. Relevant air quality standard levels are shown in brackets in the legends.

Thus, we expect on average a different chemical situation now and into the near future compared to the time periods of the ESQUIF and MEGAPOLI measurement campaigns. For example, NO₂ levels decreased by 24%, CO levels by 43% and BTEX levels by 46% from 2008 to 2018. Note that these one-year averages smooth out air quality episodes and seasonal changes, so they are not directly representative of conditions during specific times of the day and year. Also shown in Figure 9 are the US EPA and European Commission (EPA; EC) air quality standards for five of the quantities.

The trends in urban air composition mostly result from reductions in emissions, but also depend on meteorological conditions in a given year and their impacts on episodes of poor air quality. Ozone amounts are correlated with temperature, so when there is a heat-wave, the ozone concentration usually increases. Changes in ozone depend on the regime of a particular urban area which is based on the abundances of precursors NO_x and VOCs and is categorized as NO_x-limited or VOC-limited with a transition regime in between (Wang et al., 2019a). When an air mass is NO_x-limited, reductions in VOC emissions have little effect on ozone. For VOC-limited conditions, NO_x emission reductions do little to reduce O₃, and can even have the opposite effect. The situation is complex because an urban area can change regimes during a day. Particulate matter in urban regions comes from a combination of direct emission and amounts that are formed in the atmosphere from photochemical processing of precursors such as NO_x, VOCs, and SO₂. Research is still being conducted to develop detailed understanding of the dependence of particle formation and growth on precursors amounts and other controlling factors.

Human health is impacted by elevated levels of atmospheric components. In France for the year 2014 (EEA Report, 2017), it has been estimated that there were 27 000 to 35000 premature deaths from high PM_{2.5} levels, 9 000 to 23 000 from NO₂, and 1600 from O₃. The range of values depends on the assumption of the lowest value which has no effect on premature death.

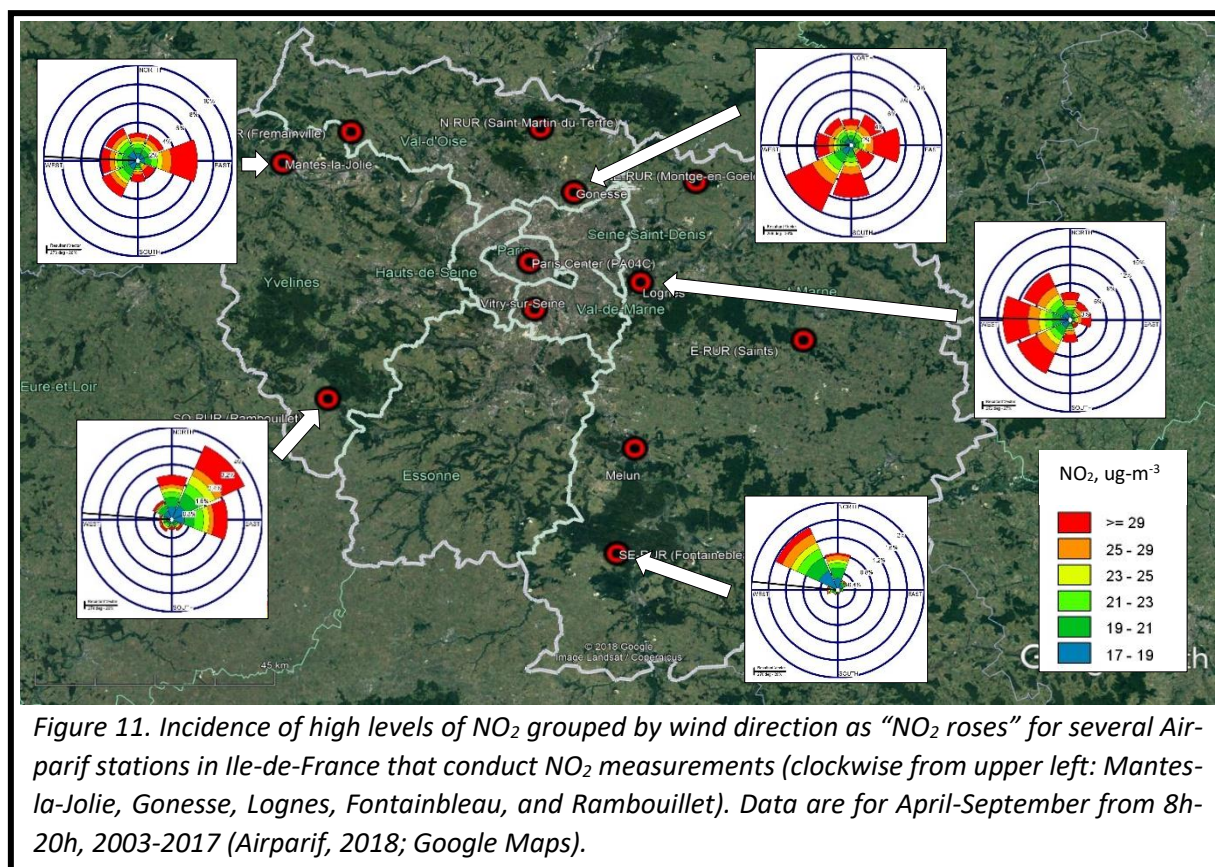


Location of a Ground-Based Supersite

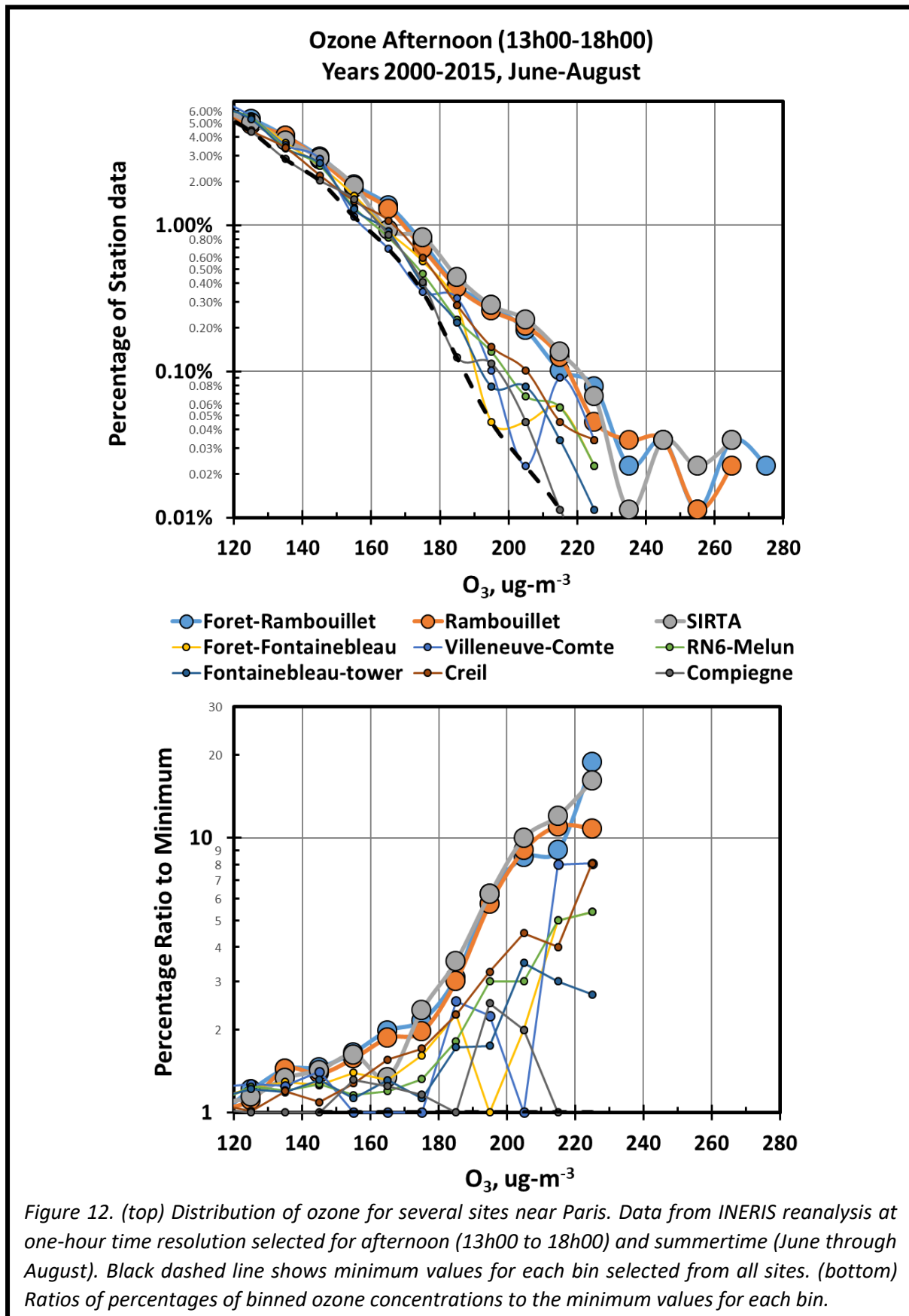
The following section provides information related to selection of a ground-based site as the focus for observations of atmospheric composition to address scientific questions related to mechanisms of air quality evolution from the interaction of urban air with nearby biogenic emissions.

Paris pollution is transported by the varying wind direction associated with specific meteorological conditions (Airparif, <https://www.airparif.asso.fr>; Airparif, 2018; Haeffelin et al., 2005; SIRTa, sirta.ipsl.fr). SIRTa is an intensive measurement site located about 18 km southwest of the center of Paris, in Palaseau. An analysis of data collected in 2003 through 2017 shows that the monthly average wind direction is quite variable from year to year. In daytime (8h to 20h) on average, it changes systematically from northwest to southwest through the summer (Figure 10). As an indication of the annual variability, the mean wind vector for June through August was 231°, 312°, 281°, 272°, 269°, 246° for years 2012 through 2017, respectively, and averaged 271° for all years. While such data give information about the average air flow around Paris, it does not indicate the meteorological conditions and associated trace component abundances for various wind directions.

To help to better understand the export of pollution from Paris during high pollution episodes, “NO₂ roses” were constructed. These are like wind roses, except that the lengths of the petals are proportional to NO₂ concentrations. They are based on SIRTa wind directions and NO₂ levels from Airparif for several stations surrounding Paris (Figure 11). To clearly show the instances of high amounts, the NO₂ ranges are adjusted to highlight the statistics for the highest NO₂ levels (>17 ug-m⁻³). For the five stations shown, air masses originating from the



Paris urban area have NO₂ concentrations that are consistently larger than from other directions. The two northern and the eastern stations do show some instances of enhanced NO₂

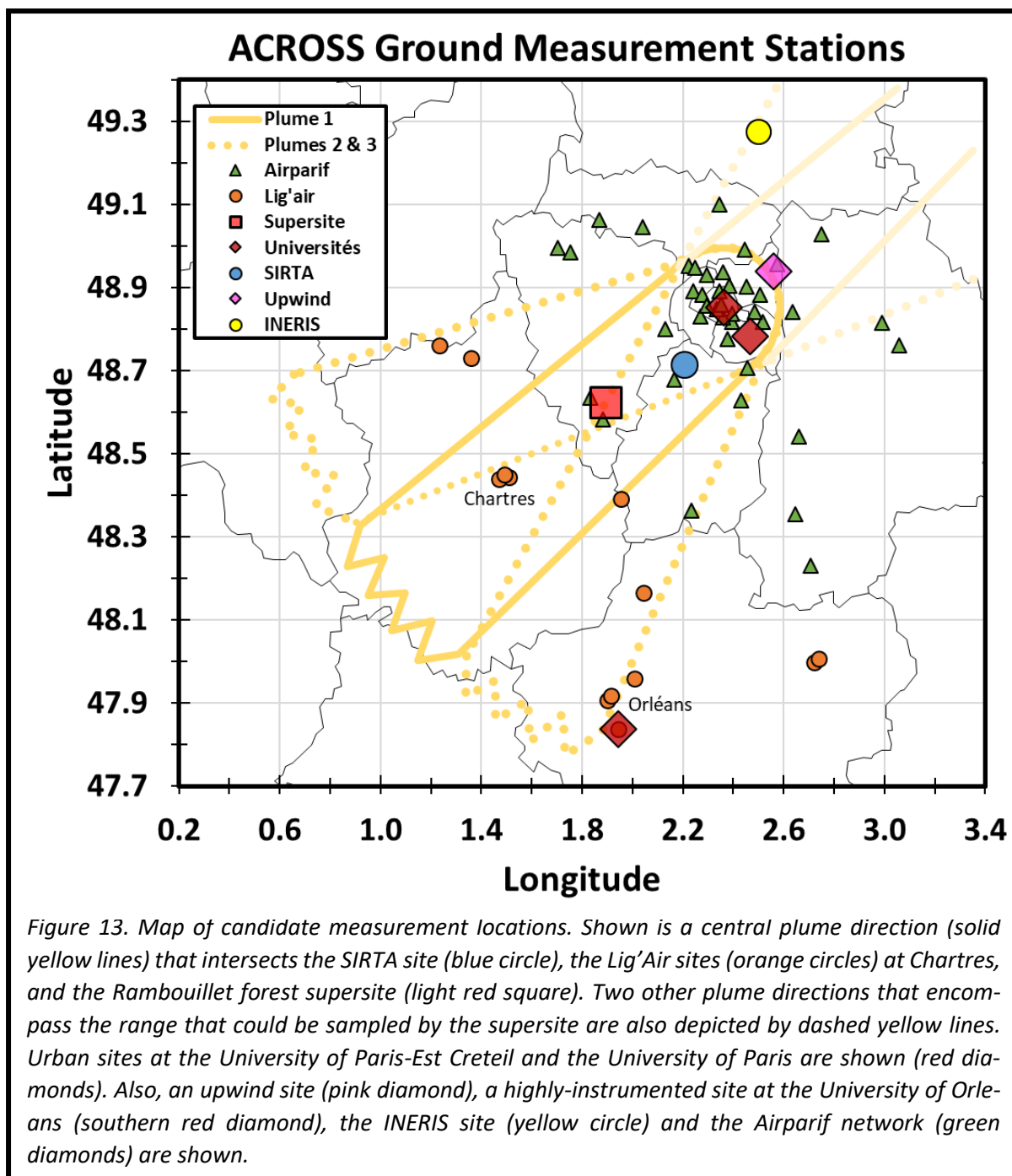


from other directions, probably from local emissions. The southeast and southwest stations show the clearest separation between high NO₂ air transported from Paris and air with lower NO₂ levels from elsewhere, with the southwest station (Rambouillet) receiving 76% of high levels from the Paris direction, and the southeast station (Fontainebleau) receiving 85%. The other three stations (Mantes-la-Jolie, Gonesse, and Lognes) have 33%, 45% and 67% of high NO₂ instances from Paris, respectively. The balance of instances is likely from local sources and recirculation of Paris air.

To aid in the selection of the ACROSS ground-based supersite, sixteen years (2000-2015) of surface ozone data at several Paris suburban sites were analyzed. These data were provided by INERIS (<https://www.ineris.fr/en>) and were processed through reanalysis, which resulted in data in a grid with 4 km resolution and one-hour averages. Several sites were selected as having the following characteristics: location in or near a forested area, located near existing infrastructure (e.g. operational or research measurement sites), and located 40-60 km from the Paris city center. Candidate sites included two locations near Rambouillet, three locations near Fontainebleau, SIRTA, two locations north of Paris (Creil and Compiègne), and one east of Paris (Villeneuve-le-Comte). For the statistics presented here, data were selected for afternoons (13h00 to 18h00) in June through August for each station and were averaged into 10 µg-m⁻³ bins to generate probability distributions. Figure 12 (top) shows the high tail of the probability distributions (>120 µg-m⁻³) of ozone for each site. The high concentration sides of the distributions are of interest, because those indicate outflow from Paris arriving at the sites at times of photochemical activity leading to production of ozone. There can also be impacts from regional pollution, but these are expected to affect all these sites about the same. Each station has 8832 one-hour ozone concentrations for the summer months in the afternoon. The sites are sorted in the legend by the percentage of data greater than 120 µg-m⁻³, largest to smallest. For reference, there are only one to three data points per bin (0.01 to 0.03%) at all sites for ozone concentrations greater than 230 µg-m⁻³. A probability of 0.1% corresponds to 9 one-hour data points per bin, and 1% is 88 points at a given site. In an average year, there are 15-28 hours of ozone greater than 150 µg-m⁻³ in the afternoon during the summer months at each site.

Three sites stand out as having higher probabilities of high ozone concentrations in Figure 12. These are the two Rambouillet and the SIRTA sites. To compare the various locations, the binned percentages from the probability distributions are ratioed to the smallest station value for that bin (Figure 12, bottom). The minimum bin values are shown by the black dashed line (Figure 12, top). The ratios reinforce the conclusion that the sites southwest of Paris have the highest ozone probabilities. For the higher concentration ozone bins (150-230 µg-m⁻³), these sites have factors of two to 20 greater probabilities than the minimum values, and they are consistently higher than the data from the other sites. For all data in this range (>150 µg-m⁻³), the total probabilities for the southwest sites are factors of 1.8 to 1.9 larger than for the lowest station (Villeneuve-le-Comte). The total probability ratios for the other stations range from 1.1 to 1.4.

The evidence favors placing the ACROSS tower supersite within the Rambouillet forest, which allows the highest probability of sampling the Paris plume with significant ozone



production while mixing with biogenic emissions. With this decision, the development of a measurement strategy that includes multiple stations along the transect between the center of the Paris emission region and Rambouillet. For a 30-40 km wide urban plume, a site in the Rambouillet forest (light red square), the measurement sites at SIRTA (blue circle), urban sites at the University of Paris-Est Creteil and the University of Paris (northern red diamonds), several of the Airparif stations (green triangles), an upwind station (pink triangle), and the Lig'Air stations at Chartres (orange circles) can expect to receive the urban plume over a range of wind directions from about 40 to 65 degrees. Wind directions from about 25 to 70 degrees will intercept these stations except Chartres but would be covered by a station at the University of Orléans (southern red diamond) for more northerly wind directions and other Lig'Air stations for more easterly winds. Candidate measurement locations, along with the full

Airparif air quality network and the northern part of the Lig'Air network (<https://www.ligair.fr>) along with three plume directions (yellow solid and dashed lines) covering a range of acceptable wind directions, are shown in Figure 13.

Characteristics of a Suburban Forest Observation Campaign

A field campaign designed to examine the interaction of the Paris urban plume with a distinct region of strong biogenic emissions is proposed to address the issues discussed. While there have been studies of this phenomenon in other areas of the world, the Ile-de-France region represents a unique situation with the Paris megacity relatively isolated from other urban centers and located near forested and agricultural regions. The Paris plume has been studied in the past, so there is considerable experience in understanding its evolution. The population of Paris ranks it among the largest European megacities. Like other large developed cities, it has shown significant reductions in levels of common pollutants (NO₂, CO, SO₂) in the last 10-20 years. This suggests that studies need to be continued to be performed to evaluate the effects of these reduced anthropogenic emissions on the location, timing, and levels of primary and secondary pollutants. The ACROSS measurement campaign will focus on contrasting the chemical evolution of urban-only, biogenically-influenced-only, and mixed urban-biogenic air masses to determine the extent of current understanding of impacts of BVOC oxidation when mixed with urban emissions.

Such a project must be well thought out in several aspects. Factors include defining scientific goals, determining the timing of intensive observation period(s), selecting types and locations of sampling platforms, prioritizing observations to be made aboard each platform, applying a variety of numerical models for forecasting and analysis, and identifying principal investigators responsible for each observation and model approach. In addition, it will be important to have procedures in place for many aspects of the campaign including those for deciding on timing and location for deploying platforms (particularly aircraft), methods for communicating with the science team, other decision-making policies, dealing with emergencies, and protocols for comparisons of similar observations and models. Each of these aspects involves several tasks that will ensure that they are accomplished in a manner most productive to success of the campaign and leading to the highest quality scientific outcomes. Some of these aspects of the campaign are presented in this document, and more complete details of the campaign planning and organization are included in the Experimental Plan document.

Overarching Scientific Questions

Scientific questions form the foundation of activities for ACROSS. The questions will lead to development of specific scientific goals and related hypotheses that will be tested by the design of the campaign and the analysis of the observations. Defining the scientific basis of the project will help to determine the types of measurements required and the appropriate methods of data analysis. The questions are grouped by chemical environment category (reactive nitrogen, free radicals, organic carbon, aerosols, and modeling) and also labeled as to their relevance in various environments (urban, biogenic, and mixed).

Reactive nitrogen chemistry and budgets:

- How large are urban and rural sources of NO_x? Are emission rates consistent with current inventories? (U, B)
- Is O₃ production within urban, biogenic and mixed environments NO_x- or VOC-limited? (U, B, M)
- Are the amounts and budgets of sink and reservoir species (i.e. HNO₃, organic nitrates, PNs, PANs) quantitatively understood? (U, B, M)
- How important are nitrogen-containing compounds in formation and growth of SOA? (U, B, M)
- Are there unknown processes that recycle sink nitrogen to NO_x? (U, B, M)
- How have recent changes in urban NO_x emissions affected atmospheric chemical pathways? What are the impacts of these changes on air quality? (U)
- What are the roles of HONO in NO_x and HO_x budgets? What are the urban and rural sources of HONO? (U, B, M)
- How do O₃ production and SOA formation and growth compare between urban, biogenic and mixed environments? (U, B, M)
- What are the temporal and spatial variabilities of NO₃ radicals and what are their roles in oxidation chemistry within the urban boundary layer (U), the forest understory, canopy and above (B), and in mixed urban-biogenic air masses (M)?

Free radical chemistry and budgets (OH, HO₂, RO₂, NO₃):

- How do the calculated loss rates of OH and NO₃ determined from individually measured reactants compare with directly measured total loss rates? What are the compounds or classes of compounds that can explain any differences? (U, B, M)
- Over the range of observed NO levels, what are the loss pathways for radicals, and are the changes reflected in the observations of sink species (e.g. HNO₃ and H₂O₂, RONO₂ and OVOCs)? (U, B, M)
- Do observed radical levels agree with box model constrained values? What are the causes of any differences? How do these compare with results from chemical transport models? (U, B, M)
- How important are recycling reactions of HO_x radicals in various environments? (U, B, M)

Organic carbon chemistry and budgets:

- What are the contributions of individual organic compounds and classes of compounds in various environments to SOA amounts? To RO₂ levels? To OVOC levels? (U, B, M)
- What are the contributions of different oxidants to the degradation of classes of organic compounds? (U, B, M)
- Do organic compound lifetimes agree with observed and calculated radical levels? (U, B, M)
- Are there species that can be used as tracers of carbon oxidation chemistry in various environments? (U, B, M)
- How do oxidation pathways vary with NO_x levels in various environments? (U, B, M)
- How quickly is carbon from a given compound or class of compounds converted to SOA for various atmospheric conditions? (U, B, M)
- How do the optical properties of SOA change with types of precursor organic compounds, HO_x levels, NO_x levels and other factors? (U, B, M)
- How do ozone production rates vary with the types of organic compounds present for given NO_x amounts and VOC reactivities? (U, B, M)

- Which emitted compounds play the most important roles in controlling oxidation and secondary product formation? (U, B, M)

Formation and growth of aerosols and their impacts:

- How does the mixing of biogenic emissions with an urban plume affect the rates and pathways for organic aerosol formation and growth? (M)
- How do measurements and constrained models compare in estimating the role of organic carbon compounds in aerosol formation and growth in various environments? (U, B, M)
- How do the optical properties of aerosols vary with chemical composition? (U, B, M)
- How does the chemical composition of aerosols affect their efficiency as condensation nuclei? (U, B, M)
- How do different oxidants affect aerosol properties? (U, B, M)
- Is it possible to quantify specific organic compounds in both the gas- and aerosol-phases? Do these compounds partition as expected? Can growth rates be quantitatively determined from this information? (U, B, M)
- How can the organic components of aerosols be better represented (beyond HOA, OOA, OPOA, BBOA, etc)? How can this representation be linked with health impacts of aerosols? (U, B, M)
- What are the conditions necessary to observe NPF in various environments? (U, B, M)

Modeling of gas-phase photo-chemistry and particle evolution:

- Do biogenic VOCs affect the production of secondary species in mixed environments? (M)
- Are emission inventories suitable to account for biological, technological or other changes in the context of climate change? (U, B, M)
- Do current parameterizations in 3D model chemical codes accurately predict both secondary photo-oxidants and secondary particles? (U, B, M)

Timing

The timing of the ACROSS campaign will be optimized by consideration of the statistics of meteorological parameters including wind direction, air temperature, and atmospheric structure, as well as the availability of platforms and collaborators, and the

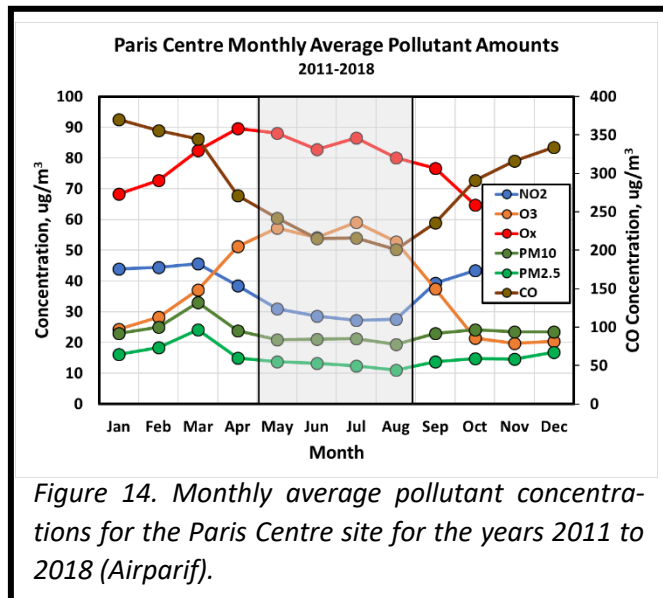


Figure 14. Monthly average pollutant concentrations for the Paris Centre site for the years 2011 to 2018 (Airparif).

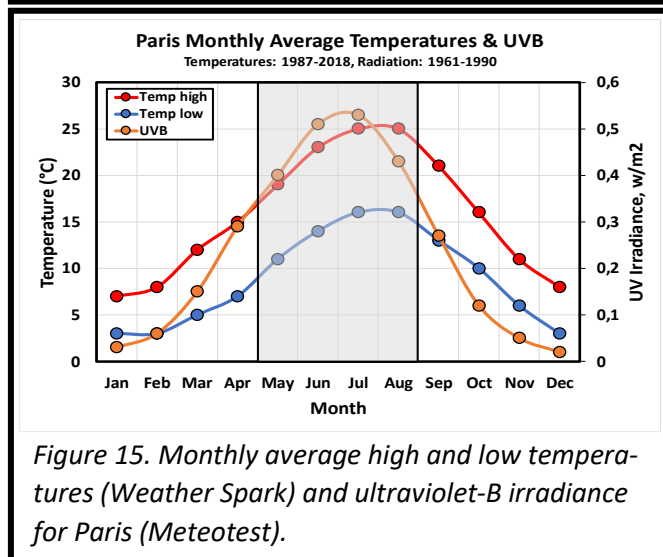


Figure 15. Monthly average high and low temperatures (Weather Spark) and ultraviolet-B irradiance for Paris (Meteotest).

temporal emission patterns of nearby forests (see Figure 6). This is developed and justified in the ACROSS Experimental Design document. We expect to focus on the mid-summer period when photochemistry activity is maximum (solar radiation that drives photolysis processes peaks in May through August) and biogenic emissions are large (peaking in June through August). Figure 14 shows monthly average amounts of common pollutants (Airparif). For the late spring and summer periods, average levels are relatively constant. Relative to winter, ozone is elevated while CO and NO₂ are depressed. Presented in Figure 15 are monthly average high and low temperatures, and monthly average ultraviolet-B (UVB) irradiance which are indicators of biogenic emission rates and photochemical activity (Weather Spark and Meteotest). These data support the selection of May through August as optimum months for the ACROSS field campaign. It is currently planned for summer of 2022.

Platforms and Locations

Several platforms for observations are envisioned for ACROSS. These include one or more aircraft, a stairway tower, tethered balloons and/or drones, and mobile platforms. Data from existing air quality networks will also be used. Some details of these platforms are described the following sections. See map of locations in Figure 13.

Aircraft

The largest research aircraft in the French fleet (SAFIRE brochure: <https://www.umr-cnrm.fr/IMG/pdf/safireenglish.pdf>; SAFIRE web page: www.safire.fr) is the ATR 42 that can carry 1500 kg at 100 m s⁻¹ for 4.5 hours (or more weight for a shorter time period). We anticipate outfitting it with many instruments and minimal operators to make observations needed to address ACROSS scientific questions. The details of the instruments are discussed later.

The general observational strategy with the aircraft in ACROSS is to observe the spatial and temporal abundance of key species related to the formation of ozone, SOA, and other secondary chemical products. This will likely involve flight patterns like those used in MEGAPOLI and other urban studies (e.g. Zhang et al., 2015; see Figures 5 and 16 herein). The urban plume will be sampled by transects approximately perpendicular to the plume direction of flow. These will be performed at various distances and altitudes both upwind and downwind of the urban

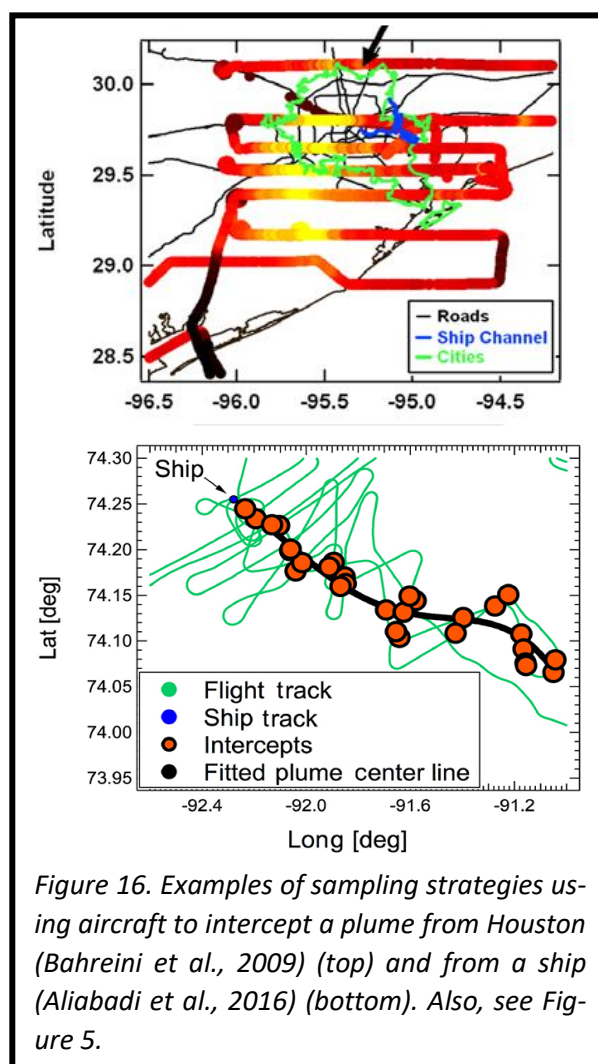


Figure 16. Examples of sampling strategies using aircraft to intercept a plume from Houston (Bahreini et al., 2009) (top) and from a ship (Aliabadi et al., 2016) (bottom). Also, see Figure 5.

region and in areas of active biogenic emissions. Sampling plumes that intersect the location of the tower platform are of highest priority, although studying plumes outflow in other directions (including those not impacted significantly by biogenic emissions) will also be interesting and valuable. Also, sampling of air masses without urban influence in the region of the tower will contribute to assessing the chemistry of the biogenic emissions having less anthropogenic impact.

Stairway Tower

A highly instrumented, tethered, stairway tower whose height is well above the local canopy height is planned. We envision designs like those used in Michigan (Carroll et al., 2001; see Figure 17 herein), Brazil (Martin et al., 2016, 2017), and Colorado (Ortega et al., 2014) with a height appropriate for the forest canopy (e.g. Fontainebleau Forest has been measured at 28.5 ± 1 meters; Shang and Chazette, 2014), exceeding the mean height by 10 to 15 meters. The tower will be capable of supporting a significant weight of instrumentation (more than 500 kilograms) and intermittently, two persons for conducting maintenance and calibrations. For species that can be sampled and analyzed at the surface, a sampling manifold (likely made of glass) will bring air from the top of the tower to fixed or mobile laboratories stationed below. The manifold at the PROPHET tower (34 m height) in Michigan transfers 3300 l s^{-1} with a residence time of less than 2 seconds. A hoist for moving instrumentation up and down will also be needed.

Tethered Balloons and UASs/Drones

While generally not capable of large payloads, tethered balloons can be used to measure a few species at altitudes between the surface and the minimum aircraft altitude, in the range of about 40 to 300 meters above ground level. Such observations can help connect the tower-based and aircraft-based measurements, revealing details about boundary layer evolution, vertical transport and mixing, and gradients of species. Depending on the size of the balloon, at a minimum we hope to obtain measurements of ozone, particles, and perhaps a few other species. Candidate platforms include Aeroballoon (<http://aeroballoon.com/products.html>), Airstar (<http://airstar.aero/en/>), and Zephyr (<https://zephyrendlessflight.com/>).

There are a wide range of capabilities of unmanned aerial systems (UASs) or drones. These range from very small types with low payload capabilities and short flight times up to very large ones with large payloads (up to 599 kg) and long flight endurance (Mamali et al., 2018; Schuyler and Guzman, 2017; Villa et al., 2016). Those in the small to medium



Figure 17. Photo of chemistry stairway tower at the PROPHET site in northern Michigan.

categories are attractive for atmospheric composition measurements because they are typically battery operated. For ACROSS, drones would provide observations of a few atmospheric components at altitudes between the tower and the aircraft. For deployment in a forested region, rotary wing models appear to be the most practical. Critical to the successful use of these platforms is the development and characterization of lightweight sensors, including careful comparison with established research-grade instruments.

Mobile Laboratories

At LISA and within the wider community, there exist instrumented laboratories in vans, trucks, and containers that can be quickly deployed for atmospheric monitoring. In LISA, there are MILEAGE (MOBILLe Laboratory for Extensive Atmospheric Gas mEasurements), which is an instrumented large panel van, and PEGASUS (PortABLE Gas and Aerosol Sampling UnitS), which consists of a pair of modified containers. One or both platforms, plus others, may be used in ACROSS to supplement the ground-based observations from air quality networks, the tower, and tethered balloon(s).

Other Ground-Based Research Sites

Aside the Rambouillet supersite the ACROSS strategy will highly benefit from other research grade research sites conveniently located along the most probable plume direction.

SIRTA (Site Instrumental de Recherche par Télédétection Atmosphérique) is an experimental site located at Ecole Polytechnique, Palaiseau, which has a heavily instrumented primary site (170 instruments), and measurements at nearby secondary sites (Haefelin et al., 2005). Data are available via FTP and the website (<https://sirta.ipsl.fr/>). As a national instrumented site it is well designed and equipped to accommodate additional research group and instruments. Being one of the key supersites during the MEGAPOLI campaign, it is now located in the middle of the distance between Paris city and the Rambouillet supersite.

The base instrumentation of SIRTA consists of observations of meteorology, radiation, aerosols and gases, and will be complemented by additional equipment. A request for access within the ACTRIS or ENVRIplus research infrastructure will be made to contribute to the cost of the guest installations.

There are existing measurement sites staged on buildings on the Université Paris-Est Créteil (UPEC) and Université de Paris (UP) campuses. The stations operate regularly at a moderate level. We plan to supplement the routine measurements with additional instrumentation to characterize the urban composition within Paris more completely than possible with standard air quality observations.

To characterize the composition of inflow air to Paris, a station will be established at Parc forestier de la Poudrerie or another suitable upwind site. This station will be outfitted with a full range of standard and research-grade instrumentation whose measurements will help establish the incremental contributions of Paris to air mass composition.

There is a well-established and highly instrumented site (Supersite Voltaire) managed by the Université d'Orléans, CNRS, and Lig'Air that can help characterize evolution of outflow downwind of the Rambouillet supersite for north-northeasterly winds.

Existing Air Quality Networks

Air quality network contributions are extremely important to the ACROSS project because they can bring to the scientific inquiry not only their deep knowledge of the regional meteorology and pollutant behavior but also their own scientific interests to maximize the impacts of ACROSS findings on societal needs. They are also key to our experimental strategy due to their rich network of permanent stations and their ability to deploy mobile facilities or to open access to research grade stations (such as the one recently opened at Paris-Les Halles by Airparif). The ACROSS domain links to two experienced air quality networks that have been contacted and have declared their scientific interest in ACROSS: Airparif and Lig'air.

Airparif (Surveillance de la qualité de l'air en Ile-de-France) is a collection of permanent and temporary monitoring stations within the Île-de-France region where measurements of NO₂, O₃, and particulate matter are made. An air quality index is also calculated based on these observations. The data are reported on a dedicated website (<https://www.airparif.asso.fr/>).

Lig'Air (Association de surveillance de la qualité de l'air en région Centre-Val de Loire) is an air quality network in the central Loire river valley to the south and southwest of the Île-de-France region. The network of stations provides measurements of standard pollutant levels and are reported on their website (<https://www.ligair.fr>).

Observations and Priorities

To understand atmospheric chemical oxidation processes in the ACROSS field campaign, several physical and chemical observations are needed. These observations provide constraints for models that can then be used to address issues such as emission rates, ozone production rates, SOA yields, and formation rates of multi-generational organic compounds. There will likely be additional measurements proposed as the project develops that can contribute to ACROSS goals.

Table 2. Observations and priorities for ACROSS platforms (see footnotes).

| Measurement | Aircraft | Tower | Balloon/ Drone | Mobile | Other Ground | Net- work |
|--|----------|-------|-------------------|--------|-----------------|--------------|
| NO _x (NO, NO ₂) | X | X | X | X | X | X |
| O ₃ | X | X | X | X | X | X |
| CO, CO ₂ , H ₂ O | X | X | X | X | X | X X |
| j-values ^a | X | X X | | | X | X |
| Other radiation ^b | X | X | X | | X | |
| VOCs (C ₁ -C ₁₅) | X | X X | | X X | X X | X X |
| OVOCs | X | X X | | X X | X X | |
| BVOCs | X | X | | X X | X X | |
| CH ₂ O | X | X | X | X | X | |
| HO _x (OH, HO ₂ , RO ₂) | | X | | X | X | |
| OH reactivity | | X | | X | X | |
| H ₂ O ₂ , ROOH, PAA | | X | | | | |
| IEPOX, ISOPOOH, ISOPN | | X X | | | | |
| NO ₃ , N ₂ O ₅ | | X | | | X | |

| | | | | | | |
|--|-----|-----|---|-----|-----|-----|
| PM _{2.5} , PM ₁₀ | | X | X | X | X | X |
| Aerosol optical ^c | X | X | | | X | |
| Aerosol size, supermicron ^d | X X | X X | X | X X | X X | |
| Aerosol size, submicron | X | X | X | X | X | |
| Aerosol size, nanometer | X | X | | X | X | |
| Aerosol f(RH) | | X | | X | X | |
| Aerosol composition ^e | X X | X X | | X X | X X | X X |
| Aerosol profiles ^f | | X | | | X | X X |
| HNO ₃ | | X | | | | |
| NO _y | X | X | | X | X | |
| Organic nitrates (ANs) | X | X X | | | | |
| Peroxy nitrates (PNs) | X | X | | | | |
| PANs | | X | | | | |
| HONO | X | X | | | X | |
| SO ₂ | | X | | | | X |
| CFCs, HCFCs, HFCs | | X | | | | |
| NH ₃ | | X | | | X | |
| N ₂ O | | X | | | | |
| Organic acids | | X | | | | |
| Tracers ^g | X X | X X | | | X X | |
| Remote Columns/profiles ^h | | X X | | | X X | X X |
| T, DP, P, RH | X | X | X | X | X | X X |
| Location | X | X | X | X | X | X |
| Surface albedo | X | X | | | X | |
| 3D winds & fluxes | X | X | | | | X X |
| Boundary layer height | X | X | | X | X | X X |

| | |
|-----|--|
| X | instrument identified and available |
| X | instrument not identified yet |
| X X | instrument identified, but more capability desired |

| | |
|--------------|--|
| Aircraft | ATR 42 |
| Tower | Rambouillet supersite |
| Balloon | TBD - deployed near supersite |
| Drone | TBD - deployed near supersite & other |
| Mobile | MILEAGE, PEGASUS, & other |
| Other ground | Rooftop stations UPEC, UP; Poudrierie; Orleans |
| Network | Airparif, SIRTA, Lig'air-Chartres, INERIS |

^a j-values desired include: O₃→O(¹D), NO₂, CH₂O (2 channels), H₂O₂, CH₃OOH, ROOH, CH₃CHO, HPALD, other carbonyl compounds, ClNO₂, others; using radiometers and spectroradiometers

^b Other radiation includes: global irradiance, UV irradiance, PAR

- ^c Aerosol optical includes: AOD vs λ , absorption and scattering vs λ , SSA vs λ , Index of refraction.
- ^d Aerosol properties include: size distribution, hygroscopicity, CN & CCN numbers, volatility, derived quantities such as surface area density.
- ^e Aerosol composition includes: WSOC, inorganic ions, organic compounds, black carbon, size resolved composition, H₂O, AMS-type parameters.
- ^f Aerosol profiles include: extinction, backscatter, depolarization.
- ^g Tracers include: CH₃CN & levoglucosan for biomass burning, aerosol ³⁵S & ¹⁰Be/⁷Be ratio for stratospheric intrusion, ethanol, HFCs, & NO_x/NO_y ratio for urban air, isoprene & monoterpenes for biogenically influenced air, DMS for marine air, and NH₃ & N₂O for agricultural activities
- ^h Trace gas columns include: O₃, NO₂, CH₂O.
-

Numerical Modeling

Numerical models of various types and configurations will be employed to plan and execute the campaign and to analyze the data collected. Such approaches are valuable because of the complex nature of the atmospheric chemistry involved in the processing of emissions from urban and rural regions. These tools can be used to reveal information about the atmospheric processes in past studies (e.g. previous aircraft sorties) to assess success of measurement strategies, to provide medium- and short-term forecasts of conditions such as plume direction and extent of photochemical activity to plan future aircraft deployments, and to be used later to extract information about the observations.

There are two main categories of models that will be used: three-dimensional (3-D) chemical transport models (CTMs) also called regional models, and zero-dimensional (0-D) box-models. CTMs provide temporal and spatial evolution of selected key species. Because of computing limitations, chemical mechanisms in such models are condensed, often by lumping similar compounds. Box-models, on the other hand, do not generally provide spatial information, but make available detailed chemical information (concentrations, production and loss rates, budgets) by employing more explicit mechanisms, and thus they can be used to gain enhanced understanding of atmospheric chemical processes. They can also be operated in constrained mode in which source species are constrained to observed amounts, and the model is used to calculate intermediates and products.

Operational Air Quality Modeling

Forecasts of the regional atmospheric composition and evolution are used to recognize when air quality episodes are expected. For ACROSS, chemical weather forecasts are needed to plan deployments of aircraft and mobile platforms. Air quality predictions are extensions of weather forecasts that include estimates of atmospheric conditions that are likely to occur and their impact on emissions and atmospheric chemistry. Such chemical weather forecasts provide the direction of Paris urban outflow and whether conditions are conducive for high photochemical activity. The national platform for air quality forecasts is PREV'AIR, which is operated by INERIS and is managed by the consortium of INERIS, Météo France, CNRS (Centre National de la Recherche Scientifique) and LCSQA (Laboratoire Central de

Surveillance de la Qualité de l'Air). Meteorological data (weather forecasts) are taken from Météo France, ECMWF (European Center for Medium-Range Weather Forecasts) and NCEP (National Centers for Environmental Prediction). Boundary conditions are derived from climatology or global forecasts. Regular observations throughout France and Europe are incorporated into the process. Four days of hourly simulations are constructed using the CHIMERE (<https://www.lmd.polytechnique.fr/chimere/>) and MOCAGE (<https://www.umr-cnrm.fr/spip.php?article128&lang=fr>) models going from the previous day (D-1) to the next two days (D+2). Ensembles are run to assess the degree of uncertainty in the forecasts. The results and their evaluations are available on the PREV'AIR website (<http://www2.prevoir.org/>)

Regional Chemical Transport Modeling

Three-Dimensional (3-D) Chemical Transport Models (CTMs) can help address several specific aspects of ACROSS research, including being used to:

- 1) Interpret observational results by, for example, employing several chemical mechanisms and by performing budget studies of key species
- 2) Place the tower supersite in a spatial context (along with aircraft measurements) by simulation of 3-D pollutant fields particularly near and within the Paris urban plume, but also throughout the study region. It will also allow prediction of the evolution of the mixed urban / biogenic plume beyond the radius of possible measurements
- 3) Perform atmospheric composition forecasts to assist in flight planning, likely in collaboration with operational air quality forecasting entities such as the French Prev'air and the European CAMS programs

Chemical transport modeling can be used to address several important questions relevant to ACROSS (related to and overlapping with questions listed earlier). Examples include:

- How will the interplay between urban and biogenic emissions affect the radical budgets, the fates of reactive nitrogen species, and the temporal behavior of aerosols? And related to this:
- How does the competition for oxidants between anthropogenic and biogenic reactants impact SOA formation rates?
- Do additional BVOC emissions change the ozone formation regime in urban plumes?
- To what extent do organic nitrates formed from biogenic VOC emissions represent reservoir species for reactive nitrogen?
- What are the impacts of various lumped chemical mechanisms in addressing these and other questions?

In addition, observations from ACROSS will allow a thorough evaluation of key parts of the models, including the ability of gas phase chemical mechanisms to yield accurate radical budgets, and SOA formation and growth schemes in the unique mixed urban / rural environment.

In the French, European and wider international communities, many state-of-the-art 3-D CTMs are available. Several (e.g. CHIMERE, <http://www.lmd.polytechnique.fr/chimere/>; Polypheumus, Mallet et al., 2007; Menut et al., 2013;

<http://cerea.enpc.fr/polyphemus/introduction.html>) have been thoroughly tested during past campaigns, such as MEGAPOLI (special issue web page: https://www.atmos-chem-phys.net/special_issue248.html). These CTMs would need to be setup in a nested fashion to achieve a desired 1 to 3 km horizontal resolution. Urban emissions in the study area are available from several available national emission inventories (e.g. AERIS, <https://en.aeris-data.fr/catalogue/>) and from the Airparif air quality network. Biogenic emissions in the area (mainly isoprene) can be estimated with inventory tools such as MEGAN (Guenther et al., 2012) and adjusted as necessary to local characteristics (detailed local land use maps and species distribution as delivered by IGN (Institut national d'information géographique et forestière, <http://www.ign.fr/>) and ONF (Office National des Forêts, <https://www.onf.fr/>)) and observed values.

Key in the successful setup of CTMs is the interaction with 0-D models that include explicit, detailed chemical and physical mechanisms. Chemical schemes of varying complexity, such as the explicit GECKO model (Aumont et al., 2005), could be tested within 0-D models, and then more simplified versions implemented within CTMs. In turn, 3-D modelling can guide evaluation and use of 0-D models by, for example, simulating plume trajectories and predicting initial and large-scale species concentrations.

Box Modeling

Within the ACROSS project, detailed and/or explicit mechanisms for organic compound oxidation can be used to:

- 1) Evaluate our current understanding of the major processes driving organic compound evolution,
- 2) Help in the interpretation of observed results at a molecular scale, and
- 3) Explore the impact of organic compounds on the environment.

Detailed and/or explicit mechanisms for organic compound oxidation involve thousands of secondary species, each bearing one or more functional moieties (alcohol, ketone, aldehyde, hydroperoxide, nitrate, etc.). There are two chemical mechanisms available and widely used in the community to describe the detailed tropospheric oxidation of organic compounds: the Master Chemical Mechanism (MCM, Jenkin et al., 1997; Saunders et al., 2003) and the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) (e.g. Aumont et al., 2005; Lee-Taylor et al., 2011). The MCM is a detailed chemical mechanism written by hand that represents the oxidation of about 150 organic compounds of tropospheric relevance. As an indication of the size of the mechanisms, for an emitted organic compound with 12 carbon atoms, such as dodecane (C₁₀H₂₂), the MCM chemical mechanism includes around 400 species and 1250 reactions. GECKO-A is a computing tool that enables the generation of explicit chemical mechanisms for an input list of precursors. The GECKO-A chemical mechanism for dodecane includes about 110 000 species and 370 000 reactions. The large sizes of these chemical mechanisms prohibit their integration into chemical transport models. They can only be solved in simple models such as box-models. Care in the setup of box-model simulations is critical in performing comparisons with atmospheric measurements; particularly important are the initial and boundary conditions of organic species. Measurements and/or chemical transport models can help in getting these conditions for a

few species. However, the concentrations of most of the organic species are not available by measurements, and/or are not provided by chemical transport models because of the significant lumping used for organic compounds.

Different methodologies can be employed and evaluated in the setup of the initial and boundary conditions for the ACROSS campaign, which includes:

- 1) Constrained box-model simulations with stable species measurements, and
- 2) Box-model simulations using concentrations provided by previous runs representing explicitly the sources and sinks of organic compounds (emissions, deposition, chemistry...) for typical environments.

Comparisons of the simulated speciation of the stable and radical organic compounds at a molecular scale with measurements (molecular or integrated scale) will help lead to better understanding of the impacts of organic species on radical chemistry, nitrogen budgets, and organic aerosol formation and growth in biogenic environments, during the aging of an urban plume, and in the interaction of urban plumes with biogenic emissions (e.g. Isaacman-VanWertz et al., 2017).

Broader Impacts of Project

It is important to recognize and articulate aspects of a project that impact science and society beyond the direct and immediate goals. These broader impacts could range from the effects of the findings on governance and impacts on daily life of citizens to enhancements in educational opportunities for students and junior scientists, and to changes in the way society views environmental issues. Some broader impacts can be planned and anticipated, while others could be unexpected. It is helpful to have persons involved in a project whose interest and expertise lie in such cross- and multi-disciplinary aspects. Ideas for possible areas of broader impacts of ACROSS are outlined below. More detailed discussion appears in the Experimental Design document.

Relations to Other Activities

In addition to the direct impact of ACROSS research on improved understanding of factors contributing to air quality in regions of suburban biogenic emissions, one would expect possible broader influence on control strategies and recognition of needs for monitoring in wider geographical regions. The findings could influence the management of forests and agriculture near urban regions through new knowledge on the two-way interactions between emissions and air quality.

Capacity Building and Diversity

A planned aspect of the ACROSS project is significant involvement of students, post-doctoral fellows, and junior scientists in the full range of research activities. We expect several Ph.D. theses to involve collection and analysis of data that are part of ACROSS. Students who were undecided on their career paths may find their calling to be in the study of the field of atmospheric chemistry. We will encourage involvement of scientists and faculty from many French and European institutions ranging from large ones focused on scientific research to smaller ones with education as their primary emphasis. We also want to include students,

scientists, and faculty from diverse backgrounds and experiences because of the benefit such diversity will bring to the project and the benefits such a project could bring to their research experience.

Technology Development and Use

For ACROSS to be successful, we expect the development of new analytical methods and improvement of existing ones. Such activities are crucial to collection of observations needed to constrain models of chemical, biological, and physical processes. The project will attempt to be a framework that allows new and emerging technology to be tested and validated by comparison with existing, established technologies. This could involve, in addition to observations during the campaign itself, the sponsoring of instrument intercomparisons of measurements in the laboratory (using available simulation chambers, for example) and ambient observations. ACROSS may also employ new platforms that could be of significant use in other observational field campaigns. Detailed information on the use of such platforms will be disseminated timely and widely.

Value to Society

Air pollution is known to cause many premature deaths, and to impact the health of ecosystems. As a society, we can improve this situation through understanding of the processes involved in emission and transformation of gases and particles to the atmosphere. We expect ACROSS findings to lead to improved numerical representations of the atmosphere, and thus improved ability to design future control strategies. We also expect to educate the public and scientific community about the goals and findings of ACROSS through presentations using a wide variety of media and platforms.

Summary

The ACROSS project will exploit the relatively unique situation of an isolated megacity (Paris) in proximity to well-defined forested areas (e.g. Rambouillet) and agricultural activities. This will allow the study of the impact of urban emissions on the chemistry of emissions from the biosphere and vice versa. Such air mass mixtures could lead to changes in yields of important secondary products of atmospheric photochemistry and thus change the abundance of species that affect air quality. Critical to the project are observations of a comprehensive suite of species and parameters from several platforms, with the goal to examine the chemistry of the Paris plume as it is exported from the urban area and encounters regions of significant emissions from the biosphere. These observations will be analyzed for consistency with current understanding and will be used to test hypotheses of unknown processes that could be important in mixed urban-biogenic air mass photochemistry.

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