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FIELD PROJECT

An Experiment to Study Atmospheric Oxidation Chemistry and Physics of Mixed Anthropogenic–Biogenic Air Masses in the Greater Paris Area

Christopher Cantrell and Vincent Michoud

The Earth system consists of numerous physical, chemical, and biological cycles operating to maintain life on our planet as it evolved over the millennia.

Within this system, human activities have perturbed the balance of many of these cycles, leading to climate, ecosystem, and biodiversity changes. In the atmosphere, there are acute situations due to the increasing burdens of greenhouse gases that trap heat and of particles that are directly emitted or come from chemical transformations. These can have direct and indirect atmospheric effects, including greenhouse and cloud modifying properties, and negative impacts on human and ecosystem health, crop yields, and quality of life.

Studies of atmospheric composition within megacities have led to significant advances in our understanding of the chemical evolution of urban atmospheres. Recent research has revealed more and more details of the complex processes involved in the atmospheric degradation of volatile organic compounds (VOCs) of anthropogenic (AVOCs) and biogenic (BVOCs) origins, including those processes that lead to incorporation into the aerosol phase. However, important scientific questions remain on how the composition and impacts of urban pollution and biogenic emissions are modified by the mixing of the components of anthropogenic and biogenic air masses. This is significant because it is common that large cities are situated close to forested areas with strong biogenic emissions. A quantitative understanding of the atmospheric chemistry of urban

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The Paris metropolitan area is the most populous urban region (more than 12 million people, www.insee.fr) in the European Union, situated in the north-central part of France more than 200 km from other major urban centers and surrounded by forested and agricultural areas (Fig. 1). As a modern megacity, Paris emits significant quantities of NO_x, AVOCs, and particulate matter (PM) from traffic, residential heating, construction, energy production, industry, and other human activities. Being bounded by rural and forested areas, these anthropogenic emissions mix, react, and interact with the surrounding emissions of BVOCs [isoprene, monoterpenes (C₁₀H₁₆), sesquiterpenes (C₁₅H₂₄) and oxygenated VOCs (OVOCs)] and particles.

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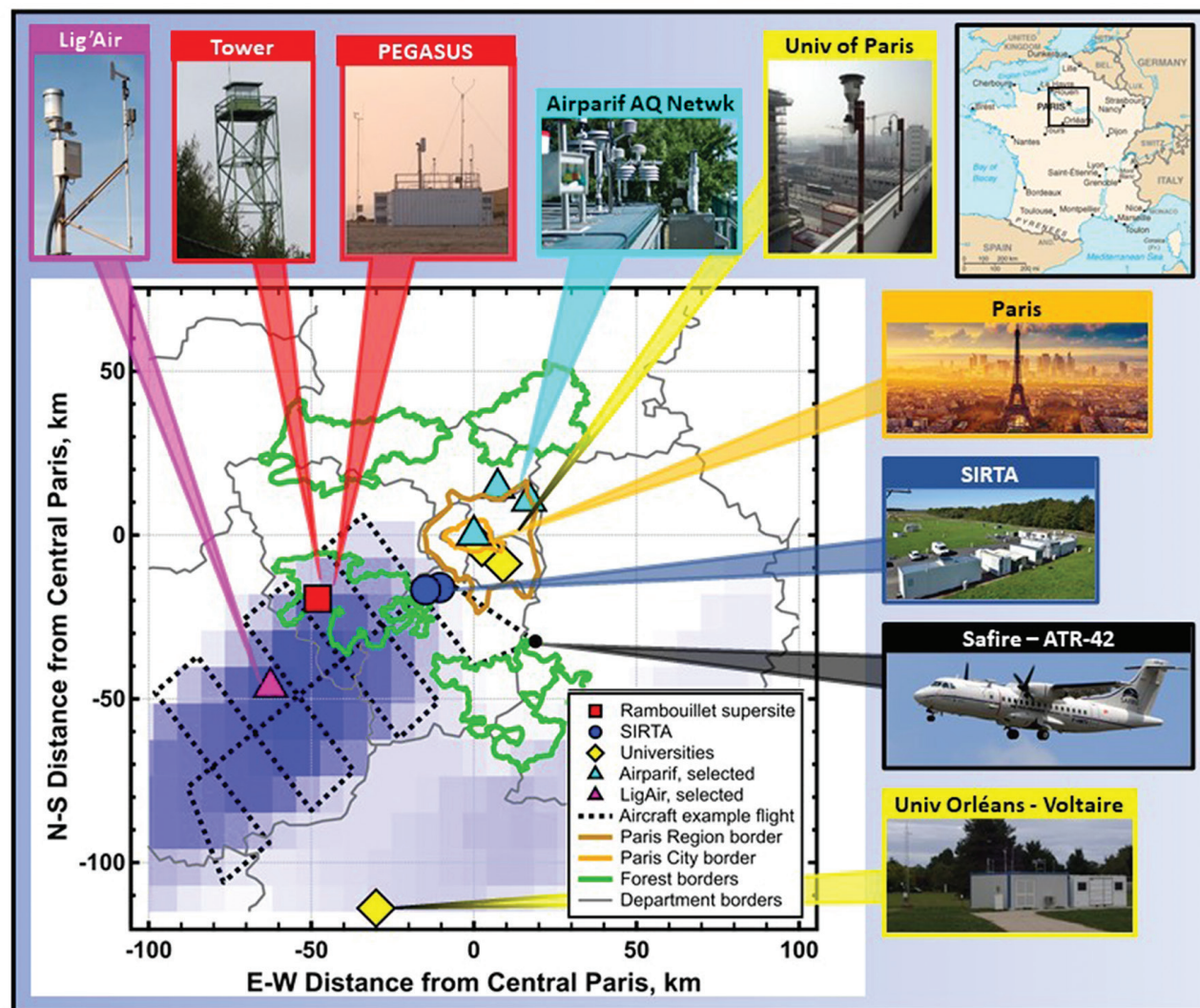


FIG. 1. Map of the ACROSS study region (white portion in lower left) including the Paris metropolitan area (dark orange outline), the city of Paris (light orange outline), and ground sites for the ACROSS measurement campaign (symbols). There are urban sites at two universities (University of Paris Cité and University of Paris-Est Creteil) shown as yellow diamonds within Paris, suburban sites at SIRTAs (blue circles), the ACROSS “supersite” in the Rambouillet Forest (red square), selected (out of 57) Airparif air quality network stations (teal triangles), one (out of 26) Lig’Air air quality network station (pink triangle), and a downwind site (Super-site Voltaire) at the University of Orléans/CNRS/Lig’Air (yellow diamond southwest of Paris). The gray lines depict department borders, and the dotted black line

shows a possible aircraft flight pattern for a Paris plume transported to the west-southwest direction. The green lines depict boundaries of forests in the Paris region. The background blue and white colors show ozone from the Copernicus Atmosphere Monitoring Service (CAMS) database (<https://atmosphere.copernicus.eu/data>) for 22 July 2021 (a nearly ideal meteorological situation), with the white color for values less than $100 \mu\text{g m}^{-3}$ and the light to dark blue colors for values between 100 and $140 \mu\text{g m}^{-3}$. The map in the upper right shows the ACROSS study region (black square), which corresponds to the area of the larger plot, in the context of France and other nearby countries. The photographs show locations and platforms that are part of ACROSS.

- Recent research has revealed more and more details of the complex processes involved in the atmospheric degradation of volatile organic compounds (VOCs) of anthropogenic (AVOCs) and biogenic (BVOCs) origins, including those processes that lead to incorporation into the aerosol phase.

Studies of urban–rural air mass interactions in the Paris region were conducted during two large experiments in the past two decades: ESQUIF (1998–2000) and MEGAPOLI (2009–2010). 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 VOCs, the formation of secondary organic aerosols (SOA), and the budgets of HO_x radicals. This lack of knowledge has direct consequences for our ability to accurately predict concentrations of secondary pollutants, in particular ozone and SOA.

The mixing of anthropogenic and biogenic emissions can affect several atmospheric chemical processes (e.g., Martin et al. 2016; McFiggans et al. 2019; Nascimento et al. 2021; Setyan et al. 2014). Competition for oxidants between AVOCs and BVOCs could lead to the formation of SOA with different yields and properties. Also, elevated NO_x (mostly of anthropogenic origin) could impact BVOC oxidation path-

ways. Many laboratory studies (but not all of them) have shown that the yield of SOA from the oxidation of α -pinene by hydroxyl radicals (OH) anticorrelates with levels of NO_x. Also, absorption of solar radiation is greater for SOA derived from AVOCs oxidized at high NO_x levels, while it is significantly reduced for SOA produced from BVOC precursors alone or from mixtures of AVOCs and BVOCs. While recent laboratory investigations support the role of anthropogenic–biogenic mixing in affecting air mass evolution and the properties of its constituents, a detailed and predictive understanding of the mechanisms occurring in such environments is not available. Such processes are then not explicitly included in chemical transport models that are used either to forecast air quality to study recent and future trends to define or validate air pollution control policies. Currently, it is difficult for such models to reproduce observed ozone trends (Colette et al. 2021). To improve representation of VOCs in models, one must account for the reductions in urban emissions as well as variations and trends of BVOC emissions, and the modifications to their atmospheric transformations in a changing climate (Fortems-Cheiney et al. 2017). The current levels of complexity in VOC emissions and chemistry in these models is limited and requires upgrading.

The ACROSS (Atmospheric Chemistry Of the Suburban Forest) project aims to improve our knowledge of atmospheric chemical processes that occur in mixed anthropogenic–biogenic air masses and their impact on air quality at the regional scale. Specifically, the main scientific questions that are addressed are as follows:

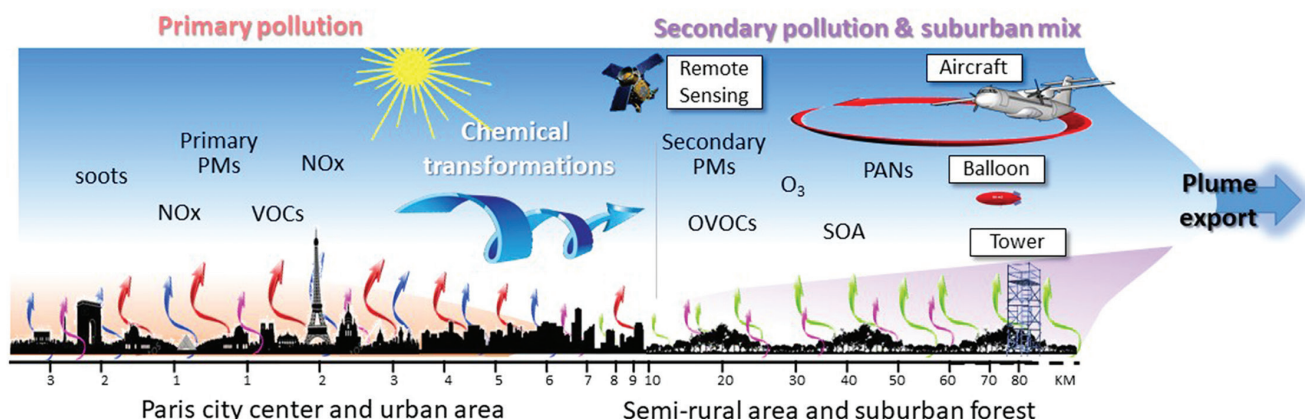


FIG. 2. Schematic diagram of the configuration of observation platforms relative to the urban and rural emission regions to be studied during the ACROSS project. The Paris urban region (left side) is an area of significant anthropogenic emissions. As these are exported from the urban area, they

encounter emissions from nearby forests and agricultural regions. These mixed air masses will be examined through comprehensive measurements from ground-based, airborne, and space-based platforms to assess and quantify the details of the chemical transformations that occur.

- 1) *How do the oxidation pathways of VOCs change when urban and biogenic air masses mix?*
- 2) *How are budgets of oxidants and reactive nitrogen compounds affected by biogenic–urban air mass mixing during both day and night?*
- 3) *How are the formation and growth of aerosols, their properties particularly related to organic carbon content, altered when urban and biogenic air masses mix?*
- 4) *What are the consequences of these factors for air quality, the health of the biosphere, and the representation of these processes in numerical models?*

ACROSS is supported under the French initiative “Make Our Planet Great Again” (MOPGA), and entails an international, large-scale, comprehensive, multiplatform, multisite field campaign conducted in the summer of 2022 in the greater Paris area.

The experimental strategy of ACROSS is based on in situ ground-based and airborne observations of atmospheric composition complemented by ground- and space-based remote sensing measurements. Figure 2 presents a schematic diagram of the principle of the experimental setup of ACROSS with the configuration of observation platforms relative to the urban and rural emission regions with winds transporting atmospheric components from left to right. It will build upon the synergy between air quality operational network measurements and research-grade comprehensively instrumented sites. The

locations of the ground sites and their proximity to the Paris metropolitan region and the locations of forested areas are shown in Fig. 1. The campaign targets a specific atmospheric flow situation, which involves northeasterly winds bringing Paris emissions to the Rambouillet Forest (and beyond) during conditions of high photochemical activity. This configuration was selected by analyzing several years of surface ozone data for areas outside of Paris, with locations in the southwest direction having the greatest probability of high ozone levels, indicating that the meteorological situation associated with northeast winds is also that which leads to high ozone production and the accompanying photochemical processes leading to secondary VOCs and SOA. The ground measurement sites will span the Paris region (urban), the Paris suburbs at Site Instrumental de Recherche par Télédétection Atmosphérique (SIRTA; early stages of processing), the Rambouillet forest “supersite” with measurements from the surface to the top of a 40-m-tall tower (mixed urban and biogenic emissions), and farther downwind in Chartres and Orléans (later stages of processing), which are 78 and 111 km from the center of Paris, respectively, and which will, for “ideal” wind directions, form a transect along a path of air mass photochemical aging.

It is expected that other atmospheric flow situations, representative of various mixing conditions, will contribute to understanding the chemical processing of mixed anthropogenic–biogenic air masses. Indeed, they include

FOR FURTHER READING

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- *Studies of atmospheric composition*
- *within megacities have led to significant*
- *advances in our understanding of the*
- *chemical evolution of urban atmospheres.*

wind directions that allow the study of biogenic air masses with little anthropogenic influence and those that present anthropogenic air masses with little biogenic influence, which thus enables examination of the behavior over a range of chemical and meteorological conditions (e.g., NO_x levels, oxidant amounts, ratios of BVOCs to AVOCs, background aerosol abundances and compositions).

The French ATR 42 environmental research aircraft of Safire will be used to explore the horizontal and vertical evolution of air masses to complement the observations from the ground sites. Composition data collected aboard the aircraft platform will be valuable to evaluate the chemical evolution during transport from the emission regions that will complement measurements from the ground sites. Forecasts from 3D chemical transport models (CTMs) and satellite observations will be helpful to deploy the aircraft to optimum sampling locations. The campaign data will be publicly available for use by interested scientists.

Instruments deployed at the various sites and platforms will be used to characterize as exhaustively as possible the atmospheric composition, including state-of-the-art measurements of inorganic gases (O_3 , NO_x , NO_y , HONO , N_2O_5 , HNO_3 , CO , CO_2 , SO_2 , H_2SO_4), radicals (NO_3 , HO_x , OH reactivity), gas-phase organic compounds (AVOCs, BVOCs, OVOCs), aerosol composition and physical properties (inorganic and organic species, size distributions, optical properties), emission and deposition fluxes by eddy covariance (CH_4 , CO_2 , NH_3 , O_3 , NO , NO_2 , VOCs, H_2O , particles), profiles of ozone and aerosols using lidar, and meteorological parameters (winds, radiation by spectroradiometer, temperature and pressure profiles at three heights on the tower, humidity, and boundary layer height by ceilometer).

In the last decade, significant progress has been made in measurement capabilities for gas- and condensed-phase chemical composition that allows more detailed scientific inquiry into these chemical processes that will be deployed in ACROSS. There have been advances in chemical ionization mass-spectrometry-based methods, in aerosol characterization and composition techniques,

and in applications of optical cavities that allow better quantification of radicals and reactive trace gases than ever before. In Paris, like elsewhere, new comprehensive datasets for OVOCs, particle abundance and properties, and oxidants are needed to support the efforts to improve CTMs.

This large instrumental deployment will lead to a unique dataset critical in answering the main scientific questions of the project that will advance our understanding of the atmospheric composition and the chemical and physical processes operative in mixed anthropogenic–biogenic environments.

To extract the maximum quantitative knowledge on the behavior of mixed anthropogenic–biogenic atmospheres from the observations, various analysis methods will be employed involving statistical and numerical modeling approaches. For example, we will compare the output of 3D CTMs with the observations to quantitatively assess and improve their accuracy in representing atmospheric composition and evolution. Zero-dimensional box models, which have detailed chemical and physical mechanisms, will be used in the analysis of the observations to test the completeness and accuracy of their configurations. The aim of such approaches is to determine if there are missing processes in current state of the art chemical mechanisms and to improve the representation of tropospheric chemistry within numerical models. Such improvements are needed to ultimately develop mitigation strategies that efficiently minimize the impacts of pollution on climate and human health.

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