Determination of unique particulate and gas-phase aviation emission tracers

Z.C.J. Decker, R. Acampora, P. Alpert, M. Schaffner, M. Gysel-Beer, J.G. Slowik, M. Ammann, A.S.H Prévôt, B. T. Brem

Aviaton Emissions

include particulate matter (PM), a pollutant that has major implications for our health, welfare and the global climate. One can often see particulate matter, such as dust or smoke in the air. However, Ultra Fine Particles (UFP), a subset of PM, are harder to see because they are about 100 times smaller than a human hair, or the size of a coil of DNA.

High concentrations of ultrafine particles (UFPs) are consistently detected near airports. This may be a problem for human health because the toxicity of UFP is greater than typical PM due to their small size and ability to penetrate the alveolar regions of the human respiratory system.

Yet, the source of UFPs near airports is not clear. Airports emit UFPs, but the emissions are complex mixtures of aircraft engine exhaust, vehicle exhaust, and other emissions such as tire rubber. Some emissions begin as particles, but others as gas-phase molecules that grow into particles. We want to untangle these emissions and learn how the emissions transform into UFPs.

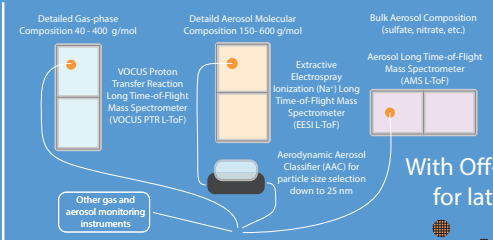
APPROPRIATE

Aviation Plume PROPeRties AT point of Exposure

We combine laboratory, test cell, and ambient field measurements to accomplish four goals

1. Find chemical indicator(s) for emissions originating at airports that distinguish airport emissions from surrounding urban emissions
2. Identify fingerprints for the fresh gas-phase and particle-phase emissions associated with specific aircraft engine states (i.e. take-off, idle, etc.).
3. Determine the contribution of solid PM (non-volatile, or nvPM) to the UFPs observed near the airport.
4. Assess the chemistry and physical changes that occur to the particle composition and shape.

We use three key on-line instruments

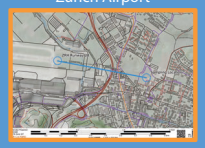


With Off-line samples for later analysis

At two field sites

SR Technics Engine Test Cell

Zürich Airport

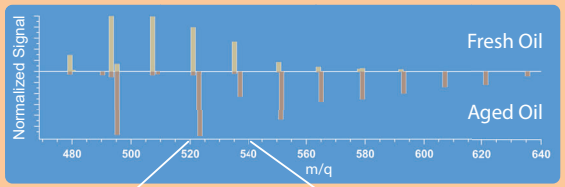


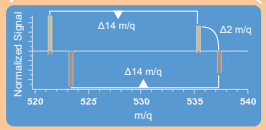
Swiss Light Source (SLS)

On-going Laboratory Experiments of Aircraft Oil Aerosol Tracers

We analyzed fresh and aged engine oil aerosol to identify key mass spectrum fingerprints

Comparison of Aerosol Molecular Fingerprints





To differentiate aircraft engine emissions from other sources in the field, such as cars, industry, or people, we need molecular fingerprints.

In the lab, we can conduct controlled experiments on fresh and aged (removed from an aircraft engine during maintenance) oils to discover these fingerprints.

To the left is an example of fingerprints from fresh and aged aircraft engine oil aerosol. We generate the aerosol in the lab and sample it with an EESI L-ToF MS.

Begininning at mass 479, a clear pattern emerges from the fresh aircraft oil at incriments of 14 mass units. Our high resolution mass spectrometer allows us to assign these signals to a molecular formula of $C_{26}H_{49}O_4P\ Na^+$.

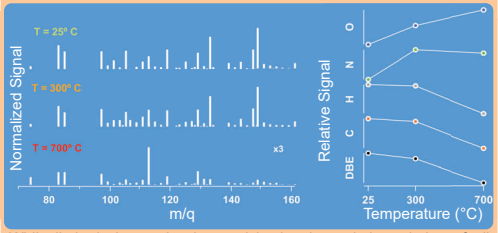
This is likely a fragmentation pattern of an ester that are known to be in aircraft engine oils (Ungeheuer et al., ACP *2021*).

Interestingly, we see a similar pattern in aged oil, but two mass units heavier. This is most likely the addiion of two oxygens and loss of five hydrogens.

Oil Vapor Degradation

Aircraft engines vent oil vapors through the hot engine exhaust flow. This short period may thermally degrade engine oil vapors.

To understand the engine oil vapor degradation, we sampled vapors from different engine oil brands after 60 s of thermal degradation at various temperatures. The resulting gas-phase molecules were then sampled with our VOCUS PTR L-ToF.



While limited change is observed in the thermal degradation of oil vapors at temperatures < 300° C, a significant change is observed at 700° C where gas-phase signals between 70 – 160 m/Q are reduced.

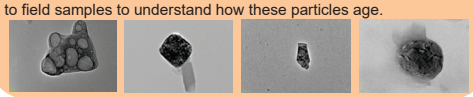
Results suggest most identified gas-phase compounds iare slightly oxygenated and unsaturated with more than 50% exhibiting a double bound equivalent (DBE) greater than three.

The right figure suggests that the oil vapor composition increases in oxidation (increasing oxygen and nitrogen with decreasing carbon and hydrogen) while also increasing in saturation (decreasing DBE).

Aerosol Imaging

Using Scanning Transmission X-ray Microscopy (STXM) coupled with Near-Edge X-ray Absorption Fine Structure (NEXAFS) at the SLS we can identify the different types of matter (e.g. organics, soot) in oil aerosol.

Below are example results of ongoing laboratory experiments on oil aerosol observed by Transmission Electron Microscopy. We can use the above methods to compare fresh and aged aerosol from the lab to field samples to understand how these particles age.



Future Work

Our fieldwork will begin in one week at the SR Technics Engine Test Cell. After two weeks of sampling, we will move to our field location outside of the Zürich airport.

Our fieldwork will inform further laboratory experiments to aid in our understanding of field data.

Then, we can combine our laboratory and results from the field to gain a holistic view on the impact of aircraft emissions on the nearby communities.

Special thanks to Swiss Federal Office of Civil Aviation SFLV 2020-080 and Frithjof Siegerist from SR Technics for providing us the oil samples