Chemical Characterization of Ultrafine Particles near a Large International Airport

Florian Ungeheuer[1], Dominik van Pinxteren[2], Diana Rose[3], Florian Ditas[3], Stefan Jacobi[3], Hartmut Herrmann[2], Alexander L. Vogel[1]

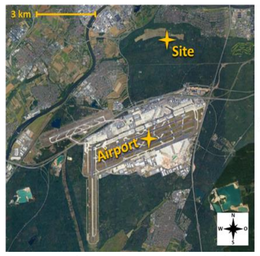
✉ ungeheuer@iau.uni-frankfurt.de

[1]Institute for Atmospheric and Environmental Sciences, Goethe-University Frankfurt, Frankfurt am Main, 60438, Germany
[2]Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, 04318, Germany
[3]Department for Ambient Air Quality, Hessian Agency for Nature Conservation, Environment and Geology, Wiesbaden, 65203, Germany

1 Abstract

We present the results from a chemical characterization study of ultrafine particles (UFP). These particles receive increasing attention due to the fact that airports are suspected to be a major source of particles smaller than 100 nm [1] [2]. UFP can be transported over long distances towards urban areas and can cause various negative health effects by being able to penetrate the pulmonary tissue [3] [4].
Cascade impactor samples were collected at an air quality monitoring station nearby Frankfurt airport, at which particle size distribution measurements show high number concentrations of particles <50 nm during the corresponding wind direction. Optimization of the filter extraction procedure, the chromatographic separation and the measurement process resulted in a sensitive method that revealed the chemical composition of the ambient UFP. For each cascade impactor stage (0.010-0.018 µm; 0.018-0.032 µm; 0.032-0.056 µm) we created molecular fingerprints (molecular weight (MW) vs retention time, Van-Krevelen-diagram, Kroll-diagram, Kendrick mass defect vs. MW) in order to visualize the complex chemical composition of the compounds detected. Unambiguous identification of molecules originating from different lubricant base stocks and its additives was achieved through matching retention time, exact mass and MS/MS fragmentation pattern compared to a selection of commercially available jet engine lubrication oils.

2 Frankfurt airport – Measuring site



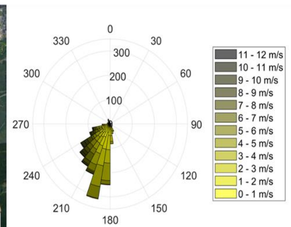


Figure 1. Map of the sampling site in a distance of 4 km to Frankfurt airport. The wind data for the sampling periods was provided by the metrological station at Frankfurt airport (ICAO-Code: EDDF) of the Deutscher Wetterdienst (DWD).

- Frankfurt airport is one of the biggest airports in Europe with more than 500,000 flight operations in 2018 shared over four runways.
- The measuring site is located in a forested area with no highly frequented streets in distance under 1 km.
- The prevailing wind direction is southwest directing towards the center of Frankfurt.

3 Method

3.1 Sampling

- Aluminium filter samples were collected with a 13 stage Micro Orifice Uniform Deposition Impactor (Nano-MOUDI, Model 115, MSP, Minneapolis, MN, USA).
- Particles are collected on the last three stages differentiated regarding their aerodynamic diameters (0.010-0.018 µm, 0.018-0.032 µm, 0.032-0.056 µm).
- Filter loadings in the sub µg range of total particle mass after 30-50 hours of sampling.

3.2 Filter extraction

- Developed to achieve the highest possible extract concentration.
- A circular section with a diameter of 2.5 cm was cut out of each filter sample.
- No pre-concentration and no filtration of the solvent extracts.

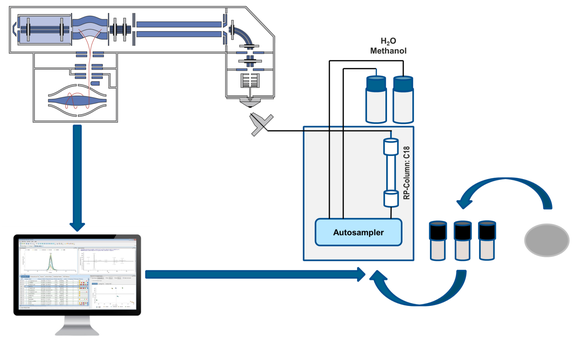


Figure 2. Chemical analysis realized by the use of ultrahigh-performance liquid-chromatography (UHPLC) (Vanquish Flex, Thermo Fisher Scientific)/ heated electrospray ionization (HESI) hyphenated with an Orbitrap high-resolution mass spectrometer (HRMS) (Q Exactive Focus Hybrid-Quadrupol-Orbitrap, Thermo Scientific) as a detector. By use of an inclusion list the samples were measured again only with fragmentation spectra recorded of the listed compounds to obtain high quality MS/MS spectra.

3.5 Fragmentation experiments

- During full scan measurement, fragmentation spectra are generated by higher-energy collisional dissociation (HCD) at which the selected compounds are accelerated against nitrogen molecules at a normalized collision energy of 30.
- Spectra were analyzed by Compound Discoverer and an inclusion list with the background corrected compounds was generated.
- Samples were measured again only with fragmentation spectra recorded of the listed compounds to obtain high quality MS/MS spectra.

3.3 UHPLC/HRMS method

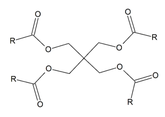
- Chromatographic separation of homologue series of hydrophobic and high molecular weight organic compounds.
- Ionization by heated electrospray ionization (HESI) in positive mode.
- Reversed phase column operated in gradient mode (H_2O/MeOH), thermostated at 40 °C.
- Detection limits of low picogram levels of organic molecules.

3.4 Non-target screening

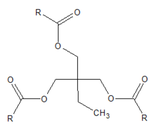
- Full scan MS-spectra analysis by the non-target software Compound Discoverer.
- Identification of substances and determination of their molecular formula.
- Utilization of their exact mass, isotopic signature, fragmentation pattern and database matching.
- Visualization by molecular fingerprints with restrictions regarding the assigned compounds.

4 Jet engine lubrication oils

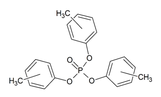
- Responsible for lubrication and cooling of turbine bearings.
- Designed to be stable against thermal stress and chemical decay.
- Composed of a synthetic base stock material and different additives.
- Lubrication oil recovery systems clean and reuse the oil in a circulating stream.
- Obstructed seals and venting systems lead to the release of jet oil droplets to the atmosphere [5].



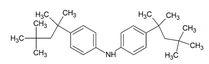
Pentaerythritol ester
($C_{27\text{-}38}H_{48\text{-}70}O_8$)



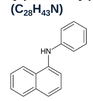
Trimethylolpropane ester
($C_{27\text{-}34}H_{50\text{-}64}O_6$)



Tris(2-methylphenyl) phosphate
($C_{21}H_{21}O_4P$)



Bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine
($C_{28}H_{43}N$)



N-Phenyl-1-naphthylamine
($C_{16}H_{13}N$)

- Synthetic esters like **pentaerythritol esters** and **trimethyolpropane esters** are used as base stock material.
- **Organophosphate** additives are used as antiwear agents and metal deactivators.
- **Amine** constituents serve as radical scavengers.

5 Compound filtering

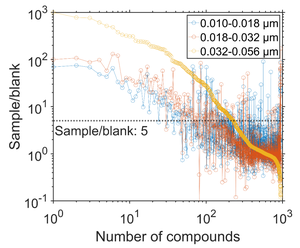


Figure 3. The sample to blank ratios of the detected compounds, averaged over all filters belonging to a certain size distribution stage (0.010-0.018 µm; 0.018-0.032 µm; 0.032-0.056 µm) are shown in logarithmic scale.

- The area of the sample signals is background corrected by the corresponding field blank.
- The sample signal must be more than five times larger than the blank signal (Fig. 3).
- The minimum area is 1.0 x 10^5.
- The minimum retention time is 0.7 min.
- Detection of compounds is accomplished with a mass tolerance of 5 ppm.
- The mass tolerance for the molecular formula prediction is reduced to 2 ppm.
- Elements for the identification: C_1 H_1 to C_{90} H_{190} Br_3 Cl_4 N_4 O_{20} P_1 S_3.
- The compounds are classified as CHO, CHN, CHNO, CHOS, CHNOS, CHOP and other.
- Over 900 detected compounds are reduced to almost 200 compounds.

6 Non-target screening

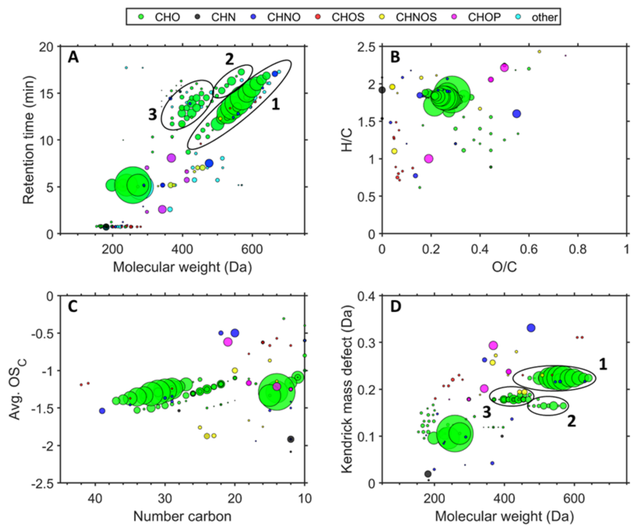


Figure 4. Molecular fingerprints (MW vs. retention time [A], Van-Krevelen-diagram [B], Kroll-diagram [C], Kendrick mass defect vs. MW [D]) of six averaged airport related ultrafine particle samples in the size range of 0.032-0.056 µm.

$$\mathrm{KMD} = \text{nominal mass} - \left(\text{IUPAC mass} * \frac{14.00000}{14.01565}\right)$$

A (MW vs retention time)

- Group 1 in Fig. 4A represents mainly the homologue series of pentaerythritol esters.
- Trimethylolpropane esters form a homologue series in group 2.
- Group 3 can be mainly attributed to fragmentation of the penta-erythritol esters in the HESI source.

B Van-Krevelen-diagram

- Describes the different compounds regarding their hydrogen to carbon (H/C) and oxygen to carbon (O/C) ratios.
- Tricresyl phosphate (TCP), contains three single-ring aromatic (cresol) moieties and appears as a magenta circle at H/C = 1 and O/C = 0.2.

C Kroll-diagram

- The Oxidation state of the complex compound composition is depicted by plotting the average carbon oxidation state (OS_C) versus the number of carbon atoms [6].

D Kendrick mass defect vs. MW

- Molecular weight (Da) is plotted against the Kendrick mass defect (KMD).
- Simplifies the identification of homologues series in complex mixtures.

7 Verification of jet engine oil constituents

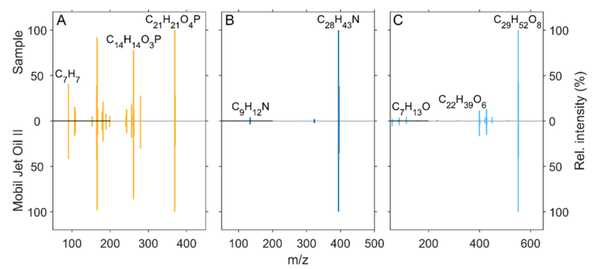


Figure 5. Comparison of the fragmentation pattern m/z vs relative intensity (%) of tricresyl phosphate ($C_{21}H_{21}O_4P$), alkylated diphenyl amine ($C_{28}H_{43}N$) and one pentaerythritol ester ($C_{29}H_{52}O_8$) measured in an ambient UFP sample (0.032-0.056 µm) and the Mobil Jet Oil II by ExxonMobil.

Fragmentation experiments

- Comparison between the fragmentation pattern of the jet engine oil constituents in the UFP samples and the Mobil Jet Oil II by ExxonMobil.

Temperature experiments

- Eastman Turbo Oil 2380 consists of a trimethylolpropane ester basestock detectable in the ultrafine particles.
- The identified trimethylolpropane phosphate ($C_6H_{11}O_4P$) was verified by temperature experiments with the Eastman Turbo Oil 2380.

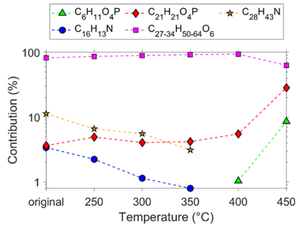


Figure 6. Development of the different constituents of the Eastman Turbo Oil 2380 during the temperature experiment.

8 Contribution of oil base stocks

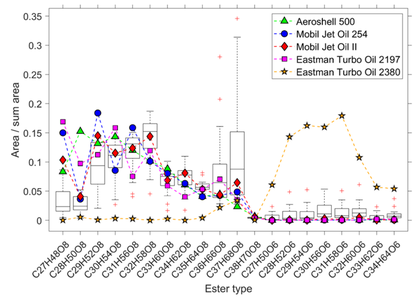


Figure 7. Comparison of the pentaerythritol- and the trimethylolpropane ester ratios of five different jet engine oils with the UFP samples. The ratio of the peak area of each ester compound to the area sum of all ester compounds is formed.

- A matching pattern of the ester compounds of the analyzed UFP samples and five different jet engine oils can be seen.
- The ester composition of four of the five jet engine lubrication oils match the pentaerythritol ester composition in UFP.
- The Eastman Turbo Oil 2380 possibly contributes to the trimethylolpropane esters detected in UFP.
- The different contribution of the ester base stocks to the UFP is presumably a result of a minor utilization of trimethylolpropane ester containing jet engine lubrication oils in the air traffic.

9 Conclusion

- We provide an analytical procedure, which allows to analyze the chemical composition of nanoparticles smaller than 56 nm.
- The whole process from sampling up to illustrating the overall composition is described.
- Results show that jet oil emissions strongly contribute to the chemical composition of particles < 56 nm nearby an airport.
- All specified constituents are detectable by HESI in positive ionization mode whereas the negative ionization mode only revealed the detection of few (<20) compounds.
- Long-term exposure health effects regarding ultrafine particles containing jet engine oil constituents should be assessed.
- It is essential to evaluate the toxicological insights in conjunction with the substances mainly dominating airport-related ultrafine particles.

ECATS 3rd Conference 13-15 October 2020

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