



Organophosphates in the UTLS - Understanding the link between meteorology and occurrence of anthropogenic aerosol tracers

Anna Breuninger¹, Christian Rolf², Patrick Konjari², Heiko Bozem³, Nicolas Emig³, Peter Hoor³, Anette Miltenberger³, Laurin Merkel¹, Arthur Kutschka⁴, Philipp Waleska⁴, Stefan Hofmann⁴, Thorsten Hoffmann⁵, and Alexander L. Vogel¹

¹Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt, Germany

²Institute of Climate and Energy System, Forschungszentrum Jülich, Germany

³Institute for Atmospheric Physics, Johannes Gutenberg University Mainz, Germany

⁴enviscope GmbH, Messtechnik für Umweltforschung, Frankfurt, Germany

⁵Department of Chemistry, Johannes Gutenberg University Mainz, Germany

The chemical composition throughout the atmosphere changes as a consequence of urbanization, developing industry and anthropogenic activities. Especially the upper troposphere and lower stratosphere (UTLS) is highly sensitive to these changes in chemical composition. With increasing anthropogenic emissions, the urgency to understand the changing chemical composition and its impact on the UTLS grows.

Organophosphates are one of the most prominent anthropogenic tracers, as they are solely man-made and found ubiquitously in the environment. They are widely used as flame retardants and plasticizers and have already been found in pristine environments such as the Arctic and are considered as chemicals of emerging concern. So far, they have been studied in air, water, sediment, and sludge and their human exposure and human and ecological risk has been assessed (Wang et al. 2020). Research on outdoor air and particle-bound organophosphates has been steadily growing over the years, however, the UTLS remains a poorly studied region.

In this study, we target the question of how meteorological conditions influence the chemical composition and thereby use organophosphates as anthropogenic tracers throughout the UTLS. Here, we present results from the TPEx campaign, conducted during June 2024 over Germany. Results from eight scientific flights, probing different regions of the UTLS during different meteorological conditions, were analyzed. With our in-house developed and manufactured Sampler for Organic Aerosol Particles (SOAP), we were able to collect a total of 27 filters throughout the whole campaign. Subsequently using ultra-high performance liquid chromatography, coupled with high-resolution Orbitrap mass spectrometry, we analyzed the organic fraction of aerosols. With this setup a non-target analysis allowed for the identification of unknown compounds and especially yet understudied organophosphates in the UTLS.

We identified five distinct meteorological conditions by using tracer-tracer correlations, cloud water content as well as water vapor content and categorized each filter respectively. For each

meteorological condition, a distinct chemical composition was identified using molecular fingerprinting. As a first result, compounds like $C_8H_{19}O_4P$ and $C_8H_{19}O_3PS$, which are found in the troposphere as well as the stratosphere, seem to disappear during cloudy conditions and are less abundant in combination with high water vapor mixing ratios. Simultaneously, a mix of thiophosphates, which are possible transformation products of organophosphates, becomes more abundant during high water vapor mixing ratios. We further aim to quantify various organophosphates and transformation products to understand occurrence, transportation and potential global distribution, as they are unambiguous tracers for the anthropogenic impact.

Wang, X., Zhu, Q., Yan, X., Wang, Y., Liao, C., Jiang, G. (2020c). A review of organophosphate flame retardants and plasticizers in the environment: Analysis, occurrence and risk assessment. *Sci. Total Environ.* 731, 139071. <https://doi.org/10.1016/j.scitotenv.2020.139071>