Molecular characterization and volatility of organonitrates: Latest observations from field and laboratory

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Organonitrates

EURAD monthly mean concentration fields for SOA from NO$_3$ oxidation together with observed concentrations of pOrgNO$_3$ (colored circles) for May 2008 (left), October 2008 (middle), and March 2009 (right), respectively.

34% to 44% of submicron aerosol nitrate measured by AMS (Kiendler-Scharr et al., GRL, 2016)

EURAD: EURopean Air pollution and Dispersion-Inverse Model (EURAD-IM) chemistry transport model (Elbern et al, 2007).
Organonitrates – why do we care?

- Reservoir or sink (temporary or permanent) of NO_x
- Impact on tropospheric O_3 levels
- Influence on SOA yields
- Influence new particle formation rates
- Nighttime chemistry: Formation via NO_3-oxidation of VOCs
- Daytime chemistry: Formation via peroxyradical reactions with NO_x

Quantification of these processes requires a better understanding of the fundamental properties of organonitrates in the gas and particle phases based on laboratory and field observations.
Karlsruhe, Germany: Higher fraction of organics and organonitrates during the night

Mass fractions of particulate organonitrates (pON) and particulate organic compounds (pOC) measured by FIGAERO-CIMS (Huang et al., EST, 2019)
Organonitrates are highly functionalized

Mass contribution to total pON of individual pON as a function of m/z ratio. Different colors indicate carbon numbers of the molecules, the labels the number of oxygen atoms per molecule (Huang et al., EST, 2019).

Similar observations in the SE US (Lee, Mohr, et al., PNAS, 2016)
Differences in diel patterns are indicative of different precursors and/or formation mechanisms.

Mean diel patterns of the mass contribution of the CxN (x = 5, 7, 10, 15) groups to total pON (Huang et al., EST, 2019). C_5 can be indicative of isoprene as a precursor, C_7 of anthropogenic VOCs, C_{10} of monoterpenes, and C_{15} of sesquiterpenes.
Chacaltaya, Bolivia: Observations of highly functionalized organic nitrates at 5240 m a.s.l.)
Organonitrates related to city pollution: Chemical formulae and volatility

Volutility Basis Set
(based on Li et al. ACP 2016)
SOA formation via NO$_3$-oxidation of biogenic VOCs in the laboratory

- **isoprene**
- **α-pinene**
- **β-caryophyllene**

SOA yield 4%

SOA yield 110%
SOA formation via NO$_3$-oxidation of biogenic VOCs in the laboratory - photolysis

- isoprene
- $\alpha$-pinene
- $\beta$-caryophyllene
NO$_3$-isoprene SOA during dark aging and photolysis

PMF separates different compound groups measured by EESI-TOF during NO$_3$-SOA formation in the dark and their behavior during photolysis.

Loss of oligomers with several nitrate groups during photolysis.
3 main points:

• Organonitrates influence SOA properties and NO\textsubscript{x} levels, knowledge of properties and fate contributes to understanding

• Recent ambient observations of organonitrates in different locations using state-of-the-art mass spectrometer techniques show they are highly functionalized and can have different organic precursors depending on environmental factors, and thus different volatilities

• Organonitrates formed during nighttime (NO\textsubscript{3} oxidation) may undergo photolysis during daytime, especially oligomers with several nitrate groups