

Nitrate Dynamics in UK Urban Environments

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Keywords: Ammonium Nitrate, Anthropogenic Aerosol, Aerosol Mass Spectrometry, Urban Aerosols, Inorganics, .

Nitrate makes a significant contribution to the concentration of PM_{2.5} and PM₁₀ with important implications for human health and regional climate forcing. This is particularly true for NW Europe, where large emissions of NH₃ and NO_x combine with comparably low temperatures and high relative humidities to create conditions that favour the production of NH₄NO₃. Despite its importance, most atmospheric chemistry models are still not modelling NH₄NO₃ very well, indicating that dynamics are still not represented correctly. In addition, due to its changing equilibrium, there are processes which operated at a sub-grid scale and are therefore difficult to simulate.

In this presentation we review new evidence on nitrate dynamics in urban environments, drawing on data from recent urban field studies, mainly, but not exclusively, in the UK. This new look is enabled through the use of new measurement technology such as Aerosol Mass Spectrometry (AMS), urban eddy-covariance flux measurements of aerosol chemical compounds and long-term nitrate measurements.

We quantify the relative contribution NH₄NO₃ to the UK aerosol, reviewing the existing UK AMS database and data from UK and European denuder/filter-pack networks.

Paired long-term measurements of aerosol concentrations in and outside of two UK urban areas (London & Edinburgh; Tang *et al.*, 2008), have provided information on the urban NO₃⁻ increment. The measurements indicate that, on average:

$$\text{NO}_3^-(\text{urban}) = 1.13 \times \text{NO}_3^-(\text{rural}) + 0.58 \mu\text{g m}^{-3},$$

with somewhat larger increments during the winter months than during summer.

Measurements of the size-distributions of sub-micron non-refractory NO₃⁻ by aerosol mass spectrometry frequently show periods of a NO₃⁻ size mode in the range 100 to 300 nm, in addition to the accumulation mode at 300 to 800 nm. This suggests that NO₃⁻ is formed by condensation on the combustion mode which is prevalent near traffic sources. The fine NO₃⁻ mode is sporadically observed, and appears to correlate with cold, humid conditions and atmospheric inversions.

The role of urban areas in producing NH₄NO₃ is further supported by the growing database of aerosol chemical compounds above urban areas, by aerosol mass spectrometry (e.g. Nemitz *et al.*, 2008), which suggests emission of NO₃⁻ from most cities, which is nevertheless highly variable between days (unlike the emission of organic aerosol).

Vertical gradient measurements above the city centre of London during the REPARTEE campaign (comparing measurements on the Telecom tower at 165 m with ground-based urban background measurements) show higher NO₃⁻ concentrations on the tower, possibly due to colder temperatures at higher heights shifting the gas/aerosol equilibrium towards the aerosol phase.

We also present evidence that the fate of NH₄NO₃ is affected by its dissociation potential. In warm conditions, NH₄NO₃ volatilises during the deposition process to semi-natural vegetation near the ground, where temperatures are raised and concentrations of NH₃ and HNO₃ lowered due to deposition. This greatly increases the effective deposition rate of NH₄NO₃ aerosol and greatly decreases its atmospheric lifetime. Since this volatilisation near the ground cannot be resolved by current CTMs, it is suggested that effective deposition rates need to be incorporated into models to account for this effect.

This work was funded by the NERC CityFlux project and by the UK Department for Environment, Food and Rural Affairs under the 'NH₄⁺ from agriculture' project.

Nemitz, E.; Jimenez, J.L.; Huffman, J.A.; Canagaratna, M.R.; Worsnop, D.R.; Guenther, A.B. (2008). *Aerosol Science and Technology*, **42** (8). 636-657.

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