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Introduction

An aerosol time-of-flight mass spectrometer (ATOFMS) was deployed at a port site (Tivoli Docks, Cork Harbour, Ireland), where it sampled ambient air for three weeks in August 2008 (summer) and February 2009 (winter). Analysis of the August data [1] found that over 66% of the total particle counts was for coal, peat and wood combustion for domestic heating. Most of these were freshly emitted, with nitrated versions only detected during four distinct events and coinciding with drops in wind speed to below 1 ms⁻¹; also no obvious growth in particle size was noted for the nitrated particles. Sampling was carried out in February 2009 to investigate any possible seasonal variations in composition and particle size. In contrast to August 2008, nitration combustion particles were observed on a daily basis and did not seem to be affected by wind speed; nitrate processing also produced some growth in particle size.

Methods

- ATOFMS fitted with aerodynamic lens (TSI ASL100) for real-time measurement of particles in size range 100-3000 nm (aerodynamic vacuum diameter).
- SMPS (scanning mobility particle sizer, TSI 3081) collected particle number concentrations & size distributions in the range 20-600 nm every 3 min.
- Over two million particle spectra were generated & classified using K-means algorithm (K = 65).
- Particle clusters with similar size distributions & composition temporality combined into 15 particle types.
- Most numerous particle types: domestic combustion (coal, peat & wood particles accounted for 61%, 23% & 2.6% of the total particles ionised).

Size Distributions

- Size distributions for ATOFMS particle counts scaled with SMPS number concentrations generated to investigate if lower temperatures & greater particle numbers in February produced growth in particle size with aging.
- Coal-amm-nit particles peak at larger diameters than coal-fresh particles (140 – 156 nm vs. 101 – 113 nm).
- Nitrate peat & wood particles counts peak at larger sizes compared to fresh counterparts.
- Each particle type appears at around 18:00 and increases from ~200 to ~400 nm at midnight, after which time they decrease in size until the source ceases emission.

Temporality

- Particle counts for each class exhibit a similar profile; increasing from 16:00 to 23:00, after which they decrease, with lowest counts during daytime hours.
- Average nitrate signals for the 3 particle types also exhibit dependence on time-night & early morning hours.
- Wood particles accumulate the most nitrate on average, followed by peat and coal.
- Differing levels of nitrate uptake among the particle types may be related to presence of sulphate or its accumulation in the same particles. Ammonia reacts preferentially with sulphate, so production of NH₄NO₃ requires an excess of gas-phase ammonia [2].
- Coal particles have the largest signal for sulfate; this is also larger than the coal nitrate signal, which may reflect ammonia reacting first with sulfate.
- Peat and wood particles contain less sulfate than coal particles, so larger nitrate signals than sulfate were expected.

Conclusions

- Fresh and nitrated particles were observed on a daily basis (in contrast to the August campaign) for each fuel.
- Nitrated particle types were more numerous, larger in mobility diameter and had larger average nitrate signals than their fresh counterparts. Temporally- and size-resolved particle counts for the three combustion types also revealed some growth each evening.
- Diurnal trends in particle counts revealed that uptake of ammonia and nitrate occurs quickly as nitrated and fresh particles had virtually identical profiles.

Further analysis:
- Mass conversions of the ATOFMS counts
- Comparison with similar data from a recent (August 2011) and similar ATOFMS 2011 campaign (Haubline, Cork Harbour (10 km SE of Tivoli site)).

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