

Abstract

Due to its prevalence over large, densely populated areas, ammonium nitrate is an important chemical species in aerosol research. However, due to its volatility at ambient temperatures and over low temperature gradients, ammonium nitrate can be a difficult species to accurately measure. The volatility of ammonium nitrate is known to be dependent on temperature, relative humidity, the internal mixing state of the particle, and availability of the precursor gas constituents. The particle's physical state affects the equilibrium constant value of the ammonium nitrate - nitric acid / ammonia exchange and helps determine the dissociation rate. For indoor aerosol research, the outdoor originating aerosol particles' exposure to the new physical conditions indoors, such as changes in temperature, humidity, and particle-surface reactions within the microenvironment all accelerate ammonium nitrate dissociation. This increased rate of partitioning can generate artifacts on datasets, increase indoor particle formation, and accelerate the corrosion of cultural antiquities through acidification. The magnitude of these impacts is uncertain due to the current lack of knowledge on particle transformation processes when outdoor originating particles migrate indoors. To address this gap in knowledge, this thesis describes 5 experiments, each carefully designed to help answer specific questions regarding particle transformations, with attention to ammonium nitrate behaviour, explicitly, but not exclusively, in regards to indoor environments.

To commence, it was necessary to establish a broad understanding of the fundamental behaviour of ammonium nitrate in a 'pure' environment. To this end, laboratory controlled experiments were carried out, and are described in Article 1. These experiments allowed for the observation of the shrinking / dissociation rates of a non-internally mixed ammonium nitrate (NH_4NO_3) - nitric acid (HNO_3) / ammonia (NH_3) exchange in a closed system. From a chosen size specific monodisperse NH_4NO_3 aerosol, results showed the 200nm particles shrank quicker than the 50/100nm particles when transported through the 2m long, laminar flow, temperature controlled reactor. Longer residence times and higher temperatures within the reactor accelerated this shrinking process. However, when dissociation rates were calculated using integrated mass measurements, the results were reversed. The smaller particles were found to lose mass faster than the larger particles. This indicated that, despite efforts to make sure the ammonium nitrate aerosol were dry, crystalline particles, it was considered likely that the particle wasn't completely dried, with further dehydration occurring as it travelled through the reactor.

To test the results of Article 1 in real-world conditions, an intensive field experiment was carried out during the summer of 2014, with the results reported in Article 2. The experimental objectives were to identify changes in particle composition between indoor and outdoor environments, under typical ambient conditions, and with a high temporal resolution. To help achieve this, a switching system was utilized to alternate between the indoor and outdoor environments, allowing almost real-time analysis of particle dynamics with online, high time-resolution instrumentation. The focus was intended to be on the indoor environment during this experiment. However, the high resolution data afforded by the instrumentation also allowed for detailed observations of a diurnal fluctuation in NH_4NO_3 - HNO_3/NH_3 concentrations outdoors. This was found to be directly influenced by temperature, solar radiation and changes in boundary layer height.

During the same campaign, a new particle formation event outdoors enabled the rapid increase of outdoor to indoor migrating particles to be observed for particles less than 100 nm. This was then

used to identify real-time I/O ratios, which were calculated by considering size, time and particle concentration dynamics. The I/O ratio obtained for this event was then set against an overall averaged I/O ratio calculated via particle number concentrations from scanning mobility particle sizer (SMPS) data, with a mobility diameter of $<0.71\mu\text{m}$. A reduction in NO_3^- mass concentrations from the outdoors to indoor environment was expected and observed. Moreover, compositional analysis carried out with aerosol mass spectrometer (AMS) measurements observed indoor chemical composition to be proportionally equivalent to that outdoors. This was explained by the similarity in temperatures indoors during daytime, reducing concentrations of ammonium nitrate before they entered indoors. These findings were supported by filter measurements taken from off-line Berner Low-Pressure Impactors which were also deployed indoors and outdoors.

Due to the volatile behaviour of NH_4NO_3 , a seasonal comparative experiment was undertaken during winter 2014-15, with the methodology consistent with the previous campaign. The results, described in Article 3, showed non-refractory (NR) - organics and NO_3^- had similar mean outdoor concentrations, with a marked increase in winter NO_3^- concentrations compared to summer. Seasonal changes in chemical composition were calculated from AMS mass concentrations, and a 33-37% decrease in I/O ratio was observed from summer to winter. The similarity in proportional loss of mass of all species presented evidence of physical rather than chemical processes. BLPI results confirmed these findings by revealing more mass indoors than outdoors on the ultrafine stages for both SO_4^{2-} and NH_4^+ . With no emission sources indoors, and particle bounce discounted due to greasing of the capture substrates, it was concluded that the particles were shrinking when penetrating indoors, and were therefore being counted in the ultrafine mode during the winter. This shrinking was not observed during the summer, nor was it as prominent on AMS measurements. However, the winter accumulation mode, obtained by SMPS measurements, showed an I/O ratio (.56) that was anomalous to those of summer (.80). It was determined that, due to higher ambient temperatures and lower relative humidity during summer, the aerosol outdoors were dry or mainly dry before entering the sampling room or the sampling inlet. In effect, during summer, the outdoor aerosols were in conditions comparable to the indoor aerosol during the winter.

Statistical tests, including Spearman Rank correlation and P-tests were carried out using winter, indoor and outdoor chemical mass concentrations, which were then set against meteorological conditions averaged over 24 hours. Wind speed was found to be well correlated with concentrations of all species. Further analysis revealed a small influence of wind direction and speed on I/O relationships. It was concluded that the increased loss of mass indoors during winter was attributed to concentrations of chemical species outdoors, the increased temperature gradient between indoors and outdoors and higher mean wind speed during the winter season.

With uncertainties between different instruments highlighted in Article 3, instrument behaviour was the focus of research detailed in Article 4. Two field campaigns were carried out during winter 2014 in Prague and summer 2015 in Barcelona to compare the response of several types of cascade impactors in two different and well-characterised aerosol airmass types, namely continental (Prague) and marine (Barcelona). The types of impactors used were: (i) Personal cascade impactor Sioutas (PCIS; 250 nm - 10 μm), (ii) Berner low-pressure impactor (BLPI; 25nm -13.5 μm), (iii) nano-Berner low-pressure impactor (nano-BLPI; 11nm-1.95 μm) and (iv) nano micro-orifice uniform deposit impactor (nano-MOUDI; 10nm-10 μm).

Taking the well characterised BLPI as an internal reference, the best agreement regarding mass size distributions was obtained with the nano-BLPI, independently of season (aerosol load) and location (aerosol chemical composition). The nano-MOUDI showed good agreement for particle sizes >320 nm, whereas, for particle diameters <320 nm this instrument recorded larger mass concentrations outdoors than the BLPI. The reason for the observed differences in these size ranges are inconclusive, yet dissociation processes of ammonium nitrate are suspected as being influential. This is especially true from the Prague results, during which, the shrinking of larger particles could have occurred due to the nano-MOUDI being located indoors, although in an unheated shed. The mechanics (rotating stages) and the metal housing of the stages may also have caused warming, and, therefore, encouraged dissociation and evaporation processes to occur. Another factor that may have reduced particle sizes within the nano-MOUDI were losses due to the spreading of the sample over the filter substrate, which increased interaction. Losses off the Teflon filter substrate may have been more significant than from the polycarbonate substrate used for the other impactors. Prior research found a significant increase in dissociation rates, especially when the sampled air temperature was >5 degrees Celsius more than the filter (Hering & Cass, 1999). Even though no absolute conclusions can be drawn for the reasons behind the different behaviours of different impactors, it is clear that nitrate plays a key part in the performance of these instruments. This highlights, once more, the importance of this work in establishing a greater understanding of ammonium nitrate on instrumentation, data collection and indoor and outdoor particle dynamics.

Finally, an experiment set in a real-world situation was undertaken in Prague metro over a period of 24 hours, with data collection carried out whilst the transportation hub was open. This placed the use of a suite of online and offline instrumentation together, in a heavily populated indoor setting. Mechanically formed particles from tracks, brakes and cables accounted for the majority of aerosol mass. However, there was also a significant presence of secondary inorganics that had migrated into the metro from street level. These findings demonstrate the importance and relevance of aerosol dynamics to human exposure in every day settings.

