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Diurnal variations in the nitrogen and oxygen isotope composition of aerosol nitrate

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Nitric acid (HNO_3) is an end product of atmospheric NO_x processing. Even though its lifetime is about one week, diurnal cycles have been reported for polluted sites on various occasions, indicating that the lifetime is short enough to reflect variations in the relative importance of atmospheric HNO_3 formation pathways. The cause of the diurnal cycles remain elusive. The diurnal variation could be a rectifier effect because of the shoaling of the nocturnal boundary layer that leads to a larger relative contribution of dry deposition to HNO_3 loss. During the day, HNO_3 levels would then be replenished from the free troposphere above. Alternatively, the increase of relative humidity during night-time may enhance absorption of HNO_3 to particles.

Here, we report on a case study using nitrogen and oxygen isotope measurements to distinguish between these different hypotheses. For example, in case of the rectifier effect, one would expect to find a decrease of the total nitrate concentration and a preferential enrichment of ^{15}N in the remaining aerosol due to kinetic isotope effects. In case of the relative humidity changes, one would expect to find no net change in the total nitrate concentration, but a potential isotope fractionation between the fine and coarse fraction of the aerosol.

Our week-long measurement campaign took place in late summer 2008 at Weybourne Atmospheric Observatory on the English coast. Throughout the campaign took relatively calm weather conditions (temperatures between 10 and 16 °C, wind speeds between 2 and 6 m s^{-1}) prevailed. We sampled every 2 h and analysed both submicron and larger aerosol particles. We observed pronounced diurnal variations in both $^{15}N/^{14}N$ ratios (a range of 12 ‰) and $^{18}O/^{16}O$ ratios (a range of 36 ‰), indicating variations in atmospheric processing pathways. In particular, the high $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios indicate a large contribution from N_2O_5 hydrolysis or reactions of NO_3. The reason is that these two compounds inherit the largest fraction of their oxygen atoms from very strongly enriched ozone.