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Short communication

Aerosol isotopic ammonium signatures over the remote Atlantic Ocean

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HIGHLIGHTS

- Aerosol NH_4 $\delta^{15}N$ measurements with improved sensitivity are reported, confirming a global isotopic distribution pattern.
- Pattern of isotopic signals may be either mixing between two end members or fractionation during aerosol transport.

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ABSTRACT

We report aerosol ammonium ^{15}N signatures for samples collected from research cruises on the South Atlantic and Caribbean using a new high sensitivity method. We confirm a pattern of isotopic signals from generally light ($\delta^{15}N$ −5 to −10‰), for aerosols with very low (<2 nmol m^{-3}) ammonium concentrations from the remote high latitude ocean, to generally heavier values ($\delta^{15}N$ +5 to +10‰), for aerosols collected in temperate and tropical latitudes and with higher ammonium concentrations (>2 nmol m^{-3}). We discuss whether this reflects a mixing of aerosols from two end-members (polluted continental and remote marine emissions), or isotopic fractionation during aerosol transport.

1. Introduction

The cycling of ammonia through the atmosphere represents a major component of the global nitrogen cycle (e.g. Fowler et al., 2013; Gruber and Galloway, 2008). The cycle involves both gaseous ammonia and aerosol ammonium, neither of which are oxidised in the atmosphere on the time scales of a few days, and can therefore be transported through the atmosphere and deposited over the oceans. In remote ocean regions, atmospheric nitrogen deposition represents an important nutrient source which can increase marine productivity (Duce et al., 2008). However, the net significance of the atmospheric ammonia/ammonium contribution to this deposition flux depends critically on whether the ammonia/ammonium source is predominantly terrestrial, and hence a new source of nitrogen to the marine environment, or from ammonia emissions from seawater that are being recycled and hence will not result in a net increase in ocean productivity. A net marine ammonia emission source to the atmosphere has been proposed (e.g. Voss et al., 2013 and references therein, Fowler et al., 2013) although it has been argued that the net direction of this flux may have been reversed in the industrial period so that it now flows from land to sea as a result of the increases in atmospheric ammonia emissions from human activity (Galloway et al., 1995). New comparisons of model and field data lead to a rather lower estimate of the global marine emission than previously suggested (Paulot et al., 2015). A recent study has suggested that the ocean ammonia emissions can be the dominant source of ammonium in rainfall on Bermuda, despite this being a region downwind of major terrestrial anthropogenic sources in North America (Altieri et al., 2014). However, another recent study has suggested that terrestrial ammonia emissions are the main source for ammonium in rainwater on Bermuda (Keene et al., 2014). Hence there is still considerable uncertainty over even the direction, leave alone the magnitude of the air-sea ammonia flux.

Due to the strong temperature dependence of ammonia solubility, it has been argued that marine ammonia emissions to the atmosphere are likely to be more important from warmer rather than cold ocean waters, with net emissions at high latitude from the ocean to the atmosphere difficult to achieve at the low water

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temperatures, under typical surface ocean and marine atmosphere conditions (Johnson et al., 2008, Paulot et al., 2015). Gas phase ammonia measurements from the remote marine atmosphere boundary layer would be useful for understanding the marine ammonia cycle. However, such gas phase ammonia concentrations are very poorly constrained, with few measurements, mostly with high uncertainties (Paulot et al., 2015). However, high sensitivity measurements suggest that gas phase ammonia and aerosol phase ammonium concentrations may be of similar magnitude to each other over the open ocean (Norman and Leck, 2005). Ammonia emissions from seawater can react rapidly in the marine atmosphere to form ammonium aerosols in the presence of acidic species. Given the rapid removal of any free nitric acid by reaction with sea-salt in the marine atmosphere (Baker et al., 2006; Andreae and Crutzen, 1997), the most likely salts to be formed by marine ammonia emissions are with sulphuric acid. We have previously assumed that these salts would not disproportionate into gas phase components (Jickells et al., 2003; Paulot et al., 2015) and hence will not isotopically fractionate once in the aerosol phase. Indeed for dry ammonium sulphate and ammonium bisulphate salts, the partial pressure of ammonia is very low. However, these salts will attract water potentially allowing a pH dependent bidirectional exchange of ammonia between aerosol and gas phases at high humidity in the marine boundary (Johnson et al., 2008, Quinn et al., 1992), consistent with limited field and laboratory data (Harrison and Kitto, 1992; Scott and Cattell, 1979). Johnson and Bell (2008) derive the following relationship from the Aerosol Inorganics Model (Clegg et al., 1998) at high relative humidity appropriate for the marine boundary layer:

$$pNH_3 = 0.00016\ e\verb|^|(0.124T + 4.6R)$$

where pNH_3 is the partial pressure of ammonia over the aerosol in nmol/m^3, T is the temperature in Celsius and R is the molar NH_4:nss-SO_4 (nss – non-sea-salt sulphate) ratio in the aerosol. This equation predicts pNH_3 comparable to or greater than typically observed marine boundary layer ammonia concentrations at NH4:nss-SO_4 ratios above ~1.2, and such ratios occur at least in parts of the Atlantic Ocean marine boundary layer (Norman and Leck, 2005). Thus ammonia-ammonium partitioning in the marine atmosphere is likely to be very dependent on aerosol pH (Johnson and Bell, 2008), which is also not particularly well known (Pszenny et al., 2004; Kerkweg et al., 2008).

The magnitude of marine ammonia emissions and their significance for ocean productivity is therefore still rather uncertain and requires further study, particularly given the scale and significance of the human perturbation of the global nitrogen cycle. Isotopic measurements have the potential to provide additional insight into the marine atmosphere ammonia cycle, and indeed the basis of the arguments for a major marine ammonia emission source dominating ammonium deposition over the North Atlantic (Altieri et al., 2014) are predominantly isotopic measurements. In the latter paper evidence from an earlier study by us of the aerosol ammonium isotopic composition in the remote marine atmosphere (Jickells et al., 2003) was used to help make the case in support of a marine source. However, while there have been several studies describing the isotopic signature of ammonia emissions and the abundance of ammonia/ammonium in rain, aerosol and the gas phase in relatively polluted areas (Yeatman et al., 2001; David Felix et al., 2013; Fukuzaki and Hayasaka, 2009; Xiao et al., 2015) there have been less studies in remote areas. In our earlier study (Jickells et al., 2003) we reported a systematic decrease in the isotopic ammonium signature with decreasing ammonium concentration which was interpreted as resulting from two end-member mixing of isotopically light marine emissions of ammonia with isotopically heavy terrestrial ammonia emissions. However, the nitrogen content of samples from the remote marine atmosphere approached our detection limit for isotopic analysis in that earlier study, and it is possible that some of the trends in isotopic composition with concentration reported could reflect uncertainties around detection limits.

We now report here analyses of aerosols collected along the Atlantic Meridional Transect AMT (Robinson et al., 2006) between the UK and Southern Ocean for ammonium ion isotopic composition using an improved method with greatly enhanced sensitivity. This allows us to test the validity of the trends seen in our previous study. The analysis of additional aerosol samples from the Caribbean is also reported and used to further consider the validity of the two end-member mixing model, between high concentration and isotopically heavy ammonia from strong terrestrial emission sources regions and a background low concentration marine emission of isotopically light ammonia.

2. Methods

Aerosol data reported here are based on samples collected on two cruises AMT15, sampling from approximately 10°N to 40°S in the Atlantic, and JC18 (Fig. 1). Our aerosol sampling and contamination control methods, as well as our procedures for calculating air-mass back trajectories, have been described in detail in previous publications (Jickells et al., 2003; Baker et al., 2010), and are therefore only briefly summarised here. Aerosol samples were collected by high volume aerosol sampling with a Sierra Type cascade impactor and the results presented here are for fine mode aerosol (<1 μm diameter aerosol and where most of ammonium is found Baker et al., 2006) collected on Whatman 41 filter. Sample filters were subsequently frozen for return to our home laboratory. Filters were later thawed, major ions water extracted from a fraction of the filter and this extract subsequently analysed by ion chromatography (anions and ammonium) and ICP-OES (for the other cations). The ammonium isotopic composition was measured on the water extract of a separate fraction of the aerosol filter using essentially the same method as Altieri et al. (2014), although independently developed and described in detail elsewhere (Lin, 2010).[1] This method is much more sensitive than the method used in our previous study. The method is based on chemical conversion of ammonium to nitrite and then to N_2O which is then cryogenically pre-concentrated and analysed by isotope-ratio mass spectrometry on a Europa GEO 20-20 (McIlvin and Altabet, 2005; Zhang et al., 2007; Altieri et al., 2014). The isotope ratios are calibrated against standard reference materials IAEA N1 and USGS 25 and 26 as well as an internal laboratory N_2O gas standard. Results are expressed here in the standard $\delta^{15}N$ notation. The method can successfully measure isotopic ratios on as little as 10 nmol of ammonium. Blanks of chemicals and sample preparation yield a beam area of only 10% or less of samples and are corrected for in the data reported here. The average precision based on replicate analyses of the standards is ±0.2‰ or better.

3. Results

Fig. 2a shows the results for AMT15 samples with the aerosol ammonium $\delta^{15}N$ isotopic composition values plotted against the ammonium concentration. Ammonium concentrations show a strong gradient of concentrations with low values at high latitudes consistent with the trend reported by Norman and Leck (2005). Since ammonia can have both marine and terrestrial sources, it is

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[1] https://ueaeprints.uea.ac.uk/19108/1/2010LinCTPhD.pdf.