On the ratio of nitrate to sulphate in CCN in the Netherlands

Harry ten Brink, Rene Otjes, Piet Jongejan
Energy research Centre of the Netherlands (ECN), Petten, The Netherlands

INTRODUCTION

Estimates of the magnitude of the first indirect aerosol effect (IAE) are based on the hypothesis that sulphate is the main manmade compound of cloud nuclei. The concentration of sulphate has drastically decreased in Europe over the last decades (Arends et al., 1996) and continues to decline. As a consequence, the indirect aerosol effects in Europe should sharply decrease too.

While sulphate rapidly decreases another hygroscopic component might become important, viz., nitrate. However a possible role of nitrate in the IAE has not been considered yet.

It is common belief that nitrate is present in particles of such a large size that the associated numbers are negligible. Moreover, the coarse nitrate does not constitute new particles, but is a result of a reaction of existing aerosol with gaseous nitric acid.

The most important reaction of nitric acid and existing coarse aerosol in our region is that with the natural seasalt, sodium chloride (ten Brink, 1998). The original seasalt particle functions as CCN and after reaction with nitric acid a particle is formed that consists of sodium nitrate. This particle is of almost equal size and has equivalent activation properties. Hence there is no principal difference with the natural situation and hence no "forcing".

The idea that nitrate mostly occurs in coarse particles is not justified for west-Europe. There is ample proof that nitrate is predominantly present as submicron ammonium nitrate (Schaap et al., 2002). Ammonium nitrate in our region almost completely derives from manmade nitrogen oxides and ammonia, which would make it a true forcing agent.

The concentration of (ammonium) nitrate is often underestimated due to evaporative losses of the semi-volatile compound during sampling. Evaporation can especially be the case for the smallest particles as is substantiated by data on nitrate in ultrafine particles in the Netherlands (Chang et al., 2001).

There may be several reasons for such a preferential loss. One is that the concentration of the gases (nitric acid and ammonia), with which ammonium nitrate is in equilibrium, is low at the final stages of a cascade-impactor due the loss of the adsorptive nitric acid in the passage of the sampling air through the impactor-train.

In addition, during the often long-term sampling (up to three days) the conditions might have changed, in the sense that with an increase in temperature volatilisation of collected material was promoted.

However, despite evaporation, the average ratio of nitrate to sulphate in this range was close to 0.3 (Chang et al., 2001). Hence it is very likely that this ratio is even higher in the somewhat larger CCN-class.

Representative sampling of nitrate in size-classes with classical impactors seems impossible and this prompted the development of a semi-continuous monitoring system with which the nitrate can be representatively measured in the same size classes.

A prototype of the monitor was used in a measuring campaign of two months, described before (ten Brink et al., 2005). Here we make an analysis of the ratio of nitrate to sulphate in the CCN-range. Also, we describe new developments in the instrumentation.

EXPERIMENTAL

The semi-continuous monitor for representative measurement of size-classified ammonium nitrate is termed the MARGA-sizer. The instrument derives the name MARGA from the possibility to simultaneously Measure AeRosol and related precursor GAses. The collection principle is that of condensing steam onto the particles to grow these to larger droplets that are easily collected. The drain-water is led to an on-line IC.

The pre-selection of the aerosol in the size-range of the CCN occurs with a set of parallel impactors. These are single-stage units taken from a commercial MOUDI-impactor. The instrument has been descried in detail before (ten Brink et al., 2005). We will present the development of a unit to preconcentrate the drain-water to improve sensitivity. This set-up will be deployed shortly in our large cloud chamber.

Activation experiments centred on nitrate will be performed along the lines described in detail by Khlystov (1998). He used study a classical Berner impactor. The approach is to measure the nitrate concentration in ambient air before and after passage through the cloud chamber. In parallel the size distribution is measured in more detail. Preliminary results will be presented at the conference.

Field measurements of the concentration of nitrate and sulphate were already made in 2002 with a prototype instrument and an evaluation of the ratio of the two components in the CCN-range will be given next.

RESULTS AND DISCUSSION

In the field campaign, performed in the summer of 2002 the average concentration of nitrate in particles smaller than 0.18 um was 0.15 ug m-3. To put it in perspective this concentration has to be compared with that of sulphate in the same range. This was close to 0.5.

There is a complication in that the LOD for sulphate was three times higher than that of nitrate. Thus the concentration of sulphate, of 0.32 ug m-3 in the CCN-range is less certain. For that reason we only used concentrations for which the uncertainty in the sulphate concentraion was less than 30%. This meant rejection of 28% of the data. Hence there is some bias in the average ratio.

An illustration of the temporal variation in the ratio is given in Figure 1.

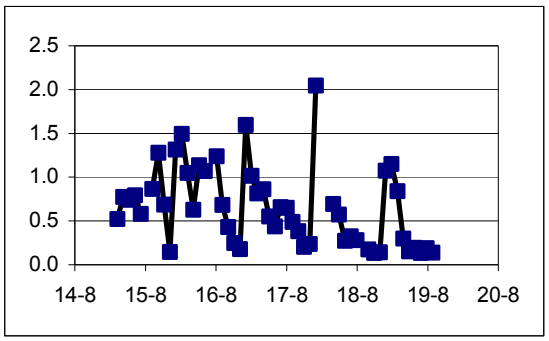

Figure 1. Ratio of nitrate to sulphate in the CCN-range, in the indicated summer period in 2002, as measured on top of the meteo-tower of Cabauw in the Netherlands.

The total campaign encompassed a period of two months in the summer. The season is important because sampling artefacts with classical cascade impactors are highest in summer. The obvious reason is the higher volatility of the ammonium nitrate. We thus obtained the first representative data on size-classified ammonium nitrate in the summer season.

One of the reasons for monitoring at a time resolution as given in Figure 1 was to search for a possible diurnal variation in CCN-nitrate. Such a pattern could be expected because the components are of a secondary nature. This means that they are not directly emitted but formed in the atmosphere in processes that depend on temperature, humidity and photochemical conditions. Moreover, the semi-volatile ammonium nitrate could exhibit a diurnal variation because its vapour pressure is a function of both temperature and relative humidity.

Nightly conditions, with lower temperatures and higher humidities should favour the preferential presence of nitrate in the aerosol phase, while at daytime the balance should be towards the gas phase. This diurnal variation could also promote a difference in the size-distribution between day and night.

Contrary to the expectations, we did not observe a diurnal cycle.

CONCLUSION

We representatively measured (ammonium) nitrate and sulphate in the fraction of the aerosol that serves as CCN. A prototype semi-continuous monitor, the MARGA-sizer was used for this purpose. The average ratio of nitrate to sulphate in the CCN size-range, defined here as particles smaller than 0.18 um, was close to 0.5. A much longer set of data is required to substantiate these first findings. This will be obtained via long-term measurements planned for the coming years with an instrument that has highly improved sensitivity.

Keywords:

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