

The need for ammonia abatement with respect to secondary PM reductions in Europe

J.W. Erisman¹ and M. Schaap^{2,*}

¹ Energy Research Centre of the Netherlands (ECN), PO Box 1, 1755 LE Petten, The Netherlands, Erisman@ecn.nl

²Institute for Marine and Atmospheric Research (IMAU), University of Utrecht, PO Box 80005, 3508 TA Utrecht, The Netherlands

* Now at TNO-MEP: m.schaap@mep.tno.nl

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Introduction

Ammonia is emitted from different sources, most notably animal manure, traffic and fertilizer application (Olivier et al. 1998). Its role in acidification and eutrophication and its impact on ecosystems and water quality is well documented (e.g. recent review by Krupa, 2003). In addition, ammonia, the major basic gas in the atmosphere, plays an important role in atmospheric chemistry, transport and deposition processes (Adams et al., 1999). Through the reactions with sulphuric and nitric acids, it contributes to the formation of secondary particulate matter in the atmosphere.

In Europe, policy to reduce the exposure of humans to particulate matter is aimed at the reduction of PM₁₀. In principle, there is no threshold for PM concentrations in relation to effects (Brunekreef and Holgate, 2002). For 2010 the targeted maximum values for PM₁₀ are 20 µg m⁻³ as

an annual average and maximal 7 daily exceedances of $50 \mu\text{g m}^{-3}$. Secondary particles constitute a large part of PM_{10} , varying from 50% to 90%. Therefore, reductions of precursor emissions could contribute significantly to reaching the future target concentrations. In this paper we assesses the effect of various reduction strategies using a box model and the 3D LOTOS long-range transport model version 5.2, developed by TNO-MEP (Schaap et al., 2003). The chemistry in the model has recently been updated to describe the equilibrium between gases and aerosol formation. Initially the background of the $\text{NH}_3\text{-NO}_3\text{-SO}_4$ system is described and then using measurements, evidence in support of the theoretical system is sought. The LOTOS model was used for different scenarios focussed on the role of ammonia in the PM formation.

$\text{NH}_4\text{-NO}_3\text{-SO}_4$ equilibrium

Secondary inorganic particles result from among others, reactions involving SO_2 , NO_x and NH_3 , in the gas and aqueous phase. The equilibrium between particulate $\text{NH}_4\text{-NO}_3\text{-SO}_4$ and gaseous HNO_3 and NH_3 has been subject to many studies (see e.g. Adams et al, 1999). Formation of ammonium sulphate and nitrate depends strongly on ambient conditions and availability of ammonia, which is determined by the physical processes like emission rate but also by the degree of sulphate neutralisation (Ansari and Pandis, 1998; Adams et al., 1999). Detailed sensitivity studies concerning these factors have been presented in the literature (e.g. Ansari and Pandis, 1998 and references therein). Here we present the nitrate partitioning, calculated with the *Isorropia* module (Nenes et al, 1998), as function of the sulphate concentration and ambient conditions.

Figure 1 shows as a function of temperature, the effect of a decrease in SO_4 on the sum of particulate $\text{SO}_4\text{+NO}_3$ concentrations, at constant TNO_3 and TNH_4 ($T = \text{total}$). This represents a

constant decrease in SO₂ emissions, but constant NH₃ and NO_x emissions. Regardless of the temperature, SIA (secondary inorganic aerosol) levels decrease almost linearly with SO₄, when sulphate is not completely neutralised. In that case, complete neutralisation occurred at about 13 µg m⁻³. When the SO₄ concentrations dropped further, NH₃ became available, the equilibrium with NO₃ (HNO₃+NH₃ ↔ NH₄NO₃) emerged as important. At low temperatures, close to 0 °C, most of the decrease in SO₄ was compensated by NO₃ formation. Such compensation occurred until all available nitrate was in the particulate phase, after which the SO₄+NO₃ concentration decreased linear with sulphate. We conclude from this exercise that after neutralisation of sulphate, nitrate may (partially) compensate for the decline in sulphate, especially at low temperatures. This led us to the evaluation of the scale of this effect in Europe and testing some of the scenarios aimed at optimisation of reductions in secondary PM.

Field evidence for the effect of ammonia on SO₄ and NO₃

During these past years, SO₂ emissions have been reduced by more than 60% in Europe. NO_x emissions have decreased by 21% and NH₃ by 14% (Erisman et al., 2003). Therefore, the case described in Figure 1 actually took place. However, it is very difficult to obtain field evidence for the observed theoretical changes, because i) time series of data are often not long enough or not all required components are measured, ii) site measurements represent the integral over different air masses with long enough residence times in the atmosphere to reach equilibrium, thus leading to a general correlation between the concentrations of different aerosol components, iii) measurements represent differences in the changing emissions, atmospheric conditions (T, rh, etc.) and deposition, and iv) measured data may be influenced by artefacts, e.g. losses of ammonium nitrate or adsorption of nitric acid (Schaap et al., 2002).

Inspection of the 90 EMEP monitoring sites in Europe, yielding 6 stations with the characterization of all aerosol components, revealed some evidence of a NO_3 increase at the end of the measurement period at Cvratouch (CZ01, Czech Republic) and K-pusta (HU02, Hungary) (www.emep.org). The examination of all other EMEP stations within Europe did not provide further indications of the increase of NO_3 concentrations. The wet deposition measurements at EMEP stations provide longer time series of data for the three components (SO_4 , NO_3 and NH_4). The precipitation measurements showed a good correlation between the three components, without any indication of increasing NO_3 concentrations at decreasing SO_4 concentrations. At several sites an increase in the $\text{NH}_4/(\text{NO}_3+2\text{SO}_4)$ ratio was observed. The trends in SO_4 and NO_3 were, however, smaller than expected from changes in emissions, especially in Western Europe. Earlier such a non-linearity effect was demonstrated by Erisman et al., (2003).

The present analysis did not provide strong evidence for the effects described with the application of the box model, confirming the limitations mentioned previously. Therefore, we extended that work by using a 3-D chemistry transport model to assess the effect of emission control strategies over Europe.

LOTOS model

LOTOS was originally developed by the Dutch research institute TNO-MEP to describe oxidant levels in Europe. Over the years, the model has been expanded into a combined aerosol and oxidant model that uses a resolution of $0.5 \times 0.25^\circ$ longitude X latitude and three dynamic layers in the vertical domain. Chemistry is described by a CBM(Carbon Bond Mechanism)-IV mechanism, *Isorropia* (Nenes et al, 1998) and explicit heterogeneous N_2O_5 hydrolysis mechanism. Cloud chemistry is represented by linear SO_2 to SO_4 conversion rate. For a detailed

description of the model version 5.2, emissions and other input variables, we refer to Schaap et al. (2003) and references therein.

Emission scenario's

A case study was performed to address the effect of nitrate buffering by ammonium in the future and examine possible and sensible strategies for reducing SIA levels. To study the effect of reductions in ammonia emission compared with SO₂ and/or NO_x reductions, several scenarios were defined (see Table 1). The base year was 1995 and changes in the European emissions are relative to that year. The calculations were done for October, during which the highest PM levels occurred over north-western and central Europe. In scenario 1-3 the effects of reductions of the individual precursor gases were assessed in a relative sense. Scenarios 4-6 were chosen to demonstrate the effect of ammonia reductions relative to current policies on SO₂ and NO_x emissions.

Figure 2 summarises the results for all scenarios expressed as SO₄, NO₃ and NH₄ concentrations (total SIA) for some regions in Europe during October 1995. These regions were chosen such that they differed in climatic conditions and pollution regimes. The first bar in the figure represents the situation in 1995 and serves as a reference. The results show that, except for south-western France and Spain, where temperatures are generally high and relative humidity low, ammonia emission reductions are more effective for decreasing SIA than SO₂ or NO_x. However, NO_x reductions lead to more homogeneous NO₃ concentration ratios, whereas NH₃ reductions lead to nitrate 'hotspots' in areas with high NH₃ emissions, as reductions are more effective in areas with low ammonia emission densities. In comparison, SO₂ reduction is relatively ineffective, and NO₃ levels increase in the high SO₄ areas.

The last three scenarios show the effect of varying NH_3 emissions in the situation where SO_2 emission is reduced by 50% and NO_x by 25%. Those scenarios show that SIA concentrations can only be reduced effectively, if apart from SO_2 and NO_x , ammonia emissions are also significantly decreased.

Synthesis

In Europe, secondary particulate matter (PM) contributes to about 50 % or more of $\text{PM}_{2.5}$. Therefore, to reduce PM concentrations it is necessary to lower precursor emissions. Since the eighties, the emissions of SO_2 have decreased by more than 60%, but particle concentrations have decreased less. In addition to NO_x , ammonia emissions decreased much less and thus the amount of neutralisation of acid SO_4 , or the free NH_4 concentration, has probably increased. Consequently, NH_4NO_3 levels may have risen. Recently increasing attention has been directed to the role of NH_3 and PM concentrations, especially concerning the equilibrium with nitric acid and NO_3 (e.g. Ten Brink et al., 1997; Adams et al., 1999; Schaap et al., 2002; 2003). Regionally NO_3 is an important constituent of SIA and is relevant to the radiative balance of the earth and to the respiratory fraction of PM. As a result of successful SO_2 abatement, SO_4 concentrations have declined but not to the same extent (Erisman et al., 2003). Depending on climatic conditions and precursor concentrations, formation of NO_3 is possible in those areas where NH_3 is in excess of SO_4 . We could not identify a buffering effect of NH_4 on NO_3 , due to a lack of representative and reliable long-term data. However, box model studies on the nitrate partitioning, using measured data as input, do indicate that the SIA levels are sensitive to NO_3 buffering, when the SO_4 levels are decreased (Ansari and Pandis, 1998). We made a first attempt to include feedback mechanisms on the lifetimes of the involved species by using a 3D long-range transport model.

Our results fully support the findings obtained with the box models and provide a first assessment of regions, which may be particularly sensitive to nitrate buffering. An extensive model analysis should provide further support for the theoretical findings.

Within the National Emission Ceiling (NEC) Directive and Gothenburg protocol, national emission ceilings for SO₂, NO_x, NH₃ and VOC have been agreed upon to reduce vegetation and ecosystem effects and to reduce human exposure to ozone. The agreements are aimed at additional future reductions in SO₂ and NO_x and for the first time, also reductions in NH₃. The scenarios used here demonstrate that for effective PM reductions, the three precursor gases should be reduced at the same time. In that sense, it could be argued that the current Directive and the protocol are inadequate to optimally reduce SIA concentrations, because NH₃ reductions are too small.

In the NEC Directive and the Gothenburg protocol, critical loads are used to optimise the emission reductions (gap closure method). That was done with a Lagrangian model where sulphur and nitrogen chemistry was not adequately coupled. The optimisation results probably would have been different, had the chemistry as described here been included in the new EMEP and LOTOS models. The reductions in different emissions lead to different transport distances in aerosols and gases due to the shifting equilibrium in the atmosphere, but also due to the influence of NH₃ in the dry deposition process (Erisman et al., 2003). These complex interactions should be taken into account in the evaluation of the current protocol and Directive, but also in the future negotiations for further reductions to meet the critical loads. That is, however, also important in respect to optimisation of strategies within CAFE (Clean Air For Europe) to reduce PM concentrations. The reduction of secondary PM needs international agreements, as it is a long-range transport problem. When reductions are optimised to meet the future targets, the

interactions of sulphur and nitrogen compounds are important as demonstrated in this paper, not only for the absolute levels, but also for the regional differentiation. In that context, the role of ammonia is very important. Finally, in the future, PM and ecosystem protection standards should both be considered at the same time in optimisation strategies, as they concern the same sources.

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Figure captions:

Figure 1. The sum of nitrate and sulphate as function of the sulphate concentration at different temperatures for the following scenario: Reflecting the constant ammonia and NO_x , total ammonia and total nitrate were chosen to be constant, 5 and 10 ug/m^3 . The sulphate concentration was set to 22.5 ug/m^3 at the start and was gradually decreased. The relative humidity was set to 80 %.

Figure 2. SIA concentrations in different European countries for all scenarios.

Tables:

Table 1. Emission reductions used for the scenarios (%)

<i>Scenarios</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>
SO_2	-25	0	0	-50	-50	-50
NO_x	0	-25	0	-25	-25	-25
NH_3	0	0	-25	0	-25	-50

Note: ship emissions were not reduced in the scenarios

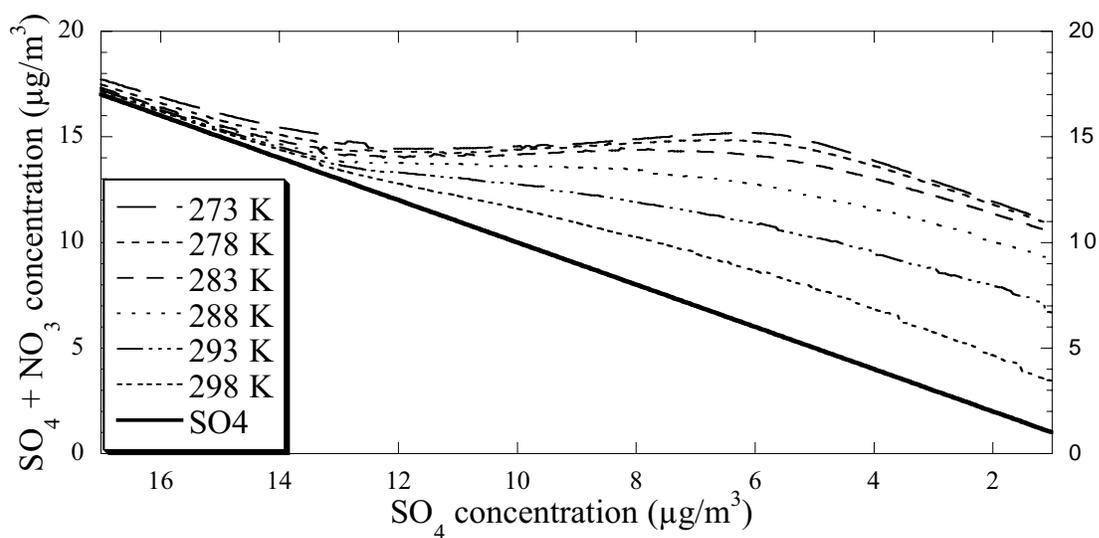


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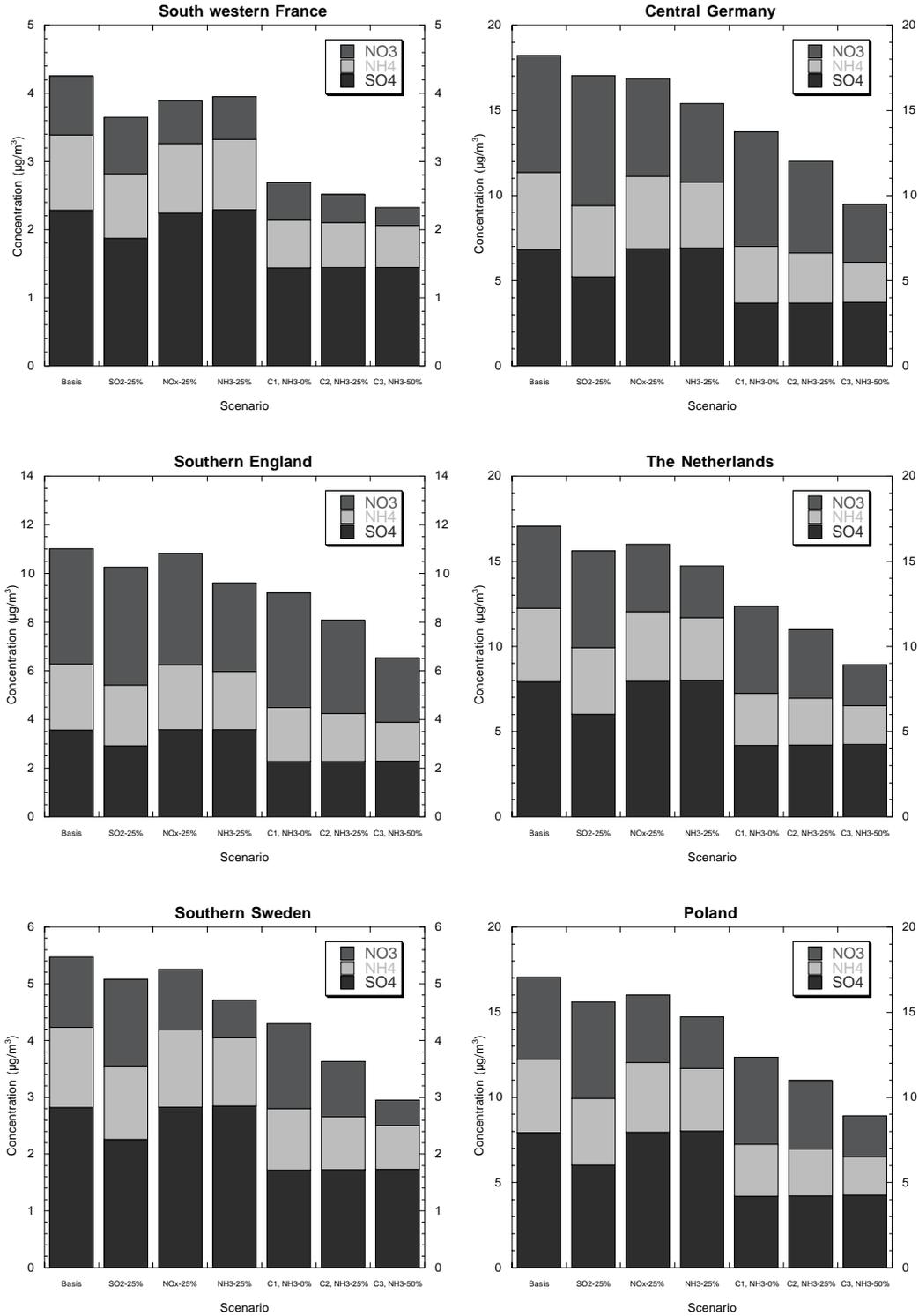


Figure 2. SIA concentrations in different European countries for all scenarios.