THE EFFECT OF SULFUR AND NITROGEN EMISSION REDUCTIONS ON PM CONCENTRATION IN VARIOUS SMOG REGIMES

Rita Van Dingenen, Jean-Philippe Putaud, Alessandro Dell'Acqua, Sebastiao Martins-Dos Santos, Luca Pozzoli, M. Grazia Perrone, Frank Raes

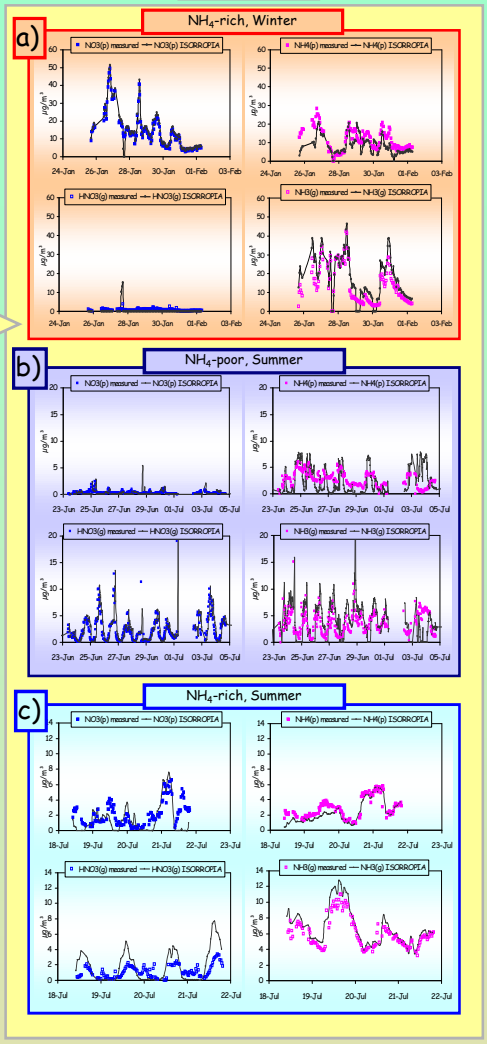
Institute for Environment and Sustainability, Joint Research Centre, Ispra

The issue

Exceedance of limit values of fine particulate matter (PM10) is still commonly occurring in large parts of Europe (Putaud et al., 2002). The same particles that cause adverse health effects, often lead to acidification and may play a role in global and regional climate change. Chemical mass closure experiments have shown that most of the PM10 (and *a fortiori* of the PM2.5) mass is made of secondary aerosol components (sulfate, nitrate, ammonium, carbonaceous matter). Efficient and cost-effective abatement strategies thus require an understanding of how much secondary aerosol is formed from emitted precursors. Nitrate, ammonium and probably many organic species occur in fact as semi-volatile compounds showing a complex gas-aerosol phase partitioning, depending on temperature, humidity and relative concentrations. Therefor, reduction measures will not necessarily lead to a linear response in PM loadings. Here we explore the link between emissions and ambient concentrations of the major ionic components of sub-micrometer particles for 3 real-world cases.

Figure 1: time series of measured and modeled partitioning between aerosol and gas phase of NH_x and $(H)NO_3$ at the three selected sites. Measurement method: Wet Annular Denuder + Steam JetAerosol Collector for high time resolution and artefact-free sampling. Model: ISORROPIA thermodynamic equilibrium; calculates aerosol/gas partitionning from total NH_4, SO_4, HNO_3, RH and T

Figure 1



Cases studied

Figure 1 a-b-c shows data from3 fields campaigns, representing duifferent smog and meteorological conditions: Ispra (rural, downwind Milan, summer 2000), Vinon-sur-Verdon (rural, downwind Marseille, summer 2001), and Bresso (urban background Milan, winter 2002). These 3 sites have been chosen because of their different characteristics: Ispra and Vinon represent both rural sites during summer, with similar amounts of total nitrate (Ispra: 1 $\mu g/m^3$, Vinon: 1.3$\mu g/m^3$) but different total ammonium (Ispra: 10$\mu g/m^3$, Vinon: 6$\mu g/m^3$). Bresso on the other hand represents an urban site in winter time with strongly increased nitrate (17$\mu g/m^3$) and ammonium (27 $\mu g/m^3$). A molar ratio SO_4:NH_x of 1:2 is required for complete neutralisation of SO_4. The molar ratios of total SO_4:NO_3:NH_x for all sites are given in Table 1, showing that Bresso and Ispra have a higher capacity for nitrate formation (i.e. availability of excess NH_3 to bind HNO_3 into particulate ammonium nitrate) than Vinon, with the lower temperature at Bresso largely favoring nitrate formation during winter time.

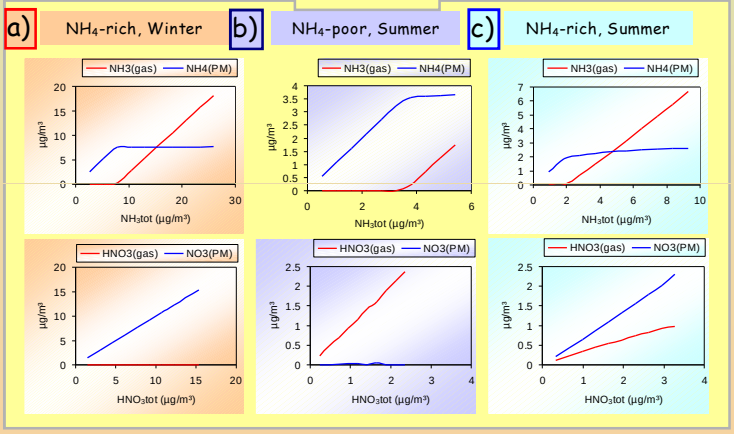
Table 1: relative molar ratios for major ions (gas + aerosol) at the three sites.

	RH	Temp	SO_4	total NH_x	total NO_3
Bresso winter	93%	3.4°C	1	16	2.5
Vinon summer	56%	23°C	1	3.2	0.3
Ispra summer	72%	19°C	1	9	0.9

Measured and modeled partitioning

We simulated the measured aerosol and gas phase contributions of sulfate and semi-volatile nitrogen compounds with the aerosol equilibrium model ISORROPIA (Nenes et al. 1998). Measured total (gas + particulate) nitrate and ammonium are given as input to ISORROPIA, together with measured sulfate, temperature and relative humidity. ISORROPIA then calculates the aerosol - gas partitioning for the given conditions , which can be compared with the measured values (Figure 1 a-b-c).

Figure 2



Simulated partitioning with reduced concentrations

Next, we explore how reducing secondary aerosol precursors affects the resulting PM mass, leaving all other conditions unaffected. This is "modelled" with ISORROPIA by reducing, one by one, total SO_4, NH_x and $(H)NO_3$ down to 10% of the observed values, and evaluating the effect on the partitioning between aerosol and gas phase of each component.

Reduction of SO_4 leads to an equal reduction in particulate SO_4 because it is completely non-volatile (not shown in the figure). For ammonium and nitrate however strong non-linear effects may occur. Figure 2 shows how a reduction in total NH3 and HNO3 (starting with the averaged observed concnetrations) affects gas and particulate concentrations:

- reduction of NH_3 has no effect on the PM concentration as long as excess NH_3 is present in the gas phase. Depending on the NH_3(g) concentration, a low (case a) to very high (case c) reduction effort is required to affect PM.
- the effect of HNO_3 reduction is further complicated by the temperature-dependent gas-aerosol equilibrium of $(NH_4)(NO_3)$; in cold conditions (case a) the equilibrium is shifted to the particulate phase, and reduction of total HNO_3 leads to equal reduction in the particulate phase. In conditions where HNO_3 is completely driven into the gas phase (case b), reduction measures won't bear any effect on PM [high temperatures, absence of NH_4 to form $(NH_4)(NO_3)$]. In case c, NO_3 partitions between gas and PM due to the availability of sufficient NH_3, and reductions are leading to a proportional decrease in both phases.

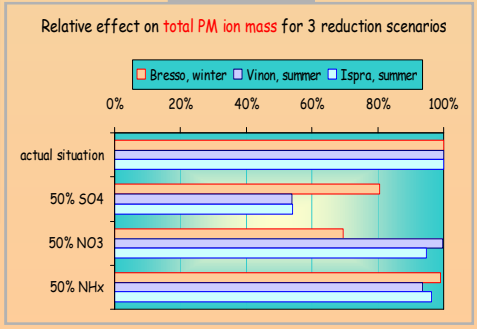
Conclusions

Abatement strategies for PM reduction will have different efficiencies in different smog regimes prevailing in Europe. Figure 3 summarizes the effect of 50% reduction in each of the inorganic compounds on total ion mass. The most efficient reduction is observed for SO_4 as it still makes up an important fraction of the PM mass and its contribution is not complicated by gas-particle partitioning. For the conditions in the 3 cases studied, a 50% reduction of ammonia has a negligible effect on PM, either because of large excess gas phase concentrations (NH_3-rich regimes), or because its contribution to PM is not significant (NH_3-poor regimes). Reduction of NO_3 finally is only efficient in winter time when it significantly contributes to PM loading (and when the PM-health problem is most stringent).

Note:

- the combined effect of agricultural (NH_3) and traffic (HNO_3) emissions cause most of the inorganic wintertime PM.
- O_3 abatement reduction strategies by reducing NO_x emissions will have a limited effect on INORGANIC PM. (but the effect on the ORGANIC contribution remains to be investigated).

Figure 3



references:

Nenes, A., Pilinis, C., Pandis, S.N. (1998) ISORROPIA: A New Thermodynamic Model for Multiphase Multicomponent Inorganic Aerosols, Aquat. Geochem., 4, 123-152

Putaud, J.P. et al (2002) A European Aerosol Phenomenology; Physical and Chemical Characteristics of Particulate Matter at Kerbside, Urban, Rural and Background Sites in Europe. Report EUR 20411 EN (http://ies.jrc.cec.eu.int/Download/cc).

European Commission, Joint Research Center, Institute for Environment and Sustainability

For more information: rita.van-dingenen@jrc.it Tel.: ++39 0332 78 93 00 Fax: ++39 0332 78 57 04