Effects of changing gaseous precursor emissions on aerosol chemical composition in Europe

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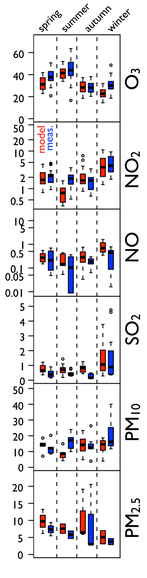
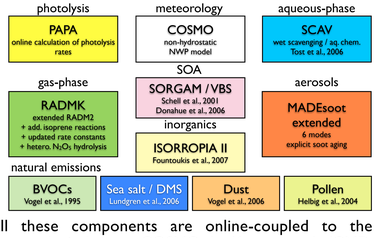
Motivation

Man-made emissions of particles and trace gases have changed substantially during the last 2 decades. Observed trends in ambient aerosol chemical composition follow emissions for SO_4^{2-}, whereas reductions in particulate nitrate are found to be lower than expected from NO_x emission changes, or not even found at all. Several hypotheses have been proposed to explain this finding, like the replacement of sulfate by nitrate as combination partner for ammonia, a change in chemical regimes, or a masking of trends by meteorological variability. In this work we investigate the effects of different emission changes on aerosol chemical composition, employing a comprehensive regional-scale numerical chemistry-transport model able to represent aerosol processes as well as its connections to the gas-phase and the liquid-phase in clouds.

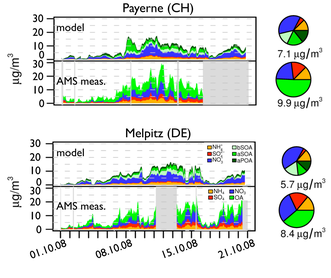
Model system and setup

COSMO-ART (Vogel et al., ACP, 2009) is an online-coupled regional-scale numerical chemistry-transport model, including state-of-the-art components for gas-phase chemistry (RADMKA), aerosols (MADEsoot extended), secondary organic aerosol formation (SORGAM), thermodynamic equilibrium calculations for inorganic salts (ISORROPIA II), washout and aqueous-phase chemistry (SCAV), a scheme to calculate photolysis rates online (PAPA), and several parameterizations for biogenic emissions.



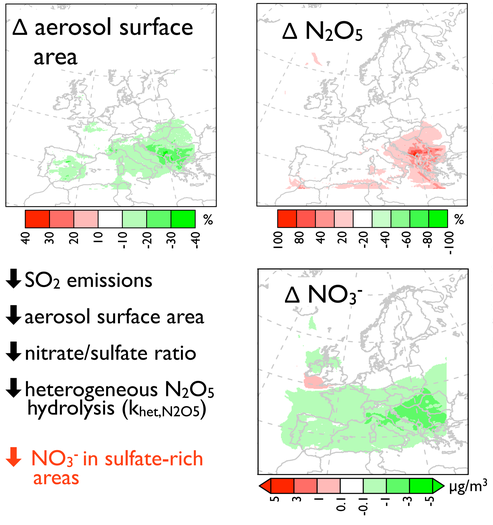


All these components are online-coupled to the meteorological core, COSMO. In Knote et al. (GMD, 2011) the model was evaluated for all seasons against a large number of surface and remote sensing observation datasets.



Modeling results

Effects of SO_2 reductions



⬇ SO_2 emissions

⬇ aerosol surface area

⬇ nitrate/sulfate ratio

⬇ heterogeneous N_2O_5 hydrolysis ($k_{het,N2O5}$)

⬇ NO_3^- in sulfate-rich areas

The model is initialized with and relaxed at the boundaries against ECMWF IFS analyses (meteorology) and MOZART-NCEP reanalyses (chemistry). Anthropogenic emissions are provided by the TNO/MACC inventory. For the sensitivity studies, emission country totals were scaled to 1990 levels using totals as reported to EMEP. A period of 1 week in January 2009 serves as study time frame.

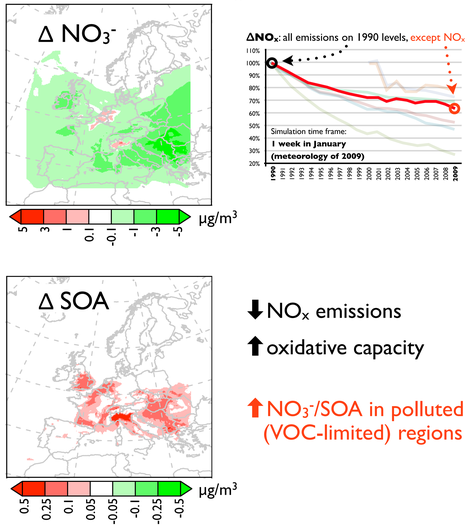
Effects of SO_2 reductions

Only in a small region over southern Ireland NO_3^- aerosols increase due to reductions in SO_2 emissions. This indicates that there NO_3 replaces SO_4^{2-} as NH_4^+-combination partner. Elsewhere, especially in southeastern Europe, NO_3^- aerosols are reduced. Less aerosol surface area and an increased nitrate-to-sulfate ratio decrease the heterogeneous HNO_3 formation pathway (Riemer et al., JGR, 2003) there.

Effects of NOx reductions

While reduced concentrations of nitrate aerosols mass are observed in most regions, especially in very polluted regions the opposite is the case. Decreasing NO_x emissions in such VOC-limited regions increase the atmospheric oxidation capacity, accelerating primary HNO_3 production. This also affects the oxidation of SOA. Here, even more areas show elevated concentrations. For NO_3^-, higher HNO_3 production is often overcompensated by significant absolute reductions in NO_x emissions.

Effects of NO_x reductions



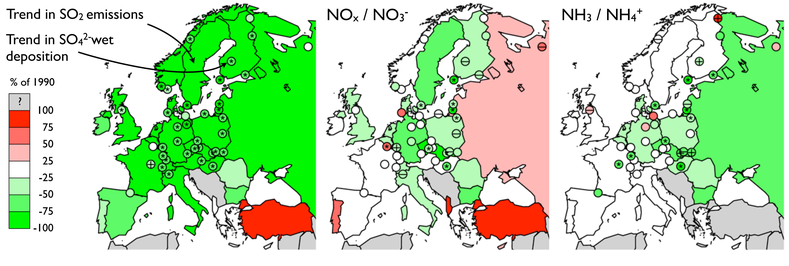
⬇ NO_x emissions

⬆ oxidative capacity

⬆ NO_3^-/SOA in polluted (VOC-limited) regions

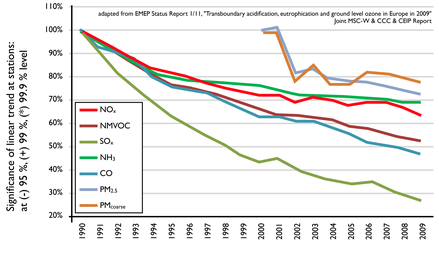
Observed trends (1990-2009)

Trends in EMEP wet deposition measurements



Emission trends: country totals as reported to EMEP (http://www.ceip.at/), *wet deposition trends:* EMEP measurements (http://www.emep.int), *trend estimation:* linear trend by least-squares-regression (emissions: annual totals, wet deposition meas.: monthly totals), *statistical significance of a monotonic trend at a station:* Mann-Kendall test.

Emission trends (EMEP region total)



Take-home messages

based on wet deposition measurements:

- sulfate aerosol mass reductions follow (strong) emission reductions
- nitrate/ammonium aerosols show smaller trends, often not significant due to meteorological variability and not-as-strong NO_x/NH_3 emission reductions

based on model results:

- „**nitrate replacing sulfate** as ammonia combination partner" hypothesis **cannot be confirmed**
- **NO_x reductions** in polluted (VOC-limited) regions **increase atmospheric oxidative capacity**, increasing NO_3^- and SOA mass, **but effect is overcompensated** in other regions **by total NO_x reductions**
- **SO_2 emission reductions** also decrease NO_3^- mass due to **decrease** in **heterogeneous N_2O_5 hydrolysis** efficiency

References

Fagerli, H. and Aas, W.: **Trends of nitrogen in air and precipitation: Model results and observations at EMEP sites in Europe, 1980–2003**, Environmental Pollution, Volume 154, Issue 3, 448-461, doi:10.1016/j.envpol.2008.01.024, 2008.

Kendall, M.: **Rank correlation measures**. Charles Griffin, London, 202, 1975.

Knote, C., Brunner, D., Vogel, H., Allan, J., Asmi, A., Äijälä, M., Carbone, S., van der Gon, H. D., Jimenez, J. L., Kiendler-Scharr, A., Mohr, C., Poulain, L., Prévôt, A. S. H., Swietlicki, E., and Vogel, B.: **Towards an online-coupled chemistry-climate model: evaluation of trace gases and aerosols in COSMO-ART,** Geosci. Model Dev., 4, 1077-1102, doi:10.5194/gmd-4-1077-2011, 2011.

Knote, C.: **Regional scale impacts of changing anthropogenic emissions on aerosols,** ETH, Zurich, http://dx.doi.org/10.3929/ethz-a-007179320, 2012.

Mann, H.: **Nonparametric tests against trend**. Econometrica: Journal of the Econometric Society, 245–259, 1945.

Riemer, N., H. Vogel, B. Vogel, B. Schell, I. Ackermann, C. Kessler, and H. Hass: **Impact of the heterogeneous hydrolysis of N_2O_5 on chemistry and nitrate aerosol formation in the lower troposphere under photosmog conditions**, J. Geophys. Res., 108 (D4), 4144, 2003.

Vogel, B., Vogel, H., Bäumer, D., Bangert, M., Lundgren, K., Rinke, R., and Stanelle, T.: **The comprehensive model system COSMO-ART – Radiative impact of aerosol on the state of the atmosphere on the regional scale**, Atmos. Chem. Phys., 9, 8661-8680, doi:10.5194/acp-9-8661-2009, 2009.

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