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Assessing sensitivity regimes of secondary inorganic aerosol formation in Europe with the CALIOPE-EU modeling system

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Sulfur dioxide and nitrogen oxides form two of largest contributors to PM2.5 in Europe; ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3). In-situ observations of many chemical components are rather sparse, and thus neither can accurately characterize the distribution of pollutants nor predict the effectiveness of emission control. Understanding (and controlling) the formation regimes for these components is important for the achievement of the reduction objectives established in the European legislation for PM2.5 (20% of PM2.5 triennial for the mean of urban background levels between 2018 and 2020). For this purpose, the present work uses the CALIOPE high-resolution air quality modeling system (12 km × 12 km, 1 h) to investigate the formation of SIA (SO_4^{2-}, NO_3^- and NH_4^+, which involve an important part of PM) and their gaseous precursors (SO_2, HNO_3 and NH_3) over Europe during the year 2004. The CALIOPE system performs well at estimating SIAs when compared to the measurements from EMEP monitoring network, but errors are larger for gaseous precursors. NH_3 is underestimated in the warmest months, HNO_3 tends to be overestimated in the summer months, and SO_2 appears to be systematically overestimated. The temporal treatment of ammonia emission is a probable source of uncertainty in the model representation of SIA. Furthermore, we discuss the annual pattern for each inorganic aerosol and gas precursor species over Europe estimated with the EMEP data and CALIOPE outputs, comparing the performance with other European studies. Spatial distribution of key indicators is used to characterize chemical regimes and understand the sensitivity of SIA components to their emission precursors. Results indicate that SO_4^{2-} is not usually fully neutralized to ammonium sulfate in ambient measurements and is usually fully neutralized in model estimates. CALIOPE and EMEP observations agree that the continental regions in Europe tend to be HNO_3-limited for nitrate formation. Regulatory strategies in such regions should focus on reductions in NO_x ($NO + NO_2$) rather than NH_3 to control ammonium nitrate. This work assesses how well the CALIOPE system reproduces the spatial and temporal variability of SIAs and their gaseous precursors over Europe and complements the measurement findings.

1. Introduction

Atmospheric PM, or aerosols, plays a central role in atmospheric processes (Fountoukis and Nenes, 2007). They have adverse effects on human health (Pope et al., 2009) and affect visibility (Altshüller, 1984), ecosystems (Niyogi et al., 2004; Bytnerowicz et al., 2007), air quality and climate change (IPCC, 2007). To alleviate some of these atmospheric problems, the control of atmospheric PM concentration

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Abbreviations: PM2.5, particles with a diameter < 2.5 μm; CALIOPE, WRF-ARW/EMEP-HERMES/CMAQ/BSC-DREAM8b; SIA, secondary inorganic aerosol; PM, particulate matter; EMEP, European Monitoring and Evaluation Programme; PM10, particles with a diameter < 10 μm; NMVOC, non methane organic volatile compounds; CTM, Chemical Transport Model; WRF-ARW, Advanced Research Weather Research and Forecasting Model; HERMES-EMEP, High-Elective Resolution Modeling Emission System-European Monitoring and Evaluation Programme; CMAQ, Models-3 Community Multiscale Air Quality Modeling System; BSC-DREAM8b, Dust REgional Atmospheric Model version 8 bins developed at the Barcelona Supercomputing Center – Centro Nacional de Supercomputación; CALIOPE-EU, The CALIOPE system applied over the European domain in 2004; CB-IV, Carbon Bond IV; SNAP, Selected Nomenclature Air Pollution; EPER, European Pollutant Emission Register; ESRI, Environmental System Research Institute; MSC-W, Meteorological Synthesizing Centre-West; MB, mean bias; RMSE, root mean square error; *r*, correlation coefficient; MFB, mean fractional bias; MFE, mean fractional error; Ratio, the ratio between modeled mean and observed mean.

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is needed. European legislation has established regulations regarding PM10 and recently for PM2.5 in order to reduce human exposure to high concentration of PM (European Commission, 2008).

PM is both emitted directly from a large variety of anthropogenic, biogenic and natural sources and formed in the atmosphere by chemical and physical processes from gas-phase precursors such as NMVOC, NO_x, SO_2 and NH_3 (Seinfeld and Pandis, 1998). Therefore, to fulfill the task of reducing human exposure to PM, policies must focus not only on the reduction of primary particulate emissions, but also on the reduction of precursor emissions for the formation of secondary particles (Wu et al., 2008; Renner and Wolke, 2010). With this purpose, in Europe within the National Emission Ceiling (NEC) directive and the multi-pollutant and multi-effect Gothenburg protocol, national emission ceilings for SO_2, NO_x, NH_3 and VOC have been agreed upon to reduce acidification and eutrophication effects and to reduce human exposure to ozone.

Several experimental studies have analyzed levels, speciation and origin of PM over Europe (Querol et al., 2004, 2009; van Dingenen et al. 2004; Putaud et al., 2004, 2010). They found that the European background levels, derived form 31 European air monitoring stations, have been 7.0 ± 4.1 μg PM10 m^{-3} and 4.8 ± 2.4 μg PM2.5 m^{-3}, over the past decade. The observed aerosol composition reveled that organic matter is a major component in PM10 and PM2.5, except at rural background sites where SIA contribution prevailed. The dominant SIA species are ammonium sulfates and ammonium nitrates salts.

The formation of SIA is a two-step process. First, the primary emissions of NO_x and SO_2 are oxidized to form nitric acid (HNO_3) and sulfuric acid (H_2SO_4), respectively, precursors of secondary aerosols. Secondly, H_2SO_4, HNO_3 and NH_3 partitions between the gas and particle phase according to thermodynamic equilibrium determined by temperature, relatively humidity and molar concentration of SO_4^{2-}, total nitrate ($TNO_3 = HNO_3 + NO_3^-$) and total ammonia ($TNH_3 = NH_3 + NH_4^+$). SO_2 emissions in Europe have been reduced ~67% from 1980 to 2000 (EMEP, 2004; Fagerli and Aas, 2008; Hamed et al., 2010). Thus, nowadays less NH_3 is converted to $(NH_4)_2SO_4$ and more NH_3 is available for the formation of NH_4NO_3. This situation leads to a higher residence time of TNO_3 in air (Fagerli and Aas, 2008).

Because of the complex relationship between SIAs (Ansari and Pandis, 1998; Vayenas et al., 2005) the control of PM2.5 is still nowadays a difficult challenge. In this sense, CTMs are important tools for air quality assessment and the evaluation of emission control policies, but it becomes necessary to assess their ability in simulating pollution quality levels. Single model evaluation studies (Schaap et al., 2004a; Sartelet et al., 2007; Stern et al., 2008; Matthias, 2008), model inter-comparisons (Hass et al., 2003; van Loon et al., 2004); and model ensembles (Vautard et al., 2009) showed that models tend to underestimate observed PM and their SIA components. The results of these studies show large uncertainties in the estimation of the meteorological input data, uncertainties in the modeling of the anthropogenic PM sources, missing natural and biogenic sources and also with gaps in the knowledge of many of the physical and chemical processes which lead to the formation of SIA.

The main purpose of this work is to characterize SIA formation regimes and understand the sensitivity of SIA vs. their gaseous counterpart over Europe by means of the CALIOPE air quality modeling system (Pay et al., 2010a; Baldasano et al., 2011) with a simulation covering the whole year 2004. This paper is structured as follows. Section 2 describes the modeling system, the observational database and the evaluation tools. Section 3 analyses the modeling results against available measured data for the year 2004 and discusses the modeled and observed annual patterns of SIA and their gas-precursors. Also a discussion about aerosol formation regimes over Europe is provided. Section 4 presents a thorough comparison of statistical evaluation results with other European studies. Finally, conclusions are drawn in Section 5.

2. Methods

2.1. Model description and setup

CALIOPE (Baldasano et al., 2008a) is a complex system that integrates a meteorological model (WRF-ARW), an emission processing model (HERMES-EMEP), a CTM (CMAQ) and a mineral dust dynamic model (BSC-DREAM8b) together coupled in an air quality modeling system (Fig. 1 of Pay et al., 2010a). CALIOPE encompasses a high-resolution air quality modeling system which provides 48-h air quality forecasts in Europe (12 km × 12 km) and Spain (4 km × 4 km) (available at: www.bsc.es/caliope). The system has been widely evaluated during its development over northeastern Spain (Jiménez et al., 2005a,b, 2006a,b, 2007), the Iberian Peninsula (Jiménez-Guerrero et al., 2008a; Baldasano et al., 2008a, 2011; Pay et al., 2010b) and Europe (Pay et al., 2010a). Furthermore, it has been used for assessing air pollution dynamics (Gonçalves et al., 2009a) and as management tool to study air quality impact of urban management strategies (Jiménez-Guerrero et al., 2008b; Gonçalves et al., 2008, 2009b; Soret et al., 2011).

The CALIOPE system applied over the European domain in 2004 is namely hereafter as CALIOPE-EU. For a detailed description of the modeling system we refer to aforementioned studies. Here, we describe the most relevant model characteristics and the setup used in this study.

Meteorological input data for the CMAQ model are processed using the WRF-ARW model version 3.6.1 (Michalakes et al., 2004; Skamarock and Klemp, 2008). Details about the performance of WRF-ARW over the European domain are provided as supplementary material.

The CMAQ model version 4.5 is a three-dimensional Eulerian CTM that uses state-of-the-science routines to model gas and particulate matter formation and removal processes (Byun and Schere, 2006; Appel et al., 2008; Roy et al., 2007). The gas-phase oxidations in the atmosphere are described in the CB-IV chemical mechanism (Gery et al., 1989) following the criteria of Jiménez et al. (2003). Aerosols are represented by the modal aerosol module AERO4 (Binkowski and Roselle, 2003) which contains a preliminary treatment of sea salt emissions and chemistry (Bhave et al., 2005; Shankar et al., 2005). Three log-normal modes spanning three size categories Aitken (0.01–0.1 μm diameter), accumulation (0.1–1 μm) and coarse (>1 μm). The aerosol within each model is internally mixed.

Fine-particle SO_4^{2-} has an anthropogenic origin and is directly emitted, generated by nucleation and/or condensation from the gas phase oxidation of SO_2 and hydroxyl radical (OH) and by heterogeneous oxidation of SO_2 in clouds (Binkowski and Roselle, 2003). The effective cloud SO_2 oxidation rate in CMAQv4.5 depends primarily on cloud liquid water content, the presence of species affecting pH (e.g., HNO_3 and NH_3), concentration of O_3 and H_2O_2 and cloud lifetime. Under optimal conditions clouds can effectively convert all ambient SO_2 into sulfate within the volume of air they process. The cloud-cover metric (fraction of total sky covered by clouds near or just above the top of the PBL) determinates heterogeneous SO_2 oxidation. The three-dimensional WRF-ARW fields of cloud water mixing ration determine the presence of resolved cloud layers in CMAQ. In CMAQv4.5 cloud treatment follows the asymmetric convective module (Pleim and Chang, 1992).

HNO_3 is produced by heterogeneous hydrolysis of N_2O_5 and by gas-phase oxidation of NO_x by OH. Atmospheric H_2SO_4 is neutralized by NH_3 to form $(NH_4)_2SO_4$. Remaining NH_3 (further denoted as free ammonia) may then combine with HNO_3 to form the semi-volatile NH_4NO_3. This equilibrium is function of ambient