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**Joint analysis of deposition fluxes and atmospheric concentrations of inorganic nitrogen and sulphur compounds predicted by six chemistry transport models in the frame of the EURODELTAIII project**

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1 **Joint analysis of deposition fluxes and atmospheric**  
2 **concentrations of inorganic nitrogen and sulphur**  
3 **compounds predicted by six chemistry transport models in**  
4 **the frame of the EURODELTAIII project**

5  
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## 7 **Abstract**

8 In the framework of the UNECE Task Force on Measurement and Modelling (TFMM) under the Convention on  
9 Long-range Transboundary Air Pollution (LRTAP), the EURODELTAIII project is evaluating how well air  
10 quality models are able to reproduce observed pollutant air concentrations and deposition fluxes in Europe. In  
11 this paper the sulphur and nitrogen deposition estimates of six state-of-the-art regional models (CAMx,  
12 CHIMERE, EMEP MSC-W, LOTOS-EUROS, MINNI and CMAQ) are evaluated and compared for four  
13 intensive EMEP measurement periods (25 Feb - 26 Mar 2009; 17 Sep - 15 Oct 2008; 8 Jan - 4 Feb 2007 and 1 -  
14 30 Jun 2006).

15 For sulphur, this study shows the importance of including sea salt sulphate emissions for obtaining better model  
16 results; CMAQ, the only model considering these emissions in its formulation, was the only model able to  
17 reproduce the high measured values of wet deposition of sulphur at coastal sites. MINNI and LOTOS-EUROS  
18 underestimate sulphate wet deposition for all periods and have low wet deposition efficiency for sulphur.

19 For reduced nitrogen, all the models underestimate both wet deposition and total air concentrations (ammonia  
20 plus ammonium) in the summer campaign, highlighting a potential lack of emissions (or incoming fluxes) in this  
21 period. In the rest of campaigns there is a general underestimation of wet deposition by all models (MINNI and  
22 CMAQ with the highest negative bias), with the exception of EMEP, which underestimates the least and even  
23 overestimates deposition in two campaigns. This model has higher scavenging deposition efficiency for the  
24 aerosol component, which seems to partly explain the different behaviour of the models.

25 For oxidized nitrogen, CMAQ, CAMx and MINNI predict the lowest wet deposition and the highest total air  
26 concentrations (nitric acid plus nitrates). Comparison with observations indicates a general underestimation of  
27 wet oxidized nitrogen deposition by these models, as well as an overestimation of total air concentration for all  
28 the campaigns, except for the 2006 campaign. This points to a low efficiency in the wet deposition of oxidized  
29 nitrogen for these models, especially with regards to the scavenging of nitric acid, which is the main driver of  
30 oxidized N deposition for all the models. CHIMERE, LOTOS-EUROS and EMEP agree better with the  
31 observations for both wet deposition and air concentration of oxidized nitrogen, although CHIMERE seems to  
32 overestimate wet deposition in the summer period. This requires further investigation, as the gas-particle  
33 equilibrium seems to be biased towards the gas phase (nitric acid) for this model.

34 In the case of MINNI, the frequent underestimation of wet deposition combined with an overestimation of  
35 atmospheric concentrations for the three pollutants indicates a low efficiency of the wet deposition processes.  
36 This can be due to several reasons, such as an underestimation of scavenging ratios, large vertical concentration  
37 gradients (resulting in small concentrations at cloud height) or a poor parameterization of clouds.

38 Large differences between models were also found for the estimates of dry deposition. However, the lack of  
39 suitable measurements makes it impossible to assess model performance for this process. These uncertainties  
40 should be addressed in future research, since dry deposition contributes significantly to the total deposition for  
41 the three deposited species, with values in the same range as wet deposition for most of the models, and with  
42 even higher values for some of them, especially for reduced nitrogen.

43

## 1 **1 Introduction**

2 Atmospheric deposition of air pollutants can lead to a range of detrimental impacts to  
3 terrestrial and aquatic ecosystems. Nitrogen (N) deposition is currently considered a major  
4 threat to European biodiversity, including sensitive habitats and species listed under the  
5 European Commission Habitats Directive (92/43/EEC) (Sutton et al., 2011; Ochoa et al.,  
6 2014). N deposition can lead to the replacement of local plant communities of species adapted  
7 to low-nutrient environments by nitrophilous species able to thrive under high-N conditions  
8 (Stevens et al., 2004). On the other hand, an alteration of soil N and carbon storage could  
9 contribute to either mitigate or reinforce the effects of climate change (Reich et al., 2006).  
10 The deposition of both sulphur (S) and nitrogen (N) can lead to the acidification of soils as  
11 well as freshwater and marine ecosystems (Longhurst, 1991). Acidification makes forests and  
12 other ecosystems more vulnerable to stress factors such as frost, drought and pests (Bouwman  
13 et al., 2002, Heij and Schneider, 1991).

14 It is generally difficult and expensive to measure the components of atmospheric deposition,  
15 especially dry deposition fluxes, and thus the use of deposition estimates simulated by  
16 chemical transport models (CTMs) has become a common practice. Nowadays modelled  
17 deposition is commonly used to evaluate a range of environmental impacts. For example,  
18 modelled deposition fluxes of nitrogen and sulphur can be used to evaluate potential  
19 ecosystem damage by comparing annual deposition rates with habitat-specific thresholds,  
20 such as critical loads for acidification and nutrient nitrogen (Nilsson et al., 1988). Maps of the  
21 exceedances of critical loads in Europe for last decades can be found in annual EMEP Status  
22 Reports ([http:// www.emep.int](http://www.emep.int)). A robust evaluation of model capabilities to correctly predict  
23 atmospheric deposition rates is, therefore, necessary, beyond the evident importance of  
24 correctly calculating air pollutant concentrations.

25

26 Atmospheric deposition can occur through dry or wet mechanisms. Wet deposition refers to  
27 the processes of scavenging of air pollutant by hydrometeors, *i.e.* cloud and fog droplets, rain  
28 or solid precipitation. One of these processes is the dissolution into cloud-drops of soluble  
29 gases such as  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{SO}_2$ , present in the interstitial cloud air. A proportion of aerosol  
30 particles (nitrates, sulphates) can also be removed within clouds by incorporation into the  
31 liquid phase. Below clouds, pollutants can be scavenged by precipitation elements between

1 the cloud base and the surface. Soluble gas species can dissolve into falling raindrops during  
2 rain, while airborne particles can be collected by raindrops through collisions. Dry deposition  
3 includes a downward transport and the subsequent uptake of the atmospheric pollutant species  
4 by surfaces, in the absence of precipitation. Models generally use an approach based on an  
5 electrical resistance analogy, defining a “resistance” to deposition, for the turbulent transport,  
6 molecular diffusion and surface processes, adding them in the same way as electrical  
7 resistances. Downward fluxes for particles can also be increased by sedimentation.

8 The presence of  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in the atmosphere is the result of a combination of  
9 processes. Whereas ammonia is directly emitted, nitric acid ( $\text{HNO}_3$ ) and sulphuric acid  
10 ( $\text{H}_2\text{SO}_4$ ) can be formed through the oxidation of nitrogen dioxide ( $\text{NO}_2$ ) and sulphur dioxide  
11 ( $\text{SO}_2$ ). Anthropogenic  $\text{SO}_2$  emissions mainly come from the combustion of fossil fuels  
12 (primarily coal and oil), whereas natural sources of atmospheric S include volcanoes and  
13 marine algae, mainly in the form of dimethyl sulphide (DMS). Nitric oxide (NO) and  $\text{NO}_2$   
14 emissions are mainly from fossil fuel combustion, biomass burning, and microbiological  
15 emissions from soils (Lee et al., 1997). In Europe  $\text{NH}_3$  mostly comes from agricultural  
16 practices such as the volatilization from animal waste and synthetic fertilizers with  
17 contributions from other sources such as biomass burning, emissions from oceans and soils  
18 under natural vegetation, emissions from waste industrial processes and transport (Bouwman  
19 et al., 1997). Ammonia is the only significant alkaline gas of significance in the atmosphere,  
20 playing an important role in neutralizing acids. Sulphates, nitrates and ammonium can be  
21 formed when  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are neutralized by  $\text{NH}_3$ , forming ammonium sulphate  
22 ( $(\text{NH}_4)_2\text{SO}_4$  and bisulphate ( $(\text{NH}_4)\text{HSO}_4$ , in the case of  $\text{H}_2\text{SO}_4$ , and ammonium nitrate  
23 ( $\text{NH}_4\text{NO}_3$ ) in the case of  $\text{HNO}_3$ . The formation of ammonium sulphate is the favoured  
24 reaction; i.e. nitrates are only formed once all sulphate is neutralized by  $\text{NH}_3$ . As ammonium  
25 nitrate can evaporate easily, the formation of nitrates is a reversible process, with the  
26 formation reaction favoured by low temperatures and high relative humidity.

27 CTMs include chemical mechanisms describing the atmospheric gas-phase chemistry, based  
28 on various reaction schemes (e.g. CB05, MELCHIOR, SAPRC99, etc.). The way these  
29 mechanisms parameterise the oxidation chemistry (i.e. NO reacting to form  $\text{NO}_2$ , which then  
30 goes on to form  $\text{HNO}_3$ ,  $\text{SO}_2$  forming  $\text{H}_2\text{SO}_4$  via oxidation of OH or other reactions affecting  
31  $\text{NO}_2$ ,  $\text{SO}_2$  and other oxidant concentrations) has an effect on the formation of  $\text{HNO}_3$  and  
32  $\text{H}_2\text{SO}_4$ . Once the concentrations of the gaseous aerosol precursors are calculated, the next step

1 in the models is to simulate their condensation onto the aerosol phase and to estimate the  
2 concentrations of aerosol species (nitrates, sulphates and ammonium, among others). In  
3 general, CTMs assume that the atmospheric gases and inorganic species (aqueous ions or  
4 precipitated solids) are in thermodynamical equilibrium, using aerosol inorganic equilibrium  
5 models such as ISORROPIA (Nenes et al., 1998) or MARS (Binkowski and Shankar, 1995)  
6 models.

7 While a large number of studies have focused on the evaluation of air pollutant concentration  
8 predictions in Europe, far fewer have looked at the deposition of nitrate, ammonium and  
9 sulphate. Estimates of total nitrogen deposition cannot be directly evaluated because of a lack  
10 of measurements, especially of dry nitrogen deposition. For gaseous nitrogen species,  
11 estimates of dry deposition are usually based on measurements of concentrations combined  
12 with estimates of the deposition velocity (Flechard et al., 2011). On the other hand, Simpson  
13 et al. (2011) highlight some uncertainties linked to the evaluation of modelled wet deposition,  
14 as a result of insufficient measurements of atmospheric concentrations of many key  
15 compounds (e.g.  $\text{HNO}_3$ , coarse-nitrate or  $\text{NO}_2$ ) or the limited availability of measurements of  
16 gas and particle compounds at the same site, among others. Moreover, model performance  
17 evaluation of wet deposition is strongly limited by the quality of meteorological input data  
18 (e.g. precipitation on complex topography) according to the same authors.

19 In Europe, some studies to evaluate wet deposition predictions for individual models have  
20 been carried out. The performance of the EMEP model for wet deposition of oxidised  
21 sulphate and oxidised and reduced nitrate has been evaluated with EMEP observations for  
22 several decades, and results can be found in EMEP status reports (<http://emep.int>). In the most  
23 recent report (for the year of 2014; Gauss et al. 2015,  
24 [http://emep.int/publ/reports/2015/sup\\_Status\\_Report\\_1\\_2015.pdf](http://emep.int/publ/reports/2015/sup_Status_Report_1_2015.pdf)) the authors found some  
25 overestimation of reduced nitrogen deposition, (12%), a small positive bias for oxidized  
26 nitrogen (1%), and an underestimation of sulphur wet deposition (-35%), considering annual  
27 accumulated values. The EMEP model was also evaluated in Simpson et al. (2006), in which  
28 the authors mention a slight overestimate of wet deposition of sulphur when compared with  
29 the measurements of the EMEP network. Aksoyoglu et al. (2014) showed that the modelled  
30 total nitrogen deposition for CAMx at various locations in Switzerland for 2006 was in the  
31 same range as the measured values. Nevertheless, comparison of the modelled wet deposition  
32 with measurements in the same study revealed an underestimation by a factor of two for

1 oxidized nitrogen, although model performance was better for the wet deposition of reduced  
2 nitrogen (Aksoyoglu et al., pers. comm.). The LOTOS-EUROS model has been evaluated for  
3 wet deposition by Schaap et al. (2004), who found an underestimation by a factor of two or  
4 more for all components, on average. In Spain, Garcia-Gómez et al. (2014) evaluated the wet  
5 deposition of oxidized and reduced N estimated by CHIMERE for the period 2005-2008,  
6 using measurement data from several networks, and including a comparison with the EMEP  
7 model. The authors obtained reasonable results for both models, with a slightly better  
8 performance for CHIMERE in the case of oxidized nitrogen, and a worse performance for  
9 reduced nitrogen (the model underestimated observed wet deposition of reduced N).

10 With regards to model intercomparisons for wet deposition, several studies have been  
11 published, some of them based on global model estimates (Lamarque et al., 2005, 2013;  
12 Dentener et al., 2006), mainly using a multi-model approach and on an annual basis. Solazzo  
13 et al. (2012) compared the performance of some models in EU and USA in the context of  
14 AQMEII, although the results are presented in a way that preserves model anonymity.  
15 Emissions and boundary conditions were common for all modelling teams but meteorology  
16 and/or grid definitions were not. The authors showed large differences between models  
17 regarding wet deposition for oxidized nitrogen. In the framework of the UNECE Task Force  
18 on Measurements and Modelling (TFMM), under the Convention on Long-range  
19 Transboundary Air Pollution (LRTAP), the EURODELTA (ED) project aims to assess how  
20 well CTMs are currently able to reproduce observed pollutant air concentrations and  
21 depositions in Europe, as well as to explain the differences between their predictions. The first  
22 two phases of the ED project have also looked at the evaluation and intercomparison of  
23 models (van Loon et al., 2007; Vautard et al., 2009, showing results for air concentration). In  
24 the third phase of this project, ED3, a more homogeneous input dataset and model  
25 configuration was used; common boundary conditions, meteorology, emissions and horizontal  
26 grid. Bessagnet et al. (2016) show the performance of six state-of-the art CTMs for air  
27 concentrations of a range of pollutants for four EMEP intensive measurement periods. Here,  
28 we evaluate the wet deposition of S (WSO<sub>x</sub>), and that of oxidized and reduced N wet  
29 deposition (WNO<sub>x</sub> and WNH<sub>x</sub>, respectively), as well as the air concentrations of the  
30 deposited species. We also include the intercomparison of dry deposition for oxidized and  
31 reduced N (DNO<sub>x</sub> and DNH<sub>x</sub>) and S (DSO<sub>x</sub>).

32

1

## 2 **2 Materials and methods**

### 3 **2.1 Model set-up and configuration**

4 Six CTMs were used to perform the simulations: CHIM (CHIMERE; version chim2013),  
5 EMEP (rv 4.1.3), LOTO (LOTOS-EUROS, V1.8), CAMX (CAMx, v5.41 VBS), MINNI  
6 (version 4.7) and CMAQ (V5.0.1). All models were run for the same domain and resolution  
7 and with the same input data (anthropogenic emissions, meteorology, and boundary  
8 conditions), with the exception of CMAQ, which used a different meteorology and  
9 geographical projection (Bessagnet et al., 2016). The meteorological variables were based on  
10 the calculations of ECMWF IFS (Integrated Forecast System) at a spatial resolution of  $0.2^\circ$ .  
11 CMAQ used meteorological variables from the COSMO model in CLimate Mode (COSMO-  
12 CLM) version 4.8 clm 11. The boundary layer height data used by CHIM, LOTO, and CAMX  
13 were calculated by ECMWF, whereas EMEP, MINNI and CMAQ used boundary layer  
14 heights as described in Bessagnet et al. (2016). For the boundary concentrations, MACC  
15 reanalysis (Inness et al., 2013; Benedetti et al., 2009) was used as input data for  $O_3$ ,  $CO$ ,  $NO_2$ ,  
16  $SO_2$ ,  $HCHO$ ,  $CO_2$ ,  $CH_4$ , sulphates, dust and carbonaceous aerosols.

17 Anthropogenic emissions were calculated by INERIS, by merging several databases: 1) TNO  
18  $0.125^\circ \times 0.0625^\circ$  for 2007 from MACC (Kuenen et al., 2011), 2) EMEP  $0.5^\circ \times 0.5^\circ$  emission  
19 inventory for 2009 (Vestreng et al., 2007) and 3) emission data from the GAINS database  
20 (<http://gains.iiasa.ac.at/gains>). Emissions were re-gridded by INERIS, as described in  
21 Bessagnet et al. (2016).

22 Table 1 summarizes some relevant aspects of the different models, such as chemical  
23 mechanisms or other specifications for the different processes. More details of the  
24 parameterizations are provided by Bessagnet et al. (2014; 2016). Here we summarize only  
25 those most relevant to N and S deposition (Table 1).

- 26 • NO soil emissions: CHIM and MINNI used version 2.04 of MEGAN and CAMX used  
27 version 2.1 of MEGAN. CMAQ used the BEIS (Biogenic Emission Inventory System)  
28 module developed by the US EPA. EMEP calculated these emissions as described in  
29 Simpson et al. (2012) and LOTO did not include this type of emissions.
- 30 • EMEP used the EmChem09 chemical scheme (Simpson et al., 2012), CHIM used  
31 MELCHIOR2 (Lattuati, 1997), CMAQ and CAMX used CB05 (Yarwood et al.,



1 2005), LOTO used a modified version of CBM-IV (Sauter et al., 2012), and MINNI  
2 used SAPRC99 (Carter, 2000).

- 3 • CMAQ, CHIM and CAMX used ISORROPIA (Nenes et al., 1999) and LOTO and  
4 MINNI the ISORROPIA II model (Fountoukis and Nenes, 2007) to estimate the  
5 formation of sulphate, nitrates and ammonium and their thermodynamic equilibria.  
6 EMEP used the equilibrium thermodynamic model MARS (Binkowski and  
7 Shankar, 1995). The system modelled by ISORROPIA includes  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  
8  $\text{SO}_4^{2-}$ , and  $\text{H}_2\text{O}$ , which are partitioned between gas, liquid and solid phases, taking into  
9 account the ambient relative humidity and temperature (Nenes et al., 1998).  
10 ISORROPIA II also includes the thermodynamics of crustal species ( $\text{Ca}_2^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ).  
11 MARS is another widely used model for the sulphate-nitrate-ammonia-water system  
12 (Saxena et al., 1986). ISORROPIA and, MARS account for the T-dependence of the  
13 equilibrium coefficients, although MARS uses activity coefficients calculated at  
14 298.15 K.
- 15 • EMEP, LOTO and CMAQ consider the formation of nitrates in the coarse fraction,  
16 originating from sea salt (all three models) and dust (only EMEP). CHIM considers a  
17 mass transfer from smaller particle sizes to larger ones, but nitrate is not directly  
18 formed in the coarse fraction. CAMX and MINNI did not consider coarse nitrate.
- 19 • EMEP, CHIM, CMAQ, CAMX and MINNI consider both, in-cloud and below-cloud  
20 wet scavenging, whereas LOTO considers just below cloud wet scavenging.
- 21 • EMEP and LOTO include a compensation point for  $\text{NH}_3$  that takes into account an  
22 equilibrium between  $\text{NH}_3/\text{NH}_4^+$  stored in plants and soil and  $\text{NH}_3$  concentrations in the  
23 air (reference EMEP, Wichink Kruit et al., 2012)
- 24 • CMAQ also includes emissions of sea salt sulphates corresponding to a proportion of  
25 7.76% of emitted sea salts split into the accumulation and coarse modes.

26 More specific information for each model regarding wet and dry deposition is included in  
27 Annex 1. For dry deposition, although many models use a similar approach for simulating  
28 dry deposition, differences can arise from the input data required to estimate the different  
29 resistances. For example, the resistance attributed to vegetative surfaces has a stomatal  
30 and non-stomatal component. For the estimation of the stomatal resistance, a minimum  
31 resistance is used, modulated by several factors that depend on light, temperature,  
32 radiation and other variables that alter this minimum resistance. These factors are

1 calculated for each type of vegetation. Therefore, both the land use database and the  
2 parameters involved in the computation of the stomatal resistance (minimum and  
3 modulating factors, assigned to each type of vegetation), can be a source of differences  
4 between model estimates.

5

## 6 **2.2 Evaluation methodology**

7 All models simulated the accumulated daily deposition of WSO<sub>x</sub> (wet deposition of oxidized  
8 sulphur species), WNH<sub>x</sub> (wet deposition of reduced nitrogen species), WNO<sub>x</sub> (wet deposition  
9 of oxidized nitrogen species), DSO<sub>x</sub> (dry deposition of oxidized sulphur species), DNH<sub>x</sub>, (dry  
10 deposition of reduced nitrogen species) and DNO<sub>x</sub> (dry deposition of oxidized nitrogen  
11 species). Species included in each group are shown in Table 2.

12 In order to evaluate model performance for WNO<sub>x</sub>, WNH<sub>x</sub> and WSO<sub>x</sub>, a statistical analysis  
13 was carried out, by comparing model outputs with observations. This comparison was also  
14 done for air concentrations of TNO<sub>3</sub> (the sum of nitric acid and nitrates), TNH<sub>4</sub> (sum of NH<sub>3</sub>  
15 and ammonium) and TSO<sub>4</sub> (sum of SO<sub>2</sub> and sulphates).

16 A similar evaluation was not possible for dry deposition of nitrates (DNO<sub>x</sub>), ammonium  
17 (DNH<sub>x</sub>) and sulphates (DSO<sub>x</sub>) due to lack of measurements.

1 Table 1.Characteristics of model codes, for some processes directly affecting wet deposition.

2 IC: in-cloud; BC below-cloud ; SC scavenging coefficients ; ASC: Aqueous SO<sub>2</sub> chemistry

MODEL	EMEP	CHIM	LOTO	CMAQ	MINNI	CAMX
<b>Wet Deposition: Gases</b>	IC& BC SC (Simpson et al., 2012)	IC& BC SC (Menut et al., 2013)	BC SC Scott (1979)	IC& BC SC Chang et al. (1987)	IC& BC SC (EMEP, 2003)	IC& BC SC (Seinfeld and Pandis, 1998)
<b>Wet Deposition: Particles</b>	IC& BC SC (Simpson et al. 2012)	IC& BC SC (Menut et al. 2013)	BC SC Scott (1979)	IC& BC SC Chang et al. (1987)	IC& BC SC EMEP (2003)	IC& BC SC (Seinfeld and Pandis, 1998)
<b>Gas Phase Chemistry</b>	EmChem09 (Simpson et al., 2012)	MELCHIOR2 (Lattuati, 1997)	TNO-CBM-IV (Sauter et al)	CB05* (Yarwood et al., 2005)	SAPRC99 (Carter, 2000)	CB05 (Yarwood et al., 2005)
<b>Cloud Chemistry: Aqueous SO<sub>2</sub> chemistry</b>	Yes (Simpson et al., 2012)	Yes and pH dependent SO <sub>2</sub> chemistry (Menut et al., 2013)	Yes (Banzhaf et al. 2012)	Yes (Walcek and Taylor, 1986)	Yes (Seinfeld and Pandis, 1998)	Yes RADM-AQ (Chang et al., 1987)
<b>Coarse Nitrate</b>	Yes	No (**)	Yes	Yes	No	No
<b>Ammonium Nitrate Equilibrium</b>	MARS (Binkowski and Shankar,1995)	ISORROPIA (Nenes et al., 1999)	ISORROPIA v.2 Fountoukis and Nenes 2007	ISORROPIAv1.7 (Nenes et al., 1998)	ISORROPIA v1.7 (Nenes et al., 1998)	ISORROPIA (Nenes et al., 1998)

3 \* with chlorine chemistry extensions

4 \*\*reaction with Ca or Na but coarse might exists with transfer from finer particles

1

2 Table 2: Composition of wet and dry deposited species

Deposition type	Deposited species
W or DSOx	SO <sub>2</sub> , SO <sub>4</sub> <sup>2-</sup> ; H <sub>2</sub> SO <sub>4</sub>
W or DNOx	HNO <sub>3</sub> , NO <sub>3</sub> <sup>-</sup> , NO, NO <sub>2</sub> (and minor species like N <sub>2</sub> O <sub>5</sub> , PAN for some models) and HONO
W or DNHx	NH <sub>3</sub> , NH <sub>4</sub> <sup>+</sup>

3

4 **2.2.1 Observation datasets**

5 For this study we used the available EMEP measurements made during four intensive periods:  
6 1–30 June 2006 (C6), 8 Jan–4 Feb 2007 (C7), 17 Sep–15 Oct 2008 (C8) and 25 Feb–26 Mar  
7 2009 (C9). The measurement data were downloaded from the EBAS database<sup>1</sup>. All the  
8 information regarding the measurement stations is available from the EBAS web site  
9 <http://www.nilu.no/projects/ccn/network/index.html>. For this study we used daily values for  
10 both deposition (WNOx, WNHx, WSOx) and mean air concentrations (TNO3, TNH4, TSO4).  
11 Measurements for a given day were taken from 24-hour sampling periods. It is important to  
12 note that the starting times of these sampling periods are not the same for all stations, and can  
13 vary in the range 00h00–09h00. It is also important to remark that the suite of pollutants  
14 measured at each site is not the same. Table S.7.2 in the Supplementary Material lists the sites  
15 and pollutants measured at each site.

16 All the sites with a temporal coverage greater than 75% were used and model values were  
17 taken only when observations were available. Two sets of sites were selected: 1) all sites with  
18 wet deposition data (W in Table 7) and 2) all sites with simultaneous measurements of wet  
19 deposition and air concentrations (WT, tables 8 and 9). The first dataset allows the most  
20 complete evaluation of wet deposition, as there are more stations with wet deposition (W)  
21 than with total precursor air concentrations (gas and aerosol components, T), whereas the

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<sup>1</sup>EBAS is a database hosting observation data of atmospheric chemical composition and physical properties. EBAS hosts data submitted by data originators in support of a number of national and international programs ranging from monitoring activities to research projects. EBAS is developed and operated by the Norwegian Institute for Air Research (NILU). For a complete list of programmes and projects for which EBAS serves as a database, please consult the information box in the Framework filter of the web interface (<http://ebas.nilu.no/>)

1 second dataset allows us to analyse the quality of the model estimates of W in terms of the  
 2 quality of modelled T, in order to help explain model performance.

3

#### 4 **2.2.2 Performance metrics used**

5 To evaluate model performance, the root mean square error (RMSE), bias and the spatial  
 6 correlation coefficient (SC) were estimated for deposition, air concentration and precipitation.

7 For deposition and precipitation, we used the accumulated values for each period. For  
 8 concentrations, we used the mean concentration for each period, based on daily values.

9 Definition of these metrics is included in Table 3.

10 Table 3. Statistics used to evaluate model performance.

Statistic	Definition
Bias	$Bias = \frac{1}{N} \sum_{i=1}^N (M_i - O_i)$
RMSE	$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (M_i - O_i)^2}$
Spatial Correlation Coefficient	$SC = \left( \sum_{i=1}^N (M_i - \bar{M})(O_i - \bar{O}) \right) / \left( \sqrt{\sum_{i=1}^N (M_i - \bar{M})^2 \times \sum_{i=1}^N (O_i - \bar{O})^2} \right)$

11 i subindex indicates a given site

12

1 To facilitate the analysis, we have defined some ratios between variables, as follows:

$$2 \quad F_w = W/(CP) \text{ and } F_d = D/(C) \quad \text{Eq. 1}$$

3 where W is wet deposition, D is dry deposition, C is the atmospheric concentration (of total  
4 reduced/oxidized nitrogen or sulphur) near ground level and P is precipitation, for each model  
5 time-step or measurement period.

6 We will refer to them as the deposition factor for wet ( $F_w$ ) and dry ( $F_d$ ) deposition throughout  
7 this paper. These ratios have been calculated for both the observed and modelled values.

8 The analysis of wet deposition can be taken a step further to separate the contributions of  
9 gaseous and aerosol species to the deposition flux. Although we can split the measured and  
10 modelled concentrations into the gaseous and aerosol components we do not know how each  
11 phase contributes to the wet deposition (W). However, these contributions can be estimated  
12 using regression techniques. If we assume that  $F_w$  has contributions from wet deposition of  
13 both gaseous and aerosol species, Equation 1 can be written as:

$$14 \quad W/P = F_{w,gas} C_{gas} + F_{w,aer} C_{aer} ,$$

15 where  $F_{w,gas}$  and  $C_{gas}$  are the deposition factor and concentration for the gaseous species and  
16  $F_{w,aer}$  and  $C_{aer}$  are the deposition factor and concentration for the aerosol species. Estimates of  
17 the phase-specific deposition factors (and their uncertainty), for the models only, were  
18 obtained using multiple linear regression, based on the equation above and considering the  
19 287 sites where measurements of any pollutant are available (S.7.1). It is important to bear in  
20 mind that the air concentrations used in the calculation are those of the first model layer (or  
21 the measurement height), while wet deposition is calculated in the models from all the layers  
22 within and below clouds. Therefore, differences in wet deposition factors of the models are  
23 not necessarily due to differences in the deposition parameterizations, they could also be due  
24 to other factors such as differences in vertical concentration profiles. However, despite these  
25 limitations we believe that these ratios are a useful tool for highlighting differences between  
26 model estimates of atmospheric deposition and providing clues as to the reasons for these  
27 differences. This analysis can provide modellers with information that can help them to  
28 understand, and if necessary, improve model estimates.

1 Maps of variability were also calculated to highlight the areas where models differ more and  
2 areas where models give more similar results. These maps were created by considering a  
3 coefficient of variation  $VAR$  of the “ensemble”, defined as follows (Bessagnet et al., 2016):

$$4 \quad VAR = \frac{1}{C_{ENS}} \sqrt{\frac{1}{M} \sum_m (C_m - C_{ENS})^2}$$

5

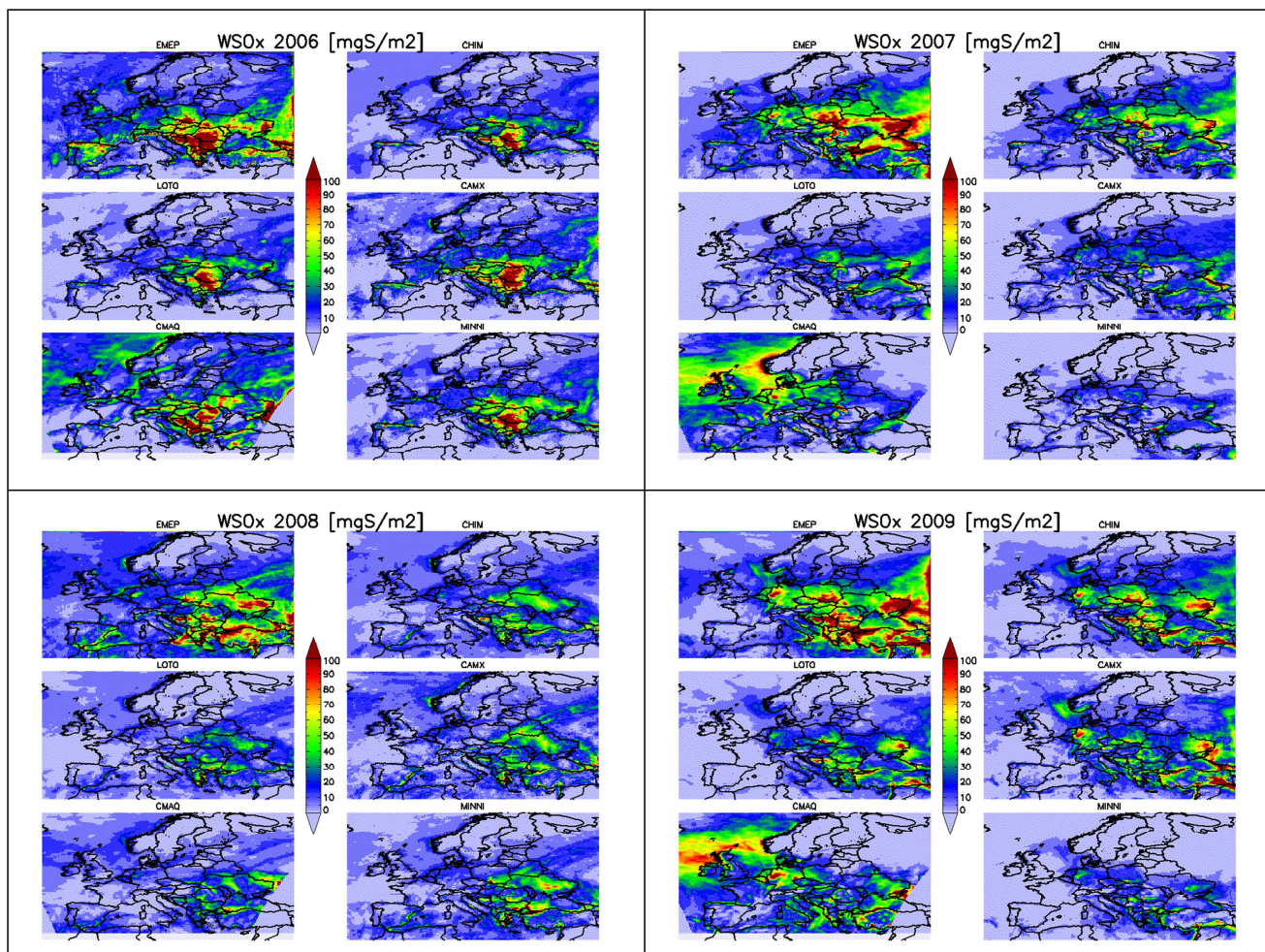
6 With  $C_m$  the concentration of individual model  $m$  included in the *ensemble* (CHIM, LOTO,  
7 MINNI and EMEP; see Bessagnet et al. 2016 for further details of the ensemble),  $M$  is the  
8 number of models, and  $C_{ENS}$  is the *ensemble* mean concentration.

9

### 10 **3 Results and discussion**

11 The following subsections include the discussion of results for sulphur and nitrogen  
12 compounds, in terms of both deposition and air concentration. For each subsection we first  
13 present an evaluation of model performance and then we compare model results. Maps  
14 showing WSO<sub>x</sub>, WNH<sub>x</sub> and WNO<sub>x</sub> for all campaigns and models are shown in Figures 1-3,  
15 and the corresponding aerosol+gas air concentrations TSO<sub>4</sub>, TNH<sub>4</sub> and TNO<sub>3</sub> are shown in  
16 Figures 4-6. For dry deposition, maps of DSO<sub>x</sub>, DNH<sub>x</sub> and DNO<sub>x</sub> are presented in the  
17 Supplementary Material S.2.1, S.2.2 and S.2.3.

18 Regarding precipitation, maps and a statistical evaluation of model performance are included  
19 in the Supplementary Material S.4.1. and Table 4 (a,b,c), respectively. The maps indicate that  
20 CMAQ has a lower accumulated rainfall for all periods, when compared with the other  
21 models (especially in C6, C8 and C9). Tables 4a, 4b, 4c, showing model performance for rain,  
22 for those sites with available measurements of WSO<sub>x</sub> (Table 4a), WNH<sub>x</sub> (Table 4b) and  
23 WNO<sub>x</sub> (Table 4c) show that this model underestimates rainfall, while the other models agree  
24 better with the observations, except in C6, when they tend to overestimate.



25

26

Figure 1. Accumulated deposition maps for WSOx (in  $\text{mgS}/\text{m}^2$ ), for all the models and periods



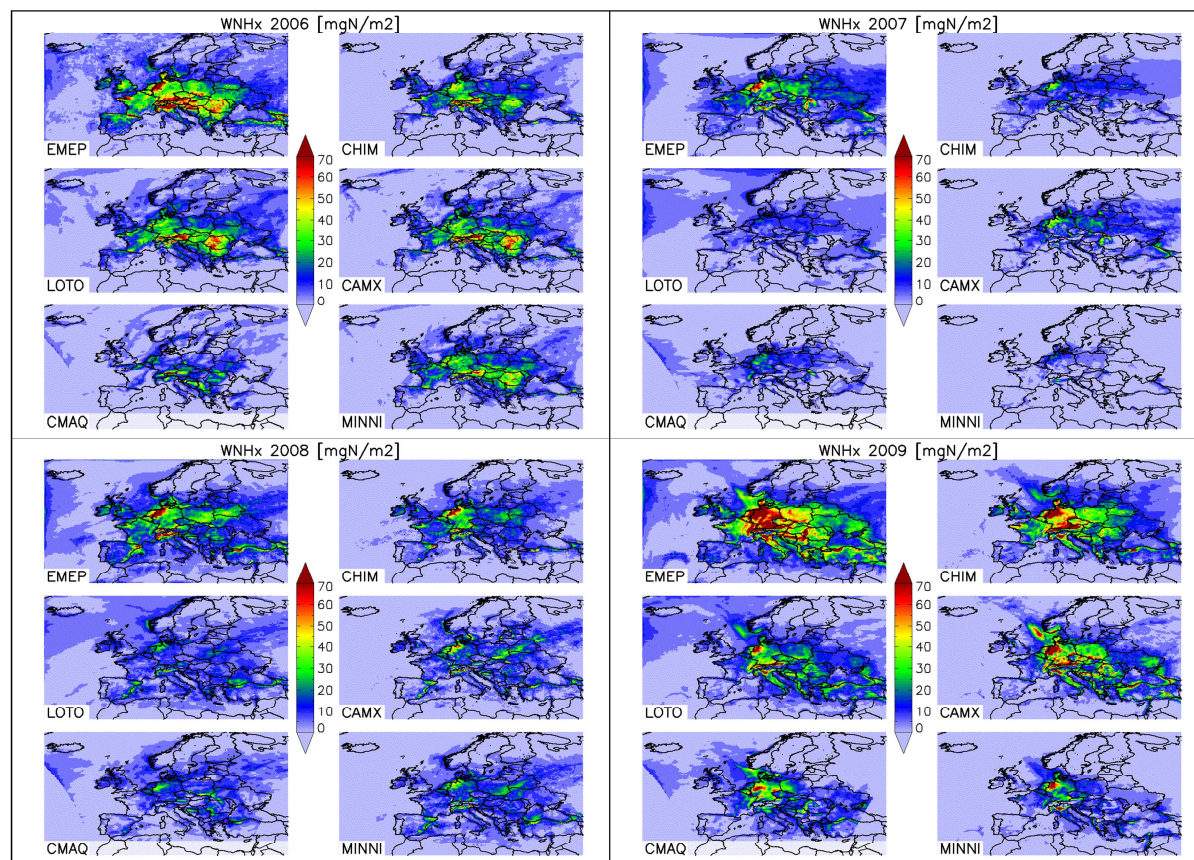
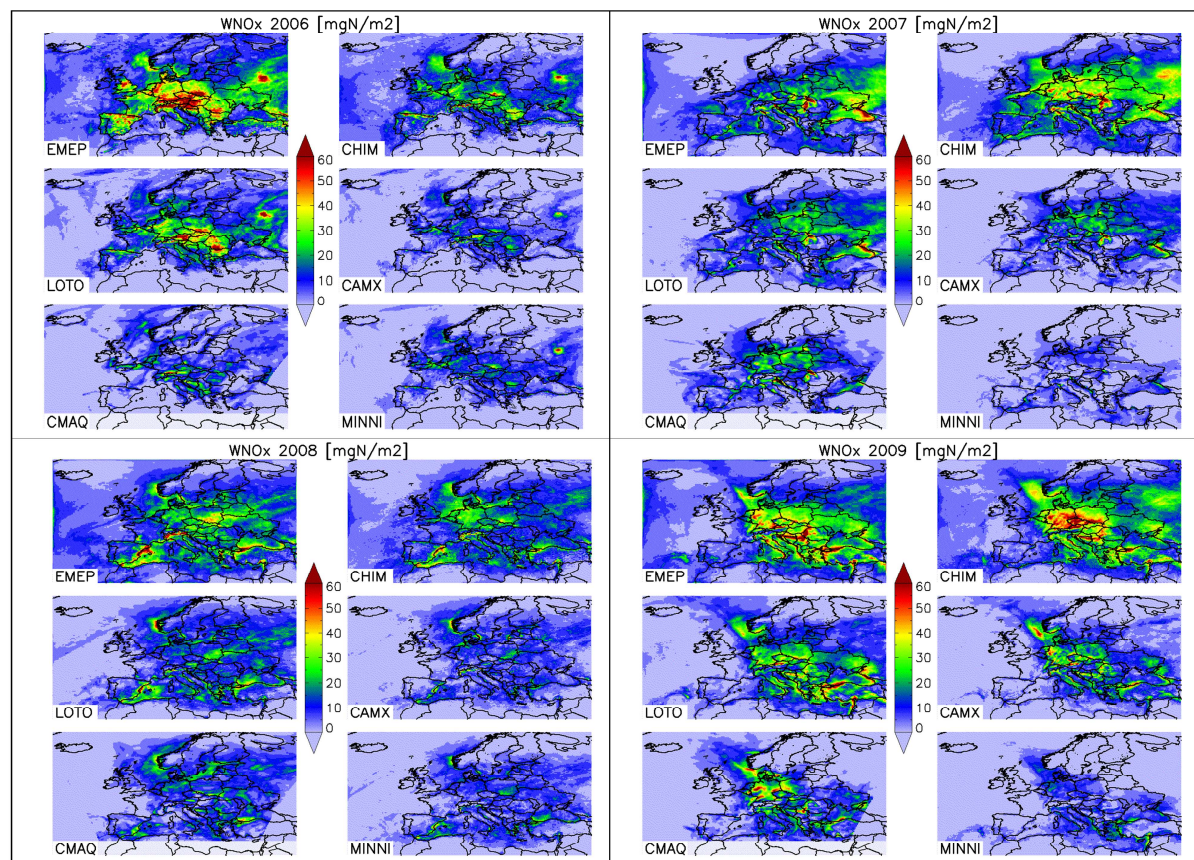


Figure 2. Accumulated deposition maps for WNHx (in  $\text{mgN/m}^2$ ) for all the models and periods.

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28  
29  
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31  
32

Figure 3. Accumulated deposition maps for WNOx (in mgN/m<sup>2</sup>) for all the models and periods.

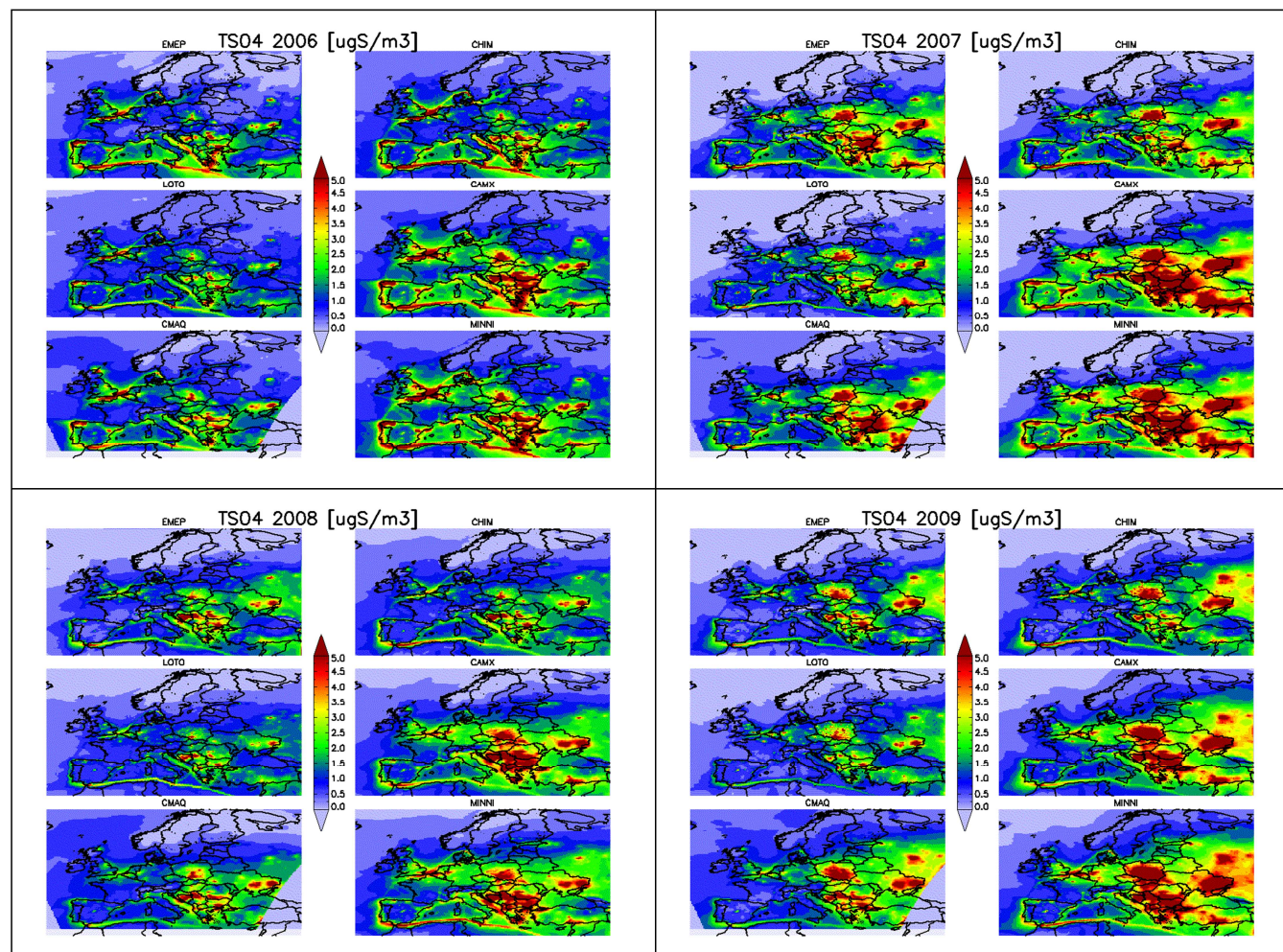


Figure 4. Maps showing the TSO4 (in  $\mu\text{gS}/\text{m}^3$ ) mean air concentration, for all the models and periods.

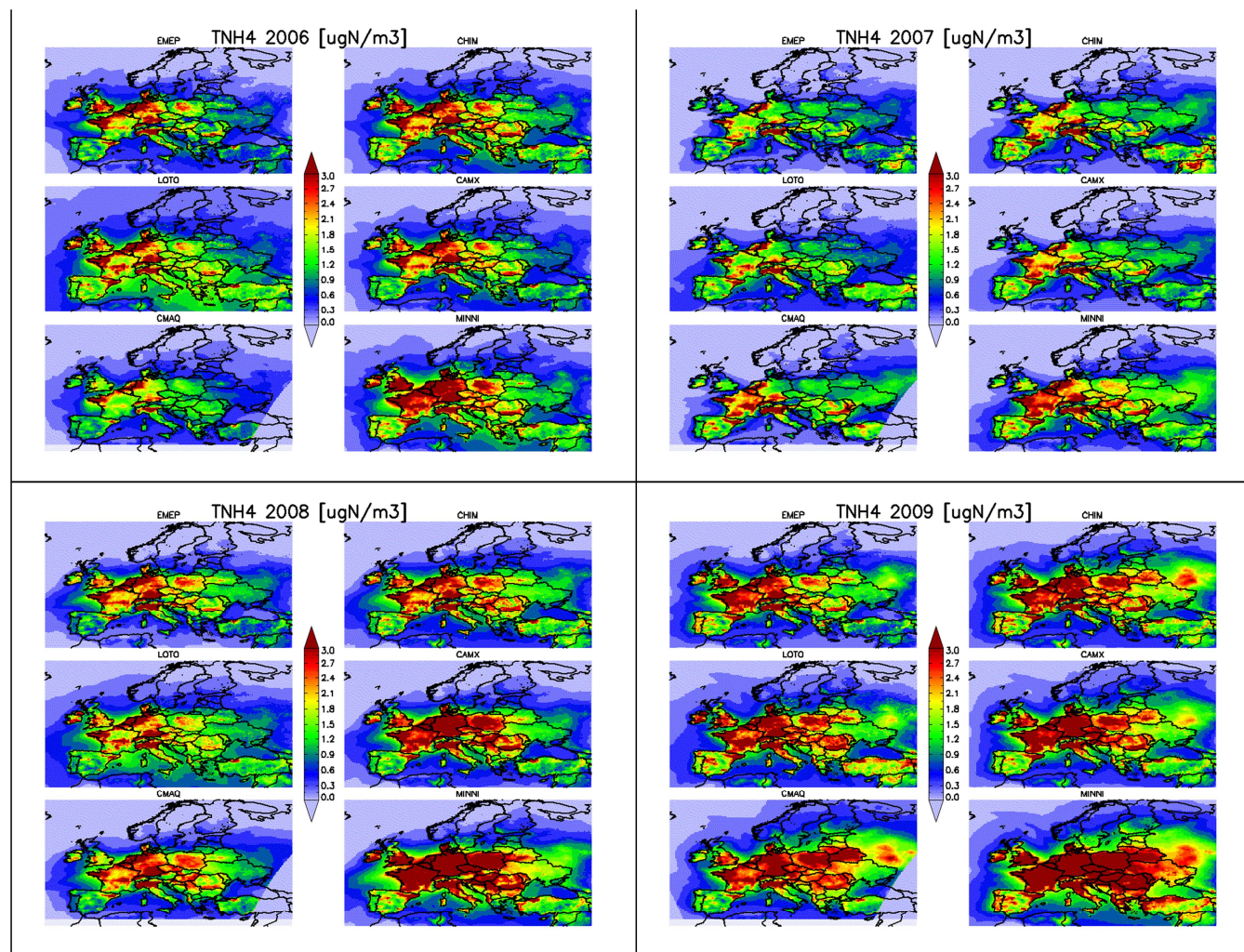
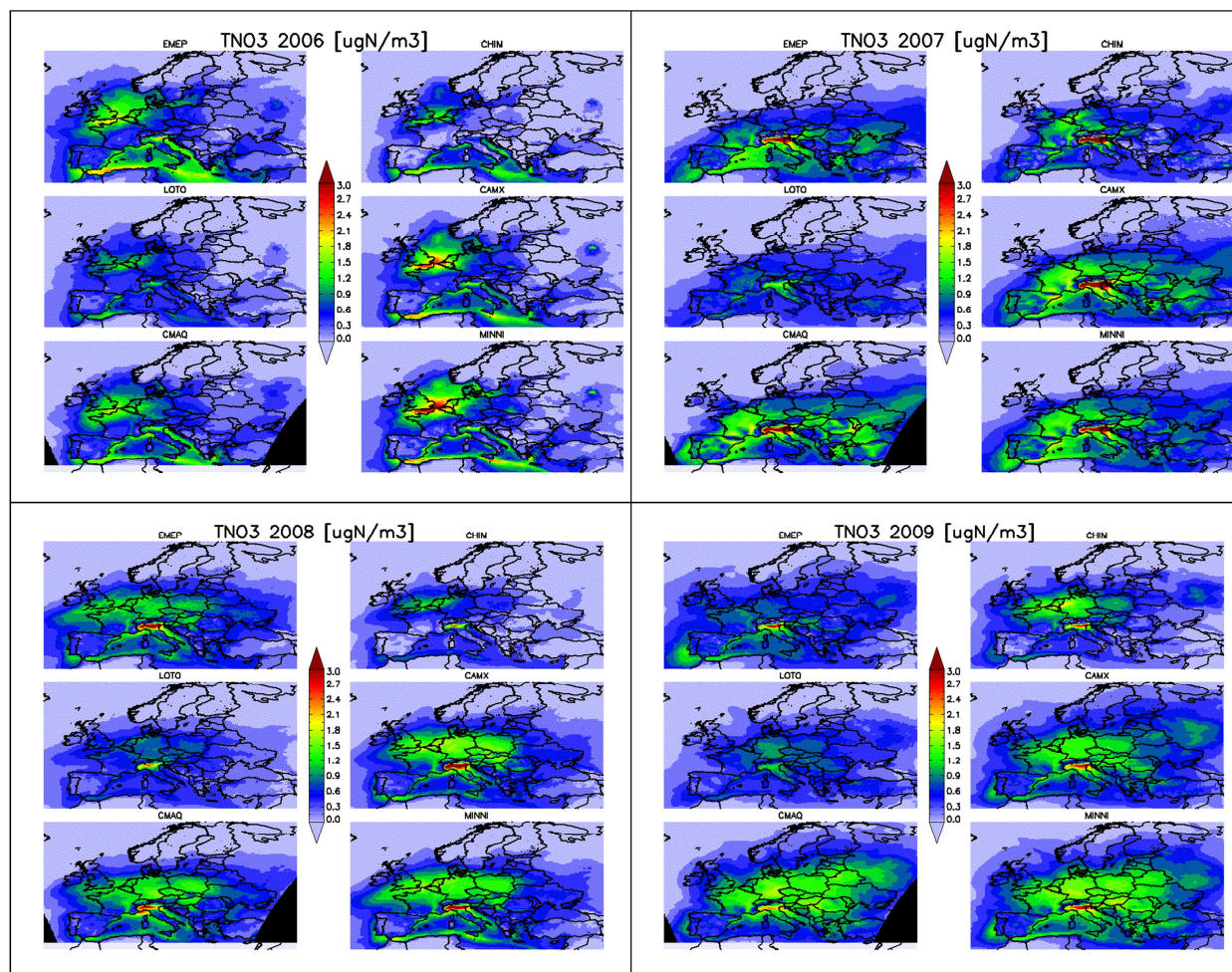


Figure 5. Maps showing the TNH4(in  $\mu\text{gN}/\text{m}^3$ ) mean air concentration, for all models and periods.



37

38

Figure 6. Maps showing the TNO3 (in  $\mu\text{gN}/\text{m}^3$ ) mean air concentration, for all the models and periods.

39 Table 4. Statistical results for rain (mm)

40 Table 4a. Statistical results for rain (mm) considering the sites with WSOx measurements

	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
Rain	2006				2007				2008				2009			
OB /N*	50.66/58				66.66/59				62.11/61				62.24/42			
CAMX	69.37	18.71	0.81	33.79	77.26	10.60	0.82	31.06	71.69	9.57	0.83	35.29	71.87	9.62	0.65	43.59
CHIM	65.21	14.55	0.82	29.99	70.84	4.18	0.82	29.48	66.25	4.14	0.83	34.02	66.78	4.54	0.65	42.18
CMAQ	39.61	-11.05	0.19	48.69	52.77	-13.89	0.27	54.83	56.16	-5.96	0.77	38.53	33.70	-28.54	0.45	57.08
EMEP	66.24	15.58	0.79	32.57	78.97	12.31	0.78	35.12	69.76	7.65	0.81	36.60	68.81	6.57	0.67	41.54
LOTO	63.88	13.21	0.82	30.05	71.59	4.93	0.83	28.71	65.77	3.65	0.82	34.81	65.38	3.14	0.68	41.10
MINNI	66.17	15.50	0.80	33.15	78.29	11.63	0.83	31.61	70.66	8.54	0.81	36.40	73.69	11.45	0.68	42.38

\*OB/N; OB: OBSERVED VALUE IN mm ; N: number of sites

41

42

43 Table 4b. Statistical results for rain (mm) considering the sites with WNHx measurements

	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
Rain	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
OB /N*	49.19/46				68.75/61				57.16/64				65.65/63			
CAMX	63.42	14.23	0.76	31.4	77.77	9.03	0.82	31.23	66.13	8.97	0.64	34.82	69.52	3.87	0.48	58.49
CHIM	59.68	10.49	0.76	28.60	71.32	2.57	0.82	30.18	61.39	4.23	0.66	33.75	64.35	-1.30	0.49	57.60
CMAQ	36.84	-12.35	0.57	32.52	52.93	-15.81	0.29	55.40	50.68	-6.47	0.59	39.05	33.40	-32.25	0.30	71.09
EMEP	62.74	13.55	0.71	31.23	79.63	10.89	0.78	35.09	64.53	7.37	0.63	36.36	65.98	0.33	0.52	56.38
LOTO	62.74	13.55	0.71	31.23	72.30	3.55	0.83	29.10	60.59	3.43	0.64	34.37	62.72	-2.93	0.50	57.62
MINNI	60.72	11.53	0.75	32.65	78.7	9.95	0.82	31.67	65.77	8.61	0.62	35.91	70.13	4.48	0.52	56.94

44 Table 4c. Statistical results for rain (mm) considering the sites with WNOx measurements

	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
Rain	53.9/62				69.31/62				62.16/65				68.2/64			
OB /N*	53.9/62				69.31/62				62.16/65				68.2/64			
CAMX	70.16	16.26	0.82	31.6	78.14	8.83	0.82	30.98	70.75	8.59	0.82	34.82	72.11	3.91	0.48	58.33
CHIM	65.91	12.01	0.82	28.05	71.68	2.37	0.82	29.96	65.38	3.21	0.82	33.75	66.67	-1.53	0.5	57.3
CMAQ	41.03	-12.87	0.66	32.91	53.8	-15.51	0.3	54.95	54.41	-7.75	0.76	39.05	34.5	-33.7	0.32	71.12
EMEP	69.38	15.48	0.78	33.01	80	10.7	0.78	34.8	68.84	6.68	0.8	36.36	68.5	0.3	0.53	55.98
LOTO	69.38	15.48	0.78	33.01	72.66	3.35	0.84	28.89	64.94	2.77	0.81	34.37	65.47	-2.72	0.51	57.35
MINNI	65.78	11.88	0.8	30.96	79.03	9.72	0.82	31.41	70.16	8	0.8	35.91	72.79	4.6	0.53	56.58

45 \*OB/N; OB: OBSERVED VALUE IN mm ; N: number of sites

## 46 3.1 Sulphur

### 47 3.1.1 WSOx: Evaluation of model results

48 The model performance statistics for WSOx are presented in Tables 5 and 6, using sea salt  
49 corrected and non-corrected observations, respectively. As mentioned above, CMAQ  
50 considers sulphate emissions that originate from sea salt, while the rest of the models do not.  
51 For this reason the statistics for all models with the exception of CMAQ should be discussed  
52 using the data in Table 5 (sea salt corrected observations), whereas for CMAQ, the data in  
53 Table 6 (not sea salt corrected) should be used. The results in Table 6 for the non-corrected  
54 data show that CMAQ performs best for C7 and C9, and is among the best for C6 (CAMX  
55 performs better). It is useful to analyse how the models behave at sites affected by sea salt  
56 emissions. Figure S.4.8 shows modelled and observed WSOx at a station located in the North  
57 of Spain (ES08). CMAQ is the only model capable of reproducing the large measured values  
58 of WSOx at this site. Figure S.4.9 shows an example for two sites located in Ireland, IE08 and  
59 IE09. This figure shows non-corrected (a) and sea salt corrected (b) data. The sea salt  
60 correction applied and available from the EBAS website shows a clear and strong effect of sea  
61 salt on WSOx at this site. In this case, we can again see how CMAQ is the only model that  
62 can reproduce the high observed values, when no sea salt correction is applied. These  
63 graphics show that 1) sulphates emitted with sea salt can have a significant contribution to  
64 deposited sulphates, and 2) models should include sea salt sulphate to adequately reproduce  
65 measured deposited rates. For the corrected data, the other models perform quite well.

66 Table 5, calculated with observed data after correction for sea salt, shows that CAMX  
67 performs best overall in C9 for WSOx (CMAQ is not included in this comparison). However,  
68 CAMX overestimates TSO4 by the largest amount, after MINNI. As pointed out in the  
69 following section, graphs in the Supplementary Material S.4.5 show that CAMX predicts the  
70 smallest dry deposition rates (along with MINNI) for a given TSO4. At the same time, maps  
71 of SO2 concentrations in the Supplementary Material (S.4.1) show that CAMX predicts the  
72 largest SO2 concentrations for most of the periods. According to Pirovano et al. (2012), this  
73 model seems to have a stronger downward mixing than the other models, enhancing the  
74 influence of elevated sources (especially relevant in the case of SO2) on ground level  
75 concentrations. All these factors can enhance the accumulation of sulphate at the surface



76 layer, and thus the good results for WSOx for CAMX could be partially due to compensating  
77 factors, and could hide problems, such as an underestimation of dry deposition.

78 MINNI and LOTO underestimate WSOx for all periods, MINNI especially in C9 and LOTO  
79 especially in C6. At the same time, MINNI overestimates TSO4. Figure S.4.4 shows that for  
80 the same amount of rain, MINNI has a lower wet deposition than the other models in C7 and  
81 C9. All these factors suggest that MINNI has a low wet deposition efficiency, which could be  
82 due to several reasons, such as an underestimation of scavenging ratios, large vertical  
83 concentration gradients, resulting in small concentrations at cloud height, or a problem with  
84 the modelling of clouds. In the case of LOTO, the underestimation of WSOx is consistent  
85 with Schaap et al. (2004). Again, Figure S.4.4 shows a lower wet deposition for this model in  
86 C6 for the same amount of rain, when compared with the other models. Figure 7, showing  
87 values of Fw for sulphur (from now on FSO4), indicates lower values of FSO4 for this model  
88 compared with the observed values, which suggests a low wet deposition efficiency for this  
89 model. This behaviour can partially be explained by the lack of in-cloud scavenging in this  
90 model, as sulphate is largely produced in the cloud aqueous phase.

91 By contrast, EMEP overestimates WSOx during all four periods, with the highest bias in C7.  
92 This model has the smallest (positive) bias for TSO4, compared with the other models, with  
93 larger values in C7 and C8, and overestimates rain, except in C9 (see Table 4a). The fact that  
94 this model overestimated WSOx without underestimating TSO4 could also indicate an  
95 underestimation of sulphur dry deposition. In fact, the scatter plots of TSO4 against dry  
96 deposition in Figure S.4.5, show that EMEP has large differences to some of the other  
97 models, such as CMAQ and CHIMERE in C6 and C7, with lower dry deposition values.

98 CHIMERE also partially overestimates TSO4 concentrations but has a very different  
99 performance for WSOx, which is underestimated in summer (C6) and overestimated in winter  
100 (C7). The behaviour in summer seems to indicate a low scavenging efficiency, producing a  
101 low WSOx and consequently high TSO4. This can be also inferred from Figure 7, where  
102 FSO4 is underestimated at some sites in C6. In C7 FSO4 for CHIMERE is correctly  
103 modelled, and thus the simultaneous overestimate of TSO4 and WSOx seems to suggest an  
104 overestimate of SO2 air concentration or an overestimate of SO2 oxidation (considering that  
105 dry deposition for this model is high, compared with the others).

106 Finally, it should be mentioned that a better spatial coverage of measurements would allow a  
107 more complete evaluation since there are areas with large differences between models, for  
108 which no evaluation is possible.

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1 Table 5. Statistical results for sea-salt corrected WSOx (mgS/m<sup>2</sup>) and TSO4 (ugS/m<sup>3</sup>) using all the available sites

all	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
<b>WSOx</b>	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
<b>OB /N*</b>	22.88/46				14.86/49				13.76/50				17.45/42			
CAMX	24.45	1.58	0.72	14.62	14.88	0.02	0.64	9.64	14.27	0.45	0.49	11.71	18.26	0.81	0.7	12.89
CHIM	16.95	-5.93	0.49	17.29	21.92	7.06	0.67	16.83	13.51	-0.3	0.5	11.26	22.19	4.74	0.54	18.6
CMAQ	23.23	0.35	0.38	18.85	27.37	12.51	0.42	22.25	9.98	-3.74	0.51	11.82	20.34	2.9	0.28	23.88
EMEP	31.02	8.14	0.57	19.89	25.97	11.11	0.64	21.35	18.37	4.62	0.45	13.19	26.6	9.15	0.68	18.82
LOTO	14.44	-8.43	0.63	15.81	12.05	-2.81	0.65	10.01	9.51	-4.25	0.54	11.76	13.54	-3.91	0.68	13.63
MINNI	18.45	-4.43	0.52	16.89	7.97	-6.88	0.62	11.55	10.61	-3.14	0.49	11.81	6.66	-10.79	0.58	18.39
<b>TSO4</b>	<b>1.06/19</b>				<b>0.69/23</b>				<b>0.61/17</b>				<b>0.86/17</b>			
CAMX	1.66	0.6	0.87	0.76	1.24	0.56	0.65	1.02	1.32	0.71	0.89	1.01	1.4	0.54	0.92	0.65
CHIM	1.24	0.18	0.66	0.65	0.86	0.17	0.55	0.71	0.88	0.27	0.83	0.43	0.95	0.09	0.8	0.39
CMAQ	1.14	0.09	0.88	0.28	0.98	0.3	0.52	0.78	0.84	0.23	0.9	0.35	1.15	0.29	0.91	0.38
EMEP	1.11	0.05	0.7	0.5	0.87	0.18	0.58	0.7	0.85	0.24	0.81	0.48	0.89	0.03	0.89	0.29
LOTO	1.06	0.01	0.77	0.36	0.78	0.09	0.56	0.7	0.76	0.14	0.84	0.3	0.8	-0.06	0.82	0.34
MINNI	1.79	0.73	0.78	1.02	1.36	0.68	0.61	1.13	1.4	0.78	0.86	1.03	1.63	0.77	0.9	0.91

2  
3 \*OB/N: OB: observed value in mgS/m<sup>2</sup> for WSOx and ugS/m<sup>3</sup> for TSO4; N: number of sites  
4

1 Table 6. Statistical results for WSOx (mgS/m<sup>2</sup>) and TSO4 (ugS/m<sup>3</sup>, without sea salt correction) using all the available sites

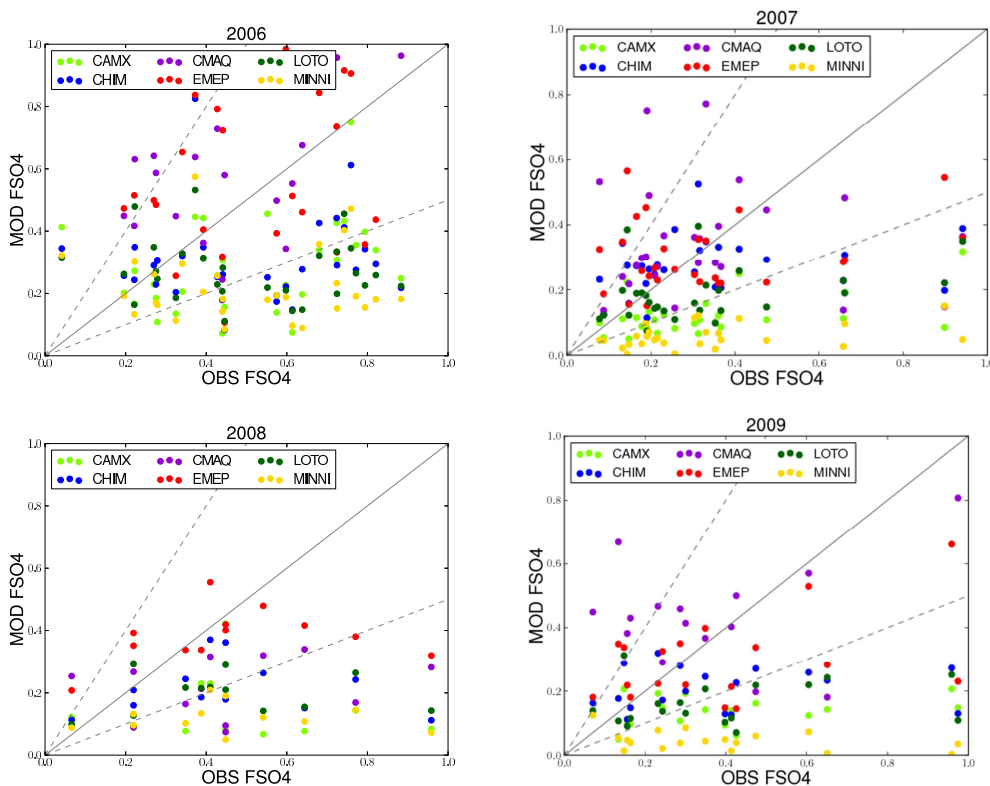
All	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
<b>WSOx</b>	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
<b>OB/N*</b>	28.25/ 57				30.17/57				24.47/ 61				22.34/62			
CAMX	28.29	0.05	0.68	17.38	14.81	-15.37	0.19	33.22	15.74	-8.73	0.54	37.86	17.55	-4.79	0.64	16.12
CHIM	20.12	-8.13	0.54	19.83	21.15	-9.03	0.08	35.11	15.12	-9.35	0.4	39.83	19.57	-2.77	0.42	20.29
CMAQ	<b>27.98</b>	<b>-0.26</b>	<b>0.66</b>	<b>17.64</b>	<b>28.18</b>	<b>-2</b>	<b>0.6</b>	<b>23.81</b>	<b>10.48</b>	<b>-13.86</b>	<b>0.38</b>	<b>42.25</b>	<b>20.86</b>	<b>-1.48</b>	<b>0.66</b>	<b>16.35</b>
EMEP	36.39	8.14	0.56	22.91	25.8	-4.38	0.12	34.87	20.98	-3.36	0.54	36.82	23.83	1.5	0.54	19.15
LOTO	17.26	-10.98	0.57	19.95	11.57	-18.6	0.07	35.84	10.44	-13.90	0.48	41.45	12.28	-10.06	0.52	19.77
MINNI	21.26	-6.98	0.48	20.92	7.87	-22.3	0.19	36.66	11.95	-12.39	0.23	42.7	6.21	-16.13	0.5	23.94
<b>TSO4</b>	<b>1.31/56</b>				<b>1.04/58</b>				<b>1.1/20</b>				<b>1.07/34</b>			
CAMX	1.98	0.68	0.68	1.16	1.89	0.84	0.67	1.3	1.74	0.64	0.61	1.04	1.55	0.49	0.77	0.69
CHIM	1.42	0.11	0.59	0.83	1.28	0.23	0.66	0.79	1.06	-0.04	0.74	0.33	0.99	-0.07	0.71	0.44
CMAQ	<b>1.38</b>	<b>0.08</b>	<b>0.66</b>	<b>0.73</b>	<b>1.39</b>	<b>0.34</b>	<b>0.6</b>	<b>0.86</b>	<b>1.22</b>	<b>0.11</b>	<b>0.63</b>	<b>0.51</b>	<b>1.2</b>	<b>0.13</b>	<b>0.68</b>	<b>0.49</b>
EMEP	1.26	-0.04	0.56	0.83	1.25	0.2	0.66	0.76	0.99	-0.11	0.66	0.4	0.97	-0.1	0.8	0.38
LOTO	1.25	-0.06	0.63	0.65	1.07	0.03	0.62	0.72	0.95	-0.15	0.74	0.36	0.9	-0.17	0.71	0.46
MINNI	2.01	0.7	0.63	1.26	1.96	0.92	0.67	1.35	1.72	0.62	0.64	0.86	1.7	0.64	0.74	0.87

2

3

\*OB/N: OB: observed value in mgS/m<sup>2</sup> for WSOx and ugS/m<sup>3</sup> for TSO4; N: number of sites

4



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2

3 Figure 7. Scatter plots showing modelled and observed FSO4 (not sea salt corrected) (in  
 4  $(\text{mgS}/\text{m}^2)/(\text{ugS}/\text{m}^3)/\text{mm}$ , for the EMEP intensive campaigns C6, C7, C8, and C9

5

### 6 3.1.2 Comparison of modelled estimates

7 Maps of WSOx show a distinct spatial pattern for CMAQ, especially in the Atlantic Ocean  
 8 and North Sea (Figure 1). This is because this model is the only one that considers sulphate  
 9 emissions from sea salt and, therefore, this model estimates higher WSOx values over marine  
 10 areas. For most of the campaigns EMEP estimates higher accumulated WSOx to terrestrial  
 11 areas than all the other models. From the maps of TSO4 ( $\text{SO}_2 + \text{SO}_4 - 10$ ) in Figure 4 we can  
 12 see that CAMX and MINNI estimate higher values than the other models, as already pointed  
 13 out by the comparison with observations. Bar charts of the modelled WSOx deposition factor  
 14 in the Supplementary Material S.4.7 show that CMAQ has the highest values for Atlantic  
 15 countries (Spain, Great Britain and France; consistent with sulphate sea salt emissions),  
 16 followed by EMEP, which has similar values to CMAQ in Germany and even higher in

1 Poland. CAMX and MINNI estimate the lowest deposition factors for all five selected  
2 countries, followed by LOTO.

3 Regarding DSO<sub>x</sub>, CMAQ estimates the highest values (S.2.3), which is also consistent with  
4 the sulphate emissions from sea salt. On the other hand, both the bar and scatter plots in the  
5 Supplementary Material S.4.7 show that CMAQ has the highest dry deposition factor,  
6 followed by CHIM. The fact that part of the sulphates in the CMAQ simulations comes from  
7 sea salt, with a fraction of these natural sulphates attributed to the coarse fraction, could be the  
8 reason for a faster deposition velocity (settling velocity), compared with sulphates formed by  
9 secondary processes. Scatter plots of TSO<sub>4</sub> versus DSO<sub>x</sub> in S.4.5 indicate that CAMX and  
10 MINNI predict a lower DSO<sub>x</sub> for a given TSO<sub>4</sub> than the rest of models. The large  
11 differences in the estimates of the models highlight the need of an evaluation of the dry  
12 deposition process with measurements, especially when, as it can be inferred from S.4.6, the  
13 magnitude of dry deposition at some points in the domain is similar to that of wet deposition,  
14 and even higher for some models, such as CHIMERE or CMAQ.

15

## 16 **3.2 Reduced Nitrogen**

### 17 **3.2.1 Evaluation of model results**

18 The model evaluation statistics for WNH<sub>x</sub> and TNH<sub>4</sub> are presented in tables 7 and 8. Results  
19 in Table 7, which use all sites with WNH<sub>x</sub> measurements, show a general underestimation for  
20 all models, with the exception of EMEP, which has lowest negative bias and even  
21 overestimates deposition in C6 and C9. These results are consistent with other publications  
22 looking at these models, such as Schaap et al. (2004) for LOTO and García-Gómez et al.  
23 (2014) for CHIMERE. In C7 the general underestimation is very pronounced, as shown in the  
24 scatter plots in Figure 8. EMEP performs best in terms of both bias and RMSE for this period  
25 while, by contrast, MINNI has the highest negative bias, accompanied by the highest RMSE.  
26 In C6 CAMX and LOTO perform best overall. For the WT sites (Table 8), all models  
27 underestimate TNH<sub>4</sub> in C6, with CMAQ having the highest negative bias, followed by  
28 EMEP. The fact that EMEP performs well for WNH<sub>x</sub> but underestimates TNH<sub>4</sub> in this period  
29 could be due to several reasons, one hypothesis being the combination of an even larger  
30 underestimation of TNH<sub>4</sub> and an overestimation of the wet deposition efficiency. As shown

1 in S.5.7 and Figure 9, FNH4 (Fw for reduced nitrogen, that is, WNHx/TNH4/rain) estimated  
2 by EMEP is generally higher than that of the other models (only CAMX in C6 is similar to  
3 EMEP, with even higher values in some countries), although in C6 and C8 EMEP tends to  
4 overestimate this factor. For colder periods (C7 and C9) FNH4 is correctly modelled by this  
5 model. The higher WNHx loads shown by EMEP are consistent with the higher removal  
6 efficiency for aerosol phase compounds shown in S.5.8., and a higher removal of the aerosol  
7 phase can lead to the results shown in S.5.3, indicating that for the same TNH4, EMEP has  
8 the highest NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> ratio. The opposite behaviour is produced by MINNI, both in S.5.8 and  
9 S.5.3, thus explaining the lowest FNH4 among all models.

10 Scatter plots of FNH4 (Figure 9) show that all the models estimate this factor better in C6  
11 than in C7 and C9. The largest underestimate of the wet deposition factor was in C7 and C9  
12 for all models, with the exception of EMEP (as already noted), being more pronounced for  
13 MINNI and LOTO. This underestimation could be related to the scavenging deposition of the  
14 aerosol component, since the cooler temperatures of this campaign favoured the aerosol phase  
15 and, as shown in S.5.8, all models have a small wet deposition factor for the aerosol  
16 component, relative to that of EMEP. This figure was produced by calculating the F factor as  
17 discussed in Subsection 2.2.2 for the gas and aerosol species, using modelled values at 287  
18 sites within the domain. By contrast, in C6 and partially in C8, when temperature conditions  
19 were more favourable for the gas phase, modelled estimates of FNH4 agree best with the  
20 observations.

21 The frequent underestimation of both WNHx and TNH4 for some models (the only exception  
22 is C9) indicates that besides the underestimation of aerosol scavenging efficiency, models are  
23 also not able to reproduce the total ammonium concentration (gas+aerosol). This could be  
24 caused, for example, by an underestimation of emissions or an overestimation of dry  
25 deposition rates. At this point it is interesting to remark that only EMEP and LOTO have a  
26 compensation point for NH<sub>3</sub> dry deposition. This fact is highlighted in S.5.3 where LOTO and  
27 EMEP have higher NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> ratios for the same TNH4 concentration, with respect to the  
28 other models. The other models do not take into account the influence of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> saturation  
29 of the soil and/or vegetation that would inhibit or, at least, strongly reduce, dry deposition  
30 over NH<sub>3</sub> high emitting areas. For example, in the case of CMAQ, Figure 9 shows that the  
31 model correctly reproduces the deposition factor, while Figure S.2.2 shows that this model  
32 has the highest DNHx in C6, which decreases the TNH4 available for wet deposition.

- 1 However the lower  $\text{NH}_3$  dry deposition rates in LOTO and EMEP do not clearly improve
- 2 their performance for  $\text{TNH}_4$  concentrations (see Table 8). Additional analyses of  $\text{NH}_3$
- 3 emission rates and their temporal variation are probably needed in the future.

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1 Table 7. Statistical results for  $\text{WNH}_x$  ( $\text{mgN}/\text{m}^2$ ) (first part of the table) and  $\text{WNO}_x$  ( $\text{mgN}/\text{m}^2$ ) (second part of the table) using all the available  
 2 EMEP sites.

3

W	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
<b>WNH<sub>x</sub></b>	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
<b>OB /N*</b>	24.38 /46				17.95/61				14.14/59				28.67/63			
CAMX	20.38	-4	0.87	12.56	9.23	-8.72	0.5	15.97	13.23	-0.90	0.55	10.96	19.32	-9.35	0.6	27.6
CHIM	17.18	-7.2	0.84	14.31	8.2	-9.75	0.27	17.9	16.29	2.15	0.37	13.18	24.85	-3.82	0.48	30.36
CMAQ	9.62	-14.76	0.8	21.84	7.46	-10.49	0.5	17.08	8.99	-5.15	0.54	11.29	10.43	-18.24	0.6	32.99
EMEP	28.44	4.06	0.78	15.44	13.69	-4.27	0.43	14.88	21.04	6.91	0.35	16.08	31.41	2.73	0.53	31.43
LOTO	20.38	-3.99	0.82	13.46	7.49	-10.47	0.5	17.34	10.61	-3.53	0.43	11.39	16.5	-12.17	0.58	29.26
MINNI	16.12	-8.26	0.79	16.25	3.58	-14.38	0.51	20.18	11.28	-2.86	0.46	11.16	7.86	-20.81	0.47	36.09
<b>WNO<sub>x</sub></b>	<b>19.39/ 62</b>				<b>17.47/62</b>				<b>13.98/65</b>				<b>22.36/64</b>			
CAMX	9.27	-10.13	0.63	16.83	10.88	-6.59	0.61	14.94	9.44	-4.55	0.51	11.71	12.28	-10.08	0.72	22.02
CHIM	16.85	-2.54	0.52	14.78	20.49	3.02	0.62	13.77	16.41	2.42	0.41	12.18	21.66	-0.69	0.65	20.18
CMAQ	8.57	-10.82	0.6	17.6	12.89	-4.58	0.63	14.06	9.59	-4.39	0.56	11.23	9.77	-12.59	0.7	24.15
EMEP	29.69	10.3	0.65	17.94	13.74	-3.73	0.54	14.67	19.52	5.54	0.38	14.34	18.66	-3.7	0.68	20.03
LOTO	19.94	0.55	0.6	14.21	13.33	-4.13	0.66	13.33	12.91	-1.07	0.49	11.1	14.3	-8.06	0.71	21.17
MINNI	9.2	-10.19	0.43	18.33	4.55	-12.92	0.55	19.65	7.55	-6.43	0.45	12.84	3.83	-18.52	0.46	31.06

4 \*OB/N; OB: OBSERVED VALUE IN  $\text{mgN}/\text{m}^2$ ; N: number of sites SC: spatial correlation

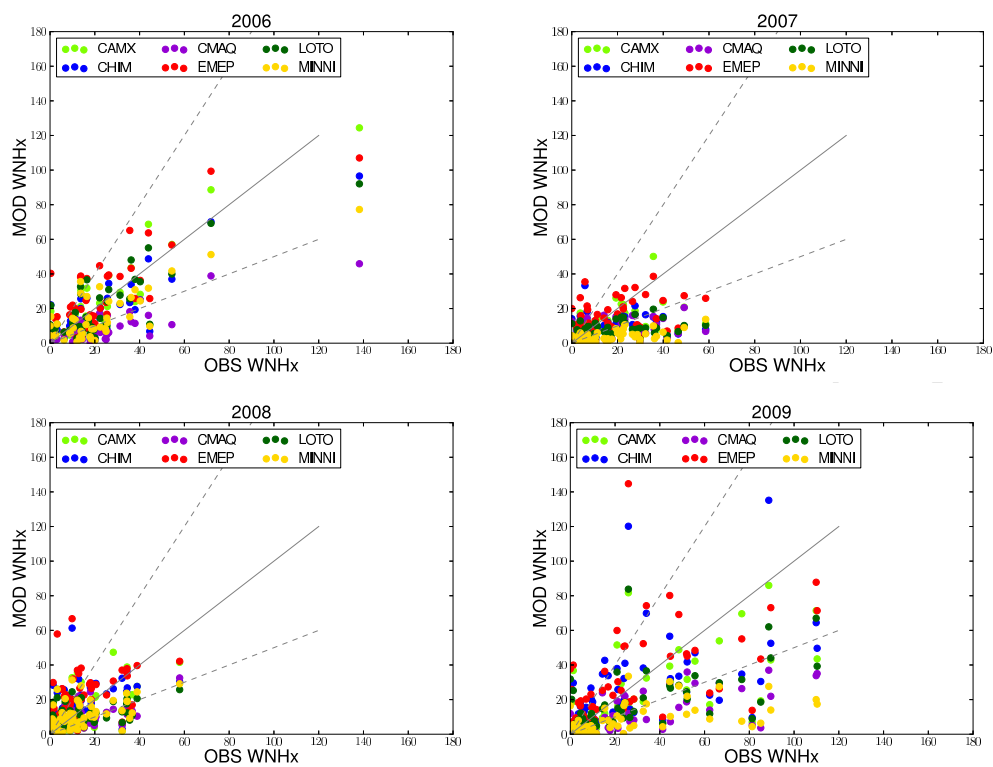
5

- 1 Table 8. Statistical results for WNHx and TNH4 (mgN/m<sup>2</sup> and ug/m<sup>3</sup> respectively) using only the available stations with simultaneous  
 2 measurements of both pollutants  
 3

WT	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
WHx	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
OB /N*	20.98/23				16.4/29				14.5/27				21.69/22			
CAMX	13.2	-7.79	0.83	12.64	8.87	-7.53	0.42	15.44	12.04	-2.46	0.35	14.46	17.92	-3.77	0.33	23.1
CHIM	10.83	-10.15	0.8	13.49	8.18	-8.23	0.13	17.51	14.07	-0.43	0.16	16.17	21.78	0.09	0.29	28.44
CMAQ	8.01	-12.97	0.7	16.34	6.87	-9.53	0.35	16.75	8.02	-6.48	0.59	12.48	7.59	-14.1	0.38	23.2
EMEP	21.51	0.52	0.8	12.52	13.02	-3.38	0.21	16.12	19.5	5	0.19	17.8	27.66	5.97	0.28	32.75
LOTO	14.09	-6.89	0.75	12.06	7.41	-8.99	0.37	16.43	9.88	-4.62	0.22	13.84	15.8	-5.9	0.31	23.24
MINNI	12.12	-8.86	0.64	14.26	3.28	-13.12	0.25	19.41	10.11	-4.39	0.26	13.87	6.79	-14.9	0.32	24.05
TNH4	2.51/23				1.67/29				1.7/27				2.23/22			
CAMX	1.64	-0.87	0.75	1.31	1.57	-0.1	0.68	1.21	1.95	0.25	0.67	1.21	2.68	0.46	0.68	1.68
CHIM	1.88	-0.63	0.8	1.2	1.69	0.02	0.66	1.33	1.76	0.05	0.71	0.97	2.49	0.27	0.74	1.22
CMAQ	1.16	-1.34	0.79	1.61	1.52	-0.15	0.79	0.97	1.57	-0.13	0.73	0.8	2.44	0.21	0.73	1.12
EMEP	1.4	-1.1	0.78	1.4	1.38	-0.29	0.56	1.4	1.5	-0.2	0.69	0.95	2.32	0.1	0.72	1.41
LOTO	1.78	-0.73	0.81	1.1	1.49	-0.18	0.63	1.25	1.62	-0.09	0.71	0.85	2.59	0.37	0.75	1.28
MINNI	2	-0.51	0.79	1.1	1.87	0.2	0.66	1.28	2.43	0.73	0.7	1.53	3.29	1.06	0.67	2.04

- 4 \*OB/N: OB: observed value in mgN/m<sup>2</sup> for WNHx and ug/m<sup>3</sup> for TNH4; N: number of sites

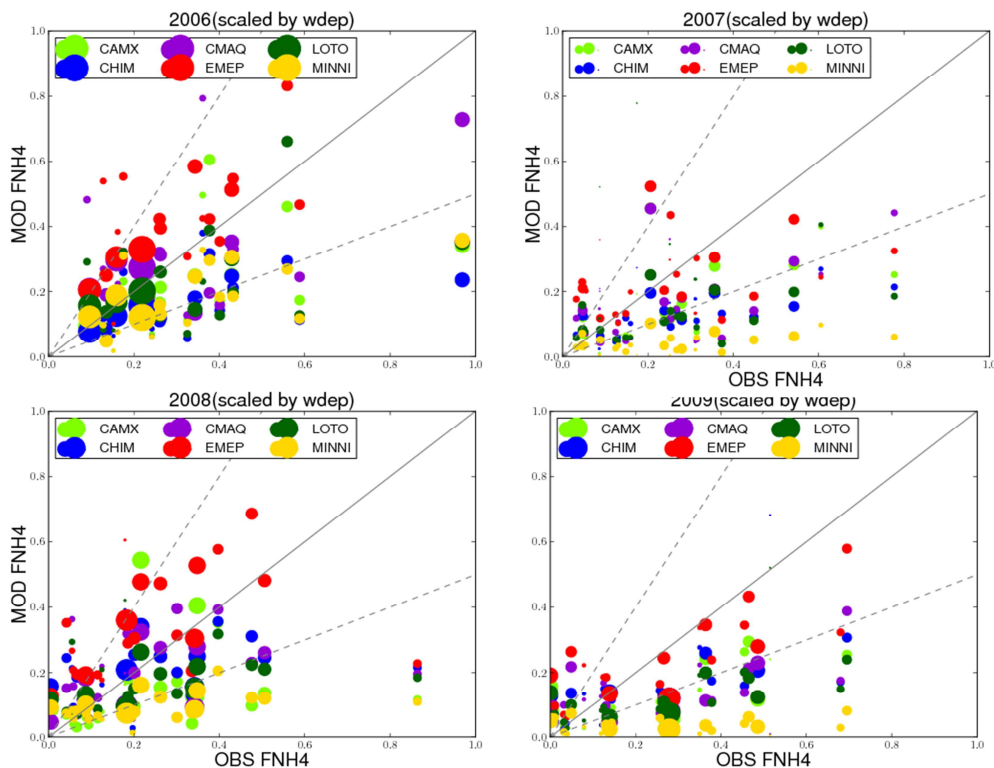
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2

3

4 Figure 8. Scatter plots showing modelled and observed WNHx (in  $\text{mgN/m}^2$ ) for the EMEP intensive campaigns  
5 C6, C7, C8, and C9



1  
2 Figure 9. Scatter plots showing modelled and observed FNH4 (in  $(\text{mgN/m}^2)/(\text{ugN/m}^3)/\text{mm}$ ) for the EMEP  
3 intensive campaigns C6, C7, C8 and C9

### 4 3.2.2 Comparison of modelled estimates

5 Maps in Figure 2 show that EMEP estimates the highest WNH<sub>x</sub> for all campaigns. Figure 5  
6 shows that MINNI estimates the highest concentrations of TNH<sub>4</sub>, with substantial  
7 differences to the other models, especially over the north Germany, northwest France and  
8 northern Italy, where the largest ammonia emissions occur. The formation of ammonium can  
9 occur in the form of both sulphates and nitrates. Ammonium concentrations were lower in C6  
10 for all models (S.5.2). As mentioned above, this result is consistent with the fact that  
11 ammonium nitrate is a volatile species, with increasing volatility at higher temperatures and  
12 lower relative humidity. Since MINNI estimates some of the largest values of TNH<sub>4</sub> (Figure  
13 5), NH<sub>3</sub> and NH<sub>4</sub>-10 (Supplementary Material S.5.1. and S.5.2) but with a similar rainfall  
14 (Supplementary Material S.1) to the other models, this again indicates that this model has a  
15 smaller wet deposition factor than the other models. EMEP and LOTO estimate the lowest  
16 values of NH<sub>4</sub>-10 for all periods except C6 (S.5.2) whereas CAMX estimates the largest  
17 values in C8. The estimated deposition factors for the gas (NH<sub>3</sub>) and aerosol (NH<sub>4</sub>-10, the  
18 ammonium component of PM<sub>10</sub>) components for all measurement locations (287) over all

1 periods (S.5.8) show that EMEP has the largest factor for both components although the  
2 difference to the other models is more marked for the aerosol phase. The deposition factor for  
3 the gaseous component of WNH<sub>x</sub> is smaller or of a similar magnitude to that of the aerosol.  
4 Nevertheless, this is probably not a result of the model parameterizations for the two  
5 components since, for example, EMEP uses a larger in-cloud scavenging ratio for NH<sub>3</sub> than  
6 for NH<sub>4</sub>-10. This suggests that the difference in the magnitude of the two factors is due to the  
7 vertical concentration profiles, a hypothesis that is backed up by the fact that Erisman et al.  
8 (1988) observed stronger decreases with height for NH<sub>3</sub> concentrations compared with the  
9 decreases in ammonium concentrations.

10 Maps in S.2.2 for **DNH<sub>x</sub>** show that CMAQ estimates some of the highest values in C6 and C9  
11 (LOTO also high in C9), CMAQ has the largest dry deposition factor (S.5.7) for the countries  
12 along the Atlantic coast (France, Great Britain and Spain) and LOTO has the largest over  
13 Germany and Poland. The deposition factors for CAMX and EMEP are also some of the  
14 highest. Scatter plots of TNH<sub>4</sub> versus dry deposition in S.5.5 show that CHIM and MINNI  
15 estimate the lowest dry deposition for a given value of TNH<sub>4</sub>, as does EMEP in C6. All  
16 models estimate the largest dry deposition in north-west France, north-west Germany and  
17 northern Italy, which are the regions with the largest ammonia emissions. Again, as discussed  
18 for DSO<sub>x</sub>, S.5.6 (a comparison of WNH<sub>x</sub> with DNH<sub>x</sub>) shows that dry deposition loads are of  
19 the same order as WNH<sub>x</sub>, or even higher for many locations in the domain and models.  
20 Therefore, it is important to have measurements that could be used to evaluate model results  
21 in order to have confidence in the N deposition calculated by models.

## 22 **3.2 Oxidized Nitrogen**

### 23 **3.3.1 Evaluation of model results**

24 Tables 7 (bottom) and 9 show the average accumulated value for WNO<sub>x</sub>, mean bias, spatial  
25 correlation and RMSE for the 4 periods. When considering all the available sites (W group,  
26 Table 7), the group of models with the lowest values of WNO<sub>x</sub> (CAMX, CMAQ and MINNI)  
27 shows a general underestimation. The predictions of MINNI have a fairly high negative bias,  
28 especially in C7 and C9, compared with the rest of the models. This confirms that the model  
29 tends to underestimate wet deposition fluxes for all three ions, despite it generally estimating  
30 higher ground level air concentrations than the other models. This means, combined with the

1 fact that all the models except CMAQ overestimate rain, that MINNI underestimates the  
2 efficiency of the wet scavenging processes at some sites, as confirmed by Figure 11. The  
3 models with the highest WNO<sub>x</sub> values (EMEP, LOTO and CHIM) seem to agree better with  
4 observations, although EMEP overestimates WNO<sub>x</sub> in C6 and C8, accompanied with high  
5 values of RMSE.

6 For the WT group (Table 9), EMEP, LOTO and CHIM have the lowest RMSE for TNO<sub>3</sub> for  
7 most of the campaigns, with the exception of CHIM having the highest RMSE in C6,  
8 accompanied by a large negative bias. The three models, on average, perform well for WNO<sub>x</sub>,  
9 TNO<sub>3</sub> and FNO<sub>3</sub> (Fw for oxidised nitrogen). The main differences between these three  
10 models and CAMx, CMAQ and MINNI relies on the deposition factor for gas phase  
11 compound that, in contrast to NH<sub>x</sub>, is more relevant for the gas phase than for the aerosol  
12 species (S.6.9). In this figure we show the deposition factors calculated for the gas and the  
13 aerosol phase (from model results at 287 sites; as explained in Section 3.2.2). We can see that  
14 for all models the scavenging efficiency of the gas phase is higher than that of the aerosol one  
15 (note that graphics in S.6.9 present a different scale for the y-axes), with EMEP having the  
16 highest values of both, followed by CHIM and LOTO.

17 The only relevant exception to this general behaviour is shown by CHIM in C6, where the  
18 model strongly underestimates TNO<sub>3</sub> concentration. Despite this, CHIM does not disagree  
19 greatly with the observations in C6 for WNO<sub>x</sub>, as shown in the scatter plots of modelled  
20 versus observed WNO<sub>x</sub> (Figure 10). This fact could hide a combination of factors, such as un  
21 underestimation of TNO<sub>3</sub> formation (we must remember that CHIMERE does not include the  
22 formation of coarse nitrates related to sea salt or dust), combined with an overestimation of  
23 wet deposition processes (pointed out in Figure 11, by the comparison of modelled and  
24 observed deposition factor (WNO<sub>x</sub>/rain/TNO<sub>3</sub>) and the overestimation of rain (Table 4c). An  
25 answer to why this model could overestimate the wet deposition factor in this campaign could  
26 come from an inadequate repartition between gas/aerosol phases for this period, when air  
27 temperatures are higher, and gas to aerosol conversion is less favoured. To investigate this  
28 idea further we have plotted TNO<sub>3</sub> against the gas to aerosol ratio (TNO<sub>3</sub> vs HNO<sub>3</sub>/NO<sub>3-10</sub>,  
29 where NO<sub>3-10</sub> is the nitrate component of PM<sub>10</sub>) for C6 for all models (S.6.4). This plot  
30 shows the model values at 287 sites (same locations as in S.7.1) and provides information on  
31 the contribution of the gaseous and aerosol phases of TNO<sub>3</sub>. Besides the fact that EMEP (red  
32 circles) estimates higher values of TNO<sub>3</sub>, CHIM predicts a HNO<sub>3</sub>/NO<sub>3-10</sub> ratio larger than

1 one at many locations, contrary to EMEP and LOTO, for example, which predict much lower  
2 ratios, with most values being lower than one. This fact combined with the higher deposition  
3 factor of  $\text{HNO}_3$  compared with the aerosol component (S.6.9) could lead to an overestimation  
4 of the wet scavenging strength for a given  $\text{TNO}_3$  concentration, and thus an overestimation of  
5  $\text{FNO}_3$ .

6 In C6 the low bias of EMEP (almost zero) for  $\text{TNO}_3$ , accompanied by an overestimation of  
7  $\text{WNO}_x$  (Table 9), could hide an overestimation of  $\text{TNO}_3$  levels, which is compensated by an  
8 overestimation of rain, at least over the area covered by WT group of observations. This  
9 potential overestimation of  $\text{TNO}_3$  by EMEP could be due to the low values of dry deposition  
10 ( $\text{DNO}_x$ ) (S.2.3). Although we cannot conclude if this value is good or not, a low dry  
11 deposition could partly explain the presence of high  $\text{TNO}_3$  in this period of the year, when  
12 dry deposition processes are more relevant. With regards to the deposition factors (deposition  
13 normalized by  $\text{TNO}_3$  and rain), EMEP has similar values to those calculated from the  
14 observations for some sites where the model overestimates  $\text{WNO}_x$  in C6 and C8 (Figure 11).

15 For the models that underestimate  $\text{WNO}_x$  (CAMX, CMAQ and MINNI), the problem seems  
16 to be different. As mentioned previously, these models overestimate  $\text{TNO}_3$  and underestimate  
17  $\text{WNO}_x$  (except in C6, when all the models with the exception of EMEP underestimate both  
18  $\text{WNO}_x$  and  $\text{TNO}_3$ ). CAMX, CMAQ and MINNI also have smaller deposition factors to those  
19 calculated from the observations (Figure 11). In the case of CMAQ, the underestimate of the  
20 deposition factor suggests that rain (underestimated for this model) is not the only reason for  
21 the underestimate of  $\text{WNO}_x$ . Plots in S.6.4 and S.6.9 indicate both a higher gas/aerosol ratio  
22 and lower deposition factors for these models. The more relevant role of the gas component,  
23 due to its higher deposition factor, suggests an underestimation of the gas scavenging  
24 efficiency for these models. S.6.4. also indicates a potential underestimation of the scavenging  
25 efficiency for the aerosol phase for these models, except for CMAQ, which has a similar  
26 factor for aerosol as LOTO. This fact could be related to the formation of coarse nitrates from  
27 sea-salt in these two models (and in EMEP) that can be more effectively scavenged than fine  
28 aerosols. Although MINNI uses a similar parameterization to EMEP for in cloud aerosol  
29 scavenging ( $7 \times 10^5$  and  $2 \times 10^5$  for accumulation and Aitkens mode, respectively), the  
30 coefficients used are lower than those used by EMEP ( $1 \times 10^6$ ).

1 In summary, we can say that WNO<sub>x</sub> deposition seems to be more strongly driven by HNO<sub>3</sub>  
2 removal than NO<sub>3</sub><sup>-</sup>. Models with higher WNO<sub>x</sub> gas deposition factors (EMEP, LOTO and  
3 CHIM, S.6.9) also estimate higher WNO<sub>x</sub> loads and better performance. In the case of  
4 EMEP and LOTO this implies that the HNO<sub>3</sub>/NO<sub>3</sub><sup>-</sup> ratio is always very low for a given TNO<sub>3</sub>  
5 concentration, because HNO<sub>3</sub> is efficiently scavenged and, therefore, TNO<sub>3</sub> is mostly  
6 composed of NO<sub>3</sub><sup>-</sup> (S.6.4). Nevertheless in C6, CHIM also agrees well for WNO<sub>x</sub> (similarly  
7 to EMEP and LOTO deposition is driven by HNO<sub>3</sub> removal ), but it seems that the model  
8 produces less total oxidized nitrogen and, moreover, the equilibrium is shifted towards the gas  
9 phase fraction (S.6.4) As a consequence modelled TNO<sub>3</sub> is underestimated and the deposition  
10 factor overestimated. This result suggests that CHIM chemical and physical processes  
11 involving oxidized nitrogen as well as aerosol-gas phase equilibrium (e.g. the role of  
12 temperature) should be analysed further. MINNI, CAMX and CMAQ seem to underestimate  
13 the gas scavenging efficiency for all campaigns (as well as that of the aerosol, although the  
14 wet scavenging of HNO<sub>3</sub> has a larger influence), leading to low wet deposition loads and high  
15 air concentration.



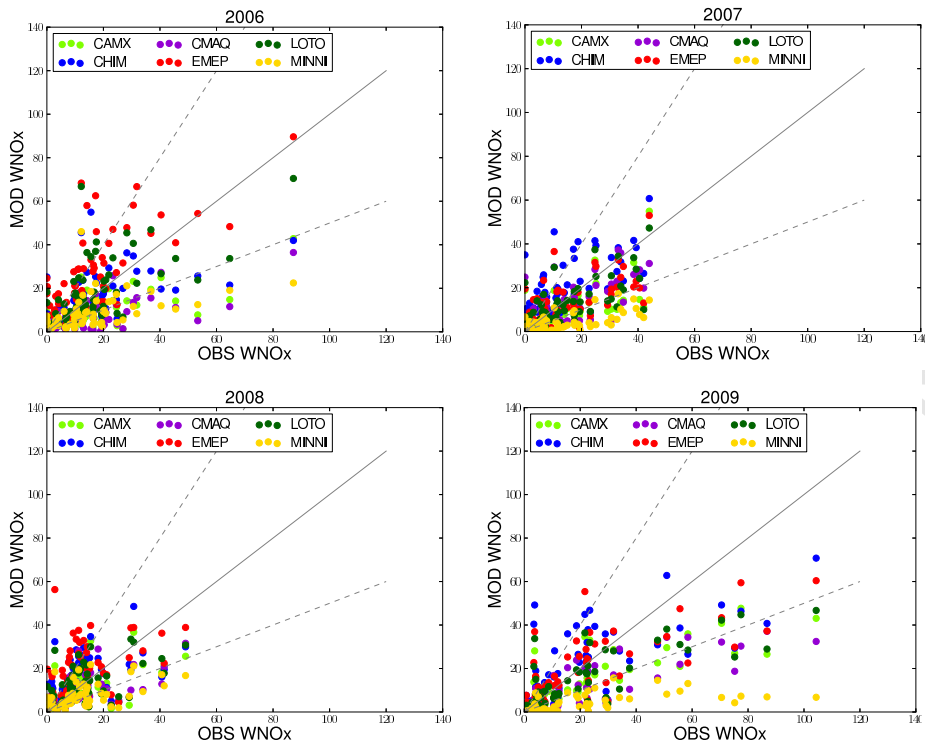
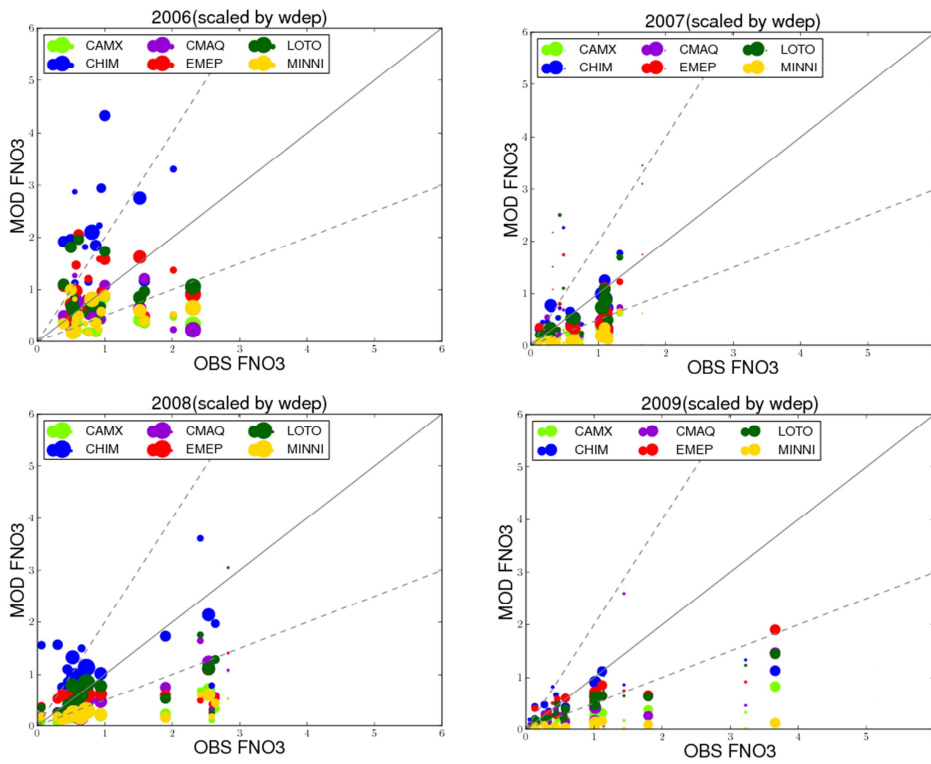
1 Table 9. Statistical results for WNOx and TNO3 (in mgN/m<sup>2</sup> and ug/m<sup>3</sup> respectively) using only the available stations with simultaneous  
 2 measurements of both pollutants

WT	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE	MOD	BIAS	SC	RMSE
<b>WNOx</b>	<b>2006</b>				<b>2007</b>				<b>2008</b>				<b>2009</b>			
<b>OB /N*</b>	21.84/25				17.64/28				16.42/28				18.85/28			
CAMX	8.31	-13.52	0.41	21.23	11.06	-6.58	0.54	18.35	10.14	-6.28	0.32	14.66	12.67	-6.18	0.81	12.24
CHIM	16.91	-4.93	0.36	17.77	20.54	2.9	0.51	17.82	17.81	1.4	0.24	14.58	20.37	1.52	0.74	12.36
CMAQ	8.49	-13.35	0.34	21.52	12.53	-5.11	0.58	17.43	10.11	-6.3	0.52	12.86	8.27	-10.59	0.78	16.22
EMEP	27.77	5.93	0.63	15.71	12.51	-5.13	0.35	19.68	21.62	5.21	0.2	16.22	18.82	-0.03	0.79	10.97
LOTO	17.85	-3.98	0.51	15.92	13.83	-3.81	0.57	17.06	14.12	-2.3	0.28	13.75	14.74	-4.12	0.83	10.9
MINNI	8.65	-13.19	0.59	20.23	4.69	-12.95	0.38	23.03	8.38	-8.03	0.25	15.29	4.07	-14.78	0.59	21.69
<b>TNO3</b>	<b>2.32 / 25</b>				<b>2.42/ 28</b>				<b>2.14/28</b>				<b>2.58/28</b>			
<b>OB /N*</b>	2.32 / 25				2.42/ 28				2.14/28				2.58/28			
CAMX	1.86	-0.47	0.67	0.9	3.66	1.24	0.77	1.96	3.29	1.15	0.78	1.75	3.3	0.72	0.73	1.37
CHIM	0.85	-1.47	0.61	1.63	2.4	-0.01	0.81	1	1.24	-0.9	0.88	1.14	2.11	-0.46	0.7	1.27
CMAQ	2.1	-0.22	0.67	0.81	3.43	1.01	0.81	1.65	3	0.86	0.82	1.43	3.58	1.01	0.57	1.87
EMEP	2.38	0.06	0.71	0.76	2.53	0.12	0.77	1.17	2.96	0.82	0.84	1.25	2.53	-0.05	0.78	1.03
LOTO	1.76	-0.57	0.73	0.84	2.14	-0.28	0.82	0.88	2.04	-0.1	0.84	0.71	2.18	-0.4	0.75	1.16
MINNI	2	-0.33	0.61	1	3.16	0.74	0.82	1.36	3.07	0.93	0.8	1.49	3.74	1.17	0.65	1.89

3 \*OB/N: OB: OBSERVED VALUE IN mgN/m<sup>2</sup> for WNOx and ug/m<sup>3</sup> for TNO3; N: number of sites

4

1

2  
3Figure 10. Scatter plots showing modelled and observed WNO<sub>x</sub> (in mgN/m<sup>2</sup>) for all the periods

4

5

Figure 11. Scatter plots showing modelled and observed FNO<sub>3</sub> (in (mgN/m<sup>2</sup>)/(ugN/m<sup>3</sup>)/mm) for all the periods

7.

1

2 **3.2.2 Comparison of modelled estimates**

3 For WNO<sub>x</sub> (Figure 3) there are large differences between the accumulated deposition  
4 estimates of the models, with CHIM, EMEP and LOTO estimating the highest values,  
5 although spatial distributions are similar. EMEP estimates particularly high values in C6 and  
6 CHIM in C9, when compared with the other models. CMAQ, CAMX and MINNI estimated  
7 the smallest accumulated deposition, with MINNI giving particularly small values for all four  
8 periods. Maps of variability in S.3.3 show that the extent to which the models differ varies  
9 depending on the period. For example, differences between models are larger in C6 over the  
10 Spanish Mediterranean coast (as they are for the other species, S.3.1 and S.3.2), whereas at  
11 the Norwegian coast differences are larger in C7 and C9. Since the June campaign (C6) is the  
12 period with the highest temperatures, gas-to-particle conversion is less favoured and so  
13 difference between model estimates for that period could be related to differences in the  
14 gas/aerosol ratio and/or the wet deposition parameterizations, especially for the gas phase  
15 component (or that of the aerosol in C7 and C8). Maps of concentrations of HNO<sub>3</sub> and NO<sub>3</sub>-  
16 10 (Supplementary Material S.6.2 and S.6.3, respectively) confirm larger values of HNO<sub>3</sub> and  
17 smaller values of nitrate for C6 than for the other periods. Finally, some of the variability  
18 observed close to the boundaries of the domain can be related to differences in how the  
19 boundary conditions are treated by each model.

20 The maps of TNO<sub>3</sub> concentrations are shown in Figure 6. All models estimate the largest  
21 TNO<sub>3</sub> concentrations in regions with large NO<sub>x</sub> emissions such as northern Italy, around The  
22 English Channel and along the shipping routes especially in the Mediterranean (LOTO has  
23 the same distribution, although it cannot be seen clearly because of the low concentration  
24 estimates). The formation of nitrates in the coarse fraction, included in EMEP and LOTO  
25 (S.6.3), gives a different spatial pattern for these two models, with higher nitrate over the sea.  
26 CAMX and CMAQ estimate the largest HNO<sub>3</sub> air concentrations, followed by MINNI. The  
27 high HNO<sub>3</sub> concentrations for these models, (besides potential differences in deposition), can  
28 be due to different reasons, such as the high NO<sub>x</sub> concentrations estimated by CMAQ  
29 compared with the low values of CAMX, (Supplementary Material S.6.1), due to low NO.  
30 Overall, the three models with the lowest WNO<sub>x</sub> (CMAQ, CAMX and MINNI) predict the  
31 largest TNO<sub>3</sub> concentrations, suggesting a lower efficiency of the deposition processes for  
32 these models. The fact that CMAQ estimates the lowest accumulated rainfall for all periods

1 (especially in C6, C8 and C9) could partly explain why this model gives smaller WNO<sub>x</sub> than  
2 EMEP, CHIM or LOTO.

3 In the Supplementary Material S.6.5 there are scatter plots of modelled WNO<sub>x</sub> versus  
4 modelled rain for all models and periods for 287 locations. As mentioned for the other  
5 pollutants, the locations correspond to all measurement sites measuring at least one of the  
6 variables (see map in S.7.1), with the sole purpose of comparing model estimates (i.e. no  
7 measurement data were used). These plots show substantial differences between the  
8 deposition estimates of the models for the same amount of rain; for instance, MINNI  
9 estimates much lower wet deposition than the other models for the same amount of  
10 precipitation, especially in C7, C8 and C9.

11 If we analyse the deposition factors, we can see in S.6.8 CHIM and EMEP have the largest  
12 wet deposition factors for WNO<sub>x</sub> (CHIM especially in C9, C8 and C7 and EMEP in C6).  
13 MINNI has the lowest values (also CAMx in C6). Differences between models are quite  
14 substantial. For example, in C9 differences between CHIM and MINNI are a factor of six in  
15 Poland. For the gas (HNO<sub>3</sub>) and aerosol (NO<sub>3</sub>-10) components, the estimated deposition  
16 factors for all measurement locations (287) over all periods (Fig S.6.4) show that CHIM and  
17 EMEP also have the largest factors for both components and MINNI and CAMX have the  
18 smallest. For all models, the deposition factor for the gaseous component is larger than that of  
19 the aerosol; i.e. the wet deposition is larger for the gaseous component for the same ground  
20 level concentration. This could be due to the different parameterisations for the gaseous and  
21 particulate phases in the models (for example, the EMEP model uses a larger in-cloud  
22 scavenging ratio for HNO<sub>3</sub> than for NO<sub>3</sub>-10, same scheme as that for MINNI) or could be due  
23 to differences in the vertical profiles of the two components. Vertical concentration profile  
24 data are not available for the models in this exercise. In the Netherlands, Erisman et al.  
25 (1988) observed increasing HNO<sub>3</sub> concentrations up to a height of 200 m and decreasing  
26 nitrate concentrations. Although these measurements were made at a specific place and time  
27 and in a different pollution climate to the current situation, such differences in the vertical  
28 profiles of the gaseous and aerosol components could explain the differences between the  
29 magnitudes of the two factors, in addition to the differences due to the parameterisations.

30 Regarding DNO<sub>x</sub>, maps in S.2.3 show large differences between models. CMAQ estimates  
31 the largest deposition rates for all periods, whereas EMEP estimates some of the lowest

1 values for C7, C8 and C9. Scatter plots of TNO<sub>3</sub> concentrations versus DNO<sub>x</sub> (S.6.6) also  
2 show low dry deposition estimates for EMEP and high estimates for CMAQ for a given value  
3 of TNO<sub>3</sub>. With regards to the deposition factor, bar plots in the Supplementary Material S.6.8  
4 show that CMAQ, CAMX and LOTO have the largest values of F<sub>d</sub>. The large differences in  
5 the DNO<sub>x</sub> estimates of the models highlights the need for an evaluation of the dry deposition  
6 process with measurement data, especially since dry deposition can be in the range of wet  
7 deposition or even higher for some models (S.6.7).

#### 8 **4 Conclusion**

9 A detailed analysis has been performed based on the results of four intensive EMEP  
10 measurement periods (25 Feb - 26 Mar, 2009; 17 Sep - 15 Oct, 2008; 8 Jan – 4 Feb, 2007 and  
11 1-30 Jun, 2006). Here we present a joint analysis of wet and dry deposition as well as air  
12 concentrations in order to determine and understand the performance and behaviour of six air  
13 quality models for nitrogen and sulphur compounds.

14 For **sulphur deposition**, the fact that CMAQ includes emissions from sea salt results in  
15 higher estimates of WSO<sub>x</sub> over marine and coastal areas; EMEP estimates higher  
16 accumulated WSO<sub>x</sub> to terrestrial areas and CAMX and MINNI estimate higher TSO<sub>4</sub> than  
17 the other models. The comparison with observations (with no sea salt corrections) shows that  
18 CMAQ performs best in C6, C7 and C9. At coastal sites, the sea salt correction applied to the  
19 measurements indicates a significant presence of sulphates. CMAQ is the only model that can  
20 reproduce the high measured values of WSO<sub>x</sub>, showing that model performance can be  
21 improved by including emissions of sea salt sulphates. MINNI and LOTO underestimate  
22 WSO<sub>x</sub> for all periods, MINNI especially in C9 and LOTO especially in C6. As MINNI  
23 overestimates TSO<sub>4</sub>, this model seems to have a low wet deposition factor for sulphur. This  
24 could be due to the vertical concentration profiles or a poor in-cloud scavenging, which in  
25 turn could be due to the parameterization of clouds in this model. By contrast, EMEP  
26 overestimates WSO<sub>x</sub>, partly due to an overestimate of precipitation, but this may also be  
27 related to an overestimate of TSO<sub>4</sub> (due to the coarse spatial resolution used, the models are  
28 expected to overestimate SO<sub>2</sub> concentrations at background locations). FSO<sub>4</sub> (wet deposition  
29 factor for sulphates) estimated by EMEP, agrees reasonably well with that calculated from the  
30 observations, although there is a tendency to overestimate at the sites with the lowest values  
31 calculated from the observations (especially in C6 and C7), and underestimate at the sites

1 with the highest values. CAMX performs best overall in C9 for the sea salt corrected dataset,  
2 although this could be due to compensating factors, as this model overestimates TSO4 by the  
3 largest amount, after MINNI. The fact that CAMX estimates the highest SO2 concentrations  
4 and the lowest dry deposition rates for a given TSO4 (along with MINNI) seems to indicate a  
5 small dry deposition factor (or deposition velocity), at least compared with other models.  
6 CMAQ estimates the highest DSOx values, consistent with the fact that this model includes  
7 sulphate emissions from sea salt. MINNI predicts lower DSOx for a given TSO4 than the rest  
8 of models.

9 With regards to **reduced nitrogen**, EMEP estimates the highest values of WNHx and also has  
10 the highest wet deposition factor. Considering all sites with WNHx measurements, there is a  
11 general underestimation by all models, with the exception of EMEP, which underestimates  
12 the least and even overestimates deposition in C6 and C9. In C7 the general underestimation  
13 is still more pronounced, with EMEP performing best (bias and RMSE). The estimates by  
14 MINNI and CMAQ have the highest negative bias, accompanied also by high RMSE values,  
15 although this is less pronounced in C6 in the case of MINNI. An analysis of the relationships  
16 between modelled wet deposition rates and the relative concentrations of gas and aerosol  
17 species, suggests that differences in how the models parameterise the wet deposition of these  
18 species (especially the aerosol) and in the vertical concentration profiles could explain the  
19 differences between models. All models underestimate TNH4 (ammonia plus ammonium) in  
20 C6, with the estimates by CMAQ having the highest negative bias, followed by EMEP. The  
21 simultaneous underestimation of WNHx and TNH4 in C6, mostly by CMAQ, but also by  
22 CAMX, CHIM, LOTO and MINNI, suggests that uncertainties or errors in the wet deposition  
23 processes cannot explain the underestimate of TNH4 in this period. An underestimate of NH<sub>3</sub>  
24 emissions or boundary concentrations, or an overestimate of dry deposition could explain this  
25 behaviour, however. In the case of MINNI; the high values of TNH4, NH<sub>3</sub> and NH<sub>4</sub>-10  
26 estimated by this model (but with a similar estimate of rainfall to the other models), could  
27 also be due to an underestimate of the wet deposition factor. This could be related to the  
28 vertical concentration profiles for this model or in-cloud processes, including the  
29 parameterization of clouds. In the case of EMEP, the good estimates of wet deposition but an  
30 underestimate of TNH4 concentrations could be due to several reasons, such as the  
31 combination of low TNH4 compensated by an overestimate of rainfall. CHIM and MINNI  
32 estimate the lowest dry deposition rates for a given value of TNH4, as does EMEP in C6.

1 Finally, regarding **oxidized nitrogen**, CMAQ, CAMX, MINNI predict the lowest WNO<sub>x</sub> and  
2 the highest TNO<sub>3</sub> (nitric acid plus nitrates). A comparison with observations indicates a  
3 general underestimation of WNO<sub>x</sub> by these models. The predictions of MINNI have a fairly  
4 high negative bias, especially in C7 and C9, compared with the rest of the models. The  
5 models with the higher WNO<sub>x</sub> estimates (EMEP, LOTO and CHIM) seem to agree better  
6 with observations, although EMEP substantially overestimates in two of the campaigns (C6  
7 and C8), accompanied with high values of RMSE. At the same time, the three models that  
8 underestimate deposition, overestimate TNO<sub>3</sub> for all the campaigns, except C6. This fact can  
9 be related to a low efficiency in the wet deposition of the gas phase, as illustrated in S.6.4, and  
10 can be due to several reasons, such as low concentrations in the upper levels of the  
11 atmosphere, a poorer estimation of cloud occurrence or an underestimation of gas-scavenging  
12 coefficients. In the case of MINNI the scavenging coefficient for aerosol may also be too low.  
13 In C6 all the models underestimate TNO<sub>3</sub>, except EMEP, which overestimates it. In this  
14 campaign all models estimate higher HNO<sub>3</sub> and lower nitrate concentrations than in the other  
15 campaigns, most likely as a result of the higher temperatures. EMEP and LOTO estimate  
16 lower HNO<sub>3</sub> concentrations than the other models, especially over the sea, which is consistent  
17 with the fact that these two models consider the formation of nitrates in the coarse fraction  
18 due to the presence of Na<sup>+</sup> in sea salt emissions. CAMX, CMAQ and MINNI, in general,  
19 estimate the highest HNO<sub>3</sub> concentrations for the whole domain.

20 The analysis of dry deposition highlights several important issues, such as 1) there were large  
21 differences between the model estimates and 2) dry deposition contributes significantly to the  
22 total deposition for the three deposited species, with values in the same range as wet  
23 deposition for most of the models, and with even higher values for some of them, especially  
24 for reduced nitrogen. This highlights the strong need for evaluating model performance for  
25 dry deposition, something not currently possible due to the lack of suitable measurements.

26

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10

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22

1 **Annexes**

2 **A.1 WET DEPOSITION SCHEMES**

3

4 **EMEP**

5 The EMEP model calculates in-and sub-cloud wet deposition. In-cloud wet scavenging of  
6 gases and aerosols is parameterised using the precipitation rate and scavenging ratios  
7 accounting for the species solubility. Below precipitating clouds, a distinction is made  
8 between wet scavenging of gases and aerosols. For gases, scavenging ratios are used, whereas  
9 the scavenging of aerosols is described based on size dependent collection efficiency of  
10 particles by the rain drops (assuming the raindrop fall speed of 5 m/s and a Marshall-Palmer  
11 size distribution of rain drops).

12 **CHIM**

13 In-cloud scavenging in CHIMERE is different to that of similar models. CHIMERE takes into  
14 account the formation of “aqueous species” due to the absorption of particulate species by  
15 clouds with a kinetic of absorption. For gases, the absorption of H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub> is considered,  
16 based on the equilibrium between the gas phase and the aqueous phase, which depends on pH  
17 following Seinfeld and Pandis (1998). Aqueous species and dissolved gases are deposited by  
18 in-cloud scavenging with a parameterization that uses a simple in-cloud scavenging  
19 coefficient. The in-cloud scavenging transfer rate  $F$  for particles is computed in two steps,  
20 based on the classical approach in one step (Berge, 1993):  $F_1$  indicates the transfer of particles  
21 into droplets and  $F_2$  indicates the scavenging of droplets in case of rain precipitation  
22 (Pernigotti *et al.*, 2012):

23

$$F_1 = -\alpha w C \quad F_2 = -\frac{P_r}{hw} C_{aq}$$

24 Where  $w$  the cloud water content ( $\text{g cm}^{-3}$ ),  $C$  is the concentration of the aerosol ( $\text{g cm}^{-3}$ ),  $C_{aq}$  is  
25 the corresponding concentration in the droplet phase ( $\text{g cm}^{-3}$ ),  $\alpha$  is a transfer coefficient ( $\text{cm}^3$   
26  $\text{g}^{-1} \text{s}^{-1}$ ),  $P_r$  is the precipitation rate ( $\text{g cm}^{-2} \text{s}^{-1}$ ) and  $h$  the height of the given grid box (cm). The  
27 advantage of this two steps scavenging process with transfer rates  $F_1$  and  $F_2$  is to lead to a

1 droplets aerosol concentration which is considered as a loss from the aerosol side but which  
2 allows for aerosol particles to reappear whenever the cloud disappears without precipitation

3 Dissolution of gases in raindrops is assumed to be irreversible in CHIMERE for both  $\text{HNO}_3$   
4 and  $\text{NH}_3$ . Particles are also scavenged by raindrops.

#### 5 **CMAQ**

6 In CMAQ, pollutant scavenging is calculated by two methods, depending on whether the  
7 pollutant participates in the cloud water chemistry (Byun and Schere, 2006). For those  
8 pollutants that participate in the cloud chemistry, the amount of scavenging depends on the  
9 Henry's law constant, dissociation constants and cloud water pH Chang et al. (1987). For  
10 pollutants that do not participate in aqueous chemistry, CMAQ uses the Henry's law  
11 equilibrium equation to calculate cloud water concentrations based on the liquid water content  
12 of the cloud. The wet deposition of a chemical species depends on the precipitation rate and  
13 the cloud water concentration.

#### 14 **CAMX**

15 The basic model implemented in CAMX uses a scavenging approach in which the local rate  
16 of concentration change within or below a precipitating cloud depends on a scavenging  
17 coefficient (ENVIRON, 2011). The scavenging coefficient is determined differently for gases  
18 and particles based on relationships described by Seinfeld and Pandis (1998). Two  
19 components are calculated for gases: direct diffusive uptake of ambient gases into falling  
20 precipitation and growth of cloud droplets containing dissolved gases. Wet scavenging of  
21 gases by precipitation occurs within and below clouds. Below the cloud, the total gas  
22 concentration in a given grid cell is available for scavenging. Within a cloudy cell the total  
23 gas concentration must first be partitioned into an aqueous fraction within cloud water and the  
24 remaining gaseous fraction within the interstitial air. Both aqueous and interstitial gases  
25 within a cloudy cell are available for scavenging, but are removed at different rates. The two  
26 components determined for particles are: impaction of ambient particles into falling  
27 precipitation with an efficiency that is dependent on particle size and growth of cloud droplets  
28 containing particle mass. Rain drops, snow flakes and graupel particles are each separately  
29 represented by a single mean size, mass and fall speed. The scavenging model in CAMX  
30 assumes that all gases can dissolve into liquid cloud and can then be scavenged by all



1 precipitation forms and that dissolved gases are in equilibrium with ambient concentrations  
2 according to Henry's law.

### 3 **LOTO**

4 LOTOS-EUROS includes a pH-dependent cloud chemistry following the approach by  
5 (Banzhaf et al 2012). In-cloud scavenging is not taken into account. Below-cloud scavenging  
6 is done using scavenging coefficients for gases and particles following Scott (1979) over the  
7 atmospheric column covered by the model (lower 3.5 km of troposphere)

### 8 **MINNI**

9 In MINNI, the parameterization of wet deposition follows EMEP (2003) approach and  
10 includes in-cloud and below-cloud scavenging of gas species and particles. Different  
11 scavenging ratios (in- and below-cloud) and collection efficiencies for gas-phase species and  
12 aerosols are considered. Sulphate production within clouds is also considered using Henry's  
13 law equilibrium equations for SO<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>.

14

## 15 **A.1 DRY DEPOSITION SCHEMES**

16

### 17 **EMEP**

18 The EMEP model uses a resistance formulation for the dry deposition of gaseous species,  
19 whereas a mass-conservative equation from Venkatram and Pleim (1999) is used to calculate  
20 aerosol dry deposition. Dry deposition velocities are surface type dependent and are  
21 calculated for 16 land-use classes. The total dry deposition in a grid-cell is the area-weighted  
22 average of all ecosystem-specific depositions within the cell.

### 23 **CHIMERE**

24 The dry deposition process is commonly described through a resistance analogy (Wesely  
25 (1989)). For each model species, three resistances are estimated; the aerodynamical  
26 resistance, the resistance to diffusivity near the ground and the surface resistance. Deposition  
27 occurs if the total resistance is low. For particles, the settling velocity is added. More  
28 information is included in Laurent et al. (2013)

### 29 **CMAQ**

1 CMAQ initially included the same description for the dry deposition of aerosols, as defined  
2 by Binkowski and Shankar (1995), but CMAQ versions higher than 4.5 use the approach of  
3 Venkatram and Pleim (1999), where the dry deposition is parameterised following a non-  
4 electrical analogy with the objective to maintain mass conservation.

5 To calculate the dry deposition velocity ( $V_d$ ) for aerosols, CMAQ considers aerosol size  
6 distributions with three log-normal modes and computes aerosol  $V_d$  as a function of particle  
7 diameter and meteorological conditions for each mode for mass, surface area and number. An  
8 integrated  $V_d$  is computed for each mode by integrating these equations over each log-normal  
9 size distribution. The modal-integrated  $V_d$  is a function of modal mass mean diameter.  
10 Aerosol treatment in CMAQ v. 5.0 includes a dynamically interactive coarse mode for  $\text{NO}_3$ ,  
11 hygroscopic growth of particles and advanced treatment of secondary organic aerosols.  
12 Recent reviews of air–surface exchange (Fowler et al., 2009) indicate the need to account for  
13 the canopy structure and its effects on particle  $V_d$ . Characterizing the fine scale morphology  
14 in a regional air quality model remains a challenge and will be a future focus area for model  
15 development.

#### 16 **CAMX**

17 The gas resistance model of Zhang et al. (2003) was used in the CAMX simulations. This  
18 scheme uses the “leaf area index” (LAI) to scale pollutant uptake by biota and uses an  
19 updated representation of non-stomatal deposition pathways. In this model, aerodynamic and  
20 boundary resistances are very similar to the original Wesely (1989) formulations but the  
21 surface resistance is calculated differently.

#### 22 **MINNI**

23 MINNI implements CMAQ aerosol model “aero3” and consequently uses the same approach  
24 to estimate aerosol dry deposition velocities.

- The estimates of N and S deposition by six regional models are evaluated
- The inclusion of sea salt sulfate emissions was found to be important
- Formation of  $\text{NH}_3+\text{NH}_4^+$  is generally underestimated in summer
- There is a general underestimation of wet deposition of reduced N by most models
- Different performance was found for the different models and pollutants

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