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Aerosol Modeling: Results and Intercomparison from European Regional-scale Modeling Systems

A contribution to the EUROTRAC-2 subproject GLOREAM

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1 Introduction

The important role of aerosols in many environmental issues as climate change, acid rain or smog is long known but there still exists some lack of knowledge in the relevant atmospheric processes, e.g. chemistry, radiative transfer and cloud formation. Models that simulate the transport and transformation of aerosols and gases are one important tool that can contribute to asses the state of knowledge. However, modeling of aerosols can require a complexity which might be beyond the one needed for photochemistry. Additional heterogeneous processes have to be treated and nighttime is getting important too. From an environmental policy point of view aerosols are longer term pollutants which requires the modeling of seasonal or annual cycles.

Several European Air Quality Modeling systems (AQM) have in the past been upgraded towards a more detailed description of the tropospheric aerosol components. Substantial developments to include the aerosol dynamical processes such as nucleation, condensation, evaporation and coagulation as well as simulating the inorganic and secondary organic compounds have been made. To better account for these processes a transition from bulk to size-resolved treatments of aerosol microphysics and chemistry has been undertaken in some AQMs. All these model development efforts contribute towards describing the gaseous and aerosol processes in the systems according to the 'one-atmosphere' approach.

In order to evaluate the capabilities, strengths and weaknesses of air quality models with respect to aerosols an intercomparison study has been started within the framework of GLOREAM, a subproject of the EUROTRAC-2 project. In this study the following modeling groups are participating: DEM (NERI), EURAD (FFA), EUROS (RIVM), LOTOS (TNO), MATCH (SMHI) and REM3/CALGRID (FU Berlin). Most of the models started as photo-oxidant simulation tools but have been considerably improved to perform aerosol calculations over larger parts of Europe. They were developed within different programs for different scientific and application purposes and, hence, the structure and complexity of these modeling systems vary substantially.

The design of this intercomparison is such that the models have been applied in the mode in which they are routinely used by the participating groups. No attempt has been made to harmonize model configurations, process descriptions and/or the input data. Under this protocol the study is limited, hence the objectives have been formulated as

- to demonstrate the capability of long-term comprehensive PM modeling covering all of Europe;
- to perform a low sensitivity evaluation of the different models and
- to perform a low sensitivity model inter-comparison focusing mainly on the different modeling approaches and inputs.

Thus we mainly analyze the variance between the models and the observations and discuss probable sources of these variances. Definite answers towards why simulation results may differ cannot be given with this type of model intercomparison. However, identifying some probable causes for the different results may still be possible. The focus is primarily on model performance for aerosol components in conjunction with the EMEP observational data that has been extended using Dutch and German special observation sites.

This intercomparison is a follow-up of a similar study performed within EUROTRAC-1 (Hass et al., 1997). However, this earlier study focused on ozone formation over Europe and here the focus is on aerosol components. The benefit of this study is also that we have included additional models covering now a larger set of modeling approaches with regard to grid sizes, vertical resolution, aerosol formation mechanisms, etc.

2 Air Quality Modeling Systems

The air quality modeling systems (AQM) for long-range-transport involved in this comparison study cover a wide range of current modeling approaches for the simulation of gaseous and particulate pollutants:

- The **Danish Eulerian Model (DEM)** is a comprehensive model calculating concentrations and depositions of all important chemical compounds on a space domain containing the whole of Europe (different time and spatial resolutions can be specified). A short description of the model and some results can be found at the following internet address: http://www.dmu.dk/AtmosphericEnvironment/DEM
- The **European Air Pollution Dispersion (EURAD/FFA)** model coupled with the aerosol modules MADE and SORGAM, is a comprehensive, multi-layer, multi-scale, Eulerian model designed to simulate relevant physical and chemical processes occuring in the troposphere. The FFA version was used for this study.
- The **European Operational Smog** (**EUROS)** model is a four layer, Eulerian (chemical) dispersion model which is used for the simulation of short and long term concentrations and deposition fluxes of ozone and precursors, particulate matter and persistent organic compounds (POP's).
- The **Long Term Ozone Simulation (LOTOS)** model, a three-layer, Eulerian photochemical model designed for the simulation of -episodic and long-term, boundary layer oxidant concentrations. The last five years the model has been extended with both primary and secondary aerosols.
- The **Multi-scale Atmospheric Transport and Chemistry (MATCH)** model has been developed as a flexible, Eulerian, transport/chemistry/deposition model for atmospheric pollutants. It is used in a range of applications ranging from urban scale studies on ~5 km or higher horizontal resolutions to continental scale studies on acid deposition, photochemistry and particulate matter. An overview of the model features is provided at the internet address http://www.smhi.se/sgn0106/if/meteorologi/match.htm**.**
- The **REM3/CALGRID** model (a combination of the former **R**egional **E**ulerian **M**odel with **3** different chemistry schemes and the **Cal**ifornia **Grid** Model), a multi-layer Eulerian grid model designed for the simulation of short- and long-term boundary layer oxidant and aerosol concentrations using a choice of two chemistry schemes and two equilibrium aerosol modules.

A descriptive summary of the six air quality modeling systems describing the model type, the development purpose and the main applications can be found in Table 2.1. Figure 2.1 displays the modeling domains used for this study. Besides REM3 the other models cover most of the European continent. The approaches of domain discretisations by the models is given in Table 10.3.

A more detailed description of the main features of the above AQMs can be found in the Appendix and in the references. As the focus in this report is on aerosols the following chapter describes the aerosol treatment of each model in more detail. Again, for references the reader is directed to the Appendix.

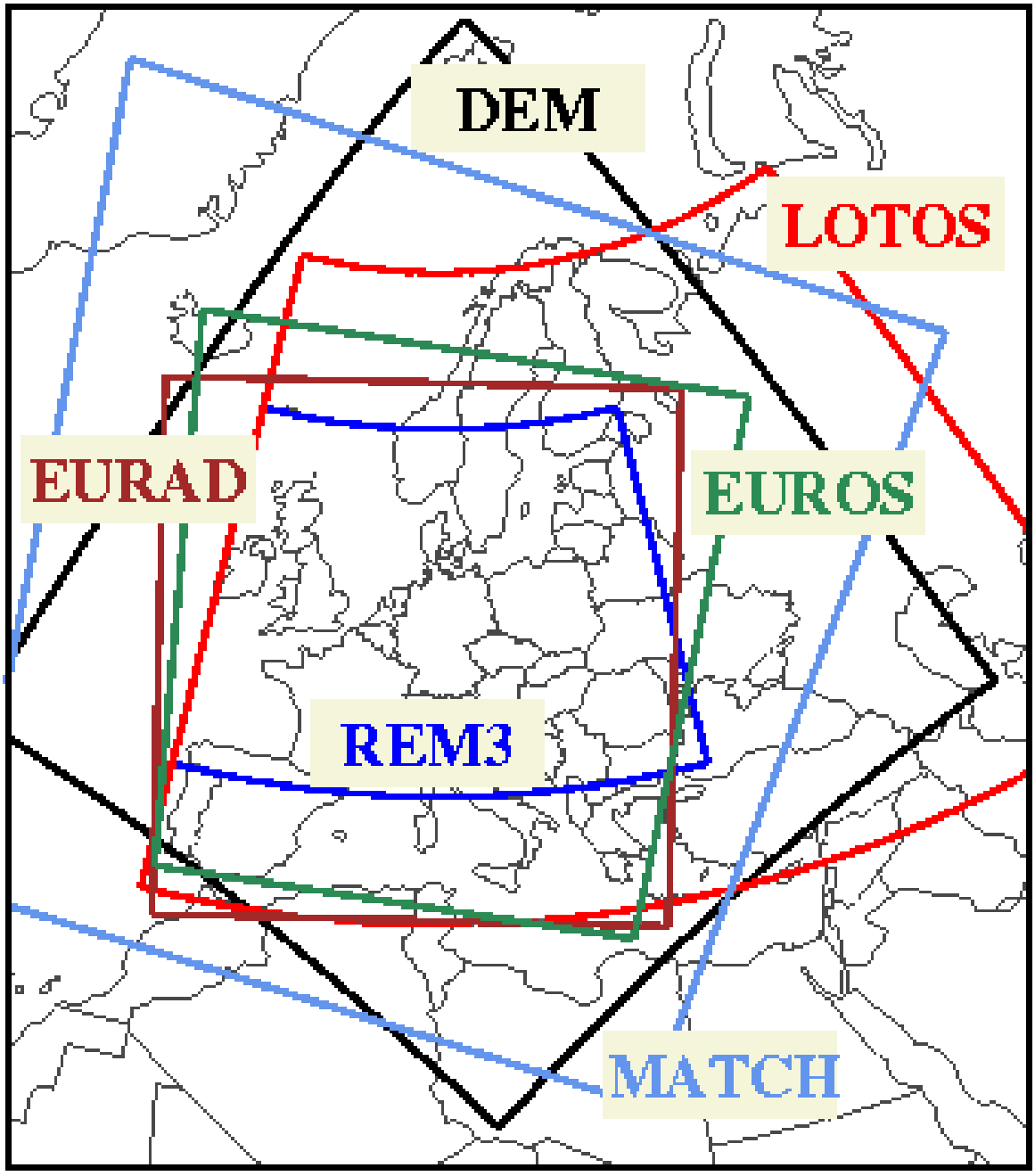

Figure 2.1. Modeling domains of the air quality modeling systems for this study.

Table 2.1. Characteristics of the Air Quality Modeling systems.

Acronym & Organisation	Full name	Model type	Purpose	Applications
DEM NERI, Denmark	**D**anish **E**ulerian **M**odel	• Eulerian • different space and time grids • Europe	Episodic and long-term calculations	• Emission scenarios • Exceedance of critical levels • Impact of biogenic emissions • Climatic changes on air pollution levels
EURAD/ FFA Ford Research Aachen	**EUR**opean **A**ir Pollution **D**ispersion Model	• Eulerian • variable grids • regional/local • Troposphere	Episodic to long term photo-oxidants and aerosol calculations	• Acidic episodes • Oxidant episodes • Process studies • Abatement strategies
EUROS RIVM, Netherlands	**EUR**opean **O**perational **S**mog model.	• Eulerian • variable grids (shifted pole) Europe • lower troposphere	Episodic and long term simulations for photo-oxidants, acidifying substances, PM and POPs	• Evaluation of directives • (inter)national outlooks assessments
LOTOS TNO, Apeldorn Netherlands	**LO**ng **T**erm **O**zone **S**imulation Model	• Eulerian • Europe • up to≈ 3.5 km Height	Episodic and long-term oxidant and PM calculations	• Air Quality assessment • Climate Air Pollution scenarios • Budget analysis
MATCH SMHI Sweden	**M**ulti-scale **A**tmospheric **T**ransport and **CH**emistry model	• Eulerian • variable grid sizes and projections • troposphere and lower stratosphere	Episodic (forecast and hindcast) and long-term calculations	• Operational emergency response • Acid deposition assessment & mapping • Surface ozone forecasts • Climate / air pollution scenarios
REM3/ CALGRID FU Berlin Germany	Combination of: **R**egional **E**ulerian **M**odel with **3** chemistry schemes and the **Cal**ifornia **Grid** model	• Eulerian • Variable grid sizes, regional to local • boundary layer and lower troposphere	Episodic and long term, oxidant and aerosol calculations	• Evaluation of long and short term abatement strategies

3 Aerosol treatment in the modeling systems

3.1 DEM

Only secondary aerosols are considered at present in DEM. Sulfate and nitrate aerosols are produced by the appropriate reactions of the condensed CBM IV chemical scheme. The CBM IV scheme is originally described in Gery et al. (1989). All chemical reactions involved in the CBM IV chemical scheme are listed in Zlatev (1995). Ammonium nitrate and ammonium sulfate are produced by a special procedure added to the CBM IV scheme (see Zlatev, 1995). This special procedure is based on the use of equilibrium principles. It is rather similar to the corresponding procedure used in EMEP (see Iversen et al., 1989, 1990 1991). However, some improvements, suggested in Harrison et al. (1994), were also implemented in the ammonia-ammonium procedure used in DEM. The dry deposition and wet deposition mechanisms are described in Zlatev et al. (1992). Some improvements were performed after 1992. The coefficient rates used in both the dry deposition mechanism and the wet deposition mechanism are varied both geographically, diurnally and seasonally. Special mechanisms are used for wet depostion over water.

3.2 EURAD/FFA

Three log-normal modes, representing the nucleation mode, accumulation mode and coarse mode, are provided to describe the dynamics of particles by MADE (Modal Aerosol Dynamics Model for Europe) (Ackermann et al., 1998) based on the work of Binkowski, 1999 and Binkowski and Shankar, 1995. The particle size distribution is described through 0^{th} moment (number) and 3^{rd} moment (proportional to mass) of the functions. The chemical composition of particles for the fine particle size range (nucleation and accumulation mode) encompasses sulfate, ammonium nitrate, water, anthropogenic and biogenic secondary organics (Schell et al., 2001), elemental carbon, primary organics and other anthropogenic derived fine particulate matter. The particulate matter in the coarse fraction include those from soil, marine and anthropogenic sources. Some basic assumptions are the internal mixture in each mode, the fixed standard deviation in each mode and dynamic mode merging by renaming. Also aerosol water is considered to be in equilibrium with the gas phase. There is also a cloud aerosol interaction integrated with the formation of Aitken mode interstitial aerosol and cloud condensation nuclei, aqueous phase cloud chemistry and vertical mixing. Particles can be removed by scavenging, sedimentation, size dependent dry deposition and by wet removal.

3.3 EUROS

Primary emitted particles are described in the EUROS model as chemically inert species divided in 5 size classes (Table 3.1). The size classes have been chosen relatively large such that processes, which affect the diameter particle, have their effect mostly on a sub size-class scale and are thus implicitly represented.

Secondary produced sulfate and nitrate is described with a condensed ozone chemical mechanism, which also parameterizes the production of particulate sulfate and nitrate. Table 3.2 lists those reactions of the scheme which concern the formation of particulate sulfate and nitrate. All secondary particulate matter is counted as PM10.

Growing and mixing of particles due to for instance cloud processes are not explicitly included. Dry deposition is modeled using the resistance approach and wet removal is based on precipitation measurements using a washout bulk removal rate. Primary particulates, at this stage, are not yet modeled to be subject to wet removal. European emission fields for anthropogenic primary PM10 are largely adapted from [Berdowski et al., 1997] with some new estimates for

Dutch emissions. Anthropogenic NOx, SOx, and VOC emissions - adapted from [Grösslinger et al., 1996] and scaled to 1995 - are used as input for the chemical scheme which simulates particulate sulfate and nitrate.

Table 3.1. PM10 size class properties used in EUROS: Diameter range (µm), surface resistance rs in (s/m), and standard Particle Size Distributions (PSD) in %. Note: this PM10 description allows about 10% of the particle mass to be in the size classes larger than 10 µm.

size class	1	2	3	4	5
diameter (µm)	< 0.95	0.95-4	4-10	10-20	> 20
rs (s/m)	1450	340	90	32	0
PSD (%)	42	33	14.5	5.9	4.6

Table 3.2. Production reactions of particulate sulfate and nitrate, which are a part of a condensed ozone chemical mechanism.

Nr.	Reactions			rate constant (k_i [298])		
1	$2NO_2 + O_3$	→	$2NO_3$aerosol	k_1	[cm^3 $molecules^{-1}$ s^{-1}]	(1)
2	$SO_2 + OH$	→	SO_4aerosol	$1.35\ 10^{-12}$	[cm^3 $molecules^{-1}$ s^{-1}]	
3	HNO_3	→	NO_3aerosol	$5.00\ 10^{-6}$	[s^{-1}]	(2)
4	SO_2	→	SO_4aerosol	$1.39\ 10^{-6}$	[s^{-1}]	(3)

(1) k_1 is a lumped rate constant based on reactions describing the (trans)formation of the nitrogen species: NO, NO_2, NO_3, N_2O_5 and HNO_3.
(2) This reaction describes the transformation of HNO_3 in cloud water and on aerosol with a rate constant of $5.0\ 10^{-6}$ [s^{-1}] with a relative humidity (RH) of 90% or less and of $1.0\ 10^{-4}$ [s^{-1}] with RH > 90%.
(3) This reaction describes the transformation of SO_2 in cloud water and on aerosol with a rate constant of $1.39\ 10^{-6}$ [s^{-1}] with a relative humidity (RH) of 90% or less and of $4.17\ 10^{-6}$ [s^{-1}] with RH > 90%.

During this study, the EUROS model has been upgraded with a new chemical reaction scheme, CB-IV_99 [Adelman, 1999], in combination with the EQSAM aerosol module [Metzger et al., 2002]. Results of the EUROS model with this new scheme and aerosol representation have not been included in this publication. The EUROS aerosol model results reported here are, therefore, limited by a simplified SO_4 and NO_3 description without NH_3/NH_4.

3.4 LOTOS

LOTOS is a 3D Eurlerian grid model of intermediate complexity. It has been designed with the aim of performing both episodic and long term simulations within acceptable computation time. For that reason in LOTOS a simple bulk approach for the aerosol modeling is used, assuming all secondary aerosols to be in the fine fraction ($PM_{2.5}$). Aerosol dynamics are not considered. The model employs the equilibrium module from MADE for secondary inorganic aerosols (Ackermann et al., 1998). The version of LOTOS used in this intercomparison did not yet include

sea-salt. The primary aerosols are assigned to two size fractions: fine mode PM2.5 and coarse mode $PM_{2.5-10}$, in agreement with the classification in the CEPMEIP emission database. In LOTOS there is no interaction between the two modes and hence the only processes concerning primary PM are emission, transport and deposition, including sedimentation for the coarse fraction. Implicitly a fixed size distribution is taken into account for the fine and coarse fraction, resulting into a set of two different deposition velocities.

SO_2 is converted to SO_4 in two ways: by the gas phase reaction with OH and by heterogeneous processes. In both cases it is assumed that the oxidation product is particulate sulfate, i.e. the intermediate product sulfuric acid is neglected. The same holds for the SO_x emissions of which 2% is assumed to be in the form of SO_4 particles directly. The heterogeneous oxidation of SO_2 to SO_4 is parameterized by a linear conversion rate. I.e. no explicit cloud chemistry is taken into account. The conversion rate is taken 8.3×10^{-5} min^{-1} in cloud free conditions with relative humidity lower than 90%. In case the cloud cover fraction is larger than zero, or the relative humidity is higher than 90%, the conversion rate is taken up to a factor 3 and 2 higher, respectively.

An important formation pathway of nitric acid (HNO_3), one of the two precursors of ammonium-nitrate, is the heterogeneous reaction of N_2O_5 on the aerosol surface. This process is taken into account following the approach of Dentener and Crutzen (1993) using a reaction probability of $\gamma = 0.1$. The concentration of SO_4 is taken as a proxy for the available aerosol surface also taking into account the (computed) water content of the aerosol.

3.5 MATCH

All secondary inorganic and aerosol-phase sulfur and nitrogen products from the chemical mechanisms are assigned to the PM2.5 fraction. In addition to that other primary particle components are currently being implemented in the model. In the present formulation we represent sea-salt particles with dry diameters from 0.062 μm to 16 μm in eight aerosol size bins which are described as chemically inert tracers. The sea-salt aerosol generation is parameterized as of Mårtensson et al. (2003), following Gong et al. (1997) as a function of size and wind speed. A correction of the source strength is applied based on the seawater salinity distribution. The particle growth from dry size to ambient size is set as a function of the relative humidity. Dry deposition is modeled using the resistance approach to three land-use classes (forest, low vegetation and no vegetation). Dry deposition to the sea surface is described in a separate approach dealing with the effect of increased downward movement of particles as a result of bubble burst activity. This approach is described in Pryor et al. (1999). Wet scavenging of sea-salt particles is assumed to be proportional to the precipitation intensity. The version of MATCH used in this intercomparison, however, did not yet consider sea salt.

3.6 REM3/CALGRID

REM3/CALGRID uses a simple bulk approach for the aerosol modeling. Aerosol dynamics are not considered. The model employs two different equilibrium aerosol modules: a) The MARS-A module (Binkowski and Shankar,1995) that treats the thermodynamics of the inorganic sulfate, nitrate, ammonium aerosols and water, slightly modified by Schaap (2000); b) the ISORROPIA module that treats in addition sodium and chloride aerosols (Nenes et al., 1998, 1999). The aerosol components are assigned to two size fractions: fine mode PM2.5 and coarse mode PM10-PM2.5. The anthropogenic emissions data base provides primary PM10 emissions split into these two size categories. The sea-salt aerosol emissions are parameterized as described by Gong et al. (1997) as a function of size and wind speed. The anthropogenic PM emissions are allocated to

two model species: $PMCO_{prim}$ = PM10-PM2.5 (coarse mode) and $PM25_{prim}$ = PM2.5 (fine mode). The photochemical mechanism includes the oxidation of SO_2 to gaseous sulfate, that is assumed to be gaseous sulfuric acid. The aerosol modules MARS or ISORROPIA treat the thermodynamics of the inorganic aerosols, depending on the gas phase concentrations of nitric acid, ammonia, sulfuric acid, HCL and humidity and temperature. In REM3/CALGRIDl, all secondary aerosols are assigned to the PM2.5 fraction. All aerosols are transported and subjected to wet and dry deposition. Gravitational settling is considered as well. PM10 concentrations are then defined as the sum of primary PM10 and secondary inorganic aerosols:

$$PM10 = PM25_{prim} + PMCO_{prim} + SO_4 + NO_3 + NH_4 + Na + CL$$

Secondary organic aerosols (SOA), that are formed by condensation of biogenic and anthropogenic hydrocarbon oxidation products, are not presently considered.

For this intercomparison study, REM3/CALGRID was applied with the ISORROPIA module (Nenes et al., 1998, 1999). ISORROPIA is a thermodynamic equilibrium aerosol module which models the sodium-ammonium-chloride-sulfate-nitrate-water aerosol system. The aerosol particles are assumed to be internally mixed, meaning that all particles of the same size have the same composition. The possible species for each phase are:

- Gas phase: NH_3, HNO_3, HCL, H_2O,
- Liquid phase: NH_4^+, Na^+, H^+, CL^-, NO_3^-, SO_4^{2-},
- Solid phase: $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NCl, NaCl, NaN, $NaHSO_4$, Na_2SO_4.

The model considers mutual deliquescence regions, the solution process is optimized for speed and robustness.

Table 3.3. Summary of aerosol treatments in the models.

	DEM	**EURAD**	**EUROS**	**LOTOS**	**MATCH**	**REM3/-CALGRID**
Aerosol module	Inorganic aerosol formation following EMEP scheme	MADE, based on Models3	see above	MADE (this study), ISORROPIA	Secondary inorganic aerosol formation from chemical mechanism; sea-salt aerosol module	Equilibrium modules: modified MARS-A and ISORROPIA. ISORROPIA was used in this study.
Size distribution	None	Modal distribution: nucleation, accumulation and coarse mode	sectional with 5 size classes	two modes: A fine mode (PM2.5) and a coarse mode (PM2.5-10).	Bulk Mass; Sectional sea-salt description with 8 size classes	2 classes: PM2.5 (fine mode) and PM10 - PM2.5 (coarse mode)
In-cloud conversion	Parameteriza-tion	Cloud module: Walcek and Taylor (1986)	parameterized with first order reaction rate for two RH classes	Linear conversion rate as a function of cloud cover and enhanced at high relative humidity	Yes, bulk with O_3 and H_2O_2 as oxidants	Not explicitly; Parameterized with a first order reaction rate
Aerosol dry deposition / sedimen-tation	Dry deposition with resistance approach	Based on size distributions and resistances (Binkowski and Shanka, 1995); Sedimentation for coarse mode only	based on size class (different resistance value per size class)	Based on assumed (fixed) size distribution. Different for the two modes. Sedimentation for coarse mode only.	based on size class	based on assumed (fixed) size distribution for gravitational settling and resistances
Hetero-geneous chemistry **N_2O_5 treatment**	N_2O_5 conversion in chemical mechanism	Walcek and Taylor (1986) N_2O_5 hydrolysis explicitly; Mentel, (1999)	implicitly in sulfate and nitrate formation reactions	N_2O_5 hydrolysis explicitly following Dentener and Crutzen (1993)	N_2O_5 and HNO_3 conversion to nitrate as in Simpson et al. (1993). NH_3-Sulfate and NH_3-HNO_3 - NH_4NO_3 reactions as in EMEP eulerian model (1998)	N_2O_5 hydrolysis on aerosol surface as represented in CBM IV
Sub-grid deposition correction	yes	Not treated		NH_3: 25% of emissions	No sub grid deposition correction	Not used.
SOA formation	not treated	SORGAM (Schell et al., 2000)	not treated	SORGAM (Schell et al., 2000)	not treated	not treated yet
Primary organic Carbon	not treated	Emissions; currently a tracer	not treated		Not treated	Not treated

4 Methodology of the intercomparison

4.1 Approach

The design of this intercomparison is such that the models have been applied in the mode in which they are routinely used by the participating groups. No attempt has been made to harmonize model configurations, process descriptions and/or the input data. The base year for the intercomparison study is 1995, with the emphasis on the growing season, namely April - September. All modeling groups have been asked to provide:

- details on their model configurations and meteorological drivers (see Appendix);
- aggregated national totals for emitted gaseous compounds and primary particles;
- daily averaged values for several compounds for a predefined set of EMEP stations together with three additional Dutch (Bilthoven, De Zilk and Wieringerwerf) and two German (Melpitz, Müncheberg) locations (see Appendix);
- the compounds are:

  aerosols: SO_4, NH_4, NO_3, Na, Cl, primary $PM_{2.5}$/PM_{10}, secondary organic (both biogenic (BSOA) and anthropogenic (ASOA));

  gas phase: HNO_3, SO_2, NO, NO_2, NH_3;

  other: wet deposition amounts of SO_4, NO_3 and NH_4.
- Each group was requested to provide the modeled station data in a prescribed spreadsheet file format and these files were the basis of the performance analysis

4.2 Statistics

The performance of models can be described quantitatively using a set of numerical performance metrics or qualitatively by visual inspection of several graphs. The set of quantitative performance measures is described in the Appendix and the use of these statistics have been discussed by e.g. Fox (1981). The preferred graphs for a qualitative inspection of performance are scatter plots, time series and pairs of spatial plots.

Both approaches to model performance need the definition of acceptance criteria or limits. Assigning these criteria often involves subjective decisions as there is still a lack of standards for air quality model performance. However, some of the quantitative measures of performance are suited to indicate the relative performance of a set of models.

In this study both quantitative and qualitative performance measures are discussed using

- tables of statistical performance metrics based on the comparison with the measurements,
- scatter plots of modeled versus measured values using different averaging options, i.e. in time or domain,
- time series to directly compare the daily performance and
- maps of performance metrics at each measurement site to identify geographical patterns.

4.3 Measurements

In the following section we will discuss the observations used in this report to compare the model results to. Verification of model results is only possible when reliable data are available. For sulfate and sulfur dioxide a large database of data exists, e.g. EMEP (EMEP, 1999). Measuring sulfate seems a straightforward procedure. Measurements of particulate nitrate are sparser and moreover most methods are not reliable because of artifacts associated with the volatility of the most common nitrate specie, ammonium nitrate, and the reactivity of nitric acid. Schaap et al (2002) made a compilation of available data in Europe and critically assessed their quality. Shortly, reliable data are only obtained with devices that remove nitric acid prior to aerosol sampling and stabilize ammonium nitrate against evaporation, e.g. denuder filter combinations. Summertime data from simpler methods were found to be more uncertain than those acquired during winter. Field campaigns in Europe indicate that evaporation from quartz filters is significant at temperatures higher than 20°C (Schaap et al, 2003). Teflon filters show higher losses than quartz filters (Eatough et al, 1988). Hence, the obtained data from these “inert” filters for nitrate (and ammonium) are lower limits. Positive artifacts occur by adsorption of nitric acid on filters. Data from cellulose filters thus represent total nitrate, the sum of aerosol nitrate and gaseous nitric acid. In winter both evaporation and adsorption of nitric acid is thought to be small.

The average precision in the monthly or seasonal average data, the data for sulfate and for nitrate from denuder filter combinations as well as total nitrate is 15 % or better (EMEP, 1998; Harrison and Kitto, 1990; Pakkanen et al, 1999, Sickels et al, 1999). For a detailed discussion see Schaap et al (2002) and references therein. A similar precision applies to the data from the "inert" filters, however the extent of evaporative loss is not defined as discussed above. Single daily data are much more uncertain. Especially at low ambient concentrations (<2 μg/m3) (total) nitrate data are associated with standard deviations considerably higher than 15 % (Ferm et al, 1988; Schaap et al, 2003). The uncertainty in (total) ammonium is probably similar or higher.

The location of the sites used for the comparison of model results with measurement data is shown in Figure 10.1. The sites commonly measure sulfate. It can be seen that there are large regions where these relatively simple measurements are not being made, most notably in south eastern Europe and central France. For nitrate and ammonium only a subset of these stations has data available. Reliable data for aerosol nitrate and ammonium, obtained with denuder filter combinations, are available for the Netherlands (RIVM, 1999), Rome (EMEP, 2002) and Müncheberg (Zimmerling et al, 2001). Data from inert filters, with associated negative artifacts, were available for Melpitz (Heintzenberg et al, 1998) and the EMEP stations in the Czech Republic and Hungary. Total nitrate and total ammonia data are available for the Scandinavian, English, Swiss, Polish and Spanish sites. Most of the stations measuring total nitrate and ammonia are located along the coast, whereas associated aerosol data are mostly found at continental sites. At coastal stations part of the nitrate might be present as sodium nitrate.

Data on nitric acid gas and ammonia gas are available at a few stations. For nitric acid we only used the data for Rome because the reference method, gas-denuders, is used there. The data obtained with Whatman 41 filters in the Czech Republic have been omitted since they may be biased high (EMEP, 1999). For ammonia only 5 sites have data of which, however, the reliability is questionable.

4.4 Data base for the study

The common database was organized as spreadsheet files. Each participant delivered one file with a matrix for each component. The matrix was set up by time versus stations.

Table 4.1. Aerosol components as delivered into the database. X denotes, that the compound has been computed/measured and was delivered in the database, (x) denotes, that a compound has been computed from other species. A dash indicates that the component is not computed or results from measurements were not available.

	SO_4	NO_3	NH_4	Na	Cl	A-SOA	B-SOA	PM 2.5	PM 10	SO_2	NH_3	NO	NO_2	HNO_3	mm	S-wet	NO_3 wet	NH_4-wet
DEM	x	x	x	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
EURAD/-FFA	x	x	x	-	-	x	x	x	(x)	x	x	x	x	x	x	x	x	x
EUROS	x	x	-	-	-	-	-	-	x	x	-	x	x	x	x	x	x	-
LOTOS	x	x	x	-	-	x	x	x	(x)	x	x	x	x	x	-	-	-	x
REM3/-CALGRID	x	x	x	x	x	-	-	x	x	x	x	x	x	x	-	-	-	-
MATCH	x	x	x	-	-	-	-	-	-	x	x	x	x	x	x	x	x	x
Measured	x	x	x	-	-	-	-	-	-	x	x	-	x	-	x	x	x	x
Possible comparisons:																		
Model to Model	6	6	5			2	2	3	4	6	5	6	6	5	4	4	4	4
Model to Measure-ment	6	6	5							6	5		6		4	4	4	4

Other Compounds (on molar basis or as noted):		
TNO_3 = NO_3 + HNO_3	**Total Nitrate (Nitrate equivalence)**	**Is directly measured or if NO3 and HNO3 are available computed**
TNHx = NH_3 + NH_4	**Total Ammonia (Ammonium equivalence)**	**Is directly measured or if NH_3 and NH_4 are available computed**
FNH_3 = TNHx –2*SO_4	**Free Ammonia**	**Computed**
GR = FNH_3 / TNO_3	**Gas Ratio**	**Computed**
S-ratio = SO_2/(SO_4+SO_2)		**Computed**

5 Emission data

Emission data for the states fully covered by the REM3/CALGRID domain are shown in Figure 5.1 for SO_2, NOx, PM and Figure 5.2 for NH_3, VOC and CO. This data and additional emitted components are tabled in the Appendix. Most models calculate biogenic emissions internally as a function of temperature, radiation and land-use.

The emission data used by the models have been compiled using EMEP and CORINAIR/TNO inventories (see Table 10.5 - Table 10.7). EURAD/FFA used the Auto-Oil-2 inventories for the EU-15 states and EMEP data otherwise for gaseous compounds. Primary PM emissions for EURAD, LOTOS and REM3 originated from TNO (1995).

Figure 5.1 shows a high agreement for country total NOx emissions except for the Baltics and its states of the former Yugoslavia. For Germany , there are also some differences in the NOx-emissions. EURAD, LOTOS and REM3 NOx-emissions are in agreement whereas the other three models use lower emissions. Road transport is a major contributor to NOx emissions and emission factors and activities are well known. This probably results in the rather consistent picture of NOx emssions as shown in Figure 5.1. For VOC emissions a similar situation has been given (see Figure 5.2).

Country total primary PM emissions are also displayed in Figure 5.1. Large differences among the models that incorporated primary PM emissions (EURAD, EUROS, LOTOS and REM3) are visible. This certainly reflects the fact that European PM emission inventories are probably not yet at a stage where gaseous emissions have been developed to. EURAD shows in nearly every country the highest total amount.

SO_2 emissions as used by the models are shown in Figure 5.1. A picture similar to NOx is visible however, there is a very large discrepancy for Germany. Here, the Auto-Oil-2 inventory used by EURAD is only about a third of what is given in the inventory of e.g. LOTOS/REM3.

Country total NH_3 emission data (Figure 5.2) used by the models are very consistent except for Hungary and the Baltic states.

Most of the differences or agreements for the emission data can be attributed towards the sources used by the models: CORINAIR/TNO, EMEP and the Auto-Oil-2. Smaller differences should be generated by the models when the inventories are gridded or re-aggregated to the national totals.

5.1 Uncertainties of emission data

Errors in the emission data are important sources of uncertainty. Comparisons between the EMEP and CORINAIR emission estimates as well as information about reported national emissions are discussed in Berge et al. (1995). Based on this, the uncertainty in annual total anthropogenic emissions is likely to be around ±20%. For individual gridpoints the uncertainties are known to be considerably larger. These induce errors in the calculated concentrations, particularly on short time scales (hours to days), and especially for primary-emitted components. Using an emission inventory for another year than the simulated year or a preliminary release of an inventory imply additional sources of error.

For biogenic components the uncertainties in the emissions are large, both for annual averages and for shorter time scales. For anthropogenic hydrocarbon emissions a potential source of error is the split of the total emissions into component-emissions. The same component-to-total ratio holds for the whole model domain. This is expected to induce errors at various locations.

Another source of error is the assigned temporal variation of the emissions, which may not be well matched by reality at some locations.

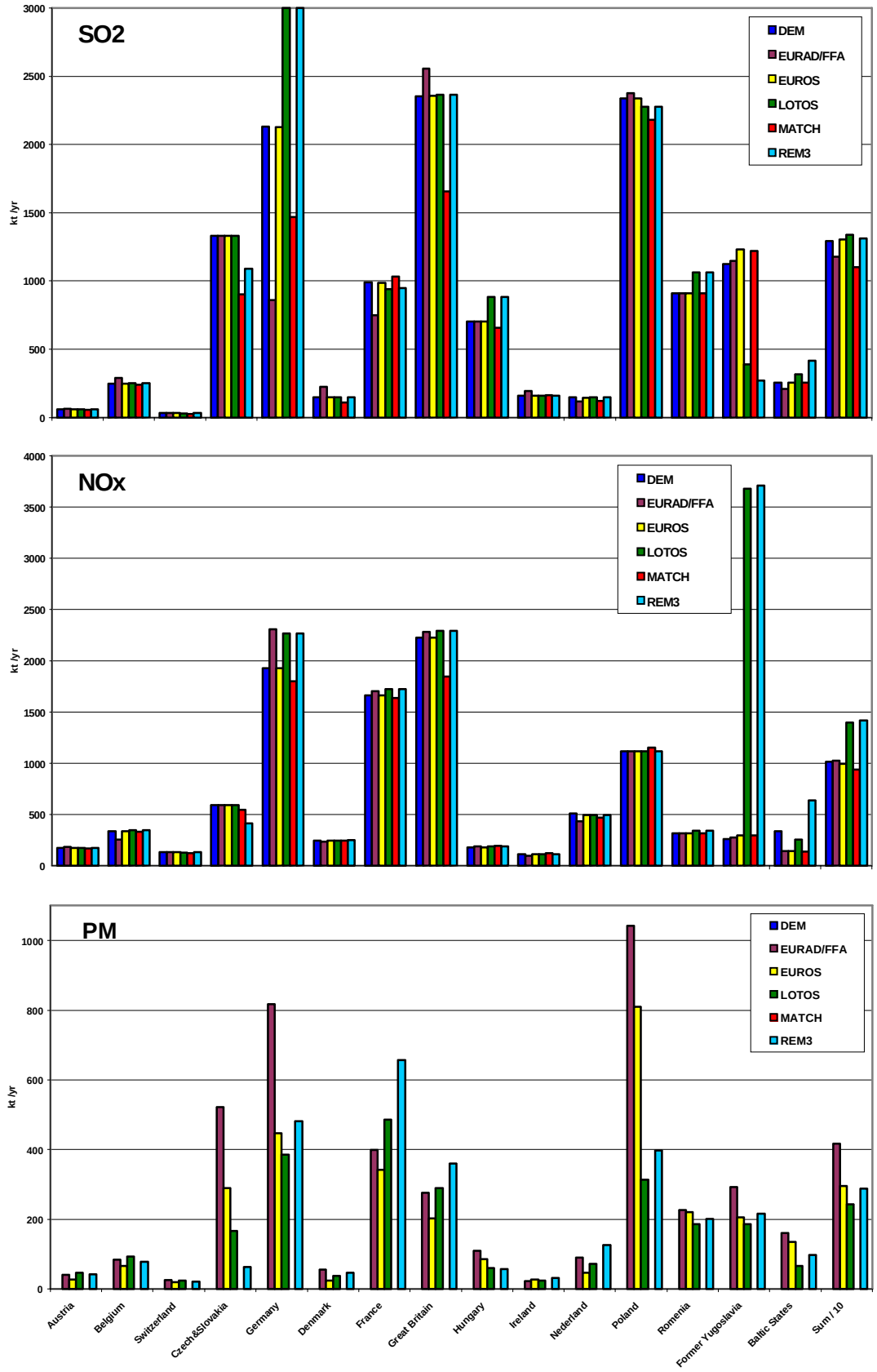

Figure 5.1. Emissions of SO_2, NOx and PM for the states fully covered by the REM3 modeling domain [kton/year].

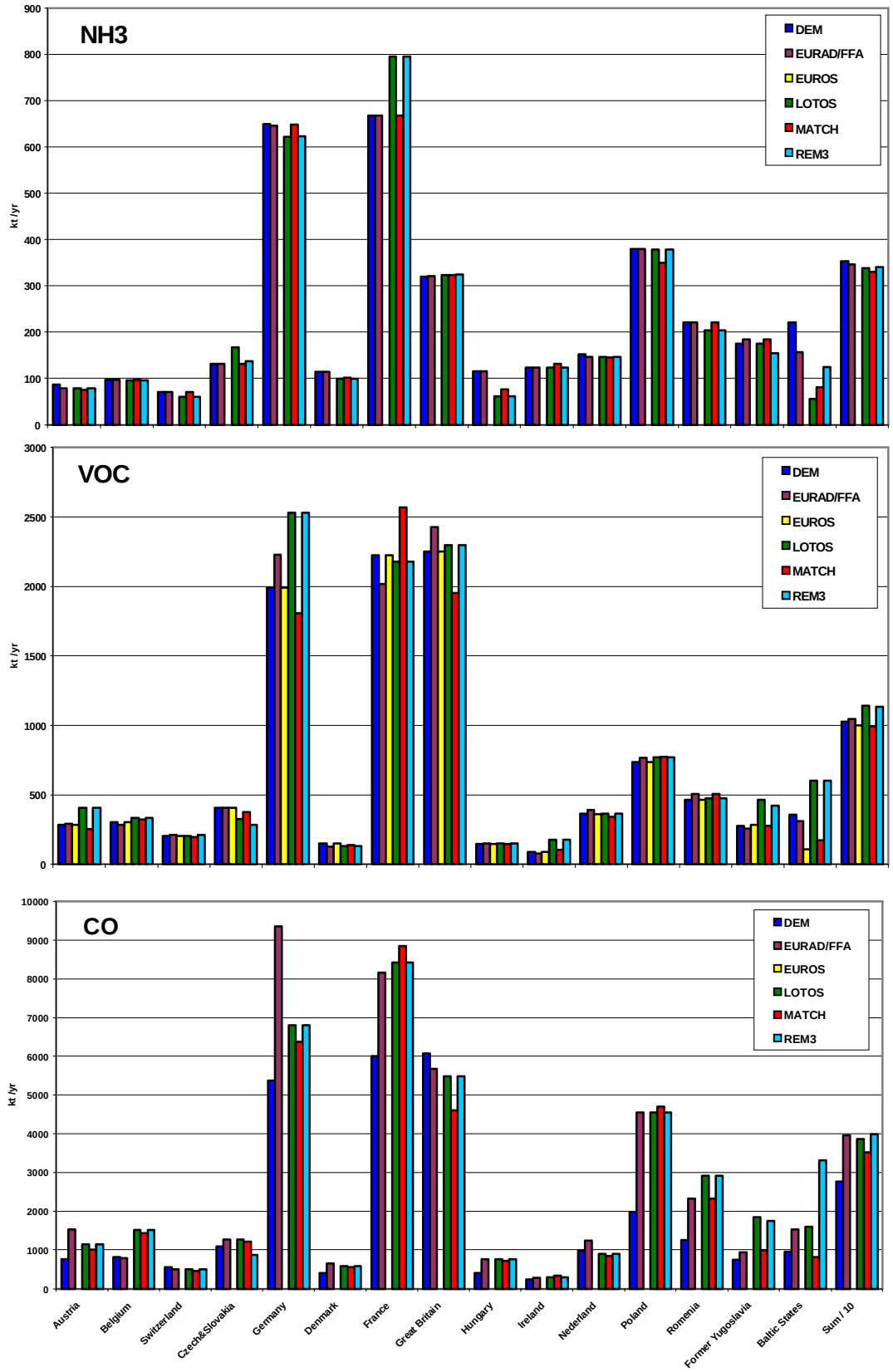

Figure 5.2. Emissions of NH_3, VOC and CO for the states fully covered by the REM3 modeling domain [kton/year].

6 Results

6.1 SO_2 and Sulfate

The performance measures for SO_4 and its precursor SO_2 are given in Table 6.1. These have been computed as mean over time and domain as defined in the Appendix.

The statistics for SO_2 show a general tendency for overprediction with DEM and MATCH performing better than the rest. The correlation coefficients are small and only one model (MATCH) is able to predict more then 50% within the factor of two range. The scatter diagram for the episode mean (Figure 6.1) indicate that REM3 and LOTOS results are very close together, EURAD overpredicts with a constant factor, the EUROS values display an S-shape figure with a midpoint at around 1μg/m^3 and DEM results are spread evenly among over- and underpredictions resulting in an excellent model to observation ratio.

From the overall SO_4 model to observation ratio one sees that four models underpredict, although two only slightly, whereas DEM and EURAD overpredict. The correlation coefficients and the success to predict within a factor of two are improved compared to SO_2. The inspection of the scatter plots (Figure 6.2) reveal that DEM and EUROS strongly underpredict the low concentrations, REM3 and LOTOS are again close together with REM3 displaying a slightly stronger underprediction, EURAD overpredicts over the observed range with about a constant factor and MATCH underpredicts.

Figure 6.3 (top) shows the episode mean values sorted according to increasing observations. For observed concentrations below about 3μg/m^3 the model results are very similar except those from EURAD. However, a scaling of the EURAD results would result in a rather coherent performance at this low concentration range. Above about 3μg/m^3 the picture is more complex and the tendency to coherently over- or underpredict is lost.

The temporal correlation coefficients for SO_4 observations and model results are also shown in Figure 6.3 (bottom). The stations have been sorted as in Figure 6.3 (top), e.g. from lowest to highest mean observed concentration. The highest correlation is often obtained with MATCH results and DEM results are very often low correlated. In the range of low observations no coherent picture among the models is visible with correlations varying between 0.2 to 0.8. Only for high observations (>4μg/m^3) a trend towards similar correlations is visible.

The spatial maps of the fractional difference (or mean normalized bias) for the SO_4 results are given in Figure 6.4 - Figure 6.6.. These graphs allow an inspection whether model performance is geographically biased. Indeed, DEM and EUROS show a strong underprediction in Scandinavia and a rather good performance in the domain center. EURAD exhibits the strongest overprediction in the domain center (Germany). MATCH underpredicts in the northwestern part of the domain, i.e. in a band ranging from the British Islands to Norway. The picture for LOTOS and REM3 is mixed with little geographical bias.

Table 6.1. Summary of statistics computed for time and space domains which include all measurement stations for SO_2 and SO_4. N is the number of stations.

SO_2	**N =41**			**JULIAN DAY 92 – 272, 1995**		
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
aver(model)/aver(meas)	1.00	2.31	1.74	1.23	1.09	1.39
Residue	1.94	4.30	3.14	2.28	1.92	2.50
RMSE	2.79	5.65	3.95	3.08	2.68	3.27
sigma (model/meas)*	1.04	0.91	0.67	0.91	0.91	0.76
Correlation Coefficient	0.43	0.39	0.39	0.39	0.45	0.35
% within factor 2	48.62	38.89	40.01	47.53	54.87	46.17

SO_4	**N = 44**			**JULIAN DAY 92 – 272, 1995**		
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
aver(model)/aver(meas)	1.11	1.52	0.98	0.91	0.84	0.81
Residue	3.16	3.05	2.74	1.89	1.74	1.93
RMSE	5.89	4.25	4.39	2.76	2.49	2.78
sigma (model/meas)*	2.18	1.17	1.84	1.21	1.17	1.20
Correlation Coefficient	0.37	0.52	0.47	0.54	0.65	0.50
% within factor 2	40.79	52.50	40.80	62.73	61.67	59.20

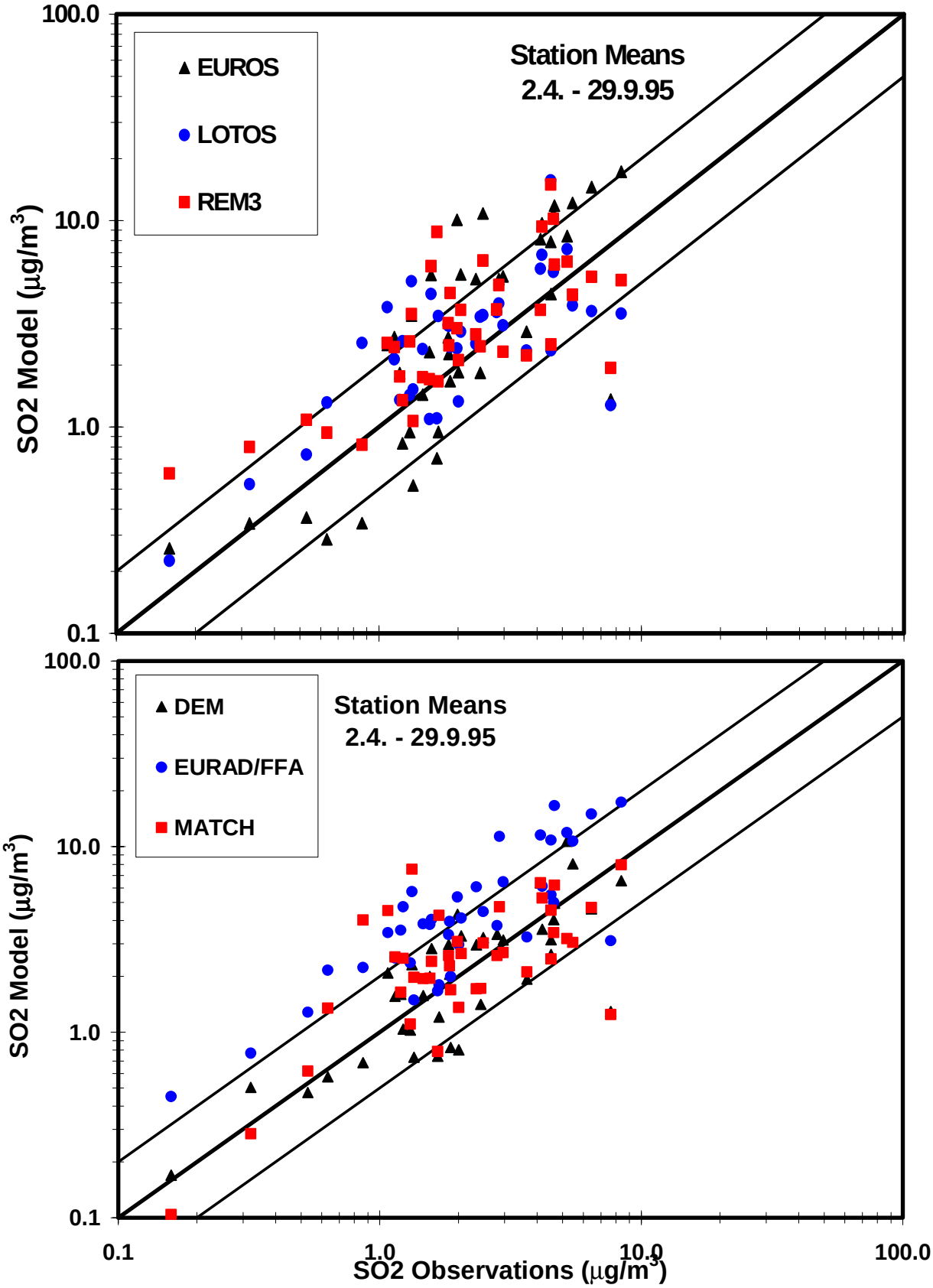

Figure 6.1. Observation of SO_2 versus model results for the episode mean. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

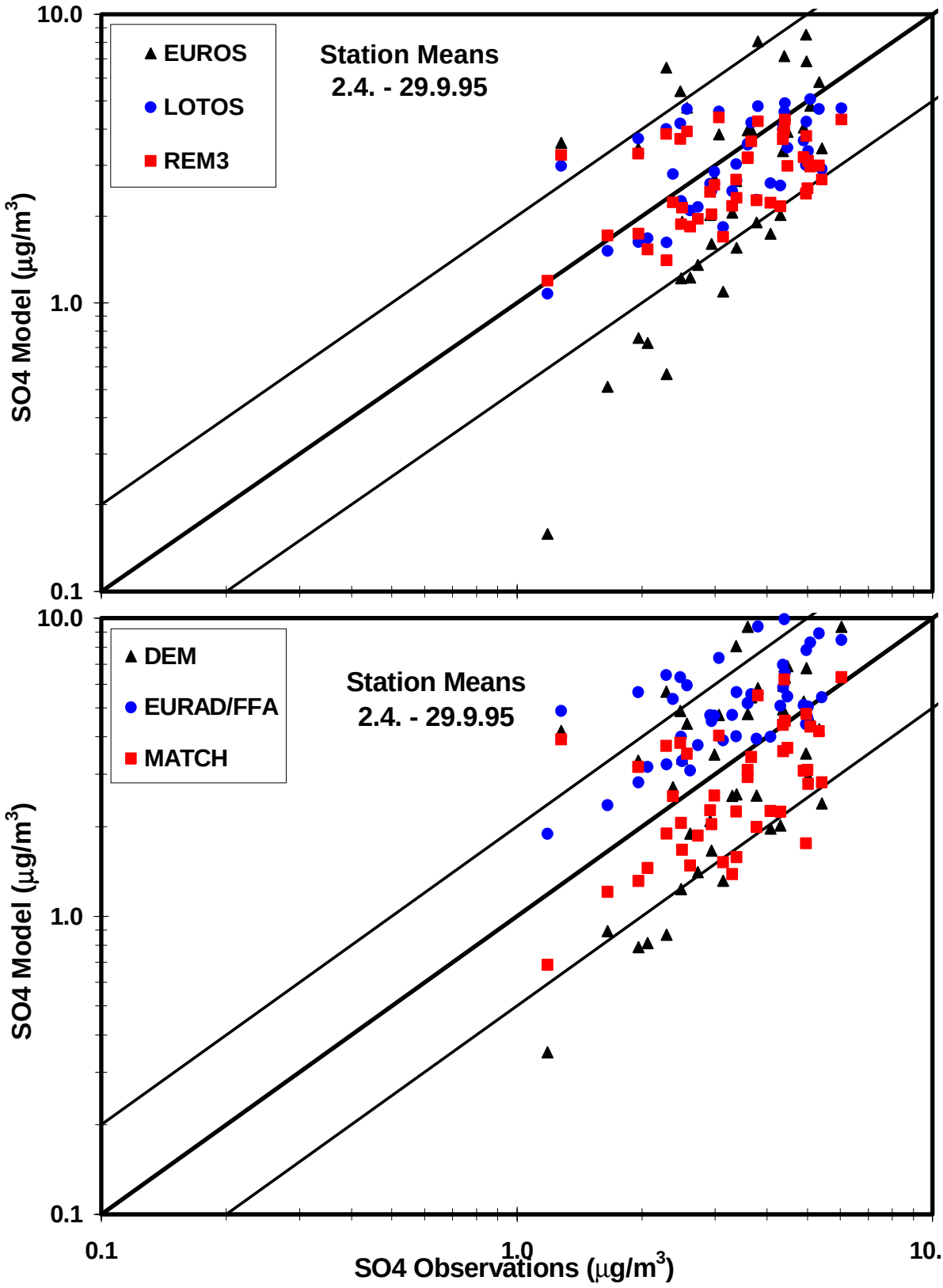

Figure 6.2. Observation of SO_4 versus model results for the episode mean. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

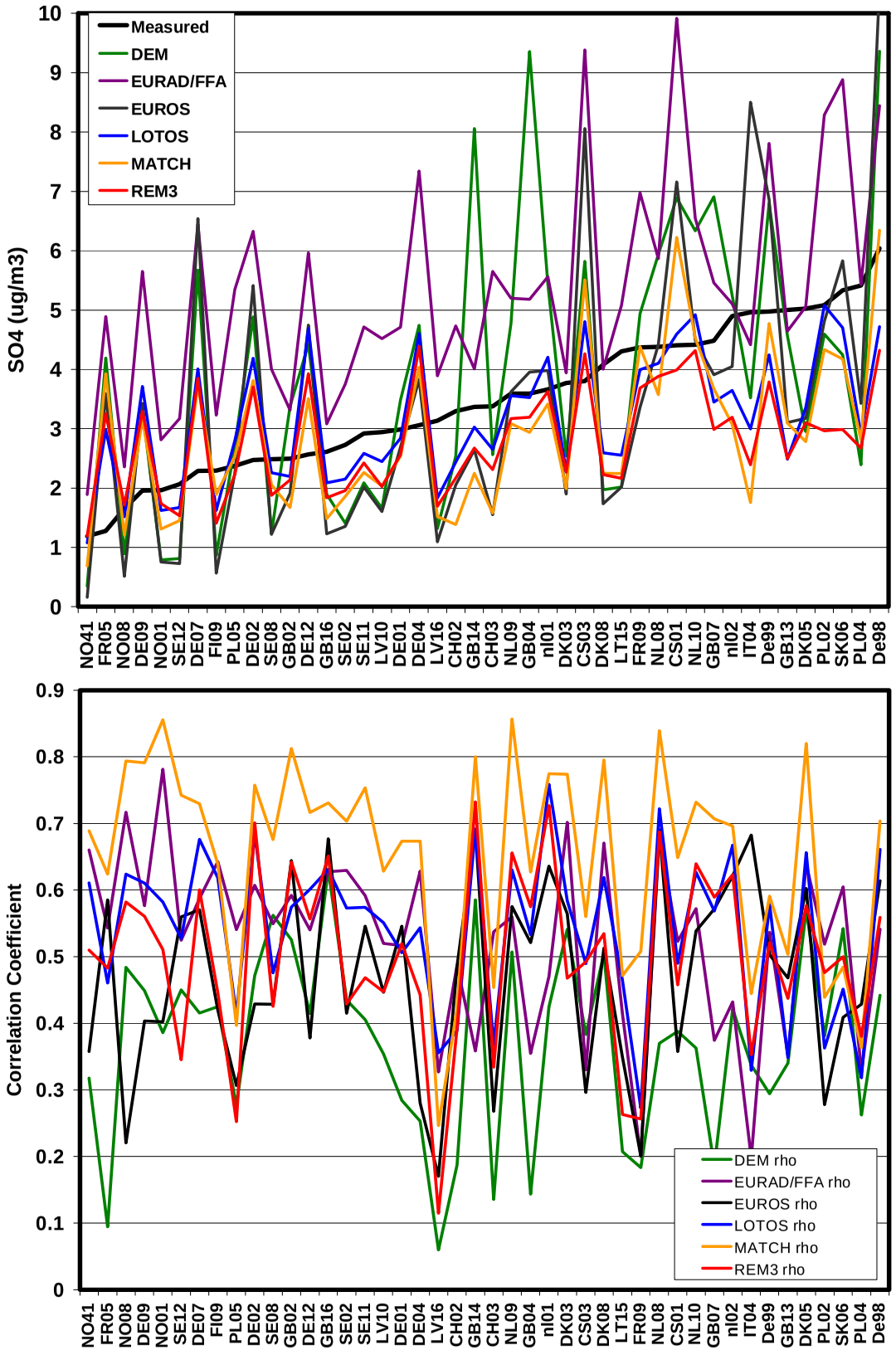

Figure 6.3. Observed and modeled mean SO_4, sorted according to increasing observations (top). Correlation coefficient for SO_4 sorted as above (bottom). Station code see Appendix 10.5.

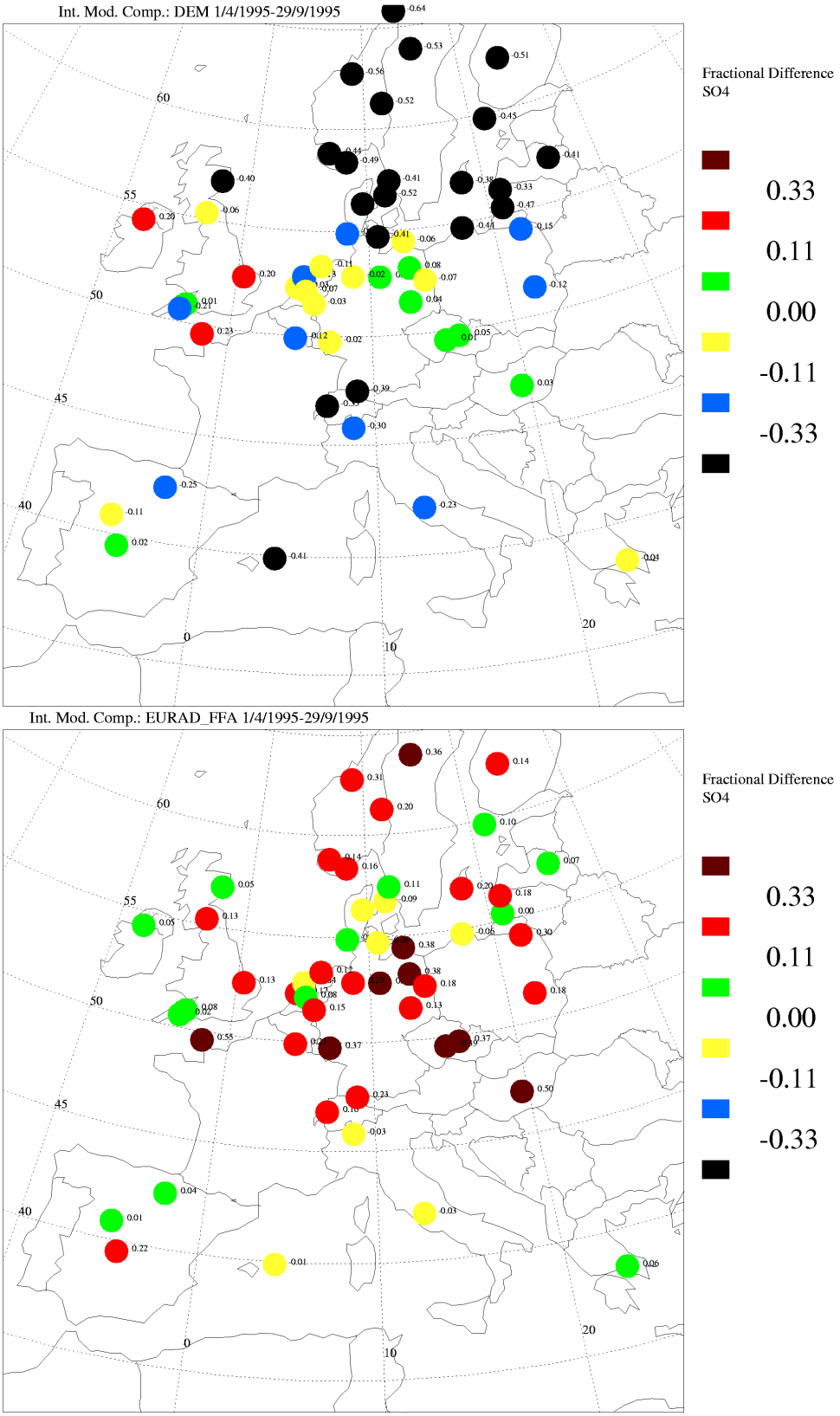

Figure 6.4. SO_4 fractional difference (for DEM and EURAD/FFA) for the modeling domain.

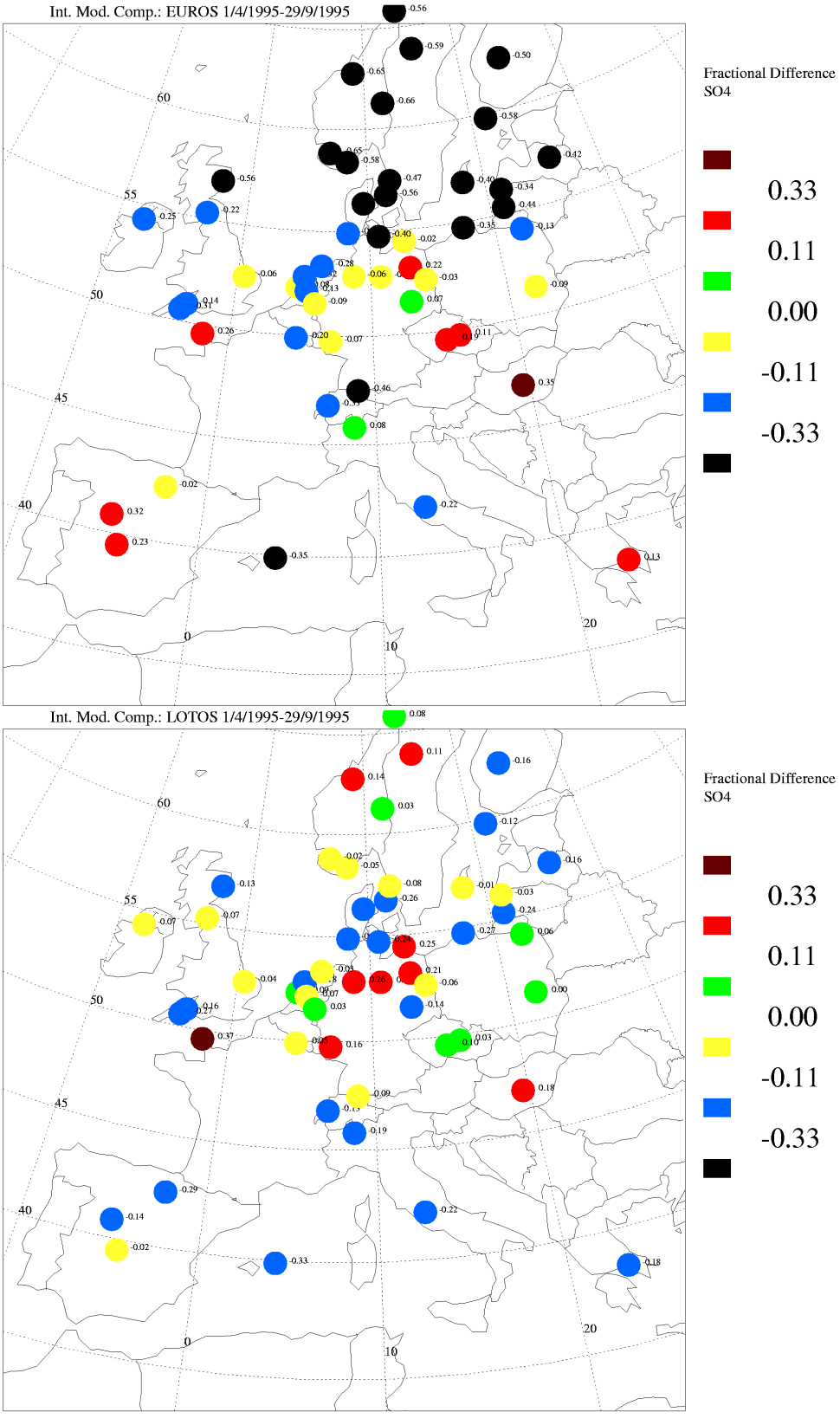

Figure 6.5. SO_4 fractional difference (for EUROS and LOTOS) for the modeling domain.

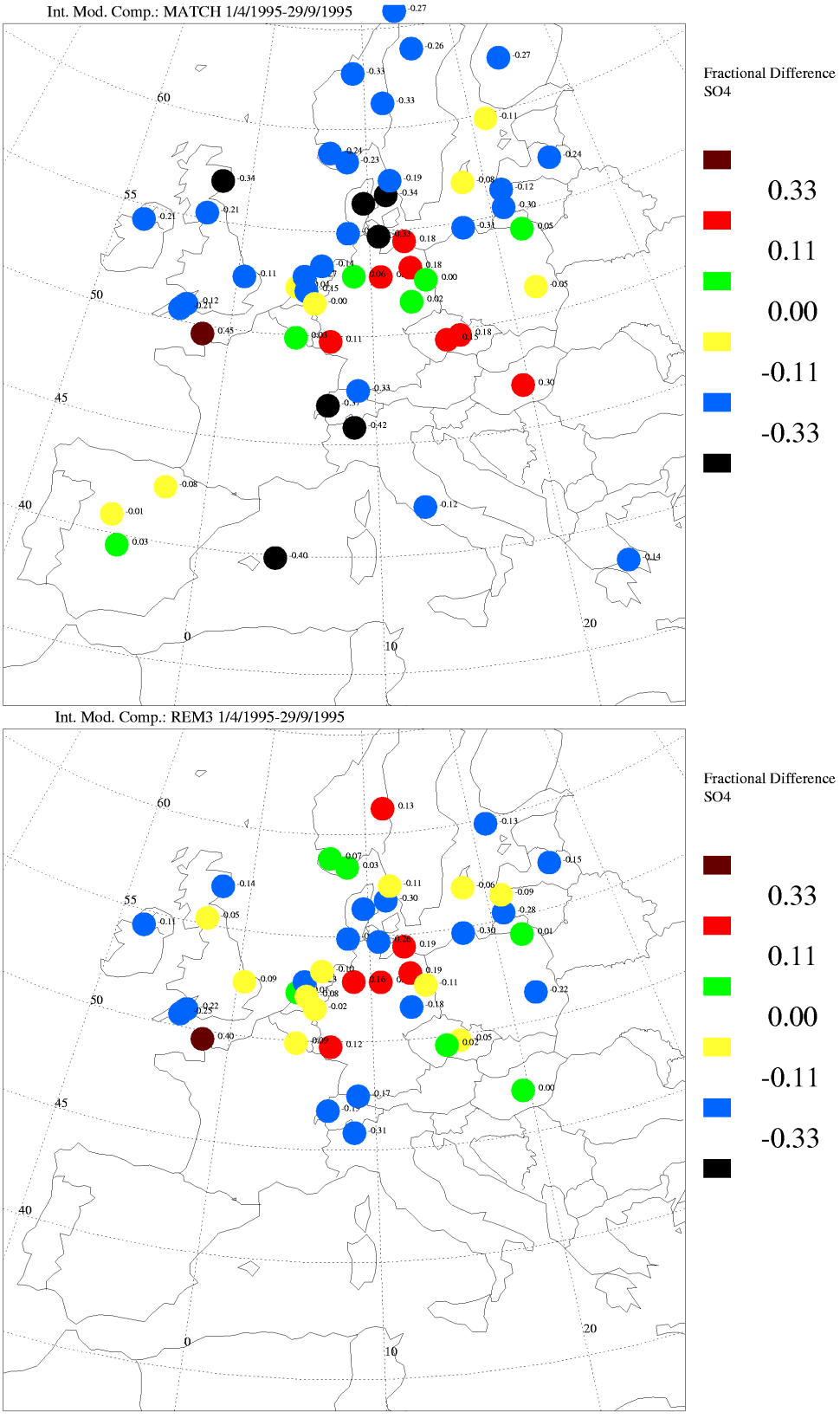

Figure 6.6. SO_4 fractional difference (for MATCH and REM3/CALGRID) for the modeling domain.

6.2 NO_2

The performance measures for NO_2 are given in Table 6.2. These have been computed as mean over time and domain as defined in the Appendix. The summary statistics show a consistent underprediction for all models with EUROS at the upper and LOTOS and DEM at the lower end respectively, although all share a low correlation coefficient. EUROS and REM3 results are rather similar as it is also seen for EURAD and MATCH.

The scatter diagrams, however, reveal that the tendency to underpredict is the result of high concentrations being strongly underpredicted whereas for smaller concentration the agreement is markedly better. This hints to the well known problem of regional models not catching more local plumes created by strong point and line sources as e.g. power stations and road traffic: Above 10 $\mu g/m^3$ in Figure 6.7 all model results fall below the 50% line.

The underprediction for LOTOS is a result of the missing surface layer in the model. Therefore, all surface emissions are mixed immediately in the mixed layer also at night. NO_2 emissions are more affected by this model concept than are SO_2 emissions as the latter are dominated by high level sources.

Table 6.2. Summary of statistics computed for time and space domains which include all measurement stations for nitrogen dioxide (N=28).

NO_2	N=28			JULIAN DAY 92 – 272, 1995		
	DEM	EURAD/FFA	EUROS	LOTOS	MATCH	REM3
aver(model)/aver(meas)	0.20	0.64	0.84	0.12	0.56	0.68
Residue	6.32	6.49	7.33	6.78	6.21	7.05
RMSE	8.67	8.90	9.45	9.18	8.52	9.33
sigma (model/meas)*	1.03	1.16	0.63	0.78	1.02	0.82
Correlation coefficient	0.23	0.16	0.07	0.03	0.23	0.13
% within fac 2	26.37	37.03	32.17	18.89	39.88	30.39

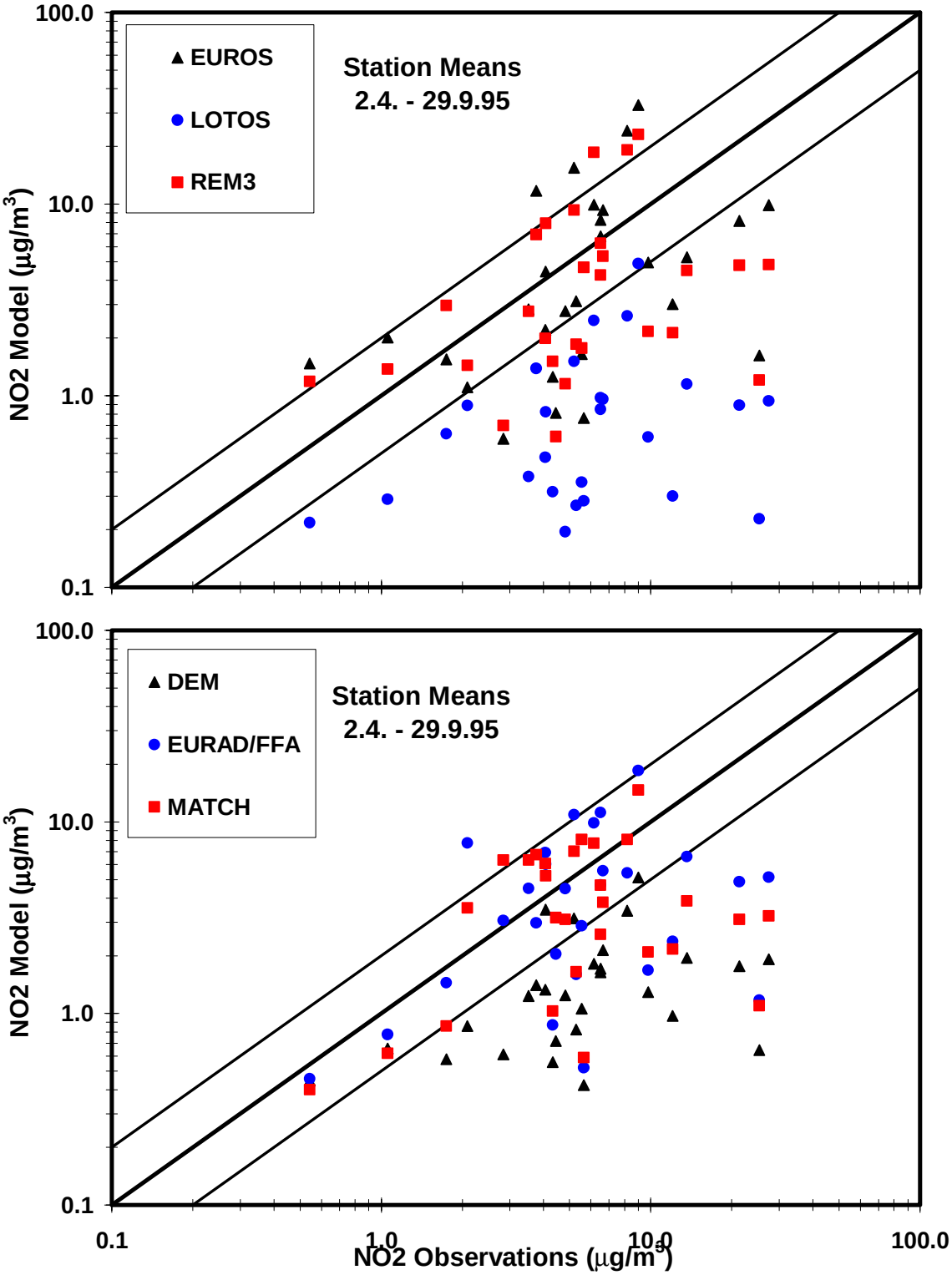

Figure 6.7. Observations of NO_2 versus modeled results. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

6.3 Nitrate and total nitrate

The performance measures for nitrate (NO_3) and total nitrate (TNO_3) are given in Table 6.3. These have been computed as mean over time and domain as defined in the Appendix.

The model-to-observation ratio for NO_3 show a close agreement for the averaged results for DEM and REM3. EURAD and EUROS overpredict while LOTOS and MATCH slightly over- and underpredict, respectively. The correlation coefficients indicate a better agreement in comparison to the small correlations computed for NO_2. With the exception of REM3 the correlation for total nitrate is improved compared to that of nitrate. All models predict total nitrate better in the factor of two range. Figure 6.9 clearly indicates the improvement for total nitrate.

The fact that so many and so different models are comparing better with total nitrate may given by the fact that the measurements of total nitrate are more reliable. This however, needs a next generation model evaluation.

EUROS and EURAD show a similar overprediction of total nitrate whereas the results of MATCH tend to stay between 1 and 3 $\mu g/m^3$ (this tight span evens out the MATCH average ratio closest to unity). In general, the scatter reproduces the tendency of the models to overpredict total nitrate. Figure 6.10 shows the mean concentrations of total nitrate sorted according to increased observation. Model results up to 2 $\mu g/m^3$ are overpredicted by the models but follow a pattern of similar behaviour at these stations. With increasing concentrations three models (EURAD, EUROS and LOTOS) stay close together with a strong overprediction. While REM3 and DEM better represent the high observations MATCH show a diverging behaviour by switching to underprediction.

The spatial maps of the fractional difference for the total nitrate are given in Figure 6.11 - Figure 6.13. DEM has an underprediction in the North and central domain and overprediction in the South. EURAD/FFA shows mostly overprediction in the North and central domain and some good agreement in the south. EUROS is consistently overpredicting with a maximum in the South. LOTOS, also with some overprediction, has close agreements in Norway and Finland. MATCH does not follow a discernible trend and the results vary strongly with location. REM3 is overpredicting at most stations except for Keldsnor, Arnholt and Rucava.

Table 6.3. Summary of statistics computed for time and space domains which include all measurement stations for nitrate (9) and total nitrate (21).

NO_3	**N = 9**				**JULIAN DAY 92 – 272, 1995**	
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
Aver(model)/aver(meas)	1.07	2.04	2.13	1.59	0.78	1.07
Residue	2.84	4.16	4.64	2.98	1.80	2.08
RMSE	4.12	6.14	6.39	4.07	2.55	3.10
sigma (model/meas)*	1.54	1.20	1.02	0.86	1.09	1.16
Correlation Coefficient	0.32	0.61	0.30	0.49	0.50	0.53
% within fac 2	40.82	41.08	38.08	47.28	53.93	56.22

TNO_3	**N = 21**				**JULIAN DAY 92 – 272, 1995**	
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
aver(model)/aver(meas)	1.09	1.85	2.49	1.67	0.94	1.20
Residue	1.69	2.39	3.67	2.00	1.26	1.42
RMSE	2.75	3.72	5.17	2.82	1.94	2.13
sigma (model/meas)*	1.86	1.35	1.03	0.98	1.35	0.93
Correlation Coefficient	0.45	0.50	0.41	0.44	0.52	0.38
% within fac 2	44.60	49.25	39.18	50.39	59.82	59.06

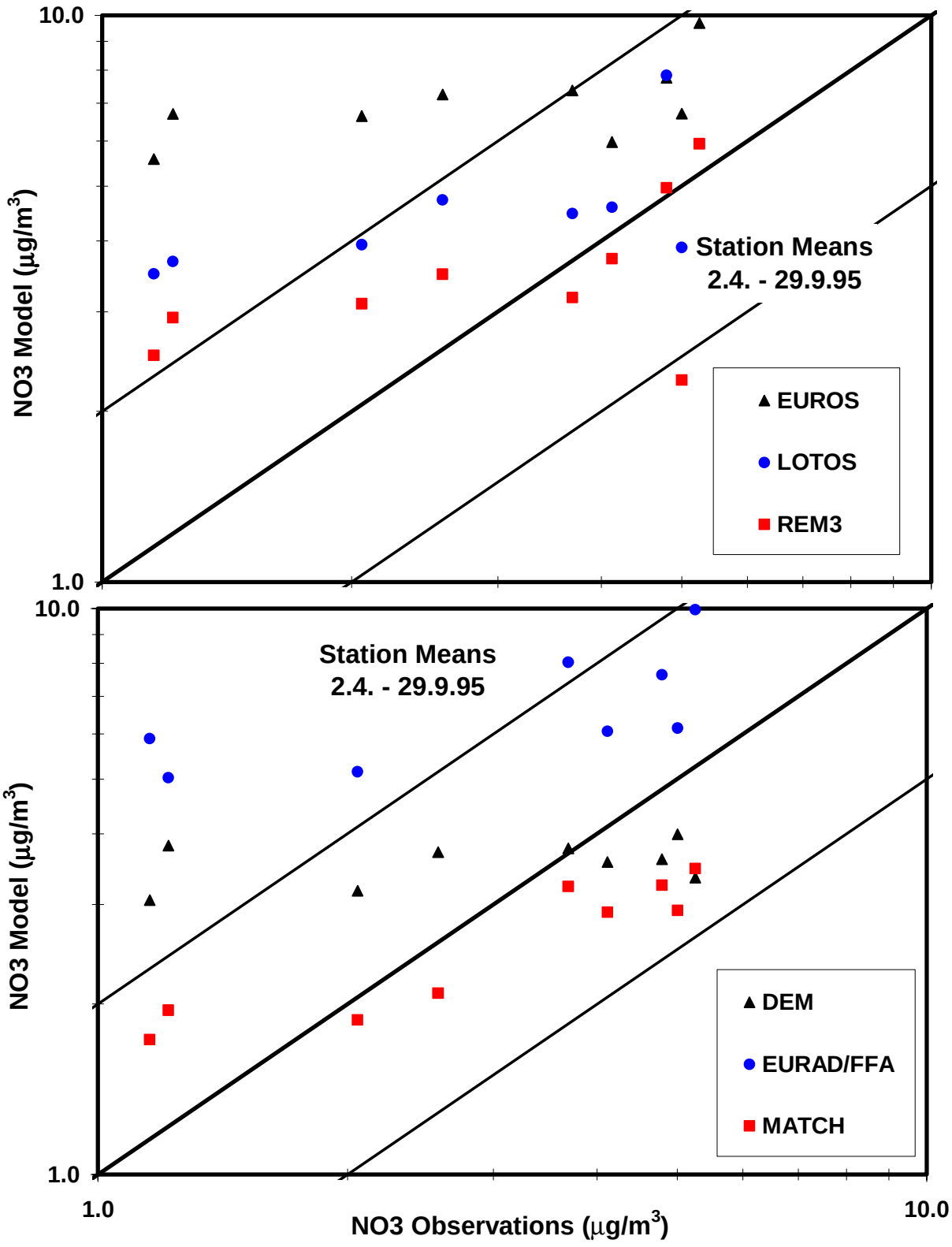

Figure 6.8. Observations of nitrate aerosols versus model results. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

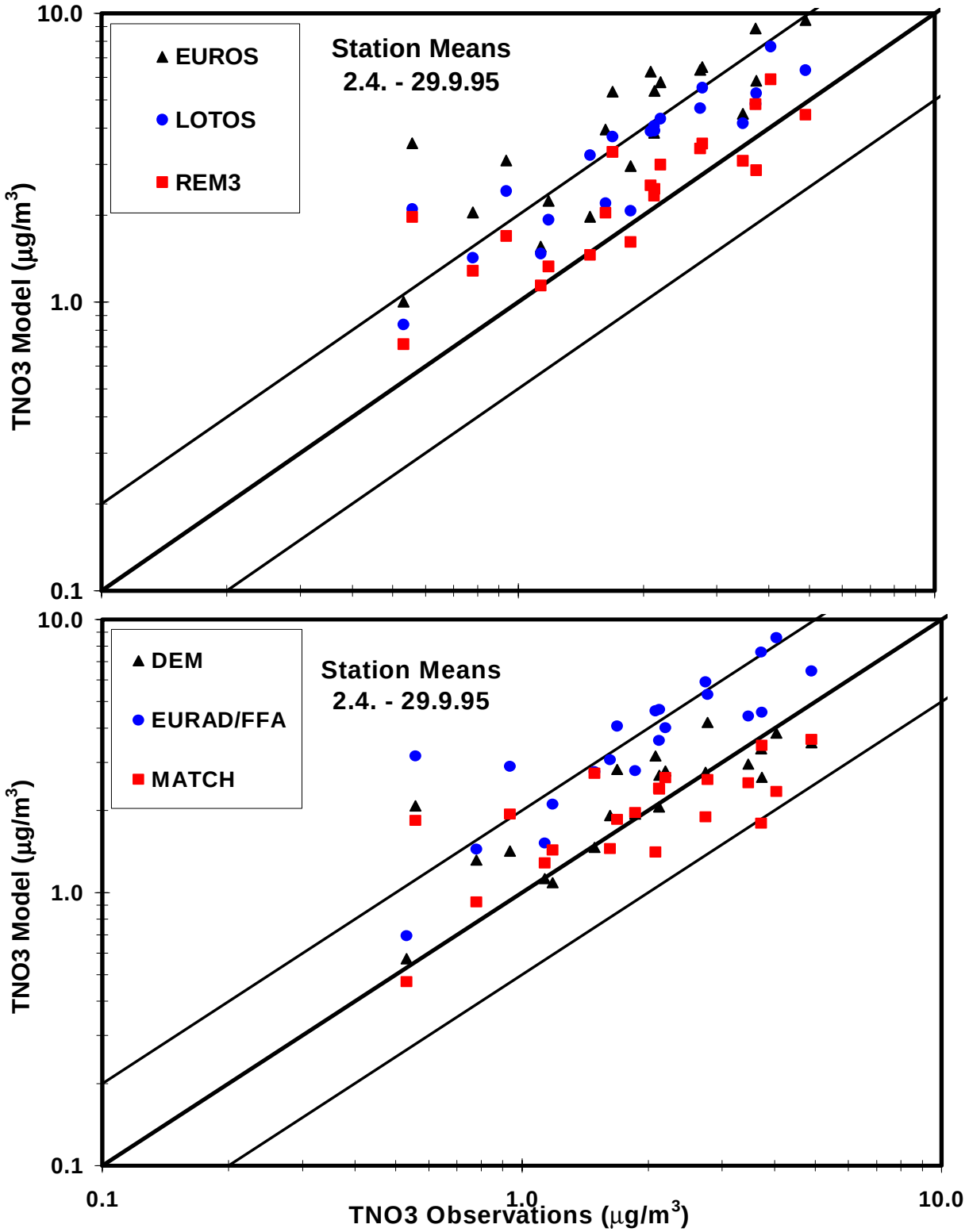

Figure 6.9. Observations of total nitrate versus model results. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

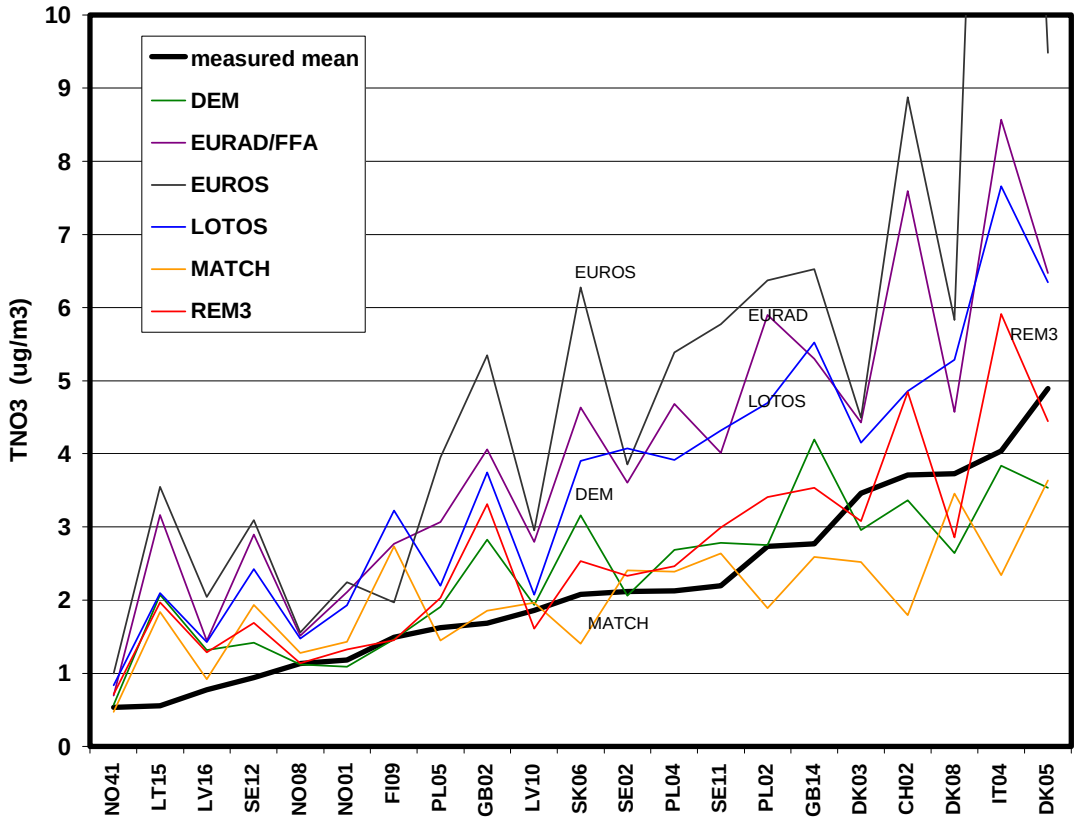

Figure 6.10. Mean total nitrate at the stations sorted according to increasing observations. Station code see Appendix 10.5.

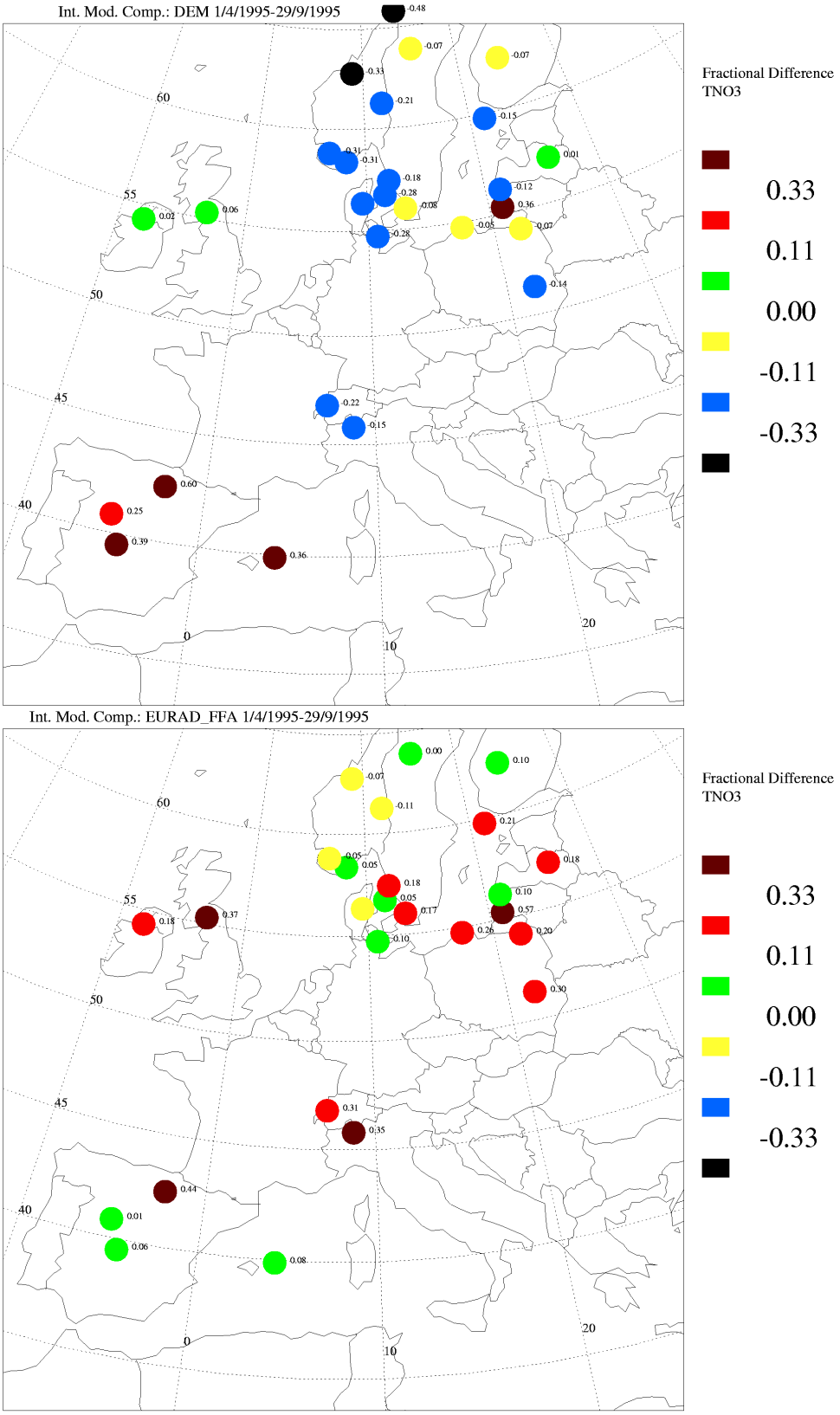

Figure 6.11. Total nitrate fractional difference (for DEM and EURAD/FFA) for the modeling domain.

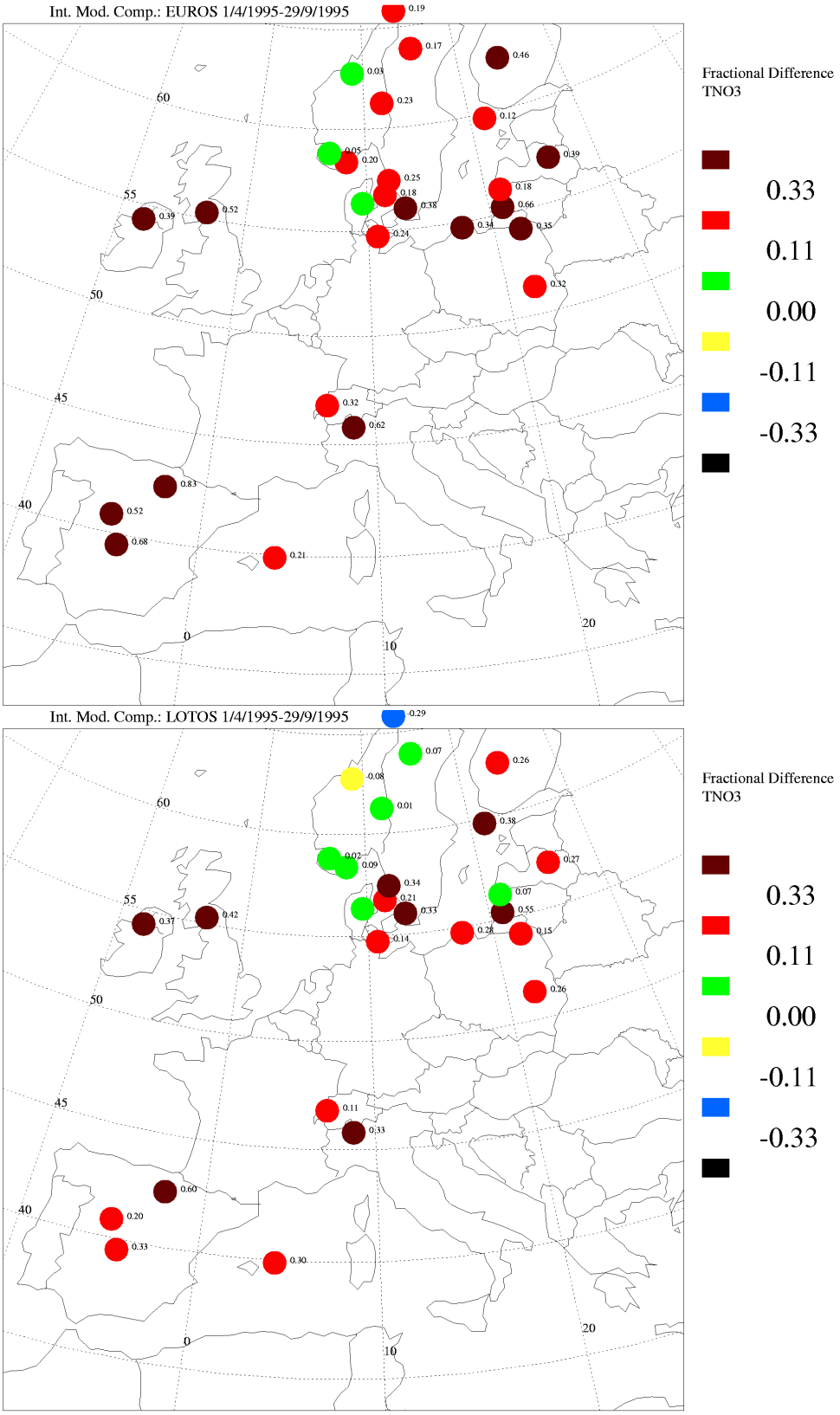

Figure 6.12. Total nitrate fractional difference (for EUROS and LOTOS) for the modeling domain.

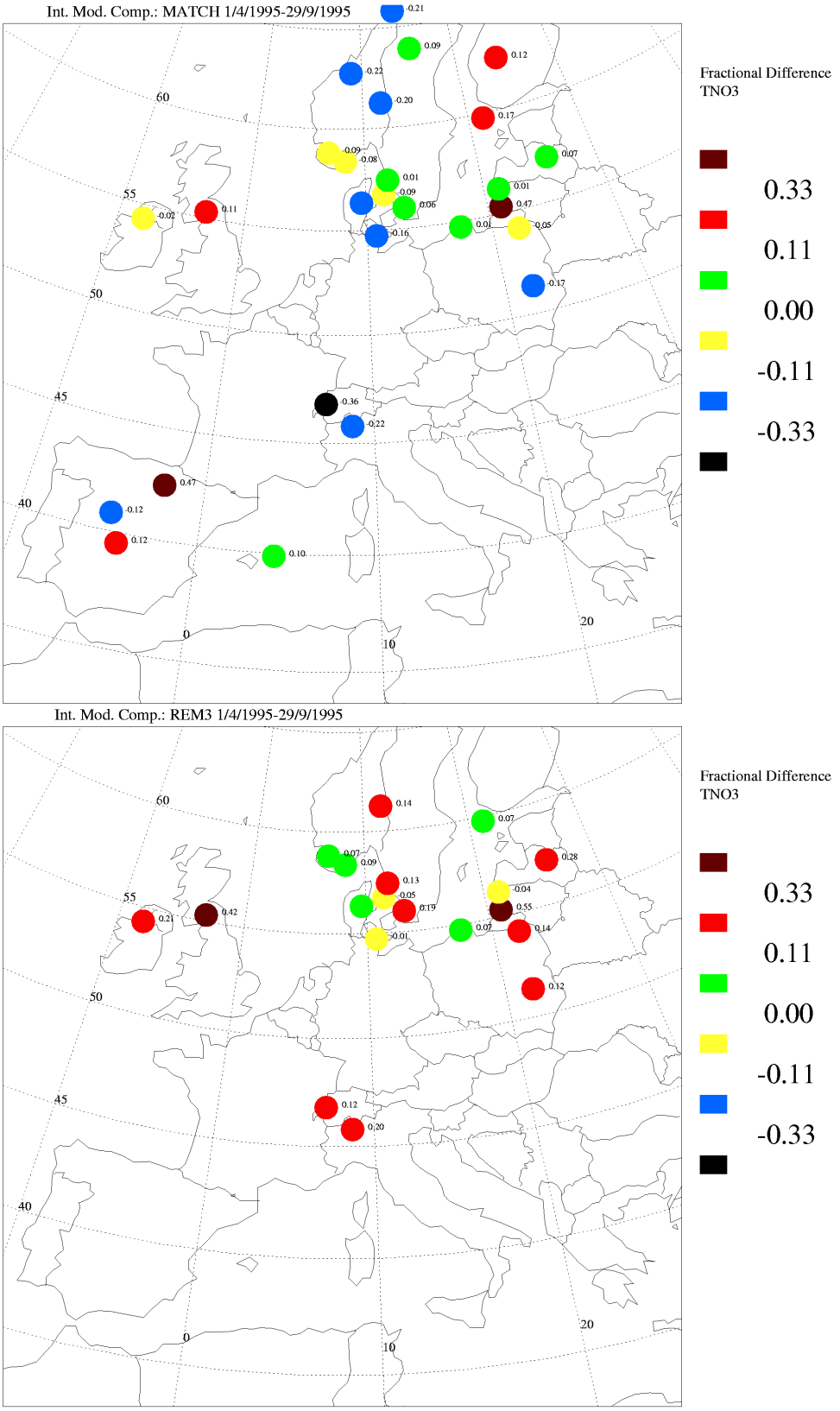

Figure 6.13. Total nitrate fractional difference (for MATCH and REM3/CALGRID) for the modeling domain.

6.4 Total Ammonia

The performance measures for ammonium, ammonia and total ammonium (TNHx) are given in Table 6.4. EUROS, at the time of the study, has not delivered these data. There are only 4 stations included for NH_3 and all models underpredict with poor statistics, e.g. large RMSE and low correlation. However, the averaged underprediction is mostly due to the very strong underprediction of the very high ammonia concentrations at the Dutch station Vredepeel. The statistics improve considerably for NH_4 and TNHx basically as more data is available.

The NH_4 scatter diagrams (Figure 6.14) show similar results for LOTOS and REM3. A underprediction is visible for MATCH and an overprediction for EURAD while DEM results scatter well.

The statistics for TNHx, which accounts for the largest set of stations, show that EURAD is the only model which overpredicts the mean values. Four models predict more than half of the stations in the within factor 2 range. From the models with low vertical resolution REM3 predicts often higher concentrations than LOTOS. Both models use the same photochemistry scheme and the same aerosol module but REM3/CALGRID employs a surface layer and two dynamic layers to resolve the mixed layer whereas LOTOS only uses one layer. For the models with higher vertical resolution the series from low to high seems to be DEM, MATCH and EURAD. The scatter plots (Figure 6.15) for all models display a 'line'-structure indicating that the observed range is covered.

Figure 6.16 shows that the low observations of TNHx in Scandinavia are well reproduced by all except EURAD. Moving to the higher observations this harmony among the models is lost besides the Norwegian site NO08. In the models this sites is remote with low predictions whereas the observations are about twice as high. Generally, the range of model results is covered by EURAD data being the highest and LOTOS being the lowest.

Table 6.4. Summary of statistics computed for time and space domains which include all measurement stations for NH_3 (4), NH_4 (15) and TNHx (21).

NH_3	**N = 4**			**JULIAN DAY 92 – 272, 1995**		
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
aver(model)/aver(meas)	0.38	0.56		0.18	0.64	0.58
Residue	6.14	4.57		6.28	4.46	4.61
RMSE	7.38	5.88		7.50	5.59	6.10
sigma (model/meas)*	4.48	2.08		1.75	1.65	2.13
Correlation Coefficient	0.27	0.15		0.05	0.33	0.09
% within fac 2	34.36	49.83		23.42	44.89	55.35

NH_4	**N = 15**			**JULIAN DAY 92 – 272, 1995**		
	DEM	**EURAD/FFA**	**EUROS**	**LOTOS**	**MATCH**	**REM3**
aver(model)/aver(meas)	0.94	1.87		1.23	0.55	1.07
Residue	1.50	2.13		1.15	1.09	1.17
RMSE	2.43	2.90		1.57	1.46	1.63
sigma (model/meas)*	1.94	1.04		0.84	1.06	1.00
Correlation Coefficient	0.39	0.50		0.51	0.61	0.43
% within fac 2	42.33	47.46		65.75	46.96	58.98

TNHx	N = 21			JULIAN DAY 92 – 272, 1995		
	DEM	EURAD/FFA	EUROS	LOTOS	MATCH	REM3
aver(model)/aver(meas)	0.79	1.24		0.58	0.84	0.91
Residue	2.77	2.67		2.13	1.98	2.30
RMSE	3.69	3.40		2.77	2.54	3.09
sigma (model/meas)*	2.16	1.15		1.02	1.00	0.97
Correlation Coefficient	0.47	0.54		0.46	0.57	0.26
% within fac 2	48.49	52.29		64.82	66.23	55.68

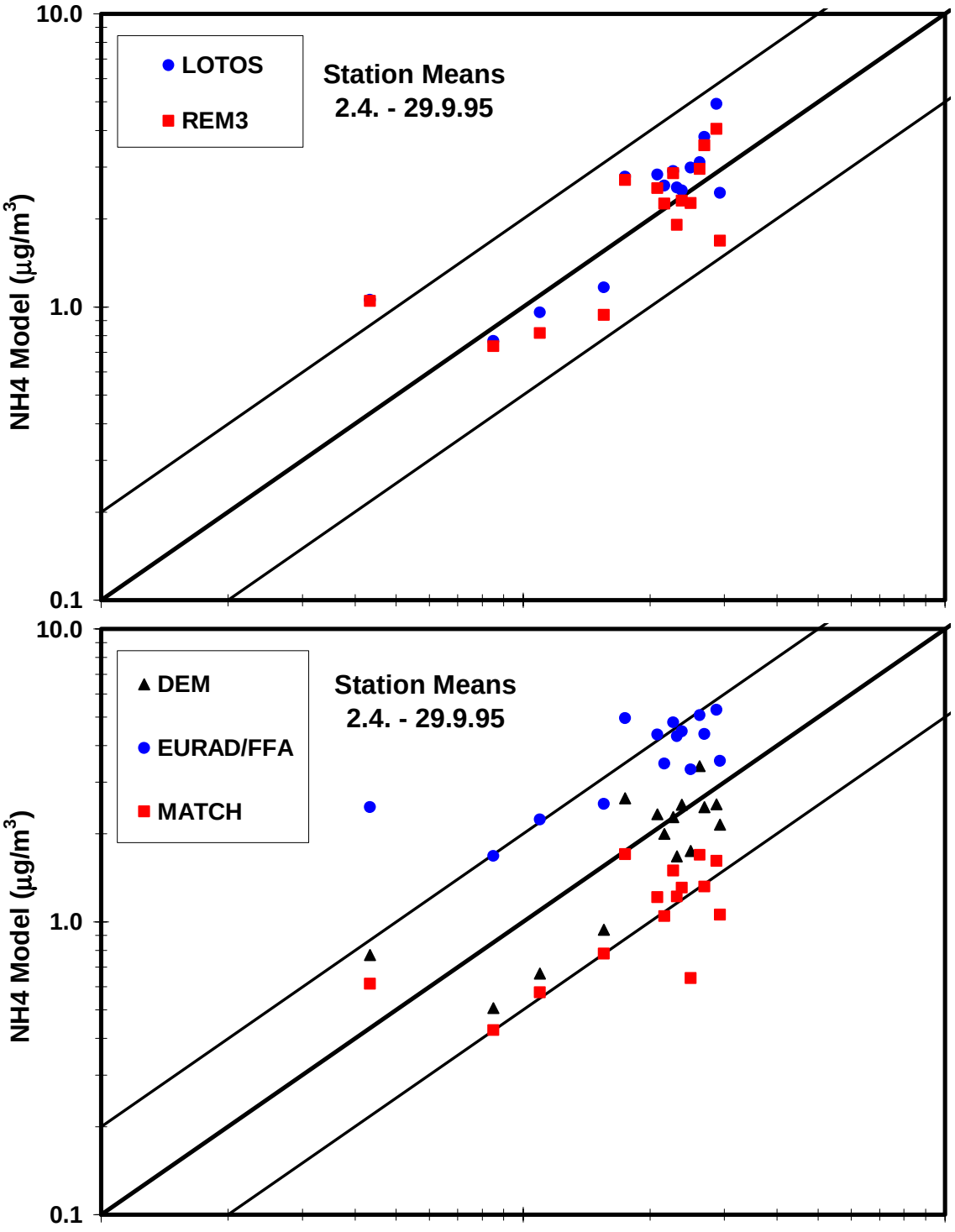

Figure 6.14. Observation of ammonium versus model results. Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

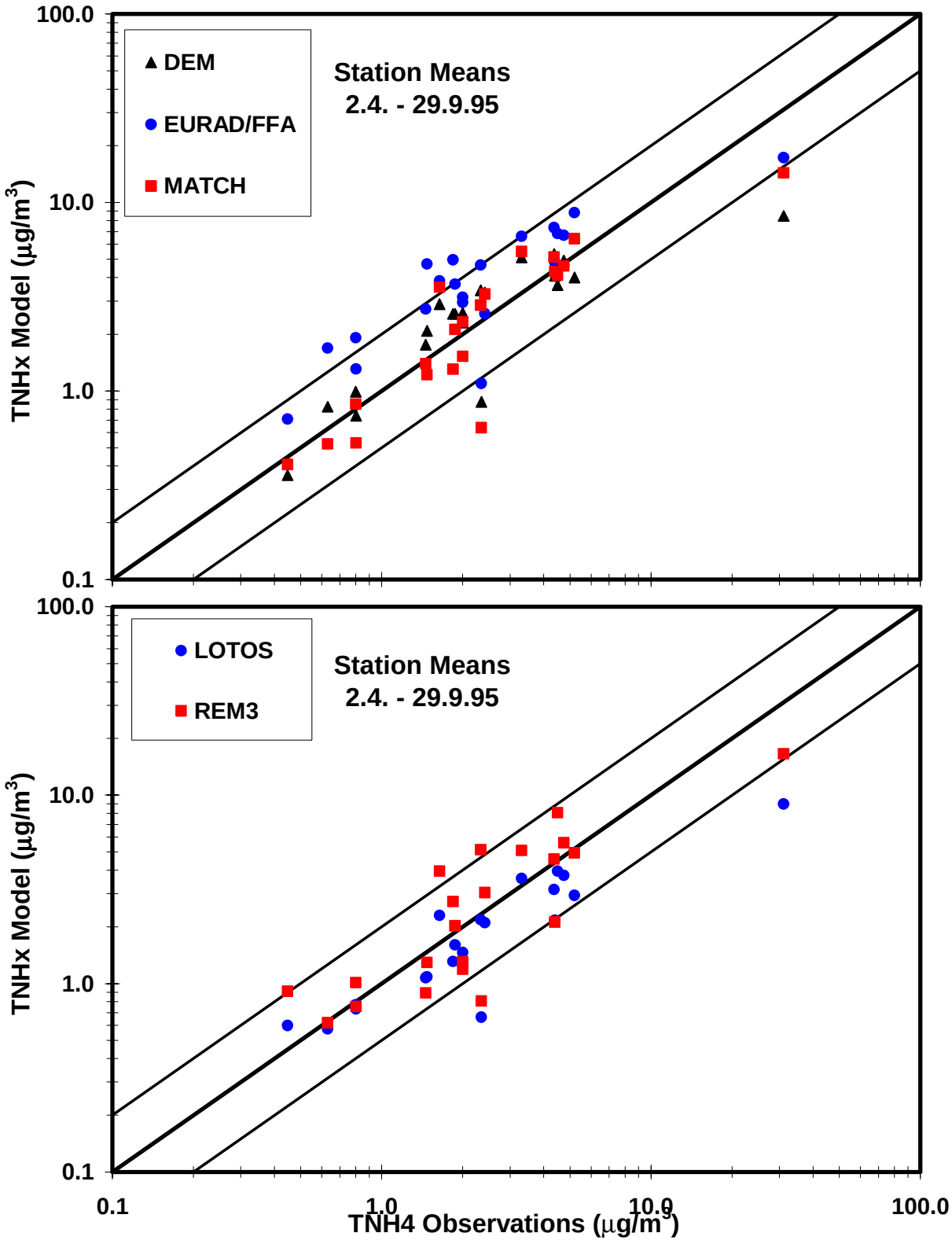

Figure 6.15. Observation of total ammonia versus model results Lines indicate the 2:1, 1:1 and 1:2 ratio, respectively.

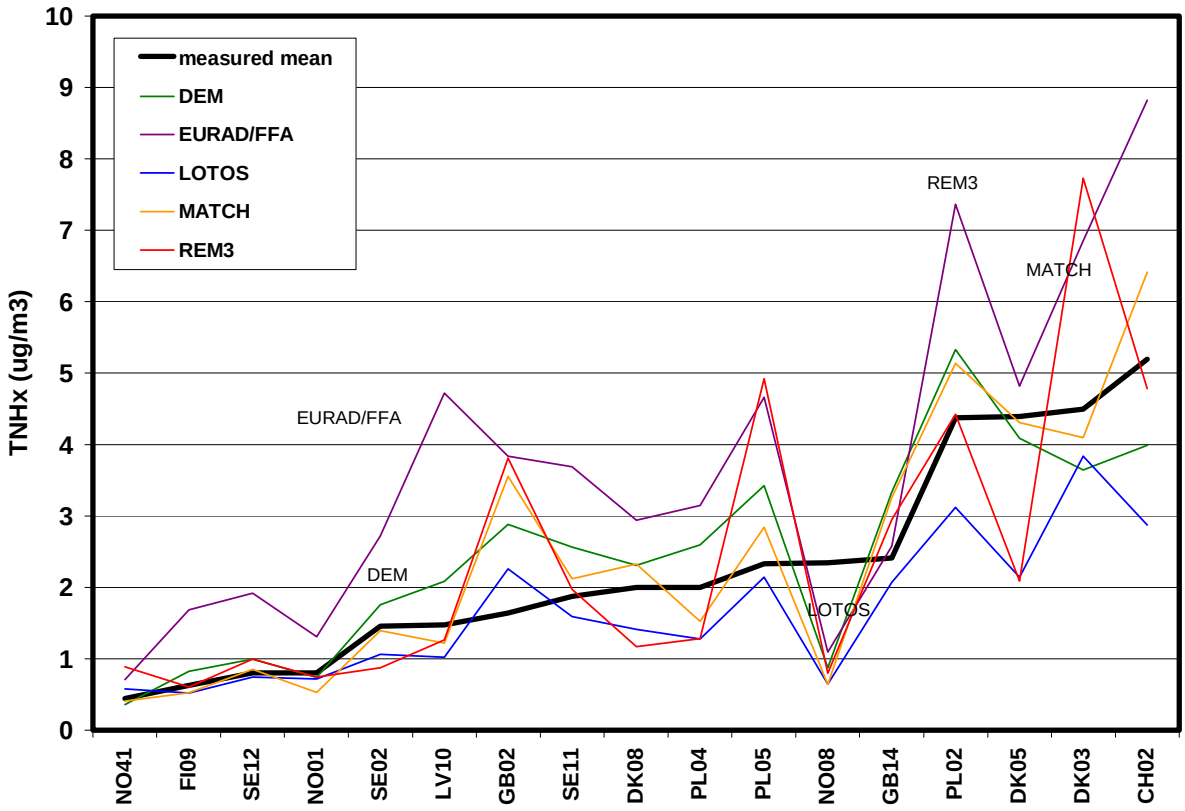

Figure 6.16. Total ammonia. Mean per station sorted according to increasing observations. Station code see Appendix 10.5.

6.5 Indicator section

The use of indicators allows to detect otherwise hidden features in the model results. We will discuss the S-ratio, the free-ammonia (FNH_3) and the gas ratio (GR), which are defined in Table 4.1.

The term S-ratio here denotes the ratio of sulfur in form of SO_2 to sulfur in form of SO_2 and sulfate. In all models the specie SO_2 is emitted, whereas sulfate is produced after transport and a reaction chain including heterogeneous processes. A ratio close to unity should indicate 'fresh' sulfur where not much of the emitted sulfur has been converted to sulfate.

Free ammonia FNH_3 is defined as the total (gas and aerosol) ammonia minus twice the sulfate concentration, i.e. $FNH_3 = TNHx - 2*SO_4$. FNH_3 is the amount of ammonia available, after neutralizing sulfate, for ammonium nitrate formation.

The gas-aerosol equilibrium in the sulfate-nitrate-ammonia system can be analysed with the gas ratio (GR), defined by Ansari and Pandis (1998) as the ratio of free ammonia over total nitrate, i.e. $GR = FNH_3 / TNO_3$. The gas ratio indicates which reactant, ammonia or nitric acid, limits the formation of ammonium nitrate. A ratio greater than 1 indicates that nitric acid is limiting, while a ratio of less than 0 indicates that ammonia is severely limiting. If the ratio is between 0 and 1 some ammonia is available for reaction with nitric acid, but ammonia is limiting.

Figure 6.17 shows the observed and modeled S-ratios as mean values at the stations. The observed S-ratio ranges from 0.15 at remote sites as Osen (NO41) to 0.74 at Svratouch (CS01) whereas the model ratios tend to be basically flat over this observed range. The low observed ratios are overpredicted indicating the fact that the models have too much SO_2. For the high

observations in Figure 6.17 an underprediction towards stations with more ‘fresh’ emissions, i.e. higher S-ratio is indicated. Part of this trend might be a result from the assumed complete mixing of emissions in the model grid volume leading to a larger dilution of sulfur emissions in the models close to the sources and a too high value in remote regions.

In similar figures in this study it was observed that the models showed a matching behaviour at certain stations. Beside the Lithuanian site (LT15) this 'harmony' among the models is hardly seen for the S-ratio.

Figure 6.18 compares the modeled free ammonia with the observed. Free ammonia is overpredicted by the models at nearly all observing sites. Ammonium nitrate formation is enhanced under this conditions in the models leading to the overprediction observed above.

Figure 6.19 compares the average modeled gas ratio with the observed one. At several station the observed ratio is greater than 1 indicating nitric acid limitation in ammonium nitrate formation. In this part of the graphic the models follow the observed increase of the gas ratio with the exception of LOTOS. LOTOS is giving a ratio below 1 for nearly all sites indicating an ammonia limitation in general. DEM on the other hand is generally displaying a ratio of above 1. Very small ratios are overpredicted by the models but LOTOS, MATCH and EURAD follow this tendency.

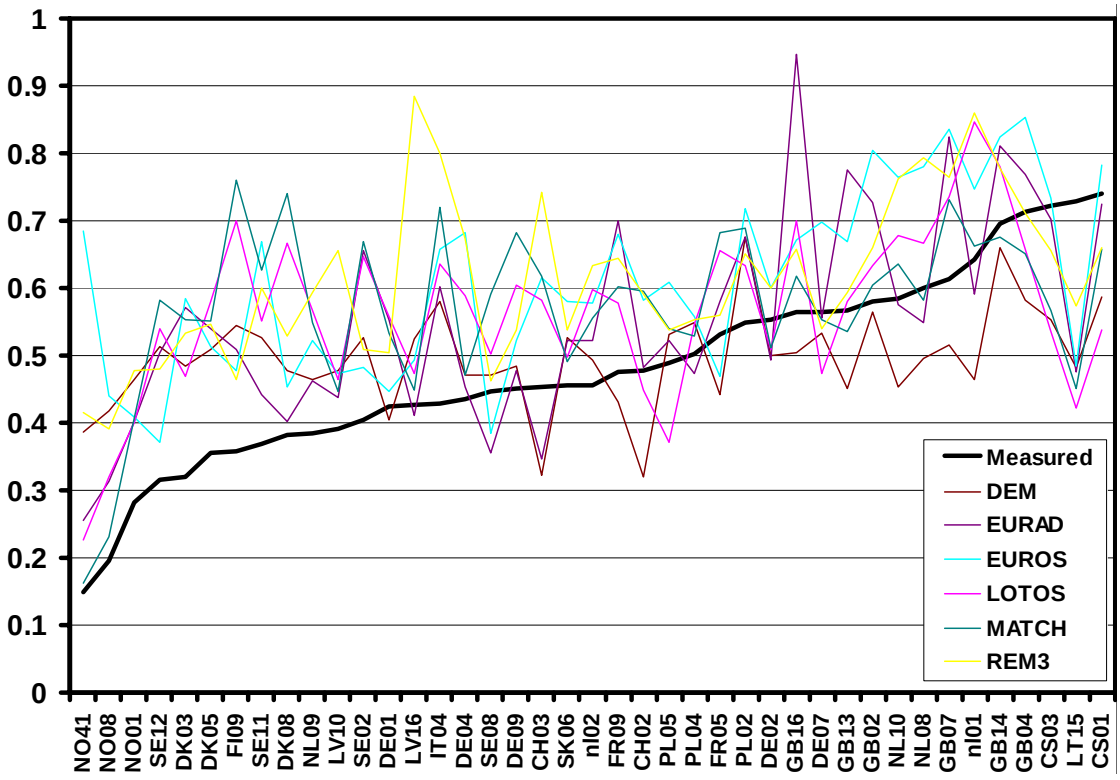

Figure 6.17. S-ratio defined as $SO_2/(SO_2 + SO_4)$: The observed ratio is the black line and values are sorted according to increased observations.

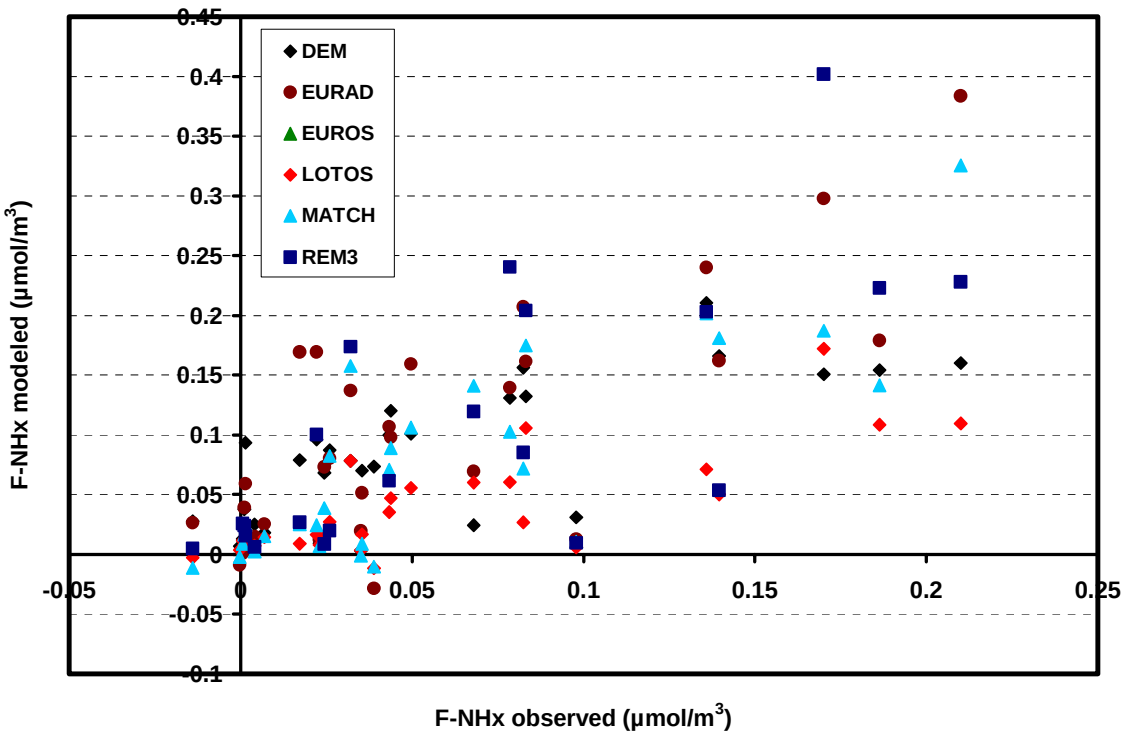

Figure 6.18 Free ammonia defined as the amount of TNHx – 2×sulfate.

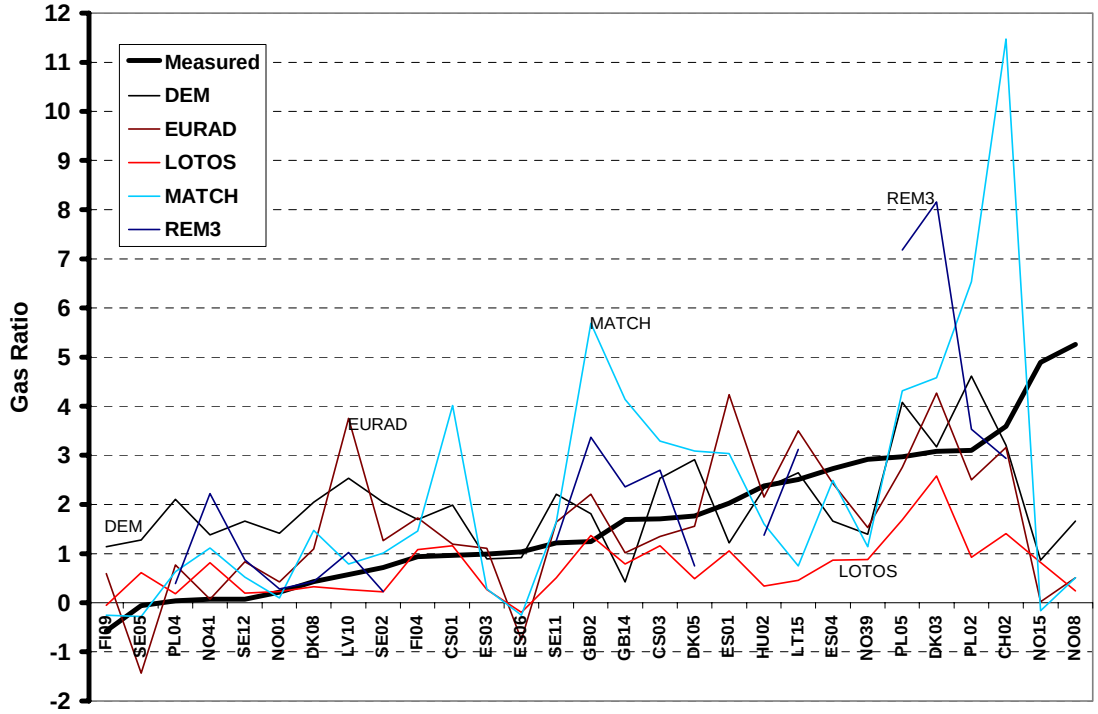

Figure 6.19 Gas ratio (free ammonia over total nitrate on molar basis) sorted according to increased observations.

7 Discussion

In Table 7.1 the ratio of time and domain averaged model results and observations is qualitatively listed for the aerosol species to provide a very general view on model performance as given by the discussion above. The following sections contain remarks to the individual model performances

Table 7.1. Ratio of model results (M) and observations (O).

	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3/ CALGRID
SO_2	=	↑	↑	↗	=	↗
SO_4	=	↑	=	=	↘	↘
NO_3	=	↑	↑	↑	↘	=
TNO_3	=	↑	↑	↑	=	↗
NH_4	=	↑		↗	↘	=
TNHx	↘	↗		↓	↘	=
NO_2	↓	↘	↘	↓	↘	↘
=	: 90% < M/O < 110%			↑	: 150% < M/O	
↗	:110% < M/O < 150%			↓	: 50% > M/O	
↘	: 90% > M/O > 50%					

7.1 SO_2 and sulfate

7.1.1 DEM

The averaged value (over the 49 stations) of the measurements of the SO_2 concentrations compares very well with the corresponding model result (see Table 6.1). The other performance measures (Residue, RMSE, Sigma and Correlation Coefficients) need to be studied carefully in order to try to obtain some improvements. An explanation for the rather poor "% within factor 2" results can be the fact that model daily values are obtained by averaging from midnight to midnight, while observation middle values are obtained by averaging from 8:00 to 8:00 at most of the stations. For the averaged over the whole period values this difference seems to be smoothed off (Fig. 6.1 shows that the comparisons for nearly all stations is indeed very good).

The results for sulfate in Table 6.2 show in general similar trends. More precisely, while the averaged value (over the 44 stations) of the measurements of the SO_4 concentrations compares reasonably well with the corresponding model result, the other parameters compared (Residue, RMSE, sigma and Correlation Coefficients) should be studied carefully in order to try to obtain some improvements. Also the conclusion about the "% within factor 2" results is similar to that made above for the SO_2 results.

7.1.2 EURAD

The model strongly overpredicts SO_2 (ratio of average of model and observations equals 2.31) and improves in the case of SO_4 but still strongly overpredicts (ratio is now 1.52). The following reasons can explain part of the overprediction. The emission data for this run was not scaled for the seasonal variation (e.g. summer emissions strength should be around 80% of yearly mean values). EURAD has the finest vertical resolution close to the ground of all the models here and rather low deposition velocities might be calculated for stably stratified periods, especially during night. Especially the parameterisation of the deposition velocity for the accumulation mode shows

a strong influence on the results under these stable conditions. Sensitivity simulations to address this are currently performed.

7.1.3 EUROS

SO_4 model results are on average very well in comparison with the observations. However the correlation coefficient is on average rather low. Modeled SO_4 concentrations in Central Europe are relatively well represented, where as low concentrations in Northern Europe are underpredicted. SO_2 concentrations are on average overestimated by the model. The correlation coefficient with observations is for time and space domains about 0.4, similar to all other presented model results. The S-ratio, $SO_2/(SO_2+SO_4)$, is better in the high sulphur concentration range than in the low concentration range.

7.1.4 LOTOS

The model overpredicts the SO_2 concentrations by some 20% on average. The overprediction is to a large extent due to high modeled concentrations over Germany relative to the observations. There are indications that the German EMEP observations are biased and underestimate the ‚true' concentrations, explaining part of the overprediction by LOTOS for SO_2. On the other hand, the SO_4 levels generally show an underprediction by LOTOS of about 10% Since there are indications of systematically biased (too low) measured values of SO_4 at the German EMEP locations similar as for SO_2, part of the underprediction may be masked by that. With respect to the total amount of sulfur (sum of SO_2 and SO_4) it seems that the model performs quite well in terms of the ratio between the modeled and observed levels. It is therefore concluded that the net conversion rate of SO_2 into SO_4 is probably too low in the model. This is confirmed by Figure 6.17, where the S-ratio for practically all stations is too high.

7.1.5 MATCH

The model slightly underestimates the average SO_2 concentrations at the 49 stations selected for comparison. The model average divided by the average of the measurement equals 0.98. However, an overprediction is pronounced over Germany and its neighbouring countries to the west and to the north. This is been discussed in the next chapter. MATCH is also lacking sub-cloud scavenging for SO_2. Particularly over source regions this may create overestimation. The overall correlation with the measurements is R=0.38.

The model underestimates the average SO_4 concentration at 55 selected stations. The model average divided by the average of the measurement equals 0.83. The rate of SO_4 formation by oxidation of SO_2 is probably too slow, indicated also by the higher SO_2/SO_4 molar ratio in the modeling results as opposed to the measurements. In addition to that, the H_2O_2, which takes part in the aqueous phase oxidation, could be underestimated. Oxidation by H_2O_2 is the dominant route for low pH (pH<5) normally encountered in clouds and rainwater. The basic meteorological information required to describe the oxidation in clouds is also sparse in the MATCH model. Both the cloud water content and the cloud cover required in these calculations are not vertically resolved. This may induce some error as well. The overall correlation with the measurements is significantly higher for SO_4 than for its primary emitted precursor SO_2, and amounts to R=0.61.

7.1.6 REM3/CALGRID

The calculated gas phase precursor SO_2 shows considerable scatter about the measurements. In particular there are very high observed summer means that are not predicted by RCG and also very high calculated summer means that are not observed. This might be caused by the horizontal and vertical grid resolution that seems insufficient to resolve major point source emissions adequately in some areas of the modeling region. On the average, sulfate is

underestimated.However, a closer look at the data shows, that most of the underestimation is due to the underestimation of the observed sulfate concentrations above 4 $\mu g/m^3$, hence, sulfate production seems too low in regions with high observed sulfate concentrations. This might be a hint that the current parameterization of the aqueous phase sulfate production by a first-order reaction rate with a fixed reaction constant is too simple to account for the photochemically enhanced aqueous phase sulfate production in the summer months.

7.2 Nitrate

7.2.1 DEM

While the NO_2 concentrations are underestimated by DEM (Table 6.2), both the NO_3 results and the total nitrate results seem to be slightly overestimated (see Table 6.3). The number of measurement stations for nitrate (NO_3) is only 9. This is why one should be careful and one should not try to draw too many conclusions from these results. The number of stations for the total nitrate is greater, 21, but still not sufficiently large. Anyway, the results in Table 6.2 and Figure 6.9 indicate that the comparison of the DEM concentrations with corresponding measurements is giving reasonably good results.

7.2.2 EURAD/FFA

EURAD/FFA shows a strong overprediction of nitrate and total nitrate. This might be correlated with the overprediction of ammonium which, in the reaction chain, leads to high nitrate and sulfate productions. As in the case of sulfur, an improved emission handling and an a careful analysis of the deposition velocities for nitrate aerosols might improve the nitrate prediction.

7.2.3 EUROS

The model results for NO_3 in the selected period greatly overestimate the observations at all stations. Total NO_3 is somewhat better modeled than NO_3 but still considerably larger than the observations. Precursor concentrations (NO_2) compare well at these stations. The correlation coefficient computed for time and space domains for NO_3 and total NO_3 with 0.3 and 0.4, respectively, form the lower end of the here reported modelled ranges, 0.3-0.6 and 0.4-0.5, respectively. It should be noted that the quality of the calculated NO_3 levels presented here is mainly limited by the fact that the used scheme does not include NH_3/NH_4.

7.2.4 LOTOS

LOTOS show a considerable overestimation of both nitrate and total nitrate. There are a number of possible explanations for this: since the SO_4 concentrations are underestimated by 10% (or more, see section 7.1.4), there is relatively more ammonia available for nitrate formation. If the conversion rate of SO_2 is increased, nitrate would go down to some extent. We do, however, not think that this would remove the overpredication completely. In comparision with other chemical mechanisms it seems that the mechanism in LOTOS (though a slightly modified version of the well-established CBM-IV mechanism) produces relatively high HNO_3 concentrations. During wintertime, when the photochemistry is less active, (total) nitrate is not overestimated by LOTOS. In addition, recent findings on the reaction probability of the heterogeneous N_2O_5 reaction, forming HNO_3, indicate a lower value than used in the present computations. This value has now been lowered, resulting into a substantial reduction of the overprediction of nitrate.

7.2.5 MATCH

The model underestimates the average particulate NO_3 concentration at 20 selected stations. The model average divided by the average of the measurement equals 0.82. This figure is increasing to 0.99 if the total NO_3 is investigated. The reason is probably the chemical partitioning between the gas phase and the particle phase. The overall correlations with the measurements are R=0.43 and

R=0.48 for NO_3 and total NO_3, respectively. Notably, in a complementary study, a correlation coefficient R=0.75 was achieved for total NO_3 when using a different subset of 26 EMEP stations.

7.2.6 REM3/CALGRID

On the average, the calculated nitrate concentrations are within 10% of the measurements with a little tendency for an overestimation. However, in the RCG modeling area there are only nine stations to compare with. The rather large residual and root mean square error is due to the strong underestimation at one station, NL02 Wieringerwerf in the Netherlands.The overestimation for TNO_3 is higher than that for NO_3. The averaged ratio between the model results and the observations is 1.2 compared to 1.07 for NO_3. Unfortunately, a station-by-station comparison of the NO_3 and TNO_3 model performance from a chemical point of view is difficult, because the stations which measure NO3 are others than those which measure TNO_3 (see Table 10.4). During the model evaluation it was recognized that the eastern lateral HNO3 boundary condition used for this study was too high due to a typo error. This error can attribute a bit to the overestimation and might be one reason, why the correlation coefficient for TNO3 is lower than that for NO_3. Note, that the lowest correlation coefficients are calculated for the stations in the eastern part of the RCG modeling area (see Table 10.21). However, it can be expected that the error propagates not too far into the modeling area because of the high removal rates for HNO_3 and therefore mainly influences low concentrations.

7.3 Ammonia

7.3.1 DEM

The number of stations used in the comparisons of the model NH_3 results with corresponding measurements is only 4. This is clearly not enough and, thus, one should again be careful when conclusions are to be drawn. Anyway, the results indicate that DEM, as the other models, underestimates the ammonia concentrations (see Table 6.4).

The numbers of stations measuring ammonium (NH_4) and total ammonium (TNHx) are greater (15 and 21 respectively), but still perhaps more stations are needed in order to draw more reliable conclusions. The results indicate that DEM slightly underestimates NH_4, while the underestimation of TNHx is considerably larger. The latter effect can perhaps be explained by the fact that DEM underestimates the NH_3 concentrations “aver(model)/aver(meas)”=0.38, see Table 6.4 and this propagates further downwards the chain.

The results shown in Figure 6.14 and Figure 6.15 indicate that the concentrations averaged over the whole period compare rather well with corresponding measurements for all stations in the case of NH_4 (Table 6.15) and for nearly all stations for TNHx (Table 6.17).

7.3.2 EURAD/FFA

The model overestimates NH_4 and, by a smaller margin, total ammonia. As with sulfate no seasonal variation has been used for the ammonia emissions and it seems that the usage of manure and slurry is high in spring.

7.3.3 EUROS

Results of the here presented EUROS model version do not include Ammonia. A recent update of the aerosol module comprises NH_3 and NH_4.

7.3.4 LOTOS

Since there is a small underprediction of SO_4 and a large overprediction of nitrate, it is no surprise that NH_4 is overpredicted. If one assumes that the amount of NH_4 should be approximately equal

to twice the amount of SO_4 plus the amount of NO_3 (on molar basis), the underestimation of SO_4 would lead to a too low contribution to the NH_4 concentrations that is more than compensated by overestimation of nitrate. Of course, this reasoning is only valid at locations where enough ammonia (NH_3) is available to fully neutralize SO_4. At most locations this is on average the case. Even when it is not the case on average, this does not imply that no nitrate is formed throughout the year. During some periods of the year there may be enough NH_3 to have excess NH_3 available for nitrate formation, for example during spring when areas are fertilized. The overprediction for (total) nitrate seems to be at all stations and not only at the station with relatively high nitrate concentrations, but ratio between the observed and modeled concentrations are largest there.

With respect to the ammonia (i.e. the gas-phase) it should be mentioned that due to the fact that LOTOS does not employ a surface layer, the ammonia concentrations are much lower in areas with strong ammonia emissions because emissions are then directly mixed into the mixing layer. Nevertheless, there is enough excess ammonia in the model to form nitrate. This formation seems to take place mainly at night

7.3.5 MATCH

The model underestimates the average NH_4 concentration at 20 selected stations. The model average divided by the average of the measurement equals 0.64. The underestimation is more pronounced over The Netherlands. The underestimation of SO_4 in the same region is probably linked to this feature. Another contributing factor to the discrepancy could be that MATCH is not using seasonally-changing emissions in the 1995-runs and neither is it employing a subsequent reemission of the NH_3 precursor from the soils. The overall correlation with the measurements is R=0.53. The total NH_4 is only slightly underestimated at 25 selected stations. This points to a failure of the partitioning between the gas phase and the particle phase. The link to the SO_4-underestimation is probably very strong. The overall correlation with the measurements is R=0.51 for total NH_4. Notably, in a complementary study of the MATCH model performance (with the same model runs), a correlation coefficient R=0.71 was achieved during comparison with a different subset of 26 EMEP stations. The free ammonia, referring to the NH_x available after full neutralisation of SO_4, is consistently negative or close to zero at most EMEP stations. The reason for this is the MATCH modeling concept for chemistry of particulate SO_4, which does not allow full neutralisation by NH_3.

7.3.6 REM3/CALGRID

The calculated NH_4 model average is within 10% of the observed average. There is no real bias in the model results, both high and low observed concentrations are under- and overestimated. The ratio between model average and observed average switches from 1.07 for NH_4 to 0.91 for TNHx, probably due to an underestimation of the gas-phase ammonia and/or due to calculated ratios of ammonium to sulfate or nitrate to sulfate that are different from those of the real world. Again, a station-to-station comparison of various measured and calculated quantities is difficult, because in the RCG modeling region there are only 3 stations which measure NH_4 and TNHx, and there is no station that measures all components that are needed to evaluate the calculated concentration ratios. The comparison of observed and modeled concentration ratios at the stations where this information is available, reveals no clear picture, probably because of the interference of the non-chemical influence parameters as emissions or transport.

7.4 Summary

The model intercomparison has shown that many model results can be found within a range of two of the modeled to observations ratio or even better. This outcome, is, at first sight, a rather

inconclusive measure of performance. However, in view of the many roads travelled to a common destination it still is astonishing. Various formulations of the models, low or high resolutions in vertical and horizontal directions and many other facets which are treated differently in each model emphasize the belief, that many routes are possible. This is especially visible by viewing the vastly differing complexity of the models as measured in their computing time. In the following some of the lessons learned during this intercomparison will be identified.

Why do most model results compare best with each other and not very well with measurements? Apperently there are some basic processes governing the concentrations which we do not capture in the models or local processes which we never can put into our models. On the other hand, the comparison of the model results showed clearly that a more complex model approach to the aerosol problem does not automatically lead to better results in a 3-dimensional application. There are too many other relevant non-chemical/physical influence parameters as the input data for emissions and the meteorological parameters or the treatment of transport and removal that have influence on the gas-phase-aerosol relationships. Hence, relationships between gas-phase and aerosol species that are derived from theory and box-model experiments might not be able to fully explain calculated and observed concentrations. LOTOS and REM3/CALGRID, for instance, use the same gas-phase chemistry, similar inorganic modules, very similar emissions, but the nitrate results and total ammonia results are quite different, probably due to a different vertical resolution of the boundary layer and a different treatment of the removal processes.

Besides of all the non-chemical influence paprameters, the evaluation of the model results for aerosols is hindered by the fact that a station-to-station comparison of measured and calculated ratios of ammonium to sulfate or nitrate to sulfate is mostly not possible because there are very few station that measure all components that would be needed to draw definite conclusions about the performance of an aerosol module on a European scale.

A striking result of our study was that the models simulated the measurements at non-EMEP sites in Germany much better than those of the very nearby EMEP-stations in Germany. On the other hand the model results agreed well with data from EMEP-stations close to the border of Germany. We observed that sulfate data for the EMEP sites are systematically lower than those reported in Germany for sites like Müncheberg (Zimmerling et al, 2000), Melpitz (Muller et al, 1998) and Keldsnor in Denmark (DK05). In Figure 7.1 we illustrate this feature. The mentioned stations are all within 100-150 km of Neuglobsow (DE07) or Zingst (DE09) and located to the north west, south and east of both stations. The reason for the low values at the EMEP stations is not clear to us.

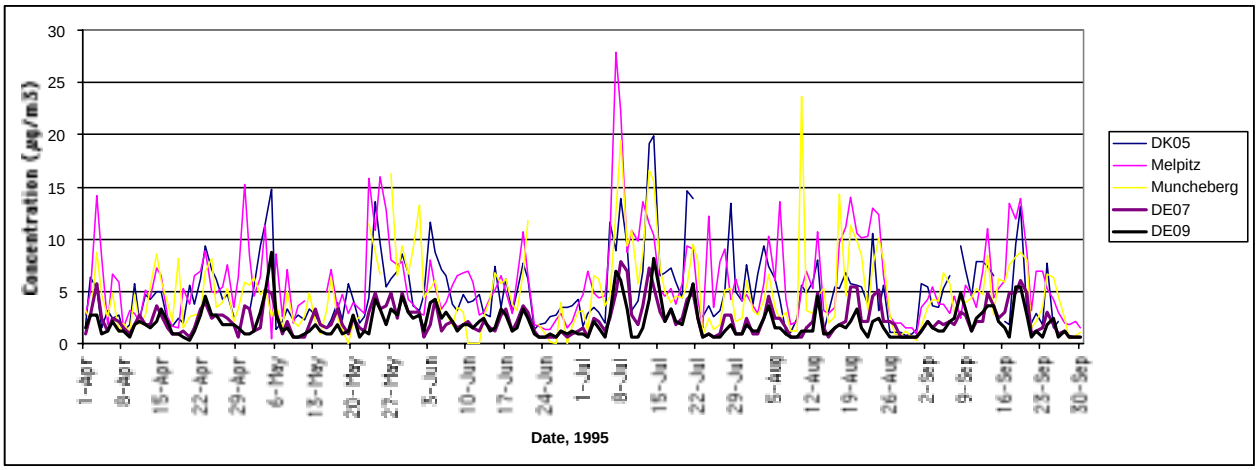

Figure 7.1. Sulfate concentration measured at Keldsnor (Dk05), Melpitz , Müncheberg and Neuglobsow (De07) and Zingst (De09) for April-September 1995.

In this intercomparison the meteorology has been taken as is, although being a key in the transport chain it would have certainly needed its own intercomparison study. To be more precise: not one meteorology but six different wind (temperature, turbulence, rain etc.) fields. Except for some comments on the stations we have taken the results of measurements as truth. An oversimplification says, that the modeller always more believes in results of measurements whereas the measurement expert, knowing the shortcomings of the instruments, tends to believe in the accuracy of computers and accept results of simulations as valid check of instrument readings. We have also accepted the emission inventories as given but there are now certain discrepancies which need to be addressed.

It has been said many times in many ways that experimentalists and modellers have their own views on the same subject, namely predicting concentrations in time and space. We feel, that this intercomparison would have gained momentum, intensity and depth by a closer cooperation between meteorologists, measurement experts, atmospheric physicists, chemists and that amorph species called modellers. However, the in-depth explanation of each single deviation between observation and model is a cumbersome task, it requires a continuous and exhaustive cooperation between many specialists and is hardly feasible without unlimited means.

So in which way should we develop our model in order to gain better results? Only more sophisticated model processes will probably not give better answers straightaway. We expect improvements from data assimilation and a more elaborate uncertainty analysis together with appropriate measurements. Nevertheless, this study has resulted in new ideas to improve modeling of particulate matter over Europe and has also shown the experience gathered in both EUROTRAC I and II projects and other international research cooperations.

7.5 Lessons learned during the excercise

In the course of this study many modelers have reviewed, adapted and/or updated their schemes and modules in response to the initial model results.

This study indicates that some ways of improving the performance of the models have to be formulated, implemented and tested. Within comprehensive modeling systems this is not an easy task and definitely requires a data set of observations which even at the time of the writing of this

report is not available in Europe. However, sensitivity simulations with changed input data, improved spatial resolution and updated aerosol physics and chemistry is a way for further improvement of the model systems.

Some experiments, in which DEM was discretized by using both a 16.67 km x 16.67 km grid and a 10 km x 10 km grid, are carried out at present. Preliminary results indicate that some improvements can clearly be seen.

The tendency to overpredict for EURAD has been recognized during this study to be caused by a missing seasonal variation in emission strength and low deposition velocities during stably stratified periods specially during nights. Especially the parameterisation of the deposition velocity for the accumulation mode shows a strong influence on the results. Sensitivity simulations to address this are currently performed.

Based on the results of this intercomparison study, the EUROS model has been updated in respect to chemical scheme and the aerosol module. Therefore, a new chemical reaction scheme is included, CB-IV_99 [Adelman, 1999], in combination with the EQSAM aerosol module [Metzger et al., 2002].

It has to be emphasized that the results for LOTOS within the intercomparison have been obtained with an older version of the model. Partly based on the experiences in the intercomparison study, the LOTOS model has further improved. Based on recent findings that indicate a lower value of the reaction probability of the heterogeneous N_2O_5 reaction (forming HNO_3) than used in the computations for this intercomparison, this value has now been lowered, resulting in a substantial reduction of the overprediction of nitrate. In addition it is concluded that the SO_2 oxidation rates are at the low side, most likely because of an underestimation of the heterogeneous conversion.

The study indicated that the oxidation rates of SO_2 in MATCH could have been higher. Furthermore, the partitioning between the gas phase and the particle phase of both nitrate and ammonium will need to be reviewed in MATCH.

The REM3/CALGRID underestimation of the high sulfate concentrations might be due to a too simple parameterization of the aqueous phase sulfate production. Sensitiviy studies are planned that address this issue. In particular it will be investigated whether the inclusion of meteorological parameters as humidity, cloud type or cloud cover can improve the model performance for sulfate. Bulk approaches to include the oxidants O_3 and H_2O_2 will also be considered.

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10 Appendix

10.1 Short model descriptions

10.1.1 DEM

The **DEM** (Zlatev, 1995, Ambelas Skjøth et al., 2000, Bastrup-Birk et al, 2001, Dimov et al., 1999, Owzarz and Zlatev, 2002, Zlatev, 2001a, 2001b, Zlatev et al, 2001) is a model for studying air pollution levels (both concentrations and depositions) in Europe. Different horizontal grids can be used (150 km x 150 km, 50 km x 50 km, 16.67 km x 16.67 km and 10 km x 10 km). Both 2-D versions and 3-D versions are available (the 3-D version containing 10 non-equidistant layers). Concentration and deposition fields on hourly (only for ozone), daily, monthly and annual bases can be prepared. The input data (both meteorological data and emission data) are obtained from EMEP. Measurements from the EMEP measurement stations network for 1989-1998 have been used during the validation of the results. The model calculates sulfur compounds, nitrogen compounds, some radicals, ozone, ammonia-ammonium and many hydrocarbons. The CBM IV chemical scheme is used. The major numerical methods used are (i) finite elements in the advection-diffusion part and an improved version of the QSSA (the Quasi-Steady-State-Approximation) method in the chemical part. The fine resolution versions are run on high-speed parallel computers (Georgiev and Zlatev, 1999, Owczarz and Zlatev, 2001, 2002, Zlatev 2001a. The splitting procedure used in DEM is discussed in Dimov et al (2001). Numerical algorithms, which are implemented in DEM, are described in Alexandrov et al. (1997), Hov et al. (1989), Zlatev (2001a, 2001b). Different studies were carried out by using DEM; see Ambelas et al. (2002), Bastrup-Birk et al. (1997), Havasi et al. (2001), Havasi and Zlatev (2002), Jensen et al. (2001), Zlatev et al. (1996, 1999, 2001).

10.1.2 EURAD/MADE/SORGAM

The **EURAD/MADE/SORGAM** model (Hass et al., 1993; 1995; Ackermann et al., 1998; Schell et al., 2001) is a flexible, multi-layer, multi-species Eulerian grid model for the simulation of the transport, chemical transformation and deposition of tropospheric constituents. The combination of EURAD with the aerosol modules MADE (Modal Aerosol Dynamics model for Europe) and SORGAM (Secondary Organic Aerosol Model) increases the capability of the system to handle also particles.

The modeling system consists of three main modules: the mesoscale meteorological model MM5 (Grell et al. 1994), that provides all the meteorological input, the EURAD emission model (EEM, Memmesheimer et al., 1995) and the chemistry-transport module CTM3 (Schell et al., 2001). MM5 forecasts the time dependent winds, temperatures and specific humidities for the period considered. A four-dimensional data assimilation procedure can be invoked to nudge the prognostic variables towards the observations (Stauffer et al., 1990; Elbern and Schmidt, 1999). The CTM3 is driven by the meteorological output of the MM5 and predicts the time-varying trace gas concentrations by solving a species continuity equation that includes parameterizations of the horizontal and vertical transport, diffusion, deposition, gas and aqueous phase conversions, and spatial redistribution and removal of pollutants by clouds (Chang et al., 1987; Hass et al., 1993). EURAD can be applied to multiple scales through nesting techniques (Jakobs et al., 1995). In this intercomparison a fixed grid size of 27×27 km^2 was used.

An extension on the RADM2 mechanism (Stockwell et al., 1990), called EuroRADM (Stockwell and Kley, 1994) is used. This chemical mechanism is further extended by a more detailed description of the isoprene chemistry (Zimmermann and Poppe, 1996).

MADE is based on the Regional Particulate Model (RPM; Binkowski and Shankar, 1995) providing detailed information about the chemical composition and the size distribution of the particles as well as the dynamic processes influencing the particle population. However, the first model version was limited to submicron particles consisting of inorganic ions and water. Further model developments and incorporation of the aerosol portion of MODELS-3 CMAQ (Binkowski, 1999) include the coarse particle size range and a more complete desciption of the fine particle chemistry (Ackermann et al., 1999). Nevertheless, recent findings required a more complex treatment of secondary organic aerosol formation. Therefore a secondary organic aerosol model was developed and implemented in the EURAD/MADE model system.

Incorporation of the secondary organic aerosol model SORGAM into the EURAD/MADE model system required some modifications of EURAD/MADE system. In order to distinguish between anthropogenic and biogenic SOA the EuroRADM2 gas-phase chemistry mechanism was extended to include additional biogenic compounds. Hence the biogenic model species API (α-pinene and other cyclic terpenes with one double bond), LIM (d-limonene and other cyclic diene terpenes), and their reactions were adapted from the RACM mechanism (Stockwell et al., 1997). This extended gas-phase mechanism is used to describe the production of low volatility product classes.

For this application SORGAM is fully integrated into the aerosol dynamics model MADE, i.e. the chemical composition of submicron particles in MADE is extended to include secondary organic compounds. Therefore SOA compounds take part in all aerosol dynamics processes considered in MADE. Particle size dependent mass transfer of low volatility organic material between the gas and the particle phase as well as particle growth is described following the parameterisations given by Whitby et al. (1997) and Binkowski and Shankar (1995).

10.1.3 EUROS

The EUROS (EURopean Operational Smog) model is an Eulerian air quality model used to simulate the dispersion and transport of components in the lower troposphere. EUROS has been developed at RIVM and is used to evaluate possible policy measures. The horizontal base grid consists of 52 × 55 grid cells with a 0.55° × 0.55° regular latitude/longitude projection with shifted pole (grid cells are about 60 x 60 km^2). The shifted pole co-ordinate system in EUROS defines the position of the equator over Denmark and is also used by the atmospheric meteorology forecast model HIRLAM.

Horizontal advection is approximated by using finite volumes, a limited $\kappa = 1/3$ advection scheme [van Leer, 1985] and a 3rd/4th order Runge-Kutta time integrator with automatic time step selection. A time step of 30 minutes is used to compute vertical exchange and horizontal diffusion, the same as for horizontal advection. Local uniform grid refinement is possible up to 4 levels resulting in a maximum longitude-latitude resolution of about 0.069° × 0.069° (about 7.5 × 7.5 km^2).

The atmospheric vertical grid structure in this version of EUROS, is modeled with four layers: the surface layer (SL), the mixing layer (ML), the reservoir-layer (RL) and the top-layer (TL). The surface layer and the mixing layer together form the atmospheric boundary layer. The depths of the four layers are uniform over the whole domain but vary in time during the day due to the growth of the mixing layer, except for the surface layer whose depth is fixed to 50 m. The mixing layer growth during daylight hours can be represented through a constant climatological growth rate or the ML height is calculated from surface meteorological variables using simple parameterizations found in the literature. The latter method is then applied for a single grid point located in the Netherlands and the derived mixing height is used for the whole of Europe.

The EUROS model has originally been developed to model winter-smog episodes (SO_2) in Europe [van Egmond and Kesseboom, 1981]. Later, the model has been used to study the temporal and spatial behaviour of not only SOx and NOx, but also of ground level ozone (O_3) volatile organic compounds (VOCs) and persistent organic pollutants (POPs), in the lower troposphere over Europe. At present EUROS is being extended to model the dispersion of primary particulate matter (PM10 PM2.5). Further an updated chemical scheme is being incorporated in combination with an aerosol module which includes NH_4 based on NH_3 gas phase concentrations. The present EUROS version includes emissions, transport processes, chemical transformation, dry and wet removal processes and first order degradation in soil and water of various compounds. This and earlier versions of the EUROS model are described in Jacobs and van Pul [1996], van Loon [1996], de Leeuw and van Rheineck Leyssius [1990], van Rheineck Leyssius et al. [1990]. More recent applications can be found in Hammingh et al. [2001] or Matthijsen et al. [2001, 2002].

10.1.4 LOTOS

The LOTOS model (Builtjes, 1991, 1992) of TNO in the Netherlands is a three-layer, Eulerian model for the simulation of the formation, transport and deposition of oxidants within the boundary layer. LOTOS uses the concept of dynamic layers, which expand or contract locally in response to changes in the meteorological conditions. The lower layer represents the well-mixed boundary layer, the middle layer represents the capping inversion, and the top layer represents the lower free troposphere reservoir layer. A purely diagnostic surface layer is used to accomplish dry deposition. The meteorological winds, temperatures and specific humidities have to be provided as 3-hourly, layer averages. Other input data includes gridded fields of mixing heights, cloud cover and precipitation rate. The meteorological input data are provided by the Free University of Berlin and are mainly based on diagnostic Optimal Interpolation of observations.

10.1.5 MATCH

The MATCH (Multi-scale Atmospheric Transport and Chemistry) model (Robertson et al., 1999) has been developed as a flexible transport/chemistry/deposition model for atmospheric pollutants. It is used in a range of applications ranging from urban scale studies on ~5 km or higher horizontal resolutions to continental scale studies on acid deposition and photochemistry (see www.smhi.se/sgn0106/if/meteorologi/match.htm). MATCH is also used operationally to provide forecasts of radioactivity in case of nuclear emergencies in Europe (Langner et al., 1998a). Here we report the model setup (v.3.9.1d) used for the GLOREAM Aerosol model intercomparison. For details on the basic transport model the reader is referred to Robertson et al. (1999). More details about the photochemistry version of the model can be found in Langner et al. (1998b) and in Tilmes et al. (2002).

The MATCH modeling domain covers almost all of Europe with about 55 km ×55 km horizontal resolution and 87x91 grid points. Data from all the 16 levels of the NWP model are used for vertical wind calculations while only the 10 lowest layers are used in the transport calculations. MATCH uses the same coordinates as the NWP model; rotated latitude longitude coordinates in the horizontal and eta coordinates (linear combination of sigma and pressure coordinates) in the vertical.

Meteorological input data at three-hourly intervals are taken from operational weather forecast runs using HIRLAM (High Resolution Limited Area Model).HIRLAM is a hydrostatic model, which currently is run at 44 and 22 km horizontal resolutions at SMHI. The 44 km model is run over an area covering Europe and the north Atlantic and Arctic regions. Boundary conditions are

taken from the ECMWF global model and initial conditions are derived from a 6-hourly intermittent data assimilation cycle.

Advection in MATCH is modeled using a Bott-type advection scheme (Bott, 1989a, b). Fifth order integral functions were used in the horizontal and an up-stream scheme in the vertical direction. Boundary layer processes, such as turbulent vertical mixing in the boundary layer and dry deposition, are parameterized using three primary parameters; the surface friction velocity, the surface sensible heat flux and the boundary layer height. Dry deposition is modeled using a resistance approach. For simplicity the same aerodynamic resistance is used for all surfaces in a grid square and only variations in the surface resistance are accounted for. Wet scavenging is assumed to be proportional to the precipitation intensity using species-specific scavenging coefficients.

Expressions for the photolysis rates, depending on solar elevation derived for clear sky situations, were taken from Derwent and Jenkin (1990). To account for the effect of clouds the photolysis rates were scaled by the ratio of the actual global radiation (corrected for clouds) to the clear sky global radiation. The gas-phase chemical mechanism used is mainly based on the EMEP MSC-W model chemistry (Simpson et al., 1993). The main difference is that for the isoprene chemistry an adapted version of the so-called Carter 1-product mechanism (Carter, 1996) has been used instead of the EMEP mechanism (Langner et al., 1998b). The photochemical model includes ca. 130 thermal and photochemical reactions between 59 chemical components and it is designed to provide a good description of the chemistry for both high and low NOx conditions. In addition to the photochemistry the reduced nitrogen chemistry from the EMEP acid deposition model is included as well as aqueous-phase oxidation of SO_2 by ozone and H_2O_2 in cloud water.

Standard numerical integration techniques following the work by Verver et al. (1996) are used to integrate the chemical mechanism. This leads to stable integrations, where the accuracy of the calculations can be controlled. We have used the Kinetics Pre-Processor (KPP) developed at the University of Iowa. The use of a standard solver coupled with KPP makes it easy to change the chemical mechanism without having to recode the solver.

Anthropogenic emissions for the simulations were derived from the 50 km ×50 km emission data provided by EMEP MSC/W at the Norwegian Meteorological Institute. The EMEP emission data are divided into emissions below and above 100 m. The emissions for 1997 for NO, SO_2, non-methane hydrocarbons (NMHC) and CO were used in the model calculations. Simple variations of the emissions with the time of day and with the day of the week were used. Biogenic emissions of isoprene (C5H8) were calculated in MATCH, based on temperature and radiation from HIRLAM, using the E-94 isoprene emission methodology proposed by Simpson et al. (1995).

10.1.6 REM3/CALGRID

The REM3/CALGRID model is an urban/regional scale model development designed to fulfill the requirements of the ambient air quality framework directive 96/62/EC of the European Commission (Stern and Yamartino, 2001). The urban-scale photochemical model CALGRID (Yamartino et al., 1992 and 1996) and the regional scale model REM3 (Stern, 1994; Hass et al., 1997) were used as the starting point for the design of a Eulerian grid model of medium complexity that can be used on the regional, as well as the urban, scale for short-term and long-term simulations of oxidant and aerosol formation.

The new model framework REM3/CALGRID includes the following model features:

- A generalized horizontal coordinate systems, including latitude-longitude coordinates;

- A vertical transport and diffusion scheme that incorporates a detailed micrometeorological boundary layer formulation, correctly accounts for atmospheric density variations in space and time, and accounts for all vertical flux components when employing either a dynamic or a fixed multi- layer system;
- A resistance-based model for the computation of dry deposition rates as a function of geophysical parameters, micrometeorological conditions, and pollutant species including the gravitational settling speed of particles;
- The latest releases of the photochemical reaction schemes SAPRC-93 and CBM-IV including Carter's (1996) 1-product isoprene scheme and SO_2 oxidation to SO_4;
- Two equilibrium aerosol modules: a) The MARS-A module (Binkowski and Shankar,1995) that treats the thermodynamics of the inorganic sulfate, nitrate, ammonium aerosols and water, slightly modified by Schaap (2000); b) the ISORROPIA module that treats in addition sodium and chloride aerosols (Nenes et al., 1998, 1999).
- A simple wet scavenging module based on precipitation rates;
- A new methodology to eliminate errors totally from operator-split transport and ensure correct transport fluxes (Yamartino, 1998) and that a constant mixing ratio field remains constant;
- Inclusion of the highly-accurate, monotonic advection scheme developed by Walcek (2000). This scheme has been further modified for REM3/CALGRID to exhibit even lower numerical diffusion for short wavelength distributions using wavelength-dependent steepening; and
- an emissions data interface for long-term applications, that enables on-the-fly calculation of hourly anthropogenic and natural emissions, and greatly facilitates emissions reduction scenario studies.

Secondary organic aerosols (SOA), that are formed by condensation of biogenic and anthropogenic hydrocarbon oxidation products, are not presently considered.

Meteorological data needed by REM3/CALGRID at hourly intervals consist of layer-averaged gridded fields of wind, temperature, humidity and density, plus 2-d gridded fields of mixing heights, several boundary layer and surface variables, precipitation rates and cloud cover. All these data are produced by the Diagnostic Meteorological Analysis System of the Free University Berlin (Reimer and Scherer, 1992). This system employs an optimum interpolation on isentropic surfaces and utilizes all available synoptic surface and upper air data.

The regional emissions data base covers all of Europe at a resolution of 0.25° latitude and 0.5° longitude. Annual anthropogenic emissions are based on CORINAIR and TNO (PM10- and PM2.5-) CEPMEIP base-year 1995 data for VOC, NOx, CO, SO_2, CH_4, NH_3, PM10, and PM2.5. Hourly emissions are derived during the model run using source group dependent, month, day-of -week and hourly factors. Biogenic VOC-emissions, sea salt Na- and Cl-emissions and PM10 wind blown dust emissions are derived on-the-fly using simple emissions parameterizations.

Table 10.1. Summary of main modeling approaches realized in the modeling systems.

	DEM	**EUROS**	**EURAD**	**LOTOS**	**REM3/-CALGRID**	**MATCH**
Type	3-D Eulerian	3-D Eulerian	3-D Eulerian	3-D Eulerian	3-D Eulerian	3-D Eulerian
Horizontal resolution	Variable: here 50 km x 50 km	variable: here 0.55° × 0.55°	variable: here 27km × 27km	0.25 degr. Lat. 0.5 degr. Lon.	Variable,here 0.25°Lat., 0.5° Lon.	Variable: here 55 x 55 km^2
Vertical resolution	variable, 10 layers	4 layers 2 layers in PBL	variable sigma-system: here 15 layers (7 below 1km)	3 layers 1 layers in PBL dynamic	Variable terrain following fixed or dynamic system, here: 4 layers, 3 layers in PBL, dynamic	variable, eta-system, here 10 layers (4 below 1 km)
Advection scheme	Finite elements	$\kappa = 1/3$ scheme (van Leer, 1985)	Bott (1989)	Shasta: Boris and Book (1973)	Walcek (2000)	Bott(1989) modified
Dry Deposition	resistance approach	resistance approach	resistance approach	resistance approach	resistance approach	resistance approach
Wet Deposition	Scavenging	scavenging	complex cloud module	scavenging	scavenging	scavenging coefficients
Chemistry	CBM IV	CBM-IV (for PM however, condensed ozone scheme (15 reactions)	Extended EuroRADM gas-phase; aqueous phase	CBM-IV and limited aqueous phase	CBM-IV or SAPRC-93, here: CBM-IV	EMEP with modified biogenic chemistry
Emissions	EMEP inventories	point- and area sources, SOx, NOx, VOC, PM10, fixed VOC split	AOPII & EMEP inventories with additional point sources, fixed VOC split	point- and area sources SOx, NOx, VOC, CO source dependent VOC split	point- and area sources SOx, NOx, VOC, CO, CH_4, NH_3, PM10, source dependent VOC split	EMEP inventories, here 1997, high and low sources, fixed VOC split, diurnal and weekday variations
Meteo-rology	EMEP meteorological data	ECMWF, upper air data set and gridded observations for surface meteo parameters	MM5 nugded forecasts, Grell et al. (1994)	LAM-150 NWP Gronås et al. (1982) mixing heights from radiosonde data	diagnostic Optimal Interpolation of observations, energy budget method for PBL variables	SMHI operational HIRLAM analysis, 3 and 6h forecasts
Boundary Conditions	Background concentrations on the boundaries with seasonal and/or diurnal variations	derived from observations	observations (climatolo-gical)	boundary from global 2-D model	observations (climatolo-gical)	Observations (climatolo-gical, with monthly variation)

10.2 Complexity

The amount of computational work for a model is difficult to specify. No specific benchmark program was available, which could count e.g. divisions or addition done in the computer code while running on a particular machine. We have therefore determined the computing performance of the machines used in this study with the same Linpack routine for all machines and the CPU times spent for the computations of the model results for one year. The shortcomings of this method are:

- computing efficient codes need less CPU-time than inefficient codes for the same task,
- parallelisation increases CPU-time,
- input/output operations increases CPU-time.

As computational complexity (CoCo) we have defined the product of speed (Million floating points per second) and CPU-time. To take into account the various model dimensions we scale this number by dividing it by the number of gridpoints. The complexity per grid point is the approximate amount of million floating point operations needed to calculate the results for one real day at one grid point.

Table 10.2. Computing times for one year model run and amount of computing per grid point (million floating point operations per grid point and day).

	Mflop/s	CPU [hours]	grid points	CoCo/point	Ratio to EURAD
DEM	259	115.6	92160	3.2	9.7%
EURAD/FFA	265	2628.0	207000	33.2	100.0%
EUROS	91	37.0	11440	2.9	8.8%
LOTOS	318	144.0	42000	10.8	32.4%
MATCH	282	333.8	79170	11.7	35.3%
REM3/CALGRID	97	111.3	25920	4.1	12.4%

Efficient parallelisation of the codes is an important tool in the efforts to reduce the computing time. Running DEM on 8 processors results in a speed up of about 7.8 (i.e the computing time given in Table 10.2 is reduced by a factor approximately equal to 8). This means that the parallel version can successfully be used for solving more and bigger tasks, which is important in complex studies where many scenarios have to be used. However, if the task is to study scenarios with only slightly changed set ups and if one has many different computers available, then one can submit the different scenarios to each of them.

10.3 Model domains

Table 10.3. Domain specifications of the models for the current study. Coordinates are given as: (Latitude, Longitude) with positive north/east.

	DEM	**EUROS**	**EURAD/ FFA**	**LOTOS**	**REM3/ CALGRID**	**MATCH**
Grid size (km)	50km × 50km	≈ 60km × 60km	27km × 27km	0,25° Lat. 0,5° Lon.	0,25° Lat. 0,5° Lon.	55km x 55km
Projection	Polar stereographic (a sub-grid of the EMEP grids)	60º shifted pole (as HIRLAM)	Lambert	Geographic	Geographic	latitude-longitude grid with shifted pole

	DEM	EUROS	EURAD/ FFA	LOTOS	REM3/ CALGRID	MATCH
LowerLeft Coordinates	(40.38, -24.68)	36.31, -9.43	(33.75, -8.86)	(35, -10)	(42, -10)	(31.8, -20.4)
LowerRight Coordinates	(24.07, 13.00)	33.42, 22.53	(33.75, 24.86)	(35, 60)	(42, 30)	(24.4, 22.0)
UpperRight Coordinates	(40.38, 50.68)	60.21, 43.99	(61.95, 37.52)	(70, 60)	(62, 30)	(57.4, 65.0)
UpperLeft Coordinates	(80.48, 13.00)	65.87, -20.38	(61.95, -21.52)	(70, –10)	(62, -10)	(74.6, -48.0)

10.4 Construction of daily averages

DEM: Daily averages are based on 15 min. concentration output. Averaging was performed from midnight to midnight.

EUROS: Daily averages are based on hourly output. Averaging was performed from 6:00 to 6:00.

EURAD: Daily averages are based on hourly output. Averaging was performed from midnight to midnight.

LOTOS: Daily averages are based on hourly output. Averaging was performed from 6:00 to 6:00.

REM3/CALGRID: Daily averages are based on hourly output. Averaging was performed from midnight to midnight.

MATCH: Daily averages are based on hourly output. Averaging was performed from midnight to midnight.

It should be noted here that the measurement data used in this study is not coherent in the way as the daily average is defined. Data from three measurement networks are used but even within the largest network, i.e. the EMEP network, the measurement interval for the daily average is varying substantially within the different national sub-networks. Also the averaging procedure within the models varies as listed above.

The impact towards the model evaluation and comparison due to these averaging differences can not be detailed here. A first estimate would be that the individual daily averages would be affected most and the impact would be decreasing the longer the considered time period would be for the averaging. As a consequence, some of the performance measures have been formulated such that the long time average is taken into account. However, for several measures the uncertainty due to different averaging procedures should be reminded in the discussions.

10.5 Performance metrics

Performance measures are commonly based on pairs of model (M) and observed (O) values. The pairs can be formed from time series for a given measurement station or from a collection of spatially distributed sites at a given time. Difference statistics using these pairs are most appropriated for model performance analysis.

The total set of selected stations is S = 56 whereas the total number of days is D = 181. However, it must be noted that not all sites measured all compounds nor did they measure perfectly over the whole time period.

We define the ratio of model results $M_{s,d}$ and results from observations $O_{s,d}$ as

$$Ratio = \frac{\sum_{s=1}^{S}\sum_{d=1}^{D} M_{s,d}}{\sum_{s=1}^{S}\sum_{d=1}^{D} O_{s,d}} = \frac{\overline{M}}{\overline{O}}.$$

The residual is the sum of the absolute deviations of model results and results from observations

$$\mathrm{Re}sidual = \frac{1}{S}\sum_{s=1}^{S}\frac{1}{D}\sum_{d=1}^{D}\left|M_{s,d} - O_{s,d}\right|.$$

The root mean square error is defined as

$$RMSE = \frac{1}{S}\sum_{s=1}^{S}\sqrt{\frac{1}{D}\sum_{d=1}^{D}\left(M_{s,d} - O_{s,d}\right)^2}.$$

The normalized ratio of standard deviation (given in the above tables as sigma (model/meas)) is

$$\sigma^* = \frac{1}{S}\sum_{1}^{S}\frac{\overline{O_s}}{\overline{M_s}} * \frac{\sigma_{s,M}}{\sigma_{s,O}} \quad \text{with the standard deviation } \sigma \text{ as} \quad \sigma_{s,O} = \sqrt{\frac{1}{D}\sum_{1}^{D}(O_{s,d} - \overline{O_s})}$$

and the observed mean at a station s

$$\overline{O_s} = \frac{1}{D}\sum_{1}^{D} O_{s,d} \quad \text{and with a similar definition for the modeled mean.}$$

The average correlation coefficient rho is defined as

$$rho = \frac{1}{S}\sum_{s=1}^{S} rho_s$$

using the correlation in time at the individual stations

$$rho_s = \frac{\sum_{d=1}^{D}(O_{s,d} - \overline{O}_s)(M_{s,d} - \overline{M}_s)}{\sigma_{s,O} * \sigma_{s,M}}.$$

The fractional difference (sometimes also referred to as Mean Relative Error) for a station s is defined as:

$$FD_s = \frac{1}{D}\sum_{d=1}^{D}\frac{M_{s,d} - O_{s,d}}{M_{s,d} + O_{s,d}}.$$

The percentage within a factor of 2 is given as number of days where

$$0.5 \le \frac{M_{s,d}}{O_{s,d}} \le 2.$$

10.6 Measurement stations

Table 10.4. Selected measurement stations which operated in the model domain in 1995. Height in m above sea level. The code XX/OO indicates, that the station is located in all domains whereas a station with X/O is located in all but REM3. A XX or X denotes available observations whereas a OO or O indicates that the observation has been calculated using observations.

ID	Name	Lat	Lon	Height	SO_2	SO_4	NO_2	HNO_3	NO_3	TNO_3	NH_3	NH_4	TNHx
CH02	Payerne	46.80	6.95	510	XX	XX	XX	-	-	XX	-	-	XX
CH03	Taenikon	47.48	8.90	540	XX	XX	XX	-	-	-	-	-	-
CS01	Svratouch	49.73	16.03	737	XX	XX	XX	XX	XX	OO	XX	XX	OO
CS03	Kosetice	49.58	15.08	534	XX	XX	XX	XX	XX	OO	XX	XX	OO
DE01	Westerland	54.92	8.30	12	XX	XX	XX	-	-	-	-	-	-
DE02	Langenbrugge	52.80	10.75	74	XX	XX	XX	-	-	-	-	-	-
DE04	Deuselbach	49.77	7.05	480	XX	XX	XX	-	-	-	-	-	-
DE06	Arkona	54.68	13.43	42	-	-	-	-	-	-	-	-	-
DE07	Neuglobsow	53.15	13.03	62	XX	XX	XX	-	-	-	-	-	-
DE09	Zingst	54.43	12.73	1	XX	XX	XX	-	-	-	-	-	-
DE12	Bassum	52.85	8.72	52	XX	XX	-	-	-	-	-	-	-
DE98	Melpitz	51.53	12.90	87	-	XX	-	-	XX	-	-	XX	-
DE99	Muencheberg	52.51	14.10	12	-	XX	-	-	XX	-	-	XX	-
DK03	Tange	56.35	9.60	13	XX	XX	-	-	-	XX	-	-	XX
DK05	Keldsnor	54.73	10.73	9	XX	XX	-	-	-	XX	-	-	XX
DK08	Anholt	56.72	11.52	40	XX	XX	XX	-	-	XX	-	-	XX
DK31	Ulborg	56.28	8.43	10	-	-	-	-	-	-	-	-	-
DK32	Frederiksborg	55.97	11.33	10	-	-	-	-	-	-	-	-	-
ES01	Toledo	39.55	-4.35	917	X	X	X	-	-	X	-	X	X
ES03	Roquetas	40.82	-0.50	50	X	X	X	-	-	X	-	X	X
ES04	Logrono	42.45	-2.35	370	X	X	X	-	-	X	-	X	X
ES06	Mahon	39.90	4.25		X	X	X	-	-	X	-	X	X
FI04	Ahtari	62.55	24.22	162	X	X	X	-	-	X	-	-	X
FI07	Virolahti	60.52	27.68	8	-	-	-	-	-	-	-	-	-
FI09	Uto	59.78	21.38	7	XX	XX	XX	-	-	XX	-	-	XX
FR05	La Hague	49.62	-1.83	133	XX	XX	-	-	-	-	-	-	-
FR09	Revin	49.90	4.63	390	XX	XX	-	-	-	-	-	-	-
GB02	Eskdalemuir	55.32	-3.20	243	XX	XX	-	-	-	XX	-	-	XX
GB04	Stoke Ferry	52.57	0.50	15	XX	XX	-	-	-	-	-	-	-
GB07	Barcombe Mills	50.87	-0.03	8	XX	XX	-	-	-	-	-	-	-
GB13	Yarner Wood	50.60	-3.72	119	XX	XX	-	-	-	-	-	-	-
GB14	High Muffles	54.33	-0.80	267	XX	XX	-	-	-	XX	-	-	XX
GB16	Glen Dye	56.97	-2.42	85	XX	XX	-	-	-	-	-	-	-
GR01	Aliartos	38.37	23.08	110	X	X	-	-	-	-	-	-	-
HU02	K-puszta	46.97	19.58	125	XX	XX	-	XX	XX	OO	XX	XX	OO
IT01	Montelibretti	42.10	12.63	48	X	X	-	X	X	O	-		-
IT04	Ispra	45.80	8.63	209	XX	XX	XX	-	-	XX	-	XX	-
LT15	Preila	55.35	21.07	5	XX	XX	XX	-	-	XX	XX	XX	OO
LV10	Rucava	56.22	21.22	18	XX	XX	XX	-	-	XX	-	XX	XX
LV16	Zoseni	57.13	25.92	183	XX	XX	XX	-	-	XX	-	XX	-
NL01	De Zilk	52.29	4.51	4	-	XX	-	-	XX	-	-	XX	-
NL02	Wieringerwerf	52.80	5.00	0	-	XX	-	-	XX	-	-	XX	-
NL08	Bilthoven	52.12	5.20	5	-	XX	-	-	XX	-	-	XX	-

ID	Name	Lat	Lon	Height	SO_2	SO_4	NO_2	HNO_3	NO_3	TNO_3	NH_3	NH_4	TNHx
NL09	Kollumerwaard	53.33	6.28	0	XX	XX	XX	-	XX	-	-	XX	-
NL10	Vreedepeel	51.53	5.85	28	XX	XX	XX	-	XX	-	XX	XX	OO
NO01	Birkenes	58.38	8.25	190	XX	XX	XX	-	-	XX	-	-	XX
NO08	Skreaadalen	58.82	6.72	475	XX	XX	XX	-	-	XX	-	-	XX
NO15	Tustervatn	65.83	13.92	439	X	X	X	-	-	X	-	-	X
NO39	Krvatn	62.78	8.88	210	X	X	X	-	-	X	-	-	X
NO41	Osen	61.25	11.78	440	XX	XX	XX	-	-	XX	-	-	XX
PL02	Jarczew	51.32	21.98	180	XX	XX	XX	-	-	XX	-	XX	XX
PL04	Leba	54.75	17.53	2	XX	XX	XX	-	-	XX	-	XX	XX
PL05	Diabla Gora	54.15	22.07	157	XX	XX	XX	-	-	XX	-	-	XX
SE02	Roervik	57.42	11.93	10	XX	XX	XX	-	-	XX	-	-	XX
SE05	Bredkaelen	63.85	15.33	404	X	X	X	-	-	X	-	-	X
SE08	Hoburg	56.92	18.15	58	X	X	X	-	-	-	-	-	-
SE11	Vavihill	56.02	13.15	172	X	X	X	-	-	X	-	-	X
SE12	Aspvreten	58.80	17.38	20	X	X	X	-	-	X	-	-	X
SK06	Starina	49.05	22.27	345	X	-	-	-	-	X	-	-	-

Figure 10.1. Location of the measurement sites of the EMEP network and additional sites from Dutch and German networks.

10.7 Emission inventories used by the models

Table 10.5. Summary of emissions [kilotonnes/year] for particulate matter (PM) and sulfur dioxide. Only countries that are fully covered by the REM3/CALGRID domain are given to allow a comparison.

PM	EURAD/FFA	EUROS	LOTOS	REM3	DEM	MATCH
Austria	41	27	47	42	0	0
Belgium	84	66	93	78	0	0
Switzerland	26	20	24	21	0	0
Czech Rep. & Slovakia	522	290	166	63	0	0
Germany	818	446	386	482	0	0
Denmark	56	24	37	46	0	0
France	399	343	486	657	0	0
Great Britain	276	203	289	360	0	0
Hungary	111	85	60	58	0	0
Ireland	23	28	24	32	0	0
Netherlands	90	47	72	127	0	0
Poland	1042	810	314	397	0	0
Romenia	227	221	187	201	0	0
Former Yugoslavia	293	205	186	216	0	0
Baltic States	161	135	66	99	0	0
Sum / 10	417	295	244	288	0	0

SO_2	EURAD/FFA	EUROS	LOTOS	REM3	DEM	MATCH
Austria	64	60	60	60	60	57
Belgium	290	247	252	252	247	240
Switzerland	34	34	29	34	34	26
Czech Rep. & Slovakia	1330	1330	1329	1091	1330	903
Germany	860	2128	2998	2998	2130	1467
Denmark	226	150	148	149	150	109
France	748	988	943	947	989	1031
Great Britain	2556	2354	2365	2365	2352	1656
Hungary	705	705	883	883	705	657
Ireland	195	161	161	161	161	165
Netherlands	119	144	147	147	147	124
Poland	2376	2337	2276	2276	2337	2181
Romenia	912	912	1064	1064	912	912
Former Yugoslavia	1146	1230	391	273	1124	1219
Baltic States	208	255	320	417	255	255
Sum / 10	1177	1304	1337	1312	1293	1100

Table 10.6. Summary of emissions [kilotonnes/year] for volatile organic compounds (VOC) and nitrogen dioxide. Only countries which are fully covered by the REM3/CALGRID domain are given to allow a comparison.

VOC	EURAD/FFA	EUROS	LOTOS	REM3	DEM	MATCH
Austria	294	283	406	406	283	253
Belgium	283	304	334	334	304	324
Switzerland	211	203	205	211	203	195
Czech Rep. & Slovakia	405	405	327	286	405	377
Germany	2230	1993	2532	2532	1993	1807
Denmark	129	150	133	133	150	137
France	2016	2223	2179	2179	2223	2570
Great Britain	2426	2250	2297	2297	2250	1954
Hungary	150	147	148	148	147	145
Ireland	78	91	175	175	91	105
Netherlands	393	362	365	365	365	340

Poland	769	735	770	770	735	774
Romenia	505	465	477	477	465	505
Former Yugoslavia	259	282	464	422	275	276
Baltic States	312	108	603	603	356	173
Sum / 10	1046	1000	1142	1134	1025	994

NOx	**EURAD/FFA**	**EUROS**	**LOTOS**	**REM3**	**DEM**	**MATCH**
Austria	187	175	176	176	175	172
Belgium	259	339	350	350	339	334
Switzerland	136	133	128	136	136	125
Czech Rep. & Slovakia	593	593	593	412	593	546
Germany	2307	1932	2266	2266	1932	1803
Denmark	234	250	250	250	250	248
France	1706	1664	1724	1726	1666	1641
Great Britain	2283	2227	2295	2295	2227	1848
Hungary	190	180	190	190	180	198
Ireland	99	115	115	115	115	124
Netherlands	436	495	498	498	514	470
Poland	1120	1120	1122	1122	1120	1158
Romenia	319	319	342	342	319	319
Former Yugoslavia	276	300	3679	3712	261	297
Baltic States	147	146	255	637	337	137
Sum / 10	1029	999	1398	1423	1016	942

Table 10.7. Summary of emissions [kilotonnes/year] for ammonia (NH_3) and carbon monoxide. Only countries which are fully covered by the REM3/CALGRID domain are given to allow a comparison.

NH_3	**EURAD/FFA**	**EUROS**	**LOTOS**	**REM3**	**DEM**	**MATCH**
Austria	78	0	79	79	87	75
Belgium	97	0	96	96	97	97
Switzerland	71	0	60	60	71	71
Czech Rep. & Slovakia	131	0	167	137	131	131
Germany	646	0	623	623	649	648
Denmark	114	0	99	99	114	102
France	668	0	795	795	668	668
Great Britain	321	0	324	324	320	323
Hungary	116	0	62	62	116	76
Ireland	124	0	124	124	124	132
Netherlands	146	0	147	147	152	145
Poland	380	0	379	379	380	350
Romenia	221	0	204	204	221	221
Former Yugoslavia	185	0	176	155	175	184
Baltic States	157	0	56	124	221	81
Sum / 10	346	0	339	341	353	330

CO	**EURAD/FFA**	**EUROS**	**LOTOS**	**REM3**	**DEM**	**MATCH**
Austria	1526	0	1147	1147	764	1012
Belgium	787	0	1515	1515	821	1434
Switzerland	510	0	500	510	548	458
Czech Rep. & Slovakia	1275	0	1273	874	1094	1222
Germany	9353	0	6797	6797	5381	6374
Denmark	654	0	588	588	405	557
France	8156	0	8421	8421	6002	8850
Great Britain	5669	0	5478	5478	6075	4610
Hungary	761	0	767	768	397	721
Ireland	279	0	304	304	246	333

Netherlands	1240	0	892	892	986	842
Poland	4547	0	4548	4548	1985	4700
Romenia	2325	0	2923	2924	1256	2325
Former Yugoslavia	941	0	1840	1749	743	992
Baltic States	1530	0	1605	3322	961	817
Sum / 10	3955	0	3860	3984	2766	3525

10.8 Statistics for the mean values at the observing sites

Table 10.8. Observed and modeled mean values for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	Obser-vation	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	3.30	2.53	4.73	2.05	2.44	1.38	2.17
CH03	3.38	2.56	5.65	1.55	2.65	1.58	2.31
CS01	4.40	6.89	9.91	7.16	4.59	6.22	3.99
CS03	3.80	5.82	9.38	8.06	4.80	5.51	4.26
DE01	2.99	3.49	4.71	2.69	2.84	2.54	2.56
DE02	2.47	4.88	6.33	5.41	4.19	3.81	3.70
DE04	3.06	4.74	7.34	3.83	4.60	4.03	4.39
DE07	2.29	5.67	6.44	6.54	4.01	3.73	3.85
DE09	1.96	3.32	5.65	3.43	3.71	3.17	3.29
DE12	2.57	4.42	5.96	4.75	4.69	3.51	3.92
De98	6.04	9.36	8.44	10.45	4.72	6.34	4.32
De99	4.97	6.80	7.81	6.86	4.25	4.77	3.79
DK03	3.77	2.54	3.94	1.90	2.28	1.99	2.27
DK05	5.02	2.95	5.05	3.18	3.36	2.78	3.10
DK08	4.08	1.97	4.00	1.73	2.60	2.25	2.22
FI09	2.29	0.87	3.23	0.57	1.62	1.89	1.40
FR05	1.28	4.19	4.89	3.59	2.98	3.93	3.26
FR09	4.37	4.94	6.97	3.36	3.99	4.38	3.68
GB02	2.50	3.38	3.31	1.91	2.19	1.67	2.14
GB04	3.59	9.36	5.18	3.95	3.52	2.94	3.19
GB07	4.48	6.91	5.46	3.91	3.45	3.67	2.98
GB13	5.00	4.57	4.64	3.10	2.49	3.09	2.49
GB14	3.37	8.06	4.01	2.64	3.03	2.25	2.68
GB16	2.61	1.90	3.08	1.23	2.09	1.48	1.84
IT04	4.96	3.52	4.42	8.50	3.00	1.76	2.39
LT15	4.31	2.02	5.08	2.01	2.55	2.24	2.16
LV10	2.94	1.66	4.52	1.60	2.44	2.03	2.02
LV16	3.13	1.31	3.89	1.09	1.83	1.52	1.70
nl01	3.66	5.43	5.56	3.98	4.20	3.42	3.63
nl02	4.90	5.25	5.10	4.05	3.65	3.07	3.19
NL08	4.38	5.93	5.86	4.42	4.10	3.57	3.88
NL09	3.59	4.77	5.20	3.62	3.56	3.09	3.17
NL10	4.42	6.33	6.55	4.49	4.92	4.53	4.32
NO01	1.96	0.79	2.81	0.76	1.63	1.31	1.74
NO08	1.65	0.89	2.35	0.51	1.51	1.21	1.71
NO41	1.19	0.35	1.89	0.16	1.08	0.69	1.19
PL02	5.08	4.59	8.29	4.81	5.08	4.33	2.97
PL04	5.41	2.39	5.43	3.43	2.91	2.81	2.68
PL05	2.37	2.71	5.35	2.25	2.80	2.53	2.23
SE02	2.73	1.41	3.75	1.35	2.15	1.86	1.96
SE08	2.48	1.23	4.00	1.22	2.26	2.06	1.88
SE11	2.92	2.09	4.72	2.01	2.58	2.26	2.42
SE12	2.07	0.81	3.17	0.73	1.67	1.45	1.53

SK06	5.33	4.25	8.88	5.83	4.70	4.17	2.99
Mean	3.48	3.86	5.29	3.42	3.17	2.93	2.81

Table 10.9. Residue for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	2.63	2.43	1.83	1.57	2.03	1.63
CH03	2.85	2.92	2.37	1.57	1.94	1.70
CS01	4.59	5.87	4.31	2.05	2.52	2.11
CS03	3.85	5.91	5.41	2.05	2.37	2.04
DE01	2.93	2.63	2.27	1.72	1.41	1.66
DE02	3.44	4.21	4.20	1.99	1.73	1.64
DE04	3.35	4.47	2.57	2.05	1.49	2.09
DE07	4.26	4.32	4.83	2.04	1.75	1.92
DE09	2.54	3.89	2.46	1.94	1.43	1.65
DE12	3.16	3.78	3.58	2.45	1.54	1.96
De98	5.43	4.10	6.18	2.33	1.97	2.75
De99	5.06	4.23	4.56	2.08	1.94	2.25
DK03	2.61	1.88	2.61	2.06	1.92	2.15
DK05	3.20	2.44	3.01	2.48	2.36	2.60
DK08	2.97	2.03	2.87	2.10	1.96	2.23
FI09	1.56	1.74	1.79	1.11	1.02	1.28
FR05	3.34	3.69	2.61	1.88	2.76	2.12
FR09	3.68	4.15	2.73	2.33	1.84	2.34
GB02	2.08	1.78	1.38	1.30	1.02	1.14
GB04	6.81	2.97	2.07	1.71	1.32	1.54
GB07	4.54	2.95	2.27	2.04	1.55	2.08
GB13	3.66	3.24	3.19	3.22	2.88	3.10
GB14	5.36	2.58	1.79	1.53	1.40	1.43
GB16	1.81	1.69	1.66	1.27	1.36	1.23
IT04	3.10	2.97	4.88	2.68	3.31	2.95
LT15	3.55	3.05	3.06	2.43	2.54	2.65
LV10	2.26	2.61	2.07	1.60	1.49	1.73
LV16	2.67	2.59	2.34	1.90	2.08	2.11
nl01	3.67	3.07	2.19	1.72	1.35	1.63
nl02	3.50	2.96	2.88	2.03	2.24	2.19
NL08	3.84	2.74	2.26	1.78	1.31	1.82
NL09	3.29	2.67	2.41	1.76	1.17	1.73
NL10	4.28	3.59	2.56	2.38	1.70	2.04
NO01	1.49	1.32	1.58	1.17	0.87	1.31
NO08	1.23	1.21	1.42	0.89	0.78	1.00
NO41	0.96	1.12	1.03	0.68	0.70	0.80
PL02	3.19	4.63	3.41	2.76	2.43	2.67
PL04	3.99	3.79	3.68	3.32	3.25	3.22
PL05	2.38	3.36	1.79	1.57	1.35	1.53
SE02	2.00	1.96	2.08	1.42	1.30	1.71
SE08	1.75	2.20	1.74	1.44	1.12	1.44
SE11	2.20	2.57	1.86	1.44	1.22	1.63
SE12	1.41	1.78	1.43	1.13	0.92	1.38
SK06	2.76	4.01	3.47	2.27	2.01	2.69
Mean	3.16	3.05	2.74	1.89	1.74	1.93

Table 10.10. RMSE for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	4.20	3.02	2.33	2.15	2.64	2.23
CH03	4.32	3.95	3.00	2.22	2.62	2.43
CS01	6.62	7.42	6.79	3.03	3.29	3.05
CS03	6.32	7.43	8.29	2.86	3.28	2.75
DE01	7.62	3.85	3.36	2.45	1.81	2.20
DE02	7.33	5.63	9.13	2.90	2.63	2.38
DE04	6.16	5.85	4.24	3.04	2.15	3.25
DE07	11.05	6.02	9.02	3.16	2.46	3.21
DE09	5.44	5.62	4.82	3.07	2.03	2.76
DE12	6.41	5.38	8.07	3.44	2.44	2.76
De98	11.31	5.79	11.42	3.39	3.14	3.91
De99	11.32	5.83	7.68	3.25	3.10	3.48
DK03	3.96	2.76	3.44	2.82	2.54	3.07
DK05	4.45	3.35	4.06	3.16	3.02	3.50
DK08	3.96	2.81	3.61	2.77	2.53	3.08
FI09	2.18	3.02	2.39	1.63	1.55	1.86
FR05	7.30	4.78	4.32	2.89	3.78	2.86
FR09	7.20	5.66	4.34	3.96	3.13	3.89
GB02	4.03	2.47	2.09	1.99	1.48	1.69
GB04	14.21	3.96	3.48	2.72	2.26	2.45
GB07	10.18	3.70	3.48	2.84	2.25	2.77
GB13	8.49	4.84	4.90	4.98	4.40	4.79
GB14	10.02	3.55	2.50	2.24	2.00	2.03
GB16	2.80	2.42	2.32	1.97	1.99	1.98
IT04	4.56	3.88	7.84	3.80	4.36	4.07
LT15	5.16	4.48	4.33	3.55	3.67	4.01
LV10	3.35	3.81	3.00	2.35	2.24	2.55
LV16	4.35	3.93	3.59	3.00	3.25	3.25
nl01	7.85	4.30	3.71	2.32	1.86	2.19
nl02	5.75	3.93	4.86	2.95	3.02	3.18
NL08	9.06	3.81	4.07	2.57	1.92	2.53
NL09	6.05	3.74	4.46	2.48	1.54	2.36
NL10	10.21	4.72	4.09	3.50	2.54	2.96
NO01	2.39	2.16	2.51	1.85	1.29	1.91
NO08	1.92	1.94	2.34	1.50	1.20	1.62
NO41	1.50	1.81	1.60	1.10	1.06	1.14
PL02	4.14	6.29	4.58	3.46	2.92	3.33
PL04	5.62	4.95	4.91	4.35	4.34	4.36
PL05	5.19	5.14	2.78	2.46	2.25	2.37
SE02	2.92	3.08	2.94	2.12	1.89	2.36
SE08	2.44	3.41	2.50	2.20	1.75	2.19
SE11	4.06	4.20	2.81	2.21	1.80	2.37
SE12	2.09	2.85	2.04	1.71	1.39	1.92
SK06	3.42	5.39	5.00	3.00	2.59	3.26
Mean	5.89	4.25	4.39	2.76	2.49	2.78

Table 10.11. Correlation coefficient rho for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	0.19	0.49	0.49	0.39	0.42	0.39
CH03	0.14	0.54	0.27	0.37	0.45	0.33
CS01	0.39	0.52	0.36	0.49	0.65	0.46
CS03	0.38	0.33	0.30	0.49	0.56	0.49
DE01	0.28	0.52	0.55	0.51	0.67	0.52
DE02	0.47	0.61	0.43	0.69	0.76	0.70
DE04	0.25	0.63	0.28	0.54	0.67	0.44
DE07	0.42	0.59	0.57	0.68	0.73	0.60
DE09	0.45	0.58	0.40	0.61	0.79	0.56
DE12	0.41	0.54	0.38	0.60	0.72	0.56
De98	0.44	0.54	0.61	0.66	0.70	0.56
De99	0.29	0.54	0.50	0.58	0.59	0.52
DK03	0.54	0.70	0.56	0.58	0.77	0.47
DK05	0.57	0.64	0.60	0.66	0.82	0.58
DK08	0.50	0.67	0.51	0.62	0.80	0.53
FI09	0.42	0.64	0.42	0.62	0.64	0.45
FR05	0.09	0.54	0.59	0.46	0.62	0.48
FR09	0.18	0.20	0.20	0.27	0.51	0.26
GB02	0.53	0.59	0.64	0.57	0.81	0.64
GB04	0.14	0.35	0.52	0.53	0.63	0.58
GB07	0.19	0.37	0.57	0.57	0.71	0.59
GB13	0.34	0.35	0.47	0.35	0.50	0.44
GB14	0.59	0.36	0.69	0.69	0.80	0.73
GB16	0.63	0.63	0.68	0.63	0.73	0.65
IT04	0.34	0.20	0.68	0.33	0.44	0.35
LT15	0.21	0.41	0.35	0.46	0.47	0.26
LV10	0.35	0.52	0.45	0.55	0.63	0.45
LV16	0.06	0.33	0.17	0.36	0.25	0.11
nl01	0.42	0.47	0.64	0.76	0.77	0.73
nl02	0.42	0.43	0.62	0.67	0.70	0.62
NL08	0.37	0.68	0.69	0.72	0.84	0.69
NL09	0.51	0.56	0.58	0.63	0.86	0.66
NL10	0.36	0.57	0.54	0.63	0.73	0.64
NO01	0.39	0.78	0.40	0.58	0.86	0.51
NO08	0.48	0.72	0.22	0.62	0.79	0.58
NO41	0.32	0.66	0.36	0.61	0.69	0.51
PL02	0.38	0.52	0.28	0.36	0.44	0.48
PL04	0.26	0.33	0.43	0.32	0.36	0.38
PL05	0.28	0.54	0.31	0.41	0.40	0.25
SE02	0.44	0.63	0.42	0.57	0.70	0.43
SE08	0.56	0.55	0.43	0.48	0.68	0.43
SE11	0.41	0.59	0.55	0.57	0.75	0.47
SE12	0.45	0.52	0.56	0.53	0.74	0.35
SK06	0.54	0.60	0.41	0.45	0.48	0.50
Mean	0.37	0.52	0.47	0.54	0.65	0.50

Table 10.12. Percentage of data within 50% for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	32.60	55.25	45.30	67.40	37.57	60.77
CH03	32.78	57.22	27.22	70.00	46.11	62.78
CS01	42.33	36.20	55.21	73.62	74.23	72.39
CS03	47.22	32.22	46.67	77.22	73.33	74.44
DE01	37.02	56.91	38.67	58.01	61.88	56.91
DE02	46.67	34.44	39.44	63.33	68.33	68.33
DE04	49.72	35.91	53.04	72.93	79.56	71.27
DE07	50.28	32.60	41.44	55.80	60.77	64.09
DE09	41.44	30.94	47.51	63.54	61.88	68.51
DE12	47.51	43.09	43.65	54.70	72.93	56.91
De98	58.99	66.85	52.25	74.72	87.08	66.85
De99	48.84	51.74	51.16	76.74	76.16	69.19
DK03	28.30	70.44	22.01	44.65	35.85	51.57
DK05	32.00	68.00	34.86	52.57	50.86	53.71
DK08	19.89	62.98	18.78	48.07	49.72	48.62
FI09	32.16	59.06	20.47	65.50	66.67	58.48
FR05	34.73	17.37	35.93	40.12	26.35	28.14
FR09	53.63	49.16	51.40	74.86	79.33	65.36
GB02	54.91	53.76	54.34	65.90	66.47	73.41
GB04	54.76	49.40	67.26	74.40	79.76	76.19
GB07	61.80	61.80	63.48	69.66	77.53	57.30
GB13	48.72	57.05	44.23	41.67	57.05	49.36
GB14	48.28	51.15	50.00	74.14	63.79	69.54
GB16	27.62	64.64	21.55	68.51	48.62	71.82
IT04	41.44	56.91	51.38	55.80	32.60	45.30
LT15	24.28	53.76	28.90	47.98	43.93	42.20
LV10	28.49	50.58	36.63	54.07	59.88	55.81
LV16	30.70	53.51	30.70	48.25	44.74	41.23
nl01	50.65	53.90	53.90	73.38	75.32	71.43
nl02	51.48	57.40	47.93	73.96	56.21	66.27
NL08	58.01	63.54	65.75	74.59	82.87	77.90
NL09	51.55	62.11	45.34	67.70	79.50	64.60
NL10	56.43	58.57	60.00	70.71	77.14	67.86
NO01	24.02	60.89	20.11	57.54	55.31	48.60
NO08	23.16	54.80	7.91	66.67	54.24	62.71
NO41	17.65	49.41	11.18	56.47	44.12	51.76
PL02	50.34	49.66	48.99	59.06	61.07	50.34
PL04	28.73	47.51	35.36	42.54	44.20	41.99
PL05	46.20	39.77	45.61	63.16	72.51	58.48
SE02	29.55	60.80	21.59	56.25	55.11	44.32
SE08	29.61	55.87	31.84	58.10	63.69	58.10
SE11	36.46	56.91	39.23	72.93	71.27	61.33
SE12	31.46	57.30	32.02	60.11	64.04	47.19
SK06	52.51	68.72	54.75	72.63	73.74	51.40
Mean	40.79	52.50	40.80	62.73	61.67	59.20

Table 10.13. Ratio of standard deviation (Observation/Model Result) for SO_4 per station (April 2 - Sep 29, 1995).

SO_4	DEM	EURAD/-FFA	EUROS	LOTOS	MATCH	REM3
CH02	2.01	1.50	0.95	0.75	0.52	0.69
CH03	1.86	1.80	0.84	0.69	0.53	0.73
CS01	2.29	2.01	2.28	1.06	1.21	1.00
CS03	3.25	2.61	3.75	1.52	1.70	1.55
DE01	4.42	2.24	2.22	1.57	1.32	1.37
DE02	4.38	2.84	5.35	1.83	1.89	1.64
DE04	3.54	2.79	2.49	1.81	1.50	1.90
DE07	7.54	3.45	5.94	2.33	1.90	2.34
DE09	4.04	3.44	3.50	2.19	1.76	2.05
DE12	4.02	2.92	5.00	2.03	1.89	1.76
De98	2.98	1.55	3.11	0.86	1.02	0.83
De99	3.17	1.63	2.33	0.85	0.83	0.76
DK03	1.57	1.36	1.16	0.82	0.70	0.80
DK05	1.37	1.24	1.29	0.86	0.67	0.82
DK08	1.29	1.31	0.93	0.83	0.72	0.68
FI09	0.51	2.02	0.37	0.83	0.93	0.54
FR05	5.69	3.07	3.58	2.23	2.78	2.00
FR09	2.03	1.28	0.94	0.90	0.80	0.81
GB02	2.18	1.35	1.22	1.03	0.80	0.81
GB04	5.03	1.39	1.54	1.14	0.91	1.02
GB07	3.71	1.31	1.54	1.10	1.03	0.90
GB13	1.96	0.86	0.93	0.48	0.63	0.42
GB14	3.69	1.21	1.17	1.04	0.77	0.85
GB16	1.45	1.24	0.92	0.81	0.71	0.61
IT04	1.26	0.83	2.68	0.62	0.37	0.56
LT15	1.13	1.32	0.86	0.60	0.49	0.46
LV10	1.06	1.52	0.93	0.80	0.61	0.57
LV16	1.01	1.28	0.46	0.48	0.40	0.32
nl01	3.06	1.56	1.74	1.26	0.99	1.13
nl02	1.90	1.21	1.84	0.98	0.82	0.84
NL08	3.32	1.65	1.90	1.28	1.11	1.14
NL09	2.67	1.59	2.12	1.22	1.10	1.17
NL10	3.50	1.67	1.57	1.44	1.20	1.22
NO01	0.72	1.48	0.89	0.86	0.76	0.76
NO08	0.96	1.47	0.84	0.95	0.96	1.00
NO41	0.55	1.73	0.15	0.94	0.78	0.74
PL02	1.49	2.21	1.56	1.14	0.86	0.67
PL04	1.18	1.35	1.31	0.64	0.65	0.62
PL05	2.41	2.23	1.12	1.02	0.83	0.70
SE02	1.08	1.59	1.04	0.85	0.78	0.72
SE08	0.96	1.59	0.69	0.85	0.75	0.58
SE11	1.67	1.84	1.17	0.82	0.73	0.69
SE12	0.58	1.65	0.49	0.81	0.72	0.68
SK06	1.75	2.26	2.47	1.43	1.06	1.05
Mean	2.41	1.78	1.80	1.10	0.99	0.97

Table 10.14. Observed and modeled mean values for TNHx per station (April 2 - Sept. 29, 1995).

TNHx	Observations	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	5.19	3.99	8.82		2.94	6.42	4.95
CS01	3.31	5.11	6.61		3.62	5.50	5.09
CS03	4.74	4.92	6.70		3.76	4.60	5.59
DK03	4.50	3.65	6.86		3.96	4.10	8.09
DK05	4.39	4.09	4.82		2.16	4.31	2.12
DK08	2.00	2.31	2.95		1.46	2.33	1.19
FI09	0.63	0.83	1.68		0.57	0.52	0.62
GB02	1.64	2.88	3.84		2.30	3.55	3.94
GB14	2.41	3.33	2.58		2.10	3.26	3.03
LT15	1.84	2.57	4.97		1.31	1.30	2.72
LV10	1.47	2.09	4.72		1.09	1.22	1.29
NL10	31.07	8.48	17.30		8.96	14.34	16.56
NO01	0.80	0.74	1.31		0.73	0.53	0.76
NO08	2.34	0.87	1.09		0.66	0.64	0.81
NO41	0.45	0.36	0.71		0.60	0.41	0.91
PL02	4.37	5.33	7.37		3.15	5.14	4.57
PL04	2.00	2.60	3.15		1.32	1.52	1.30
PL05	2.33	3.42	4.66		2.18	2.85	5.13
SE02	1.46	1.76	2.72		1.07	1.40	0.89
SE11	1.87	2.57	3.69		1.61	2.12	2.02
SE12	0.80	0.99	1.92		0.77	0.85	1.01

Table 10.15. Residue for TNHx per station (April 2 - Sep 29, 1995).

TNHx	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	2.89	3.88		2.53	2.49	2.37
CS01	2.84	3.33		1.33	2.44	2.30
CS03	3.20	2.76		1.86	1.87	2.36
DK03	2.39	2.76		1.77	1.75	4.09
DK05	2.51	1.66		2.27	1.62	2.39
DK08	1.54	1.17		0.88	1.08	1.03
FI09	0.49	1.10		0.27	0.24	0.46
GB02	1.49	2.26		1.09	1.96	2.54
GB14	1.87	1.48		0.93	1.49	1.49
LT15	1.89	3.22		0.93	0.93	1.52
LV10	1.34	3.25		0.67	0.53	0.74
NL10	22.87	14.74		22.10	16.88	15.58
NO01	0.60	0.60		0.44	0.36	0.55
NO08	1.75	1.48		1.76	1.72	1.62
NO41	0.33	0.36		0.28	0.21	0.60
PL02	2.84	3.32		1.79	1.96	1.93
PL04	1.59	1.60		0.92	0.80	1.03
PL05	2.41	2.57		1.15	1.41	3.34
SE02	1.17	1.38		0.62	0.65	0.78
SE11	1.48	1.89		0.76	0.78	0.96
SE12	0.62	1.14		0.41	0.37	0.60

Table 10.16. RMSE for TNHx per station (April 2 - Sept. 29 1995).

TNHx	DEM	EURAD/	EUROS	LOTOS	MATCH	REM3

		FFA			
CH02	3.86	4.69	3.27	3.24	2.94
CS01	3.72	3.85	1.71	2.91	3.09
CS03	4.00	3.35	2.47	2.44	3.02
DK03	3.01	3.68	2.51	2.36	5.42
DK05	3.66	2.26	3.16	2.29	3.27
DK08	2.45	1.73	1.62	1.89	1.78
FI09	0.73	1.53	0.39	0.34	0.57
GB02	2.52	2.73	1.40	2.24	3.06
GB14	3.06	2.10	1.52	1.98	2.07
LT15	2.84	3.70	1.26	1.24	2.16
LV10	2.05	3.81	0.97	0.81	1.06
NL10	26.67	19.12	26.07	20.48	20.56
NO01	1.11	1.01	0.72	0.59	0.80
NO08	2.29	2.06	2.39	2.30	2.29
NO41	0.58	0.60	0.38	0.32	0.75
PL02	3.62	3.82	2.55	2.54	2.62
PL04	2.49	2.22	1.39	1.14	1.50
PL05	3.45	3.11	1.51	1.79	4.45
SE02	2.02	1.90	1.14	0.92	1.29
SE11	2.52	2.50	1.20	1.07	1.42
SE12	0.94	1.54	0.60	0.49	0.79

Table 10.17. Correlation coefficient for TNHx per station (April 2 - Sep 29, 1995).

TNHx	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	0.39	0.28		0.31	0.36	0.05
CS01	0.48	0.43		0.28	0.43	0.04
CS03	0.23	0.22		0.28	0.34	0.13
DK03	0.60	0.62		0.40	0.59	0.15
DK05	0.44	0.65		0.56	0.62	0.46
DK08	0.52	0.75		0.55	0.59	0.49
FI09	0.57	0.68		0.59	0.74	0.04
GB02	0.75	0.73		0.67	0.73	0.44
GB14	0.61	0.56		0.80	0.63	0.57
LT15	0.17	0.30		0.23	0.29	0.28
LV10	0.49	0.43		0.43	0.59	0.30
NL10	0.40	0.52		0.54	0.71	0.36
NO01	0.58	0.77		0.61	0.84	0.46
NO08	0.38	0.38		0.24	0.50	0.23
NO41	0.48	0.65		0.65	0.70	0.11
PL02	0.39	0.52		0.35	0.45	0.18
PL04	0.53	0.49		0.44	0.64	0.40
PL05	0.23	0.39		0.23	0.24	-0.23
SE02	0.49	0.69		0.51	0.69	0.38
SE11	0.57	0.64		0.56	0.69	0.34
SE12	0.51	0.61		0.52	0.72	0.27

Table 10.18. Percentage of data within 50% for TNHx per station (April 2 - Sep 29, 1995).

TNHx	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	52.53	56.96		59.49	77.85	74.68
CS01	52.22	46.67		81.11	62.22	68.33

CS03	50.28	73.18	82.68	81.56	79.89
DK03	49.08	71.17	81.60	77.91	56.44
DK05	61.14	83.43	50.86	86.29	46.86
DK08	51.93	72.38	79.56	75.14	62.98
FI09	54.27	37.20	76.22	72.56	40.85
GB02	61.88	30.63	56.25	30.63	23.13
GB14	55.41	54.05	80.41	59.46	65.54
LT15	44.63	30.58	61.16	55.37	54.55
LV10	51.05	19.58	67.13	77.62	64.34
NL10	12.59	62.22	10.37	44.44	57.78
NO01	42.54	60.22	63.54	71.82	52.49
NO08	20.56	35.56	19.44	15.00	29.44
NO41	40.57	61.14	62.29	68.00	39.43
PL02	57.87	62.92	74.72	78.09	76.40
PL04	52.84	61.36	65.91	72.16	50.57
PL05	41.24	44.63	68.36	62.15	46.33
SE02	50.29	51.43	75.43	72.57	58.86
SE11	61.67	50.00	83.33	83.33	68.33
SE12	53.80	32.75	61.40	66.67	52.05

Table 10.19. Ratio of standard deviation (Observation/Model Result) for TNHx per station (April 2 - Sep 29, 1995).

TNHx	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	1.57	1.02		0.48	1.16	0.71
CS01	2.31	1.27		0.71	1.21	1.26
CS03	1.69	0.89		0.52	0.84	0.92
DK03	1.38	1.38		0.63	0.98	1.35
DK05	1.47	0.99		0.43	0.98	0.46
DK08	1.55	1.18		0.49	1.22	0.43
FI09	1.83	2.94		0.82	0.87	0.72
GB02	1.93	1.46		0.82	0.96	1.30
GB14	1.61	0.96		0.54	0.74	0.85
LT15	2.64	1.97		0.75	0.80	1.92
LV10	2.40	2.35		0.72	0.76	0.88
NL10	0.40	0.44		0.24	0.42	0.51
NO01	1.52	1.52		0.73	0.63	0.60
NO08	0.77	0.57		0.32	0.31	0.31
NO41	1.43	1.62		0.90	0.73	1.01
PL02	1.53	1.04		0.43	0.93	0.68
PL04	2.14	1.62		0.59	0.75	0.79
PL05	2.28	1.49		0.59	0.92	1.96
SE02	1.83	1.57		0.58	0.83	0.49
SE11	2.06	1.56		0.55	0.78	0.67
SE12	1.51	1.90		0.58	0.78	0.79

Table 10.20. Observed and modeled mean values for TNO_3 per station (April 2 - Sept. 29, 1995).

TNO_3	Observation	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	3.71	3.36	7.59	8.87	4.86	1.80	4.85
DK03	3.46	2.96	4.43	4.49	4.16	2.52	3.08
DK05	4.89	3.53	6.47	9.49	6.34	3.64	4.45
DK08	3.73	2.65	4.57	5.83	5.29	3.45	2.86

FI09	1.49	1.47	2.77	1.97	3.23	2.74	1.45
GB02	1.69	2.83	4.06	5.35	3.75	1.85	3.31
GB14	2.77	4.20	5.30	6.52	5.53	2.59	3.54
IT04	4.04	3.84	8.57	22.98	7.66	2.34	5.91
LT15	0.56	2.07	3.16	3.55	2.10	1.83	1.97
LV10	1.86	1.94	2.80	2.95	2.07	1.96	1.62
LV16	0.78	1.31	1.44	2.04	1.43	0.92	1.28
NO01	1.18	1.09	2.11	2.24	1.93	1.43	1.33
NO08	1.13	1.12	1.52	1.56	1.47	1.28	1.14
NO41	0.53	0.57	0.69	1.00	0.83	0.47	0.71
PL02	2.74	2.75	5.90	6.37	4.70	1.89	3.41
PL04	2.13	2.69	4.68	5.38	3.92	2.39	2.46
PL05	1.62	1.91	3.07	3.96	2.19	1.45	2.03
SE02	2.12	2.06	3.61	3.86	4.07	2.41	2.33
SE11	2.20	2.79	4.02	5.77	4.32	2.64	2.99
SE12	0.94	1.42	2.90	3.09	2.42	1.93	1.69
SK06	2.08	3.16	4.63	6.28	3.90	1.41	2.54

Table 10.21. Residue for TNO_3 per station (April 2 - Sep 29, 1995).

TNO_3	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	2.33	4.31	5.50	1.88	1.97	1.86
DK03	2.01	1.93	2.24	1.97	1.62	1.54
DK05	2.80	3.00	5.62	2.96	2.27	2.35
DK08	2.26	1.97	3.34	2.51	1.77	1.83
FI09	0.90	1.51	1.26	1.82	1.54	0.81
GB02	1.77	2.57	4.01	2.48	0.90	2.13
GB14	2.40	3.46	4.00	2.95	1.22	1.62
IT04	2.57	5.59	19.10	4.74	2.28	3.83
LT15	1.73	2.72	3.03	1.64	1.42	1.50
LV10	1.36	1.64	1.69	1.07	1.11	0.92
LV16	1.17	1.07	1.48	0.91	0.65	0.79
NO01	1.04	1.31	1.43	1.21	0.78	0.74
NO08	0.91	0.95	1.04	0.86	0.73	0.69
NO41	0.53	0.50	0.62	0.62	0.35	0.43
PL02	1.79	3.63	3.93	2.33	1.32	1.42
PL04	1.64	2.87	3.37	2.08	0.98	1.19
PL05	1.55	2.00	2.74	1.28	1.00	1.10
SE02	1.54	1.88	2.26	2.38	1.15	1.34
SE11	1.98	2.32	3.77	2.43	1.24	1.50
SE12	0.97	2.02	2.24	1.57	1.15	0.95
SK06	2.15	2.89	4.36	2.22	0.99	1.28

Table 10.22. RMSE for TNO3 per station (April 2 - Sep 29, 1995).

TNO_3	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	3.57	5.76	7.13	2.50	2.52	2.56
DK03	2.94	3.38	3.71	3.21	2.64	2.84
DK05	4.05	4.44	8.84	4.57	3.64	3.93
DK08	3.53	3.24	5.28	3.92	3.02	3.21
FI09	1.33	2.40	1.69	2.30	2.58	1.09
GB02	3.55	4.45	6.75	3.53	1.53	2.94
GB14	4.89	6.33	6.11	4.44	2.05	2.28

IT04	4.03	7.94	23.94	6.22	3.64	5.61
LT15	2.97	4.18	4.11	2.11	2.10	2.01
LV10	2.08	2.66	2.56	1.59	1.77	1.54
LV16	2.18	2.02	2.10	1.34	1.13	1.16
NO01	1.87	2.44	2.40	2.15	1.29	1.06
NO08	1.71	1.87	1.86	1.44	1.22	1.06
NO41	0.99	0.87	1.01	1.11	0.49	0.58
PL02	2.64	4.86	5.33	2.81	1.78	1.81
PL04	2.62	4.44	4.66	2.78	1.38	1.88
PL05	2.20	3.36	3.53	1.66	1.39	1.50
SE02	2.34	3.03	3.48	3.37	1.66	2.23
SE11	3.17	3.57	5.30	3.30	1.85	2.31
SE12	1.59	3.08	3.16	2.10	1.75	1.25
SK06	3.46	3.91	5.67	2.86	1.30	1.79

Table 10.23. Correlation coefficient for TNO_3 per station (April 2 - Sep 29, 1995).

TNO_3	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	0.33	0.26	0.53	0.51	0.49	0.50
DK03	0.69	0.81	0.63	0.56	0.67	0.55
DK05	0.59	0.68	0.44	0.51	0.63	0.52
DK08	0.54	0.75	0.46	0.49	0.60	0.47
FI09	0.57	0.59	0.27	0.61	0.58	0.32
GB02	0.62	0.80	0.56	0.61	0.75	0.56
GB14	0.71	0.62	0.72	0.76	0.80	0.78
IT04	0.46	0.12	0.28	0.15	0.43	0.11
LT15	0.00	0.02	0.13	0.03	-0.08	0.09
LV10	0.50	0.40	0.43	0.48	0.42	0.40
LV16	0.08	0.09	0.15	0.17	0.09	0.02
NO01	0.53	0.72	0.49	0.47	0.73	0.48
NO08	0.74	0.69	0.45	0.58	0.73	0.48
NO41	0.18	0.46	0.26	0.39	0.49	0.27
PL02	0.39	0.51	0.38	0.47	0.32	0.47
PL04	0.43	0.49	0.59	0.43	0.67	0.22
PL05	0.23	0.30	0.26	0.30	0.26	0.30
SE02	0.53	0.77	0.47	0.41	0.73	0.30
SE11	0.57	0.70	0.51	0.51	0.64	0.43
SE12	0.45	0.39	0.36	0.37	0.56	0.33
SK06	0.28	0.29	0.21	0.33	0.31	0.35

Table 10.24. Percentage of data within 50% for TNO_3 per station (April 2 - Sep 29, 1995).

TNO_3	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	55.07	47.83	41.30	74.64	47.10	78.99
DK03	42.94	68.71	66.26	76.69	60.12	79.14
DK05	46.29	68.57	53.14	71.43	65.71	73.71
DK08	44.75	75.14	55.80	60.22	72.38	67.96
FI09	55.15	56.97	45.45	36.97	61.82	62.42
GB02	51.95	39.61	20.13	30.52	66.23	30.52
GB14	53.22	38.60	37.43	39.18	74.27	61.40
IT04	53.04	40.88	14.92	43.65	56.35	44.75
LT15	28.65	19.10	12.92	23.03	30.34	26.97
LV10	44.76	49.65	49.65	65.03	62.24	68.53

LV16	29.79	48.94	29.79	47.87	51.06	46.81
NO01	34.25	51.38	40.33	55.25	59.12	58.01
NO08	33.70	53.59	47.51	59.67	54.70	53.59
NO41	40.57	48.00	50.29	46.86	45.71	48.57
PL02	52.63	43.27	43.86	52.63	67.84	69.01
PL04	51.93	46.96	37.57	49.17	77.90	76.24
PL05	40.74	46.30	33.33	49.38	58.64	57.41
SE02	44.32	59.66	49.43	42.05	65.34	60.23
SE11	43.58	50.84	35.75	50.28	67.04	64.80
SE12	42.37	36.16	28.25	31.07	53.11	45.20
SK06	46.93	44.13	29.61	52.51	59.22	65.92

Table 10.25. Ratio of standard deviation (Observation/Model Result) for TNO_3 per station (April 2 - Sep 29, 1995).

TNO_3	DEM	EURAD/ FFA	EUROS	LOTOS	MATCH	REM3
CH02	1.98	2.31	3.02	1.33	0.60	1.37
DK03	1.17	1.59	1.37	1.01	0.75	0.68
DK05	0.91	1.27	1.90	0.98	0.65	0.76
DK08	1.01	1.34	1.52	1.04	0.92	0.57
FI09	1.44	2.23	1.37	1.71	2.45	0.60
GB02	1.96	2.43	3.05	1.67	1.01	1.33
GB14	1.91	2.16	1.98	1.58	0.89	0.92
IT04	1.17	1.67	4.29	1.19	0.54	1.23
LT15	4.55	5.90	5.20	2.45	2.79	2.49
LV10	1.55	1.75	1.65	1.03	1.14	0.80
LV16	3.00	2.69	2.40	1.57	1.39	1.18
NO01	2.24	2.91	2.51	2.33	1.83	1.09
NO08	2.06	2.10	1.73	1.48	1.53	0.74
NO41	2.56	2.50	2.36	2.99	1.39	1.31
PL02	1.88	2.79	2.78	1.46	0.74	1.14
PL04	1.97	2.87	2.77	1.60	1.24	1.07
PL05	1.70	2.56	2.17	1.12	0.82	0.98
SE02	1.22	1.82	1.57	1.31	1.08	0.72
SE11	1.81	1.97	2.16	1.35	1.02	0.94
SE12	2.75	4.13	3.99	2.61	2.73	1.66
SK06	3.75	3.39	4.28	2.56	1.07	2.00

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