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Ozone Impacts of Gas-Aerosol Uptake in Global Chemistry Transport Models

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Abstract.

The impact of six heterogeneous gas-aerosol uptake reactions on tropospheric ozone and nitrogen species was studied using two chemical transport models, EMEP MSC-W and ECHAM-HAMMOZ. Species undergoing heterogeneous reactions in both models include N_2O_5, NO_3, NO_2, O_3, HNO_3 and HO_2. Since heterogeneous reactions take place at the aerosol surface area, the modeled surface area density S_a of both models was compared to a satellite product retrieving the surface area. This comparison shows a good agreement in global pattern and especially the capability of both models to capture the extreme aerosol loadings in East Asia.

The impact of the heterogeneous reactions was evaluated by the simulation of a reference run containing all heterogeneous reactions and several sensitivity runs. One reaction was turned off in each sensitivity run to compare it with the reference run. The analysis of the sensitivity runs confirms that the globally most important heterogeneous reaction is the one of N_2O_5. Nevertheless, NO_2, HNO_3 and HO_2 heterogeneous reaction gain relevance particularly in East Asia due to the presence of high NO_x concentrations and high S_a in the same region, although ECHAM-HAMMOZ showed much stronger responses than EMEP in this respect. The heterogeneous reaction of O_3 itself on dust is of minor relevance compared to the other heterogeneous reactions. The impacts of the N_2O_5 reactions show strong seasonal variations, with biggest impacts on O_3 in spring time when photochemical reactions are active and N_2O_5 levels still high. Evaluation of the models with northern hemispheric ozone surface observations yields a better agreement of the models with observations in terms of concentration levels, variability, and temporal correlations at most sites when the heterogeneous reactions are incorporated.

1 Introduction

Nitrogen species, ozone and atmospheric aerosols are major pollutants in the atmosphere, having strong impacts on ecosystems and human health, and also interacting with climate (Ainsworth et al., 2012; Harrison and Yin, 2000; Simpson et al., 2014; IPCC, 2013). In regions, where gas phase and aerosol pollutants meet, heterogeneous chemistry can play a significant role (Jacob, 2000). The first heterogeneous process to become prominent in atmospheric chemistry was the heterogeneous destruction

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of stratospheric ozone on polar stratospheric clouds (Solomon, 1999). However, heterogeneous processes are also relevant in the lower atmosphere, influencing tropospheric ozone and therefore oxidation capacity of the atmosphere (Pöschl, 2005; Seinfeld and Pandis, 2012). An important example is the heterogeneous reaction of N_2O_5 on aerosols, which is known to impact the NO_x-O_3 cycle while mainly removing NO_x from the troposphere (Mozurkewich and Calvert, 1988; Dentener and Crutzen, 1993; Evans and Jacob, 2005; Chang et al., 2011b; Brown and Stutz, 2012), which can lead to ozone reduction (Macintyre and Evans, 2010). Other oxidised nitrogen species also undergo heterogeneous reactions on different aerosol types. NO_2, HNO_3 and NO_3 react on wet surfaces of different aerosol types and increase aerosol nitrate content (Rudich et al., 1998; Goodman et al., 1999). HNO_3 reacts also with dust and sea salt particles which is again a sink for NO_x and a source for particulate nitrate (Davies and Cox, 1998; Hanisch and Crowley, 2001). Moreover, heterogeneous reaction of NO_2 produces HONO which plays the role of a reservoir specie for NO and OH production (Platt et al., 1980). Other species also undergo heterogeneous reactions. O_3 reacts on dust particles and this has been estimated to lead to an ozone loss of about 20% in dusty regions (Usher et al., 2003). HO_2 reacts on wet particles leading to H_2O_2 production (Thornton and Abbatt, 2005). Furthermore, heterogeneous reactions lead to halogen release from sea salt aerosols (Frenzel et al., 1998; Yang et al., 2008; Lowe et al., 2011). Many modeling studies have been conducted over the years on these processes, but usually heterogeneous reactions were studied individually, and typically considering annual global budgets rather than detailed temporal or spatial resolution of the impacts (Dentener and Crutzen, 1993; Rudich et al., 1998; Saathoff et al., 2001; Bauer et al., 2004; Hodzic et al., 2006; Thornton et al., 2008; Chang et al., 2011b).

This paper presents estimates of the global impact of heterogeneous reactions of N_2O_5, NO_3, NO_2, HNO_3, HO_2 and O_3 and evaluates each reaction in a systematic way. The influence of each reaction on the magnitude and spatial and temporal variation in surface ozone is illustrated. The greatest impacts are seen in northern hemispheric regions of North America, Europe, South and East Asia. The N_2O_5 reaction is shown to significantly affect the spring-peak of surface O_3 at sites in all these regions. Although the impact of N_2O_5 reaction on O_3 is analysed, due to technical limitations in both models no $ClNO_2$ chemistry is included, which could decrease the impact of N_2O_5 on O_3, since it is a competing NO_x loss process.

Section 2 presents the two global scale chemical transport models, EMEP MSC-W and ECHAM-HAMMOZ, as well as details of the reaction parameterisations and sensitivity tests. In section 3 a short review of the range of reaction probabilities for each heterogeneous reaction is given. Model setups and sensitivity runs are described in section 4. Section 5 first presents a comparison of the simulated surface area from the models with satellite derived product, since the surface area of aerosols is crucial for heterogeneous chemistry. Especially in polluted regions where high trace gas concentrations meet large surface areas provided by aerosols heterogeneous chemistry might be of significant importance explaining aerosol composition and trace gas mixing ratios (Jacob, 2000; Pathak et al., 2009). Furthermore, section 5 presents the results of the sensitivity tests, and comparisons of daily maximum ozone time series for 2012 with surface station observations for selected sites. Finally, section 6 summarizes the results and implications for atmospheric chemistry.

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2 Model description

Two models, the chemical transport model EMEP MSC-W (v4.14) (Simpson et al., 2012, 2017) and the global chemistry aerosol climate model ECHAM6.3-HAM2.3MOZ1.0 (Schultz et al., in preparation) were used to study the heterogeneous chemistry of various compounds in the atmosphere.

2.1 EMEP

The EMEP MSC-W chemical transport model has been described in detail by Simpson et al. (2012), but substantial updates were made in the treatment of aerosols, biogenic emissions and chemistry in recent years, see Simpson et al. (2015, 2017) (and refs therein). The default model setup includes 20 vertical layers up to 100 hPa, using terrain-following coordinates, and the lowest layer has a thickness of about 90 m. Although originally designed for European applications (previously using a grid of resolution 50 km, more recently 28 km), the model is very flexible and is now applied on scales ranging from global (Jonson et al., 2010) to local (1-7 km grids), e.g. Vieno et al. (2010, 2014), Schaap et al. (2015). Anthropogenic emissions from land-based sources are here taken from the so-called PANHAM database from the EU PANDA project (http://panda-project.eu), which combined emissions from the global HTAP data base (http://edgar.jrc.ec.europa.eu/htap_v2/index.php?SECURE=123) with the MIEC database for China (http://www.meicmodel.org/).

Emissions of VOC from biogenic sources are calculated in the model based upon land-cover and meteorological conditions. Emission factors for earlier versions of the EMEP model were mainly intended for European simulations (Simpson et al., 1999, 2012), but during 2016-2017 the factors used in non-European areas were substantially revised - see Simpson et al. (2017) for details. For details of other emissions (soil-NO, lightning, aircraft, biomass-burning), see Simpson et al. (2012). For the present study meteorological data from the European Centre for Medium Range Weather Forecasting Integrated Forecasting System (ECMWF-IFS) model (http://www.ecmwf.int/research/ifsdocs/) were used, and the model runs with $1 \times 1^{\circ}$ latitude-longitude resolution.

The chemical scheme in the EMEP MSC-W model, denoted 'EmChem16', consists of a standard gas-phase mechanism (132 species, 183 reactions, a recent update of the earlier EmChem03 evaluated by Andersson-Sköld and Simpson 1999), extended with organic aerosols using a volatility-basis-set scheme (Bergström et al., 2012; Simpson et al., 2012), plus sea-salt (Tsyro et al., 2011) and dust aerosol. Unlike ECHAM-HAMMOZ, the EMEP model includes NH_3 and handles the resulting interactions with sulphate, HNO_3 and ammonium-nitrate through the use of the MARS equilibrium solver (Binkowski and Shankar, 1995). Unfortunately, interactions with sea-salt have not yet been implemented in EMEP-MARS. The chemical equations are solved using the TWOSTEP algorithm (Verwer and Simpson, 1995; Verwer et al., 1996).

The EMEP MSC-W model has been extensively compared with measurements of many different compounds with generally good performance (e.g. Simpson et al., 2006a, b; Fagerli and Aas, 2008; Aas et al., 2012; Gauss et al., 2011), although most of these studies have focused on Europe. Still, in comparisons with global data and other models, the EMEP MSC-W model seems to perform well, especially more recent versions (Jonson et al., 2010, 2015; Angelbratt et al., 2011; Bian et al., 2017).

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As of EMEP MSC-W model version rv4.7 (Simpson et al., 2015), aerosol surface area (S_a) is estimated using the empirical relations of Gerber (1985), which simply requires aerosol mass concentrations and assumed aerosol density and size-parameters. Values of S_a are calculated for fine and coarse particulate matter (PM_f, PM_c) both as totals (including all components, for reaction R1-3,5 in Table 1), and separately for coarse sea-salt and dust particles - which we denote as S_{ss} and S_{du} respectively. The distinction between total area S and S_{ss} and S_{du} was made to allow the use of Gerber's specific parameterizations for sea-salt and dust for reactions R5 and R6 (Table 1), with the assumption that where concentrations are large (eg over oceans, deserts) these give a better estimate of S than the rural parameterisation would give. Further, for S_{du} the aerosol is assumed to be dry; which is not always true but is intended to reflect the nature of desert dust dominated aerosol. The EMEP model does not include fine-mode formation of NO_3^- through reaction R4, since the relationship between HNO_3 and fine-mode nitrate is given by the thermodynamic equilibrium solver MARS.

2.2 ECHAM-HAMMOZ

ECHAM-HAMMOZ is an aerosol chemistry climate model capable of performing interactive aerosol chemistry simulations. For this study simulations were done using version ECHAM6.3-HAM2.3MOZ1.0 (https://redmine.hammoz.ethz.ch/projects/hammoz/wiki/Echam630-ham23-moz10). The model system ECHAM-HAMMOZ consists of the general circulation model ECHAM6.3 (Stevens et al., 2013), the aerosol model HAM2.3 (Neubauer et al., in preparation; Zhang et al., 2012) and the chemistry model MOZ1.0 (Schultz et al., in preparation). ECHAM calculates meteorological variables, cloud processes and radiative transfer considering greenhouse gases and aerosols. The simulations in this study make use hybrid sigma coordinates with 47 vertical layers, while the surface layer thickness is about 50 m. The horizontal resolution T63 leads to an associated 1.875°$\times$ 1.875 °Gaussian grid.

HAM simulates the evolution of aerosols considering aerosol and aerosol precursor emissions, microphysical processes as nucleation, coagulation, accumulation, sedimentation, dry and wet deposition. Via direct and indirect aerosol effects a feedback to climate system is simulated (Neubauer et al., in preparation). The aerosols in HAM are assumed to be internally mixed and consist of up to 5 components: sulphate, sea salt, dust, organic carbon and black carbon. To describe the aerosol number the microphysical driver M7 uses distribution seven log normal functions describing four wet aerosol modes and three dry aerosol modes. Hence, the wet functions cover nucleation, Aitken, accumulation, and coarse modes and the dry functions do not cover the nucleation mode. The height and median radius of the distribution are calculated, just its width is fixed. Due to aerosol aging it is possible for insoluble particles to become soluble (Vignati et al., 2004). Dust and sea salt emissions are interactively calculated considering the wind speed at 10 m. Dimethylsulphate emissions are parametrized and emissions of sulphate dioxide, sulphate aerosol, black carbon and organic carbon are taken from the Representative Concentration Pathway (RCP) 8.5 emissions (Van Vuuren et al., 2011). Finally, optical properties of the aerosol are calculated and impact the atmospheric circulation in ECHAM (Zhang et al., 2012).

Atmospheric chemistry is simulated by MOZ which is based on MOZART3.5 (Model for Ozone and Related chemical Tracers version 3.5) (Stein et al., 2012) connecting tropospheric chemistry of MOZART4 (Emmons et al., 2010) and stratospheric chemistry of MOZART3 (Kinnison et al., 2007). Further development since Stein et al. (2012) lead to MOZ being a chemical

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mechanism resembling to CAM-chem (Community Atmosphere Model with Chemistry) (Lamarque et al., 2012) with several revisions, extended chemistry of aromatic compounds and a more detailed isoprene chemistry based on Taraborrelli et al. (2009). The version MOZ1.0 used here consists of 242 tracers, 733 chemical reactions which contain 142 photolysis reactions, 6 heterogeneous tropospheric reactions and 16 stratospheric heterogeneous reactions. Further, MOZ calculates dry and wet deposition of gases. Anthropogenic emissions are taken from the emission inventory RCP 8.5 (Van Vuuren et al., 2011). Biogenic emissions of VOC and NO_2 are calculated interactively by MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006; Henrot et al., 2017). NO lightning emission are parametrized as described by Grewe et al. (2001).

HAM and MOZ interact via two physical processes. First, assuming spherical aerosols, the surface area density for heterogeneous reactions is calculated using aerosol distribution and median radius. Second, MOZ provides fields of oxidants for aerosol formation from gas-phase precursors. The HAMMOZ coupling does not include ammonium nitrate formation due to the lack of nitrate aerosol in the current HAM version. Therefore, reactive uptake of nitric acid leads to a total loss, based on the assumption of a quick loss of gas phase HNO_3 and particulate nitrate. To underline, heterogeneous reactions in ECHAM-HAMMOZ do not form HNO_3 in the gas phase, but introduce a direct loss to the products HNO_3 and NO_3^-.

3 Heterogeneous reactive uptake

Experimental studies show that oxidised nitrogen species, ozone and the hydroperoxy radical undergo heterogeneous reactions on wet and dry aerosols. Heterogeneous reactions can be modeled as a pseudo-first order process (Ammann et al., 2013).

$$\frac{d[\mathrm{X}]_g}{dt} = -k_{\mathrm{X}}[\mathrm{X}]_g \tag{1}$$

The change in gas phase concentration of the species X = N_2O_5, NO_3,NO_2, HNO_3, HO_2, O_3 is proportional to its gas phase concentration $[\mathrm{X}]_g$ and a reaction rate coefficient k_{X} (Schwartz, 1986)

$$k_{\mathrm{X}} = \left(\frac{r_p}{D_g} + \frac{4}{c_{\mathrm{X}} \cdot \gamma_{\mathrm{X}}} \right)^{-1} S_a \tag{2}$$

where D_g represents the gas phase diffusion coefficient, r_p is the particle radius, c_{X} is the mean molecular velocity of the species X, γ_{X} represents the reaction probability and S_a the surface area density. The γ_{X} values are generally determined from laboratory measurements. The first term in Eqn. 2 is very small for particles of accumulation mode and larger, and is neglected in the EMEP model. The main challenges for chemistry transport models are the calculation of a proper surface area density S_a and the parametrization of the reaction probability γ_{X}.

First, Table 1 summarizes the heterogeneous reactions investigated in this study. Second, sections 3.1-3.6 discuss literature values of γ associated with each reaction. An overview of the parametrization and values used for the different reaction probabilities is given in Table 2. ECHAM-HAMMOZ and EMEP MSC-W use the same reaction probabilities or functions for many reaction, with the most important difference being the lack of ammonium nitrate aerosol in ECHAM-HAMMOZ. Lastly, to check if the surface area density is realistic, simulated S_a is compared to a satellite-model-product in section 5.1.

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3.1 N_2O_5

N_2O_5 reaction probability depends on aerosol water content and aerosol composition. Therefore, several laboratory studies measured γ values on different aerosol types leading to the possibility to derive detailed parametrizations (Riemer et al., 2003b, 2009; Evans and Jacob, 2005; Liao and Seinfeld, 2005; Davis et al., 2008; Bertram and Thornton, 2009; Griffiths et al., 2009; Brown and Stutz, 2012). For dry sulphate aerosol, reaction probabilities range between 10^{-4} and 10^{-3}; for wet aerosol γ ranges between 10^{-3} and 8.6×10^{-2} depending on relative humidity. The N_2O_5 heterogeneous reaction humidity dependence also explains the range of reaction probabilities of sea salt aerosol of 6×10^{-3} to 4×10^{-2}. On nitrate containing aerosol lower reaction probabilities were found due to nitrate effect (Wahner et al., 1998), between 3×10^{-4} and 3×10^{-3} (Chang et al. 2011b, and references therein). Moreover, N_2O_5 can react on organic aerosol under dry conditions with low reaction probabilities in the order of 10^{-6} and 10^{-5} (Gross et al., 2009). This value increases to 10^{-4} – 10^{-3} under wet conditions, because the higher water content allows N_2O_5 to hydrolyze (Thornton et al., 2003). Even dust aerosols can be covered by a layer of water leading to a reaction probability between 3×10^{-3} at 30 % and 2×10^{-2} at 70% relative humidity (Bauer et al., 2004). For N_2O_5 reaction on black carbon, Sander et al. (2006) reported a wide range of reaction probabilities, between 2×10^{-2} – 10^{-6}.

Most studies have used laboratory data to estimate γ values, but some have made use of ambient data. Brown et al. (2009) used aircraft measurements over Texas, and found observation-based γ values of ca. 5×10^{-1}–6×10^{-3}, usually substantially lower (often a factor of 10) than values calculated using laboratory-based values. Using aircraft measurements around the United Kingdom, Morgan et al. (2015) found rather high γ values for N_2O_5, from ca. 1×10^{-2}–3×10^{-2}, with strong dependencies on sulphate, and a clear suppression of γ due to nitrate. They concluded that including the suppressive effect of organic aerosol in the uptake parameterisation leads to significant underprediction of the γ values. Further, direct N_2O_5 measurements retrieved a highly daily variation of $\gamma_{N_2O_5}$ also explained by the nitrate effect leading to a mean value of 5.4×10^{-3} ranging from $3\cdot10^{-5}$ to $2.9\cdot10^{-2}$(Riedel et al., 2012). In Stone et al. (2014) and Wagner et al. (2013) in situ measurements of N_2O_5 were used to retrieve the reaction probability within the framework of a box model. In Stone et al. (2014) $\gamma_{N_2O_5}$ is varied over a range of values between 0 and 1, and found that values of $2\cdot10^{-1}$ – $2\cdot10^{-2}$ agreed best with observations. Wagner et al. (2013) retrieved the reaction probability of N_2O_5 using a box model driven by ambient wintertime observations. The reaction probability distribution ranges between $2\cdot10^{-3}$ and $1\cdot10^{-1}$, displaying a maximum at $2\cdot10^{-2}$.

It is clear from the above mentioned studies that great uncertainties surround both the magnitude and the chemical dependence of γ values for N_2O_5. Even thorough evaluations such as those of Davis et al. (2008) or Chang et al. (2011a) have little consideration of important components of the aerosol such as organic matter, and even such schemes seem to be inconsistent with the aircraft-observations discussed above. For our modelling studies, we have not tried to develop or use yet another scheme, but rather to make use of the γ schemes already implemented in each model, with some small efforts at harmonisation to build similar reference schemes.

The equations used for EMEP MSC-W and ECHAM-HAMMOZ can be found in Table 2. Both models make extensive use of the parameterizations developed by Evans and Jacob (2005), with the largest difference being that EMEP includes ammonium nitrate (in fine particles) among the nitrate species. For N_2O_5 the uptake coefficients for sulphate, sea salt and

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organic aerosol are identical in the two models. For the reaction on dust, both models rely on Bauer et al. (2004) which was interpreted differently by Evans and Jacob (2005) and Liao and Seinfeld (2005). This small difference in the uptake coefficient formulation on dust does not lead to large differences in the resulting uptake coefficient.

EMEP MSC-W also modifies the γ value for secondary inorganic aerosol to account for a nitrate inhibition effect (Wahner et al., 1998; Riemer et al., 2003a). This makes use of the γ_{NO_3} factor presented in Davis et al. (2008) for ammonium nitrate, and merged with the sulphate factor in a manner reminiscent of Riemer et al. (2003b). First a sulphate mass fraction within the secondary inorganic aerosol is calculated (SIA), $f_{SO_4} = m_{SO_4}/(m_{SO_4} + m_{NO_3})$, then γ_{SIA} as

$$\gamma_{SIA} = f_{SO_4}\gamma_{SO_4} + (1 - f_{SO_4})\gamma_{NO_3}. \quad (3)$$

Figure 1 illustrates the γ values for sulphate aerosol from Evans and Jacob (2005) as a function of relative humidity (RH) and temperature for sulphate, and the RH dependency of γ for nitrate from the Davis et al. (2008) formulation. The negative temperature dependence after 280K can be explained by increasing volatility with increasing temperature leading to less uptake on the aerosol. As described before, reaction probability increases with increasing water content in the aerosol due to enhanced N_2O_5 hydrolysis. Even at high RH, reaction probability on nitrate containing aerosol is not as high as in sulphate aerosol. Nevertheless, the very high γ values found at high RH seem questionable, because the aerosol itself becomes saturated at high RH and these small water content changes should not have such a huge impact on the heterogeneous reaction.

No further parameterization considering organic coatings is used in either EMEP MSC-W or ECHAM-HAMMOZ due to the large uncertainties in this effect (e.g. Brown et al., 2009; Morgan et al., 2015), and the fact that ambient OM and its thermodynamic properties are so poorly understood (Hallquist et al., 2009). Further, sensitivity runs done with ECHAM-HAMMOZ have shown minor global impact of organic coatings (Stadtler, 2015).

3.2 NO_3

Hydrolysis of the nitrate radical NO_3 happens on various aerosol types depending on the water content. NO_3 heterogeneous reaction produces HNO_3 and OH in the aqueous particle phase and can be counted as a NO_x sink (Rudich et al., 1998). Several laboratory studies shown γ ranging between 10^{-4} and 10^{-3} (Rudich et al., 1996; Moise et al., 2002). Jacob (2000) recommended to use $\gamma = 10^{-3}$ for atmospheric chemistry model simulations, and this value was adopted for EMEP and ECHAM-HAMMOZ.

3.3 NO_2

NO_2 heterogeneous reaction leads to the production of HNO_3 and HONO. Especially in humid environments, the heterogeneous reaction may account for up to 95% of HONO production (Goodman et al., 1999). During nighttime HONO can accumulate in the atmosphere and therefore be an efficient OH radical source during the morning when sun rise starts photolysis (ibid). Estimates of γ for NO_2 vary widely, however, with several laboratory studies giving a range between 10^{-8} and 10^{-3}

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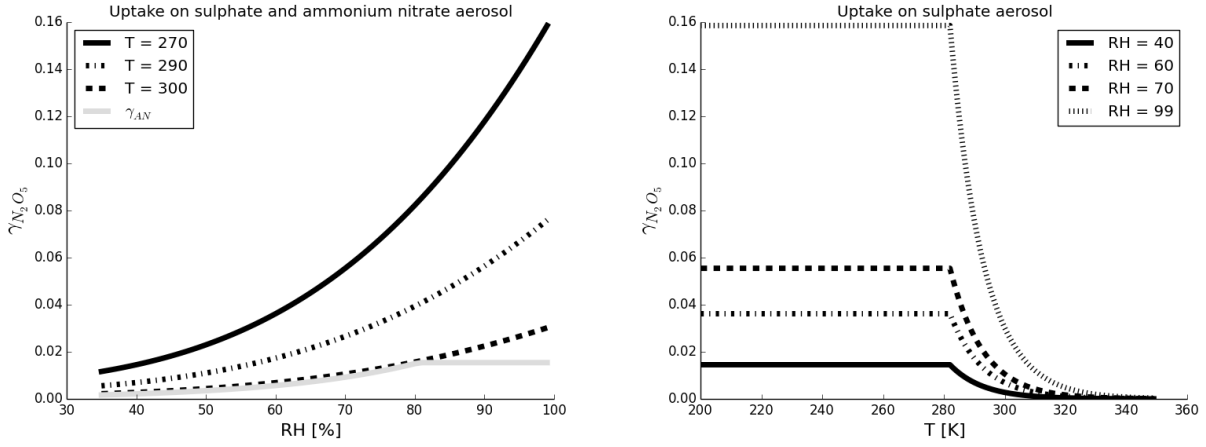

Figure 1. Upper plot: N_2O_5 reaction probability dependence on relative humidity for sulphate (black) and nitrate (grey) aerosol. For sulfate aerosol three temperatures are shown. Lower plot: N_2O_5 reaction probability temperature dependence on sulphate aerosol for four relative humidity. Parameterizations from Evans and Jacob (2005) and Davis et al. (2008), see text.

(Harrison and Collins, 1998; Kleffmann et al., 1998; Arens et al., 2001; Underwood et al., 2001). Jacob (2000) recommended $\gamma = 10^{-4}$ and this value is used for this study.

3.4 HNO_3

Nitric acid reacts on sea salt and dust aerosol surfaces, producing nitrate which stays in the aerosol phase (Davies and Cox, 1998; Hodzic et al., 2006). Experimentally derived γ values for HNO_3 on sea salt range between 10^{-4} and 10^{-2} (Davies and Cox 1998, and references therein). A relative humidity dependent uptake coefficient was proposed in Hauglustaine et al. (2014) increasing γ from 10^{-3} and 10^{-1} to cover low and high relative humidity. No such relative humidity dependence was used in this study, because for the conditions in the marine boundary layer, the value of 10^{-2} fits well and is used here.

Heterogeneous reaction of HNO_3 on dust was studied on different types of minerals, atmospheric dust types and for a range of relative humidities giving γ in the range of 10^{-6} and 10^{-1} (Hanisch and Crowley, 2001; Usher et al., 2003; Liu et al., 2008; Hauglustaine et al., 2014). Although in Fairlie et al. (2010) a relative humidity dependence of varying γ between 10^{-5} and 10^{-3} is described, the value is used here is based on Hodzic et al. (2006), who tested γ values between 10^{-6} and 0.3, deriving 0.1 as the best γ value minimizing the model error compared to observations. Compared to the other referenced studies, this is an upper limit.

3.5 O_3

Studies of the heterogeneous reaction of ozone on dust give a wide range for possible reaction probabilities, from 10^{-10} to 10^{-4} (Reus et al., 2000; Usher et al., 2003; Mogili et al., 2006; George et al., 2015). Reus et al. (2000) gives 10^{-4} as an upper

limit for this reaction probability, but George et al. (2015) suggests a more conservative upper limit value of 10^{-5}. Nevertheless, Nicolas et al. (2009) conclude that a reaction probability of 10^{-6} is a realistic number in terms of atmospheric environmental conditions, and this value was adopted here.

3.6 HO_2

HO_2 reaction probability is highly variable and strongly depends on transition metal ions contained in the aerosol (Tilgner et al., 2005; Mao et al., 2013; George et al., 2013; Huijnen et al., 2014). Furthermore, this reaction can also take place on cloud droplets. Estimates for γ range between 0.02 and 1 (Jacob, 2000; Remorov et al., 2002; Thornton and Abbatt, 2005; Taketani et al., 2008; George et al., 2013; Mao et al., 2013). Whalley et al. (2015) measured HO_2 in clouds and found a decrease in HO_2 concentrations up to 90%. Depending on the compounds in the particle aqueous phase heterogeneous reaction of HO_2 produces either H_2O_2 or H_2O. Consequently, this heterogeneous reaction can be a terminal radical sink or not (Mao et al., 2013; Whalley et al., 2015). Here we do not account for a terminal sink, but let the heterogeneous reaction of HO_2 produce H_2O_2 and use the γ recommended by Jacob (2000) of 0.2.

4 Setup of sensitivity runs

To test the six heterogeneous reactions (see Table 1), six sensitivity runs were designed and performed with both models. For EMEP MSC-W a spin up of six months and for ECHAM-HAMMOZ one of twelve months is used. Afterwards the results for the whole year 2012 are evaluated. The reference run REF contains all heterogeneous reactions with the parameterizations given in Table 2. Each sensitivity run is done with five out of six heterogeneous reactions; the names of the runs show which compound does not undergo heterogeneous reaction. For example, in the noN2O5 run, only N_2O_5 heterogeneous reaction is turned off. An overview of the simulation is given in Table 3.

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Table 1. Heterogeneous reactions in the EMEP MSC-W and ECHAM-HAMMOZ models. The second column specifies the aerosol type on which the reaction proceeds in the models:. SS: seasalt, DU: dust, PM: particulate matter

No.	Reaction		Aerosol type	Notes
R1	N_2O_5	$\longrightarrow 2\,HNO_3$	PM	1
R2	NO_3	$\longrightarrow HNO_3$	PM	2
R3	NO_2	$\longrightarrow \frac{1}{2}HNO_3 + \frac{1}{2}HONO$	PM	2
R4	HNO_3	$\longrightarrow NO_3^-$	SS, DU	2,3
R5	HO_2	$\longrightarrow \frac{1}{2}\,H_2O_2$	PM	2
R6	O_3	$\longrightarrow HO_2$	DU	

[1] Just for RH>40% in EMEP.

[2] Just on wet aerosol in ECHAM-HAMMOZ.

[3] Just on coarse mode dust and sea-salt in EMEP, using S_{ss} and/or S_{du}, see Sect. 2.1.

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Table 2. Reaction probabilities for the different species. Unless explicitly labelled (in parentheses afer the equation), both models use the same formulation. Here, RH denotes relative humidity in range, RH $\in (0, 100)$, and fRH denotes fractional relative humidity in range, fRH $\in (0, 1)$.

Specie	γ	Reference
N_2O_5	$\gamma_{SS} = \begin{cases} 0.005, \text{RH} \leq 62\ \% \\ 0.03, \text{RH} \geq 62\ \% \end{cases}$	EVA05
	$\gamma_{SU} = \alpha \cdot 10^{-\beta}$	EVA05
	$\alpha = 2.79 \cdot 10^{-4}\text{fRH} + 1.3 \cdot 10^{-4}\text{fRH} - 3.43 \cdot 10^{-6}\text{fRH}^2 + 7.52 \cdot 10^{-8}\text{fRH}^3$	
	$\beta = \begin{cases} 4 \cdot 10^{-2}(\text{T} - 294), T > 282\ \text{K} \\ -0.48, T \leq 282\ \text{K} \end{cases}$	
	$\gamma_{DU} = 0.01$ (EMEP)	EVA05
	$\gamma_{DU} = 4.25 \cdot 10^{-4}\text{RH} - 9.75 \cdot 10^{-3} (30\% \leq \text{RH} \leq 70\%)$ (ECHAM)	LIA05
	$\gamma_{OC} = \begin{cases} 0.03, \text{RH} > 57\% \\ 5.2 \cdot 10^{-2}, \text{RH} \leq 57\% \end{cases}$	
	$\gamma_{BC} = 0.005$	EVA05
	$\gamma_{AN} = \min(0.0154, 1/(1 + \exp(8.10774 - 0.04902 \cdot \text{RH})))$ (EMEP)	DAV08
NO_3	$\gamma = 0.001$	JAC00
NO_2	$\gamma = 10^{-4}$	JAC00
HNO_3	$\gamma_{SS} = 0.01$	DAV98
	$\gamma_{DU} = 0.1$	HOD06
HO_2	$\gamma = 0.2$	JAC00
O_3	$\gamma_{DU} = 10^{-6}$	NIC09

The subscripts refer to the aerosol compounds as given in Table 1, plus OC:Organic carbon/Organic matter, SU: Sulphate;BC black carbon.

Refs: DAV98 Davies and Cox (1998), DAV08 Davis et al. (2008), EVA05 Evans and Jacob (2005), JAC00 Jacob (2000), LIA05 Liao and Seinfeld (2005), THO08 Thornton et al. (2008), HOD06 Hodzic et al. (2006), NIC09 Nicolas et al. (2009)

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Table 3. Overview of sensitivity runs.

Run	Description
REF	All heterogeneous reactions
noN2O5	All except N_2O_5 reaction
noNO3	All except NO_3 reaction
noNO2	All except NO_2 reaction
noHNO3	All except HNO_3 reaction
noHO2	All except HO_2 reaction
noO3	All except O_3 reaction

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5 Results and Discussion

5.1 Surface area density

Aerosols consist of a variety of compounds in the gas, liquid or solid phase, and the shapes of aerosols vary greatly (Pöschl, 2005). Large scale models can not explicitly treat the morphology of aerosols. In EMEP MSC-W and ECHAM-HAMMOZ distribution functions and median radii are used to simulate the aerosol population. Based on this approach surface area density S_a is calculated considering the aerosol distribution, the median radius and assuming spherical particles. This assumption is good for liquid aerosols behaving as small water droplets. For dry particles this assumption can lead to an underestimation of S_a due to folded or porous structures (Buseck and Posfai, 1999).

In van Donkelaar et al. (2015) satellite retrievals and the GEOS-Chem chemical transport model are used to derive global surface $PM_{2.5}$ estimates with a resolution of 10 km $\times$ 10 km in the time period between 1998 and 2012. The physical relation between AOD and surface area is described in the supplementary material of van Donkelaar et al. (2015).

Figure 2 shows the estimated $PM_{2.5}$ surface area by van Donkelaar et al. (2015) and the modeled surface area density S_a from EMEP MSC-W and ECHAM-HAMMOZ as annual mean 2012 over land. Although these data-sets are not strictly comparable, since the van Donkelaar et al. 2015 estimate in itself relies partly on various assumptions of a third chemical transport model, GEOS-Chem (*ibid*), the general patterns of the models agree well with the surface area density estimation. Both models capture the east west gradient in S_a over North America even if the total S_a value is comparably lower in both models. Similarly, Europe in the satellite GEOS-Chem product has slightly higher S_a values than the models produce. In contrast, the S_a values over India are captured very well, and the peak values in East Asia are also produced by both models, while ECHAM-HAMMOZ simulates highest S_a values among the three data sets in East Asia. An overestimation of both models compared to satellite GEOS-Chem happens over North Africa. In South America EMEP MSC-W performs better than ECHAM-HAMMOZ due to larger contributions from secondary organic aerosol (SOA) formation. EMEP uses a more complex SOA scheme (Bergström et al., 2012; Simpson et al., 2012) which allows for oxidation ('aging') of semivolatile organic vapours. In ECHAM-HAMMOZ an adjusted amount of organic material covering also SOA is emitted, but the amount does not close the gap leading to a lower S_a compared to EMEP MSC-W and satellite GEOS-Chem.

5.2 Impacts of sensitivity tests

To evaluate the impact of our heterogeneous reactions, the six sensitivity runs were compared to the reference run containing all heterogeneous reactions. By turning off one heterogeneous reaction in each sensitivity run, the impact of each reaction can be estimated. Table 4 and 5 show the differences between the sensitivity runs and the reference run for EMEP MSC-W and ECHAM-HAMMOZ, as averaged over regions of North America (NA), Europe (EUR), East Asia (EA) and South Asia (SA) defined like in Fiore et al. 2009. The main focus of this evaluation lies on the effect of the heterogeneous reactions on ozone mixing ratios.

For the reference runs, EMEP MSC-W and ECHAM-HAMMOZ simulate very similar values for ozone, ECHAM-HAMMOZ giving somewhat lower mixing ratios. Also NO_x values are similar in Asia, but differ 50 % to 100 % in North America and

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Table 4. Impacts of gas-aerosol reactions on regional average mixing ratios of O_3 and key NOy compounds: EMEP model.

Region	Run	O_3 (ppb)	NO_x (ppb)	NO_y (ppb)	HNO_3 (ppb)	PAN (ppb)	N_2O_5 (ppt)	NO_3 (ppt)
NA	REF	39.830	0.863	1.824	0.213	0.513	12.27	5.01
NA	noN2O5	-3.788	-0.122	-0.210	0.012	-0.086	-34.02	-4.13
NA	noHO2	-0.061	0.010	0.001	-0.002	-0.007	0.25	0.50
NA	noHNO3	-0.121	0.0	0.041	-0.038	-0.0	0.01	-0.01
NA	noNO2	-0.190	-0.018	-0.014	0.001	-0.001	-0.47	-0.11
NA	noNO3	-0.084	-0.0	-0.001	0.0	-0.001	-0.10	-0.17
NA	noO3	-0.012	0.0	0.0	-0.0	-0.0	-0.00	-0.00
EUR	REF	40.607	1.023	2.432	0.256	0.508	16.43	7.33
EUR	noN2O5	-4.539	-0.292	-0.360	0.029	-0.104	-86.73	-8.06
EUR	noHO2	-0.300	0.027	0.004	-0.002	-0.020	0.64	0.94
EUR	noHNO3	-0.273	0.0	0.153	-0.149	-0.0	0.00	-0.20
EUR	noNO2	-0.160	-0.046	-0.028	0.001	0.004	-0.96	-0.30
EUR	noNO3	-0.163	-0.001	-0.003	0.0	-0.001	-0.38	-0.80
EUR	noO3	-0.051	0.0	0.0	-0.0	0.0	-0.00	-0.01
EA	REF	43.441	2.271	4.657	0.548	0.842	28.29	6.29
EA	noN2O5	-5.637	-0.481	-0.591	0.073	-0.180	-123.3	-10.17
EA	noHO2	-0.815	0.080	0.006	-0.011	-0.063	-0.04	0.48
EA	noHNO3	-0.114	0.002	0.083	-0.073	-0.0	0.02	0.00
EA	noNO2	0.354	-0.677	-0.421	0.060	0.067	-3.96	-0.30
EA	noNO3	-0.096	-0.0	-0.001	0.0	-0.001	-0.39	-0.21
EA	noO3	-0.017	0.0	0.0	-0.0	-0.0	-0.00	-0.00
SA	REF	47.010	1.140	2.932	0.421	0.313	24.38	12.86
SA	noN2O5	-3.799	-0.146	-0.120	0.007	-0.059	-40.12	-9.36
SA	noHO2	-0.273	0.033	0.010	-0.004	-0.016	1.22	1.59
SA	noHNO3	-0.680	-0.0	0.236	-0.260	-0.001	-0.23	-0.49
SA	noNO2	-0.357	-0.048	-0.036	0.001	-0.003	-2.56	-0.70
SA	noNO3	-0.469	-0.003	-0.008	-0.0	-0.002	-1.33	-1.44
SA	noO3	-0.043	0.0	-0.0	-0.0	-0.0	-0.00	-0.01

The first column refers to the region over which the annual mean is spatially averaged, and the second column refers to the corresponding run. Values shown for the reference run are total mixing ratios in ppbv. For all sensitivity runs only field averaged differences in ppbv are shown. Since the the sensitivity runs were subtracted from the reference run, positive values mean higher mixing ratios in the reference run than in the sensitivity runs and vice versa. Regions are defined as follows: NA (15°N–55°N; 60°W–125°W), EU (25 °N–65°N; 10°W-50°E), EA (15°N–50°N; 95°E–160°E), and SA (5°N–35°N; 50°E–95°E).

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Table 5. Same as table 4, but for ECHAM-HAMMOZ.

Region	Run	O_3 (ppb)	NO_x (ppb)	NO_y (ppb)	HNO_3 (ppb)	PAN (ppb)	N_2O_5 (ppt)	NO_3 (ppt)
NA	REF	38.936	1.293	1.591	0.146	0.135	14.85	2.71
NA	noN2O5	-2.163	-0.086	-0.125	-0.012	-0.011	-13.99	-1.52
NA	noHO2	-0.089	0.014	0.009	-0.003	-0.002	0.04	0.07
NA	noHNO3	-2.233	0.01	-0.18	-0.186	-0.003	-0.91	-0.29
NA	noNO2	-0.186	-0.027	-0.025	0.001	0.001	-0.46	-0.06
NA	noNO3	-0.039	0.0	0.001	0.0	0.0	-0.05	-0.04
NA	noO3	-0.071	0.001	0.001	-0.0	0.0	-0.05	-0.01
EUR	REF	39.566	2.034	2.376	0.154	0.161	21.51	4.7
EUR	noN2O5	-2.815	-0.215	-0.297	-0.019	-0.022	-38.0	-2.88
EUR	noHO2	-0.385	0.036	0.023	-0.005	-0.009	0.16	0.17
EUR	noHNO3	-2.163	0.019	-0.335	-0.349	-0.003	-1.37	-0.68
EUR	noNO2	-0.113	-0.118	-0.106	0.005	0.008	-1.16	-0.15
EUR	noNO3	-0.052	-0.0	-0.001	-0.0	0.0	-0.13	-0.13
EUR	noO3	-0.09	0.003	0.003	0.0	0.0	-0.07	-0.02
EA	REF	38.505	2.101	2.541	0.17	0.258	10.05	2.64
EA	noN2O5	-3.333	-0.24	-0.338	-0.026	-0.038	-31.27	-3.02
EA	noHO2	-0.816	0.098	0.054	-0.009	-0.034	-0.14	0.05
EA	noHNO3	-1.852	0.013	-0.242	-0.252	-0.003	-0.52	-0.24
EA	noNO2	0.062	-0.606	-0.542	0.013	0.053	-0.97	-0.12
EA	noNO3	-0.02	-0.001	-0.001	-0.0	0.001	-0.04	-0.05
EA	noO3	-0.053	-0.001	-0.0	-0.0	0.0	-0.02	-0.0
SA	REF	44.255	1.29	1.535	0.099	0.125	15.5	6.15
SA	noN2O5	-2.219	-0.083	-0.13	-0.013	-0.017	-14.85	-2.18
SA	noHO2	-0.287	0.036	0.024	-0.005	-0.007	0.1	0.22
SA	noHNO3	-3.453	0.009	-0.604	-0.606	-0.005	-1.27	-1.06
SA	noNO2	-0.33	-0.046	-0.047	0.001	0.0	-1.25	-0.3
SA	noNO3	-0.115	0.001	-0.001	-0.0	-0.0	-0.26	-0.21
SA	noO3	-0.077	-0.0	-0.001	-0.0	-0.0	-0.04	-0.02

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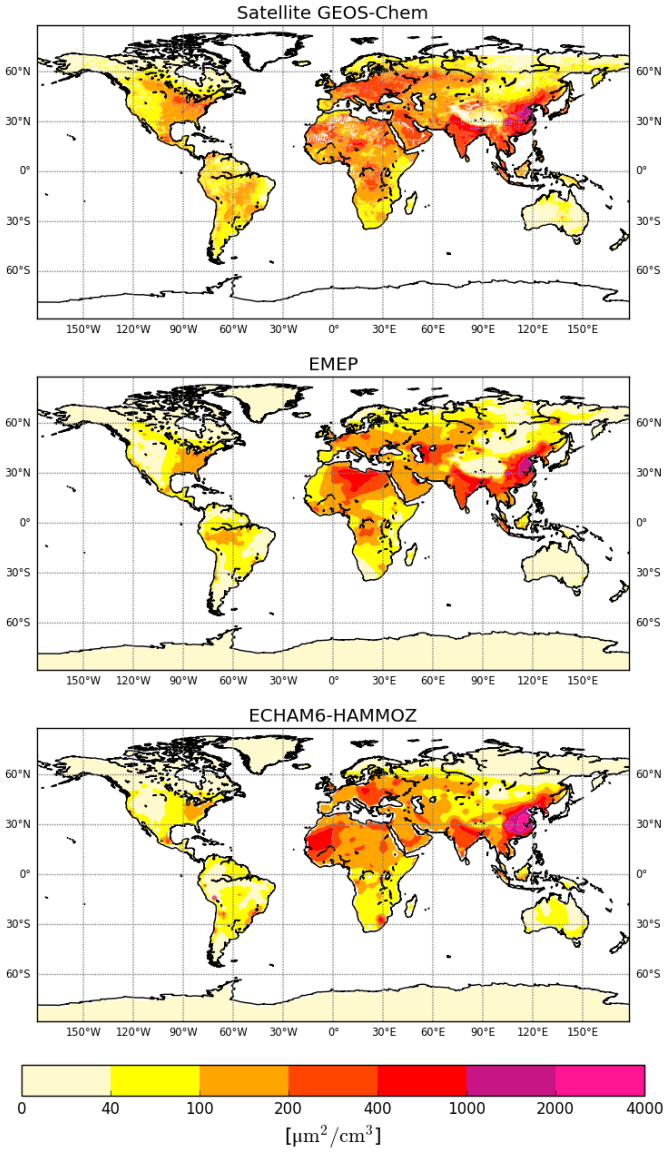

Figure 2. Satellite estimated (top) and simulated surface area densities by EMEP (middle) and ECHAM-HAMMOZ (bottom). The Satellite data is an average value for the time period 2010 - 2012, from van Donkelaar et al. (2015). The model data is for 2012.

Europe. In terms of other reactive nitrogen species, EMEP MSC-W has overall higher NO_y levels and especially PAN. This difference in NO_y availability is expected given the impact of EMEP's NH_3 emissions in the formation of ammonium nitrate, thus extending the lifetime of reactive nitrogen species.

Tables 4–5 clearly show reductions in O_3 from all the sensitivity runs, except for the sensitivity run without heterogeneous NO_2 reaction in East Asia. In this region the special case of ozone titration (Wild and Akimoto, 2001) leads to an ozone loss due to NO_2 instead of production: lowering NO_2 in this region of very high NO_x regions means reducing a loss process. Even if the models agree on the direction of the impact of heterogeneous reaction on O_3, they do not agree on the strength of the reactions.

For both models the N_2O_5 reactions have generally (ECHAM-HAMMOZ) or always (EMEP) the biggest effect on O_3, with changes of ca. 2–6 ppb. The EMEP model shows a consistently larger response in all regions. Some other heterogeneous reactions (especially NO_2, HO_2 and HNO_3) gain some significance in highly polluted areas where aerosol surface areas are high, but the two models show quite different response though in their response to these other gas-aerosol reactions. The EMEP model actually shows rather small impacts of all reactions except N_2O_5, except in East and South Asia where some impacts can approach 10-20% of that of N_2O_5. ECHAM-HAMMOZ, on the other hand, shows quite marked responses to especially the HNO_3 reactions, but also the HO_2 reactions.

The strong response of O_3 in ECHAM-HAMMOZ to the HNO_3 reaction compared to EMEP seems to be the result of a number of factors. The simplest is that EMEP allows this reaction only on coarse aerosol, and so has a smaller surface area for this reaction, especially on dust. Another explanation is that the model sensitivities to NO_x changes may be different, possibly caused by chemical differences or the different horizontal resolutions of the models. Ozone chemistry (and even the switch from production to loss) can be very sensitive to NO_x concentration levels, especially in unpolluted areas (Crutzen et al., 1999; Sillman et al., 1990). NO_x plumes from ships or power plants emitted into large model grid cells might well produce more O_3 in one model than the other, leading to different sensitivities to NO_x emissions (von Glasow et al., 2003; Vinken et al., 2011). The EMEP model has in fact a psuedo-species 'SHIPNOx' by which 50% of NO_x from ship plumes are given a pathway to HNO_3 production, skipping the intermediate NO_2 production associated with overestimating O_3 production from NO in pristine environments (Simpson et al., 2015). A further factor is the lack of nitrate aerosol in ECHAM-HAMMOZ. In the EMEP model HNO_3 can take part in ammonium nitrate aerosol (AN) formation, thus extending the lifetime of NO_y. Due to the AN, some HNO_3 can be recycled back into the atmosphere stabilizing the HNO_3 and NO_3 mixing ratios.

Table 5 shows that for ECHAM-HAMMOZ omitting the HNO_3 reaction on dust and sea salt aerosol increases NO_x by ca. 10-20 ppt, whereas in EMEP the change is tiny. The impact in ECHAM-HAMMOZ can be found over the whole globe, but especially over the oceans, where NO_x is low, but still much higher than NO_z. Changes in NO_z are far higher in ECHAM-HAMMOZ than in EMEP. Even if heterogeneous HNO_3 loss does not hugely impact NO_x, a small NO_x increase, even if really small, is ubiquitous and shifts the equilibrium between ozone production and loss towards more production, reaching a higher steady state O_3 concentration. Also, this reaction has a significant effect on NO_3, reducing it in the northern oceans by about 10 % (not shown). NO_3 rapidly photolyses, and resulting NO_2 likewise, so has a high ozone-formation potential. Reducing HNO_3 and therefore NO_3 drastically by the surface reaction in this highly sensitive region leads to a nonlinear response of the model

changing the gross ozone production in ECHAM-HAMMOZ by 350 Tg, which is a reduction of 7 %. This leads to a global more or less uniformly distributed difference of 1 - 4 ppbv in ozone mixing ratios.

Analyzing all the possible differences in these two different models is beyond of the scope of this study, but it may well be that ECHAM-HAMMOZ overestimates the impact of HNO_3 due to missing nitrate aerosol formation and EMEP underestimates the impact, due to the use of only coarse sea salt and dust aerosol for the HNO_3 and HO_2 reactions.

As the N_2O_5 reactions have the greatest impact on tracer concentrations among our sensitivity tests, the spatial and temporal differences between the reference run and the sensitivity run noN2O5 have been investigated in more detail. Figs. 3 and 4 show the difference between the mixing ratios of O_3 and NO_x in the reference run and in the sensitivity run without the N_2O_5 reactions. Both models show the largest changes in regions where high aerosol loadings and high NO_x emissions can be found, such as Northeast America, Europe, South and East Asia.

Converting N_2O_5 to HNO_3 on aerosol surfaces introduces an additional sink for NO_x, because HNO_3 is rapidly (in EMEP MSC-W) or immediately (in ECHAM-HAMMOZ) lost via dry, wet deposition and reactive uptake on aerosols after it is produced. Therefore, NO_x mixing ratios are lowered in the reference run REF compared to the simulation without the heterogeneous reaction noN2O5, as can be seen in Figure 4.

For ozone, the differences propagate through the whole northern hemisphere due to the longer lifetime of O_3 compared to NO_x (Fig. 3). Again both models simulate similar patterns with regard to the spatial distribution of changes due to N_2O_5. As described before, EMEP MSC-W shows a bigger impact on O_3 concentrations than ECHAM-HAMMOZ because of O_3 is already lowered due to the direct heterogeneous loss of HNO_3.

Especially for East Asia the impact of heterogeneous reactions cannot be neglected. High nitrate loadings in ammonium poor regions verify the importance shown by the models (Pathak et al., 2008). In the southern hemisphere, N_2O_5 and the other heterogeneous reactions evaluated in this study have much smaller impacts on ozone and NO_x than seen in the northern hemisphere (Figures 3, 4).

To explore the seasonal impact of N_2O_5 reactions, Fig. 5 shows monthly values for tracer mixing ratios and surface area density from both models for the different northern hemispheric regions. In general, the models produce comparable seasonal cycles for the gas tracers and surface area density. Strongest seasonal cycles are found in the noN2O5 run and in ozone for both runs. In the noN2O5 run, N_2O_5 builds up during winter time, because it is thermally unstable and photolabile. Including the heterogeneous uptake leads to a strong N_2O_5 reduction in both models, yielding a flat seasonal curve. The loss of N_2O_5 leads to a decrease in NO_2, NO_3 and PAN. Here models slightly differ. EMEP displays a stronger reduction in NO_3 and PAN, since it has in both runs higher mixing ratios compared to ECHAM-HAMMOZ. Removing NO_2 from the system leads in both models to a reduction of ozone. Although, the impact of N_2O_5 heterogeneous reaction on NO_2 is higher in winter and lowest during summer, the greatest change in O_3 can be found during spring. This can be explained by the availability of N_2O_5 and ozone production strength. As stated before, N_2O_5 is formed during night time, therefore less sun is favorable. In contrast, to form ozone light is needed. Still high N_2O_5 concentrations, enough surface area and a sufficiently high ozone production can be found during spring, leading to the biggest change in O_3 production during this season. During winter, nights are longer and the sun is less active, therefore also heterogeneous chemistry is efficient, but less ozone production reduction occurs.

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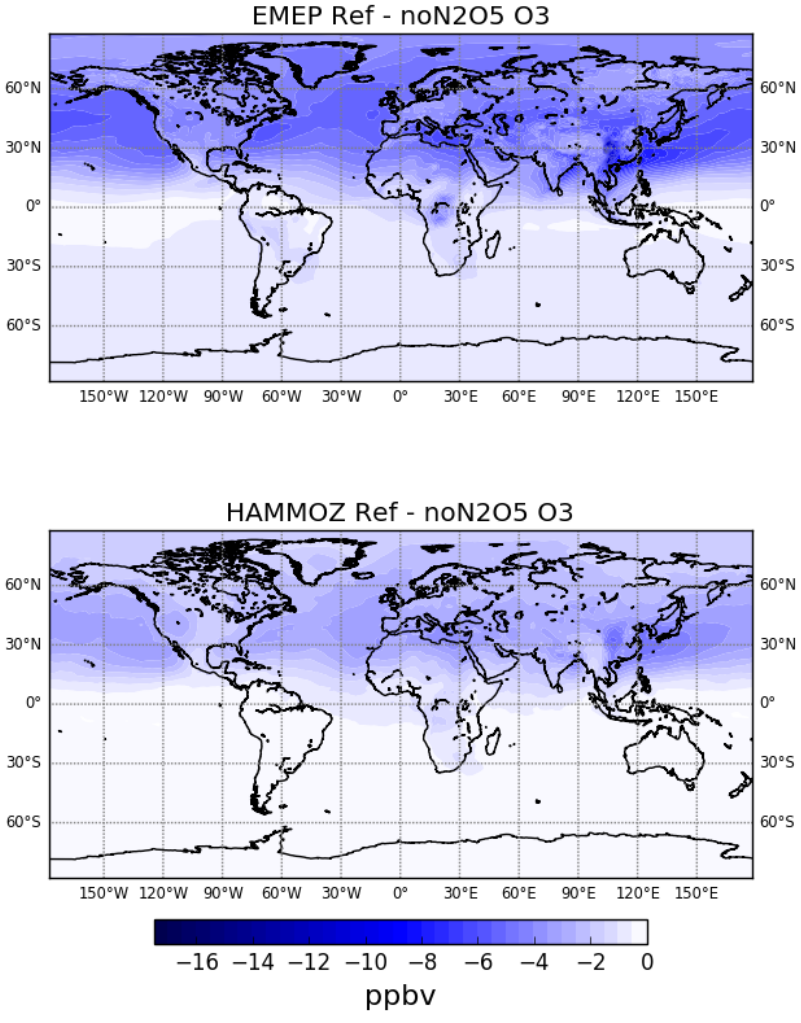

Figure 3. Differences in annual mean ozone mixing ratio between the reference run REF and the sensitivity run noN2O5 for 2012. Since the sensitivity run was subtracted from the reference run, negative values show higher values in noN2O5 than in REF.

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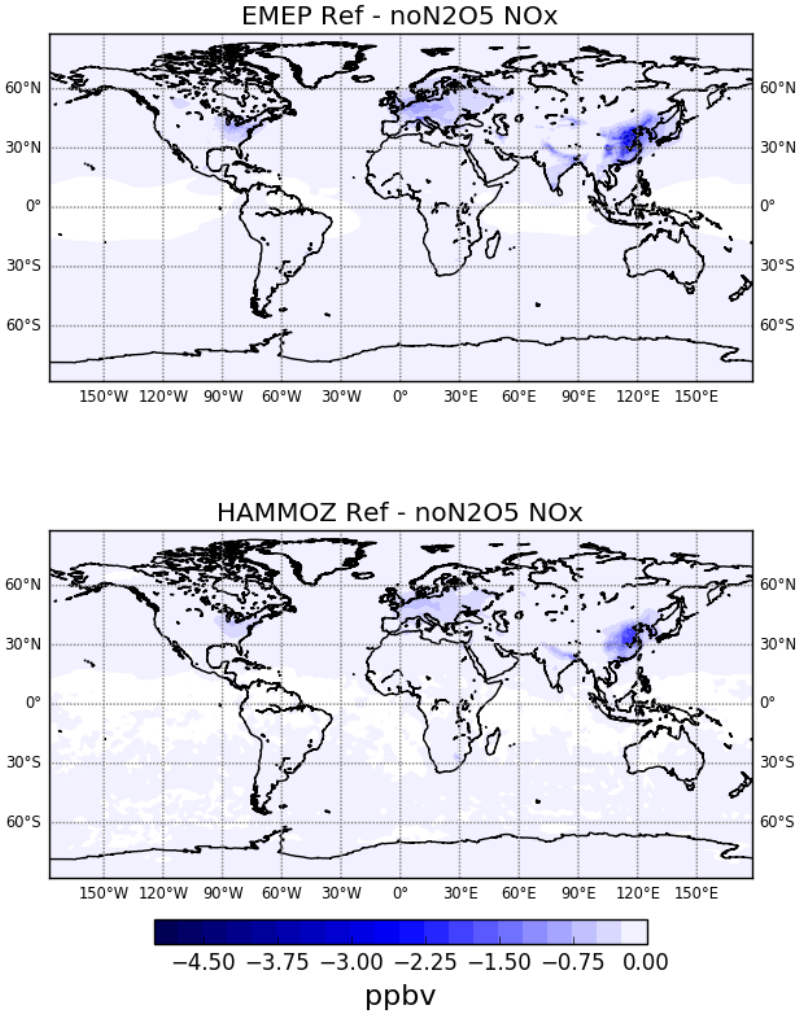

Figure 4. Differences in annual mean NO_x mixing ratio between the reference run REF and the sensitivity run noN2O5 for 2012. Since the sensitivity run was subtracted from the reference run, negative values show higher values in noN2O5 than in REF.

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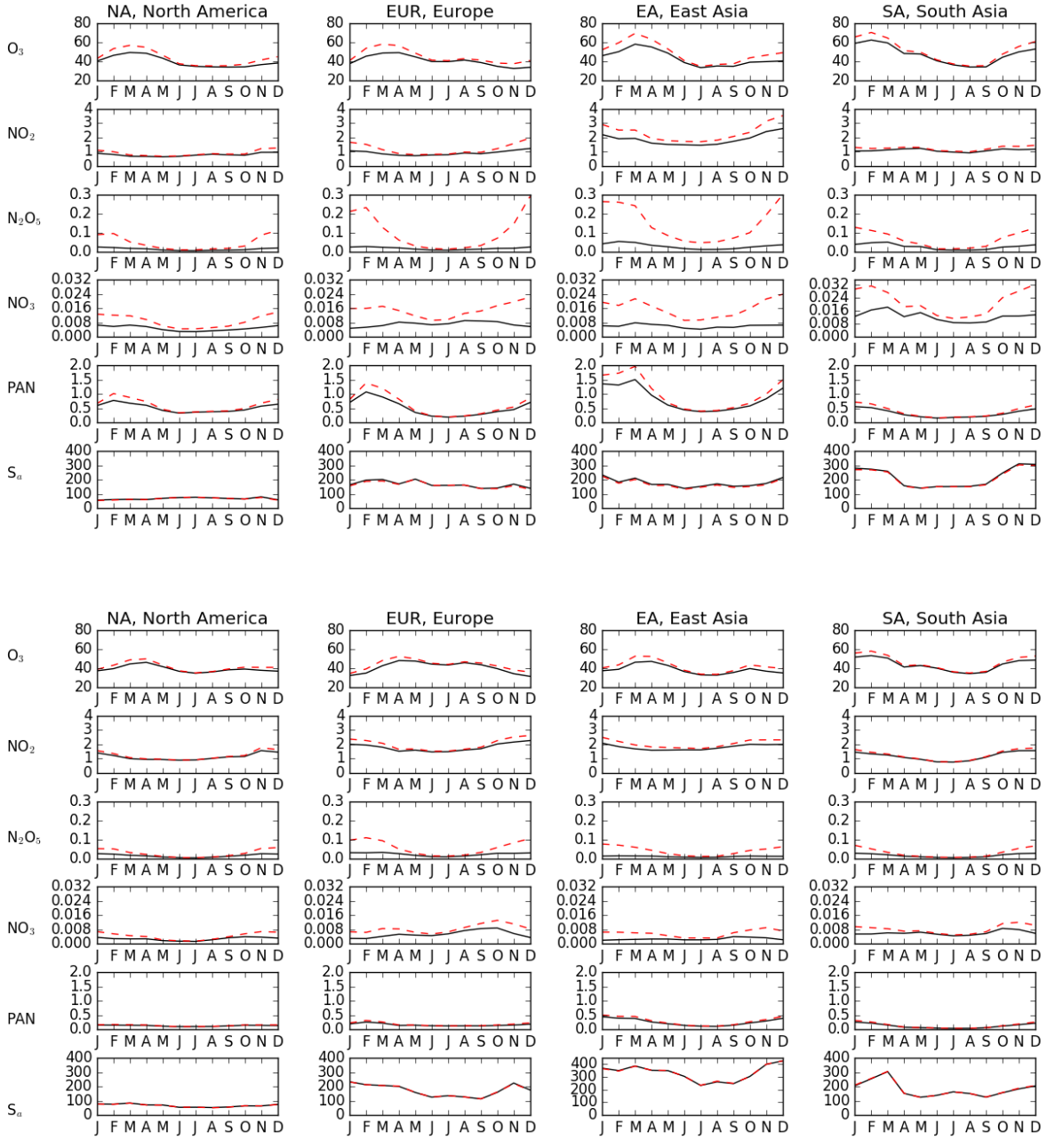

Figure 5. Changes in O_3, NO_2, N_2O_5, NO_3, PAN and S_a for the base-case (solid black line) and noN2O5 case (dashed red line) for EMEP (top) and ECHAM-HAMMOZ (bottom). Plots show monthly gas phase mixing ratios in ppbv and surface area density in $\mu m^2 cm^{-3}$ for different regions as defined above.

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5.3 Comparison with observations

Surface observations from 20 sites of the GAW and TOAR networks (Global Atmospheric Watch, Schultz et al. 2015, 2017), with stations distributed over the world, were used to evaluate ozone concentrations in the reference and N_2O_5 sensitivity runs of both models. The GAW data set consists of many sites in North America and Europe, but unfortunately few in Asia (e.g. none in China for 2012). Still, sites exist in Japan and these should provide a good indication of ozone formation downwind of the mainland. Mountain sites were excluded from this comparison in order to avoid problems with the interpretation of which model level is most appropriate for comparison. Trinidad Head on the west coast of USA and Mace Head on the west coast of Ireland are also good background stations which capture trends in hemispheric air masses arriving from the Pacific and Atlantic respectively (Parrish et al., 2009, 2014). To capture the seasonal dependence of N_2O_5 uptake on aerosol, daily maximum ozone values were compared with the corresponding interpolated model data. Since the stations were selected to be relatively remote and low-elevation, ground stations the comparison with the coarse grids of the models might be representative.

Six out of the twenty stations are shown in Figs. 6, 7 and 8. Both models generally capture the seasonal variation well, fine structures and fluctuations are often reproduced, but not equally well by both models and depending on the station. For example in Tsukuba, Japan both models simulate the increasing variability during summer time, nevertheless maximum concentrations are still underestimated. EMEP calculates higher peak values, than ECHAM-HAMMOZ, in contrast in Waldhof, Germany, ECHAM-HAMMOZ simulates higher peak values, partially overestimating them compared to the observations.

A closer look at the dashed line compared to the solid line reveals the seasonal highest impact of N_2O_5 during spring time. The high impact in spring pattern can be found in both model simulations, but is stronger in EMEP, since ECHAM-HAMMOZ includes the year through ozone reduction due to direct HNO_3 loss explained in the previous section 5.2. For example in Mace Head, Ireland the springtime ozone formation is clearly decreased by N_2O_5 reaction, while during summer the impact is marginal and increases again during winter. Both models start with a spin-up from the reference run, therefore the winter impact can not be seen in January. If the models would run for another month, this would show too, indicated by the gap between reference run and noN2O5 sensitivity run at the very end of the year.

Concluding, the impact of N_2O_5 heterogeneous reactions on chemical ozone production leads to a better agreement of EMEP and ECHAM-HAMMOZ and daily maximum ozone station observations in remote stations. Both models show improvements due to prior slight ozone overestimation. Heterogeneous chemistry removing ozone in models which tend to overestimate it, logically improve the model. This improvements could also be done introducing other nitrogen species loss process to reduce ozone production, less NO_x emissions or dynamically inhibiting downward transport of stratospheric ozone. Especially the stratospheric ozone intrusion is assumed to strongly happen during spring time, which would cause the same pattern as we see here in Figures 6, 7 and 8.

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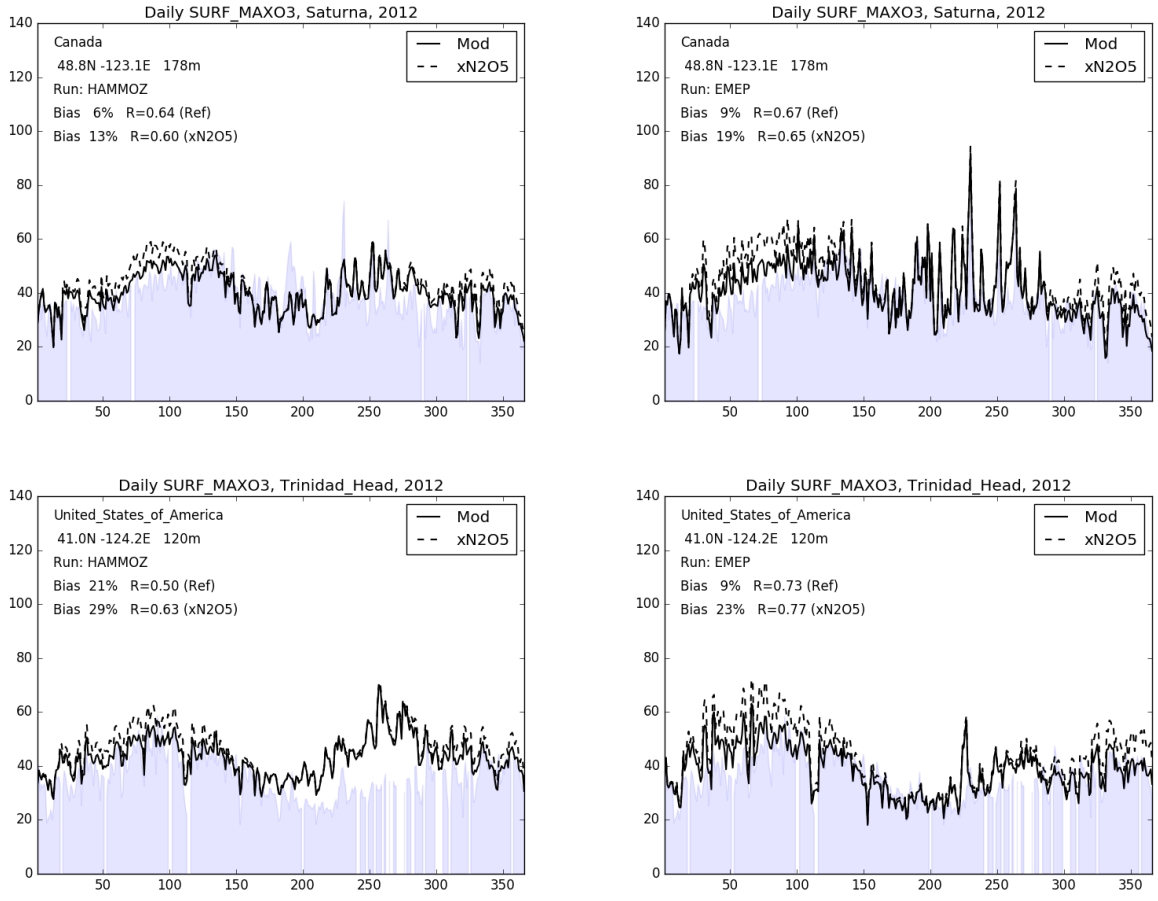

Figure 6. Modelled versus observed daily maximum ozone (ppbv) for two North American sites (Saturna, Canada, Trinidad Head, USA). The shaded area refers to surface station observations, the solid line is the reference run of the model and the dashed line the sensitivity run noN2O5 excluding heterogenous N_2O_5 reaction. On the upper left corner the station location, model, bias and correlation R are specified.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-566
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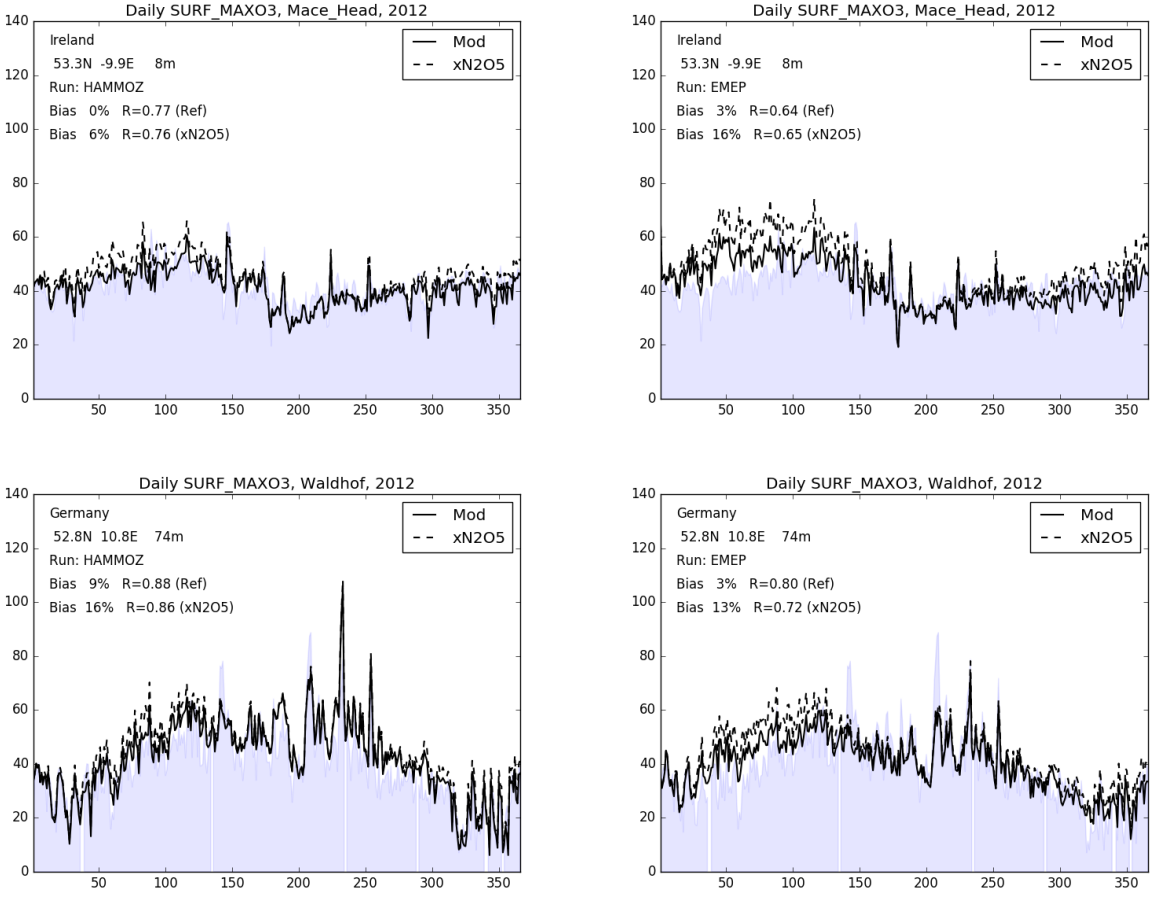

Figure 7. As Fig. 6 but for two European sites, Mace Head (Ireland) and Waldhof (Germany).

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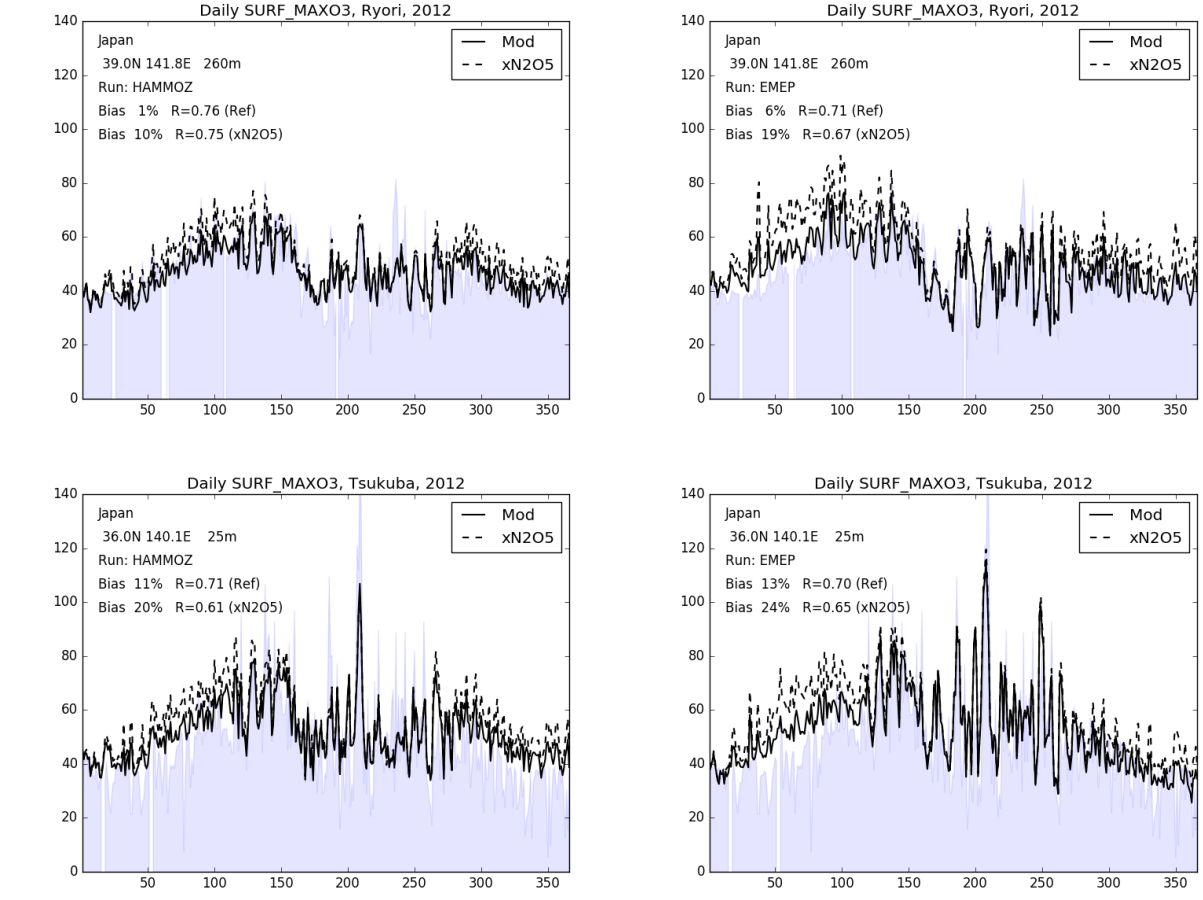

Figure 8. As Fig. 6 but for two Japanese sites, Ryori and Tsukuba.

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Atmospheric Chemistry and Physics Discussions

6 Conclusions

Two global transport models were used to investigate the implications of six heterogeneous (gas-aerosol uptake) reactions on ground-level ozone concentrations. Both models were harmonized to use similar parameterizations for most of these reactions, enabling us to compare the impacts of N_2O_5, NO_3, NO_2, O_3, HNO_3, and HO_2 on ozone mixing ratios. Each reaction was evaluated systematically comparing the reference run to sensitivity simulations excluding one reaction at a time. Since heterogeneous reactions take place at the aerosol surface area, the modeled surface area density S_a of both models was compared to a satellite product retrieving the surface area. This comparison shows a good agreement in global pattern and especially the capability of both models to capture the extreme aerosol loadings in East Asia.

The analysis of the sensitivity runs confirms that the globally most important heterogeneous reaction is the one of N_2O_5. This impact was expected from previous studies, with the surface reactions of N_2O_5 having an impact on ozone mixing ratios through removal of reactive NO_x species. Some other heterogeneous reactions (especially the ones of NO_2, HO_2 and HNO_3) gain some significance in highly polluted areas where aerosol surface areas are high, but the two models show quite different response in their response to these other gas-aerosol reactions. The EMEP model actually shows rather small impacts of these reactions, except in East and South Asia where some impacts can approach 10-20% of that of N_2O_5. ECHAM-HAMMOZ, on the other hand, shows quite marked responses to especially the HNO_3 reactions. The reasons for this are related to differences in nitrate chemistry and surface area assumptions in the models, and to the differing spatial resolutions. It may well be that ECHAM-HAMMOZ overestimates the impact of HNO_3 due to missing nitrate aerosol formation and EMEP underestimates the impact, due to the use of only coarse sea salt and dust aerosol for the HNO_3 and HO_2 reactions.

The reactions of O_3 on dust and NO_3 on aerosols were found to have only minor effects on ozone in comparison to the other reactions in both models. In terms of global spatial impact, all reactions related to nitrogen species alter atmospheric chemistry downwind of source areas to some extent, with changes being much larger in the polluted northern hemisphere than in the southern hemisphere.

Evaluation of the models with northern hemispheric ozone surface observations from the GAW/TOAR networks yields a better agreement of the models with observations in terms of daily maximum concentrations, variability and temporal correlations at most sites when the heterogeneous reactions are incorporated. The impacts of the N_2O_5 reactions show strong seasonal variations, with biggest impacts in spring time when photochemical reactions are active and N_2O_5 levels still high.

Due to lack of direct observations substantial uncertainties remain regarding the impact of heterogeneous reactions on tropospheric reactive gases. It should be noted, that neither model had animplementation of the particle-liquid-water/nitrate/chloride effects suggested by Bertram and Thornton (2009) and tested by e.g. Lowe et al. (2015). Further, neither model includes halogen chemistry, which is also known to impact O_3 in polluted regions (e.g. Sarwar et al., 2014; Li et al., 2016). The large impact of N_2O_5 seen in our work might be somewhat overestimated compared to that we would obtain if the chemistry of $ClNO_2$ (which would recycle NO_x) and other halogens could be included. Such improvements should result in better particle phase chemistry, and will be the subject of future work.

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