

**In-cloud oxalate
formation in the
global troposphere**

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In-cloud oxalate formation in the global troposphere: a 3-D modeling study

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Abstract

Organic acids attract increasing attention as contributors to atmospheric acidity, secondary organic aerosol mass and aerosol hygroscopicity. Oxalic acid is globally the most abundant dicarboxylic acid, formed via chemical oxidation of gas-phase precursors in the aqueous phase of aerosols and droplets. Its lifecycle and atmospheric global distribution remain highly uncertain and are the focus of this study. The first global spatial and temporal distribution of oxalate, simulated using a state-of-the-art aqueous phase chemical scheme embedded within the global 3-dimensional chemistry/transport model TM4-ECPL, is here presented. The model accounts for comprehensive gas-phase chemistry and its coupling with major aerosol constituents (including secondary organic aerosol). Model results are consistent with ambient observations of oxalate at rural and remote locations (slope = 0.83 ± 0.06 , $r^2=0.67$, $N=106$) and suggest that aqueous phase chemistry contributes significantly to the global atmospheric burden of secondary organic aerosol. In TM4-ECPL most oxalate is formed in-clouds and less than 10% is produced in aerosol water. About 61% of the oxalate is removed via wet deposition, 35% by in-cloud reaction with hydroxyl radical and 4% by dry deposition. The global oxalate net chemical production is calculated to be about $17\text{--}27\text{ Tg yr}^{-1}$ with almost 91% originating from biogenic hydrocarbons, mainly isoprene. This condensed phase net source of oxalate in conjunction with a global mean turnover time against deposition of about 5 days, maintain oxalate's global tropospheric burden of $0.24\text{--}0.39\text{ Tg}$ that is about 13–19% of calculated total organic aerosol burden.

1 Introduction

Atmospheric aerosols are composed of water, inorganic salts, crustal material, carbonaceous compounds and trace metals. Organic aerosols (OA) account for a significant fraction of the fine particulate mass in the atmosphere (e.g., Kanakidou et al.,

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2005; Zhang et al., 2007). However, many uncertainties exist regarding their sources, composition, properties and transformation mechanisms, impeding the evaluation of OA impacts on atmospheric composition, climate, human health and ecosystems (Kanakidou et al., 2005). OA can also affect the hygroscopicity of cloud nucleation by modifying cloud condensation nuclei (CCN) number and efficiency (Yu, 2000; Sun and Ariya, 2006).

OA components can be directly emitted in the atmosphere in the particulate phase (primary organic aerosols; hereafter POA) or chemically formed in the atmosphere (secondary organic aerosols; hereafter SOA). A large fraction of “traditional” POA is also semi-volatile, being a dynamic mixture of compounds with vapor pressures that span several orders of magnitude (Robinson et al., 2007). SOA is formed from the semi-volatile partitioning of volatile organic compound (VOCs) oxidized by e.g., ozone (O₃), hydroxyl (OH) and nitrate (NO₃) radicals (e.g., Kanakidou et al., 2005; Hallquist et al., 2009).

Aerosol Mass Spectrometer (AMS) observations (Zhang et al., 2007; Jimenez et al., 2009) indicate that a large fraction of the ambient OA in the fine mode is chemically processed (oxygenated). Although the gas-to-particle partitioning mechanism is included in many state of the art global atmospheric models (e.g., Tsigaridis and Kanakidou, 2003, 2007; Heald et al., 2005, 2006; Hoyle et al., 2009; Pye and Seinfeld, 2010), the predicted organic aerosol burden is significantly underestimated (5–100 times in the upper troposphere) compared to OA measurements upon comparison (de Gouw et al., 2008; Heald et al., 2005; Volkamer et al., 2006). This discrepancy might arise from atmospheric processes (mechanisms and/or precursor species) not adequately represented or omitted in global models.

Aqueous-phase chemistry provides a complementary pathway for SOA formation to non-aqueous gas-particle partitioning (“traditional” description of SOA) and has the potential to enhance OA concentrations in the atmosphere and particularly in the free troposphere (Gelencser and Varga, 2005; Sorooshian et al., 2007; Ervens et al., 2008). Weber et al. (2007) showed that up to 50% of the organic aerosol mass can be

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attributed to aqueous phase production. During SOA formation in the gas-phase, the precursors are mostly high molecular weight (MW) molecules ($>C_7$) able to produce semi-volatile compounds. In the case of aqueous phase SOA formation, the precursors need to be water soluble and therefore can be smaller and oxidized molecules (Volkamer et al., 2007). Their oxidation products have higher O:C content than their precursor molecules (Jimenez et al., 2009). During gas-phase oxidation, C–C bonds can often be cleaved, yielding smaller and therefore more volatile compounds. On the contrary, in the aqueous phase C–C bonds are preserved, since organic compounds oxidation by OH radicals forms multi-functional compounds (Carlton et al., 2007). In addition, condensed-phase OH reactions are shown to enhance O:C ratio in the products (Lim et al., 2010) more than the gas-phase reactions (Jimenez et al., 2009) because the oxidation occurs on low-MW precursors. Such processes can explain the high O:C ratio (close to 1 or even higher) observed in aged ambient aerosols (Aiken et al., 2008; Altieri et al., 2009) and thus bring models closer to observations (Ervens and Volkamer, 2010; Jimenez et al., 2009). One of the most important aqueous phase products is oxalic acid, $(COOH)_2$, which has high O:C ratio of 2.

Formation of low-volatility organic compounds by multiphase processes has been observed during both field (Kawamura et al., 1996; Matsunaga et al., 2003; Liggio and McLaren, 2003; Garcia-Alonso et al., 2006; Volkamer et al., 2007; Hecobian et al., 2010) and laboratory studies (Ervens and Volkamer, 2010; Lim et al., 2010) of glyoxal (CHOCHO; hereafter GLY). GLY is produced via the oxidation of $C_{n \geq 2}$ -hydrocarbons, with a global chemical production estimated to be $45\text{--}100 \text{ Tgyr}^{-1}$ (Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrou et al., 2009). Stavrou et al. (2009) showed through inverse modeling that only half of the over land observed GLY columns can be understood in terms of identified sources (primary and secondary). GLY is highly reactive in the aqueous phase (Buxton et al., 1997) and has been suggested to participate in heterogeneous reactions producing SOA (Ervens and Volkamer, 2010; Lim et al., 2010). By applying an irreversible uptake (γ) of GLY on aqueous particles and cloud drops ($\gamma = 2.9 \times 10^{-3}$; Liggio et al., 2005a), Fu et al. (2008) and Stavrou et al.

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(2009) calculated that about 90% of GLY is subject to dissolution in atmospheric water (clouds and wet aerosols) contributing to SOA formation by 6.4 to 13 Tg yr⁻¹. However, observations of GLY atmospheric columns from the SCIAMACHY satellite sensor are generally underestimated by chemistry transport models (Wittrock et al., 2006; Myriokefalitakis et al., 2008), in particular over the oceans. Myriokefalitakis et al. (2008) suggested the existence of a source of GLY (~20 Tg yr⁻¹) over the oceans to support GLY columns observed over the tropical oceans. High GLY columns have been also recorded by recent surface-based measurements of GLY over the oceans (Sinreich et al., 2010; Volkamer et al., 2010). Their significance on the GLY budget and involvement in SOA formation remains to be determined.

The main atmospheric reservoirs of liquid water are cloud droplets and wet aerosols; their main difference lies in the amount of liquid water per particle (often well described by the liquid water content, LWC) (Fig. 1). Clouds are formed from condensation of water vapor onto CCN, cover ~60% of the Earth's surface and occupy about 7% of the tropospheric total volume (Lelieveld et al., 1989; Pruppacher and Jaenicke, 1995). Clouds provide medium for chemical transformations that are either not taking place, or proceed very slowly in the gas-phase (e.g. non-sea-salt sulfate (nss-SO₄²⁻) production; Fuzzi et al., 2001). Aerosol water can be about five orders of magnitude less than cloud LWC (0.1–1 vs. 10⁻⁶–10⁻⁴ g m⁻³, respectively; Ervens and Volkamer, 2010; Hennigan et al., 2008a) therefore the concentration of dissolved substances can vary orders of magnitude between the two systems. In the condensed medium of wet aerosols, organics can react with themselves or with other aerosol components such as sulfate, ammonium, amides, to form sulfur and nitrogen containing organic compounds (Perri et al., 2009; Noziere et al., 2008; Ervens and Volkamer, 2010; Lim et al., 2010).

Water-soluble organic compounds can be transferred and react into atmospheric liquid water, forming lower volatility compounds such as organic acids (Warneck, 2003; Ervens et al., 2004; Lim et al., 2005; Carlton et al., 2006; Perri et al., 2009), oligomers (Tan et al., 2009; Altieri et al., 2006, 2008; Perri et al., 2009) and organosulfates (Liggio et al., 2005a; Galloway et al., 2009). The low volatile organic products remain (at

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least partly) in the particulate phase after droplet evaporation, contributing to OA mass (Sorooshian et al., 2007, 2010; Hennigan et al., 2008b). Hennigan et al. (2009) showed that a substantial amount of gas-phase organic species partition onto aerosol during late morning in the South East US; the organic mass is semi-volatile (but does not evaporate together with the aerosol water) and can contribute substantially, up to 50% of the total SOA mass, in this region of the globe. Low molecular weight dicarboxylic acids are recognized as ubiquitous aerosol constituents (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994; Kawamura et al., 1995a, b; Kawamura and Sakaguchi, 2009), contributing to a few percent on the water soluble mass (Sorooshian et al., 2007, 2010).

Lim et al. (2005) suggested that carbonyls like glycolaldehyde (HOCH_2CHO ; hereafter GLYAL) and methylglyoxal (CH_3COCHO ; hereafter MGLY) could contribute similarly to GLY to the global SOA formation. GLY, GLYAL and MGLY are gas-phase high solubility oxidation products of biogenic and anthropogenic VOCs. In the presence of liquid water, these aldehydes dissolve in the aqueous phase following Henry's law. Hydrated aldehydes are oxidized by OH radicals producing oxalate (hereafter OXL), mostly via glyoxylic acid oxidation (CHOCOOH ; hereafter GLX). OXL is a low volatility product that upon cloud evaporation tends to remain in the particulate phase (especially if it is neutralized by e.g., ammonium or sodium).

Lim et al. (2005) and Carlton et al. (2007) presented a chemical scheme of GLY, GLYAL and MGLY in the aqueous phase producing oxalic acid that remains mainly in the particulate phase as OXL. Isoprene is the biogenic hydrocarbon with the highest emissions of about 500 Tg yr^{-1} (Guenther et al., 1995), followed by terpenes (about 140 Tg yr^{-1} ; Guenther et al., 1995), which are the main precursors of light aldehydes in the atmosphere like GLY, GLYAL and MGLY (Myriokefalitakis et al., 2008). Box model calculations by Lim et al. (2005) suggested that cloud processing of isoprene contributes to at least 1.6 Tg yr^{-1} on the global biogenic SOA production.

OXL is globally the most abundant dicarboxylic acid with concentrations ranging from tens of ng m^{-3} in remote locations (Sciare et al., 2009) to hundreds of ng m^{-3} in urban

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regions (Kawamura and Ikushima, 1993; Sorooshian et al., 2007; Legrand et al., 2007) and up to more than $1 \mu\text{g m}^{-3}$ in highly forested areas like the Amazon basin (Falkovich et al., 2005) and Central Africa (Ruellan et al., 1999). The observed correlation between nss-SO_4^{2-} and OXL at various locations denotes a common formation pathway (Yu et al., 2005; Sorooshian et al., 2006), most probably associated with aqueous phase chemistry. Modeling studies also support the in-cloud oxalic acid formation (Warneck, 2003; Ervens et al., 2003, 2004; Lim et al., 2005, 2010) from GLY (Carlton et al., 2007) and other GLY-like gas-phase precursors like GLYAL (Perri et al., 2009) and MGLY via pyruvic acid (CH_3COCOOH ; hereafter PRV) oxidation (Altieri et al., 2008).

Primary sources, albeit weak, have also been identified for oxalic acid. Yamasoe et al. (2000) showed that OXL accounts for about 0.1% of the total aerosol mass emitted during the burning of tropical forests. Schmidl et al. (2008) found that the average concentration of OXL in smoke from the burning of wood ranges between 0.1–0.3% of the total emitted mass (almost 400 times lower than that of OC concentrations). Moreover, incomplete combustion of aromatic hydrocarbons (benzene, toluene, naphthalenes, and others) in gasoline engines could be a potential primary source of atmospheric diacids, with oxalic acid concentrations accounting for almost 25–50% of the total dicarboxylic acid emitted mass (Kawamura and Kaplan, 1987). Nevertheless, vehicle exhaust is not expected to be a significant primary source of oxalic acid in the atmosphere (Huang and Yu, 2007).

In the current study we present the first 3-dimensional chemistry-transport modeling (CTM) study of occurrence and fate of oxalate in the global troposphere. The temporal and spatial OXL distributions are simulated using the 3-dimensional global CTM, TM4-ECPL, coupled with a multiphase chemistry module. Section 2 describes the modeling tool and the simulations that have been performed for this study. The OXL global budget calculations are presented in Sect. 3 where the contributions of biogenic and anthropogenic sources to OXL chemical production are distinguished and the impact of the OXL removal processes taken into account by the model is discussed. In Sect. 4 the computed OXL distributions are presented and compared, in Sect. 5, with observations

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of OXL available in literature to evaluate model uncertainties. The implications of the findings for the OA global budget are discussed in Sect. 6.

2 Model description

The chemistry-transport global model TM4 is used for the present study (van Noije et al., 2004). The model version applied here (TM4-ECPL) contains a comprehensive gas-phase chemistry mechanism (Myriokefalitakis et al., 2008) and organic aerosol parameterizations from Tsigaridis et al. (2006), Tsigaridis and Kanakidou (2007) and Myriokefalitakis et al. (2010). Gas-particle partitioning of inorganic species components is solved using the ISORROPIA II aerosol thermodynamics model that also calculates aerosol water content (Nenes et al., 1998; Fountoukis and Nenes, 2007). The resolution of TM4-ECPL is 34 vertical hybrid layers from the surface to 0.1 hPa and $4^\circ \times 6^\circ$ horizontal resolution in latitude and longitude, using a time-step of 1 h. In this study, the meteorological fields come from ECMWF (European Center for Medium-Range Weather Forecasts) operational data for year 2005 and are updated every 6 h using short range forecasts over 6 or 12 h.

2.1 Emissions

TM4-ECPL uses the monthly average $1^\circ \times 1^\circ$ gridded VOC, nitrogen oxides (NO_x), carbon monoxide (CO) and biomass burning trace gas (biogenic and anthropogenic) emissions from the POET database (Granier et al., 2005) for the year 2000. Biomass burning emissions of carbonaceous aerosols for the respective year are adopted from the Global Fire Emissions Database version 2 (GFED v2; Van der Werf et al., 2006). Marine emissions of POA, hydrocarbons and sea-salt particles, are calculated online as presented in Myriokefalitakis et al. (2010). Dust emissions from AEROCOM (Aerosol Comparison between Observations and Models; Dentener et al., 2006) updated to year 2005 are also used.

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2.2 Aqueous-phase chemistry scheme

The chemical mechanism in TM4-ECPL is based on recently published box modeling studies (Ervens et al., 2004; Lim et al., 2005; Sorroshian et al., 2006; Carlton et al., 2007; Ervens and Volkamer, 2010). Chemical production of OXL occurs only in the aqueous phase, as there are no known gas-phase chemical reactions that produce the compound. In the presence of cloud droplets, GLYAL, GLY, MGLY, HCOOH, CH₃COOH and PRV are transferred from the gas to the aqueous phase, where GLYAL, GLY, MGLY and PRV are oxidized by OH radicals to produce OXL via GLX oxidation. In the presence of clouds, GLX and OXL are also considered to repartition between the gas and aqueous phases.

The 27 aqueous phase reactions taken into account in the model include 13 species and are listed in Table S1 (supplementary material), together with the adopted reaction rates. The pH-dependence of aqueous phase chemistry is considered via the equilibrium reactions given in Table S2 (supplementary material). Using TM4-ECPL, in-cloud [H⁺] concentration is calculated from the strong acids and bases as

$$[\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{MS}^-] + [\text{HNO}_3] + [\text{NO}_3^-] - [\text{NH}_4^+]$$

where MS⁻ is the methansulfonate; HNO₃ is nitric acid NO₃⁻ is nitrate ion and NH₄⁺ is ammonium ion. For pH > 4.3 the dissociation of the weak acids, CO₂, SO₂, and of the base NH₃ are also taken into account (Jeuken et al., 2001). For the present study OXL is also taken into account. The composition, phase state (solid/liquid phase) speciation, aerosol water, and pH are obtained from the ISORROPIA II aerosol thermodynamic equilibrium model (Fountoukis and Nenes, 2007).

The partitioning between the gas and aqueous phases of O₃, OH and HO₂ radicals, hydroperoxide (H₂O₂), GLY, GLYAL, MGLY, HCOOH, CH₃COOH, PRV and OXL is parameterized based on the Henry's law (Table S3, supplementary material). For most species, the transfer between the gas and aqueous phases is parameterized using the phase ratio. This expresses the amount of gas in a given volume of air that resides in the aqueous phase relative to the amount in the interstitial gas-phase (Lelieveld and

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Crutzen, 1991). Using the phase ratios for each species the partitioning between the gas and aqueous phases is calculated. However, mass transfer limitations are taken into account for species with high reactivity in the aqueous phase (Schwartz, 1986). In the present study, the transfer of OH and HO₂ radicals between gas and aqueous phases follow mass diffusion processes (see details in Supplementary material A1).

2.3 Simulations

Several sources of uncertainty in the predictions have been investigated in the simulations (e.g., the dependence of OXL production on temperature, on the cloud pH, on the phase-transfer of the precursor molecules, the potential OXL primary emissions and the OXL chemical formation in aerosol water). For these investigations, simulation S1 has been used as a reference case for simulations S1.1 to S1.3, S2, S3 and S4. The differences between these simulations and S1 are summarized in Table 1.

The base simulation (S1) assumes that the in-cloud OXL formation is the only source of OXL in the atmosphere. After cloud evaporation, OXL is considered to remain entirely in the aerosol phase. This phase change is governed by Henry's law, where the effective Henry's law constants depend on the aqueous medium composition. Cloud droplets are not pure water but also contain sulfate, ammonium and other components; the presence of salts tends to enhance the Henry constant values (Ip et al., 2009). In particular, GLY partitioning measurements in Na₂SO₄ solutions with ionic strength within the range of observations for atmospheric aerosols, clouds and rain (spanning from 10⁻⁶ to a few tens of M; Herrmann, 2003) show enhanced Henry's values by about 2 orders of magnitude. In S1, in order to take into account the ionic strength effect of cloud droplets, the effective Henry's law constant values for GLY, GLYAL and MGLY are increased by 2 orders of magnitude (Ip et al., 2009).

Nevertheless, the ionic composition and strength of cloud droplets is largely uncertain, therefore an additional simulation (S1.1) is carried out that neglects any water ionic composition impact on Henry law constants. The phase transfer of the gaseous precursors into the interstitial cloud is critical for the abundance of OXL. Therefore,

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even though some ionic strength always is present in cloud, S1.1 is used rather as the lower limit for OXL formation. The temperature dependence of Henry law constants can be a significant source of uncertainty in a global modeling study where temperature is spanning over a large range of values. High temperatures are associated with low solubility constants, which imply lower aqueous phase OXL concentrations near the surface (higher temperatures) and higher in the free troposphere (lower temperatures) than when neglecting the temperature dependence. The temperature effect on species solubility (hence OXL production) has been investigated by an additional simulation (S1.2) where Henry's constants for 298 K (H_{298} ; Table S3, Supplement) have been used throughout the model domain. Moreover, the effect of pH on OXL formation has been studied analyzing simulation S1.3 in which aqueous phase partitioning and chemical rates are computed based at a constant pH (4.5) reflective of a mean value for urban and remote conditions (Herrmann et al., 2000).

Simulation S2 is similar to S1, but also considers the (potential) combustion primary sources of oxalic acid (i.e., biomass burning and fossil fuel combustion). Due to the scarcity of available oxalic acid emission factors, biomass burning processes and fossil fuel combustion emissions have been scaled to the organic carbon (OC) observations by Schmidl et al. (2008), and the OC emissions from biomass burning and anthropogenic combustion processes. The adopted biomass burning OC emissions in TM4-ECPL for the year 2005 amount to roughly 22 Tg C yr^{-1} (GFED v2; Van der Werf et al., 2006). For this simulation, 1% of these OC emissions ($\sim 0.1 \text{ Tg C yr}^{-1}$) is assumed to be in the form of oxalic acid.

Simulation S3 is similar to S2 but also considers OXL formation into aerosol aqueous phase (Fig. 1c,d). Lim et al. (2010) showed that SOA formed by GLY in aerosol water are predominantly (>80% by mass) in the form of oligomers; in contrast, OXL dominates SOA formed in cloud water. Ervens and Volkamer (2010) suggested that the chemistry in aerosol water is governed by photochemical processes during daytime that can be described by a lumped reaction rate, which varies between 0.8 s^{-1} and 7 s^{-1} depending on the hygroscopicity of seed aerosol. During nighttime, SOA

are mostly produced via NH_4^+ reactions in the aerosol water, which can be described by a reaction rate constant that depends on the ionic strength and ranges from $1.3 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$ to $4.3 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$ (Noziere et al., 2009; Ervens and Volkamer, 2010). For simplicity, in the present study we assume that during daytime GLY produces SOA that are 80% oligomers and 20% OXL (by mass; Table S1, Supplement). For this photochemical process, a pseudo-first order reaction rate of 4 s^{-1} is adopted, which corresponds to an average rate of SOA production on ammonium sulfate seed in agreement with Ervens and Volkamer (2010). To account for the impact of light intensity on this photochemical process, the pseudo-first order reaction rate is scaled to the photolysis frequencies of H_2O_2 . In the absence of light, GLY is considered to exclusively react with ammonium (NH_4^+) in the aerosol water (Noziere et al., 2009) producing 100% SOA (identified by Noziere et al. (2009) to be mostly oligomeric species; B. Ervens, 2010, personal communication; Table S1, Supplement). Ervens and Volkamer (2010) showed that for aerosol water, depending on the aerosol composition, the GLY's effective Henry's law constant spans more than 3 orders of magnitude, compared to pure water. Therefore for simulation S3, the Henry's law constant of GLY for aerosol water has been further increased by an order of magnitude compared to S1.

Simulation S4 is similar to S3 but also considers a potential GLY source over the oceans as suggested by comparison of our model results with satellite observations (Myriokefalitakis et al., 2008). For this explorative simulation, GLY emissions of 20 Tg yr^{-1} (Myriokefalitakis et al., 2008) have been taken into account in TM4-ECPL. They are distributed geographically and monthly based on the difference between the TM4-ECPL modeled and SCIAMACHY observed GLY columns shown in Myriokefalitakis et al. (2008).

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3 Budget calculations

OXL abundance is strictly connected to the concentration of its aqueous phase precursors that are both of anthropogenic and biogenic origin. OXL precursors are chemically formed in the aqueous phase or emitted from anthropogenic and natural (terrestrial and oceanic) sources. According to S1, the global in-cloud chemical production of OXL equals to about 37 Tg yr^{-1} , corresponding to a net chemical atmospheric source (difference between in-cloud chemical production and in-cloud chemical destruction by OH radicals) of about 24 Tg yr^{-1} . TM4-ECPL global annual mean OXL burden equals to 0.34 Tg , corresponding to a global mean turnover time over deposition of about 5 days. Here below, we elaborate on the strength of biogenic and anthropogenic sources on OXL formation and also on each separate sink of OXL for simulation S1. Budget calculations for the simulations performed to quantify the uncertainty of our results are presented in Table 2.

3.1 Biogenic sources

According to TM4-ECPL calculations (S1), biogenic volatile organic compounds oxidation is responsible for the 91% of the global OXL chemical production. Isoprene is the most important precursor of OXL, contributing to about 79% ($\sim 29 \text{ Tg yr}^{-1}$) to the global OXL production, followed by terpenes that contribute to about 12% ($\sim 5 \text{ Tg yr}^{-1}$). Isoprene and terpenes form OXL through their oxidation products GLY, GLYAL and MGLY. Isoprene oxidation by OH radicals contributes almost 60% of GLY, 82% of GLYAL and 81% of MGLY chemical production globally, whereas terpenes account for almost 7%, 14%, and 13%, respectively. OXL is produced by about 46% from GLY, ($\sim 17 \text{ Tg yr}^{-1}$), 15% from GLYAL ($\sim 6 \text{ Tg yr}^{-1}$) and about 39% ($\sim 14 \text{ Tg yr}^{-1}$) from MGLY.

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3.2 Anthropogenic sources

Anthropogenic hydrocarbons contribute by about 9% ($\sim 3 \text{ Tg yr}^{-1}$) to the global OXL chemical production. TM4-ECPL takes into account the chemistry of ethene (C_2H_4), propene (C_3H_6), acetylene (C_2H_2) and aromatics (benzene, toluene and xylene), which contribute to OXL precursors abundance through their impact on GLY, GLYAL and MGLY formation (Myriokefalitakis et al., 2008). Aromatics contribute almost 13% and acetylene almost 18% to GLY chemical formation. Moreover, according to TM4-ECPL model calculations, ethene contributes almost 4% to GLYAL production. TM4-ECPL simulations show that propene and aromatics contribute about 2% and 3% to MGLY global chemical formation, respectively. Alkenes (ethene and propene), acetylene and aromatics (benzene, toluene and xylene) contribute 2%, 4% and 3%, respectively (about 1 Tg yr^{-1} each) to global OXL production.

3.3 Sinks of oxalate

In TM4-ECPL, OXL is removed from the atmosphere by OH radical in-cloud oxidation, wet and dry deposition. The rate constant for the in-cloud oxidation of OXL by OH radicals ranges between $1.4 \times 10^6 \text{ mol}^{-1} \text{ L s}^{-1}$ to $4.7 \times 10^7 \text{ mol}^{-1} \text{ L s}^{-1}$ depending on the droplet's pH (Table S1; Supplement). According to model calculations (simulation S1), OXL in-cloud oxidation by OH radicals consumes about 35% ($\sim 13 \text{ Tg yr}^{-1}$) of the in-cloud produced amount of OXL. The resulting global mean turnover time of OXL due to in-cloud oxidation by OH is calculated to be about 10 days.

OXL is drastically removed from the atmosphere via wet deposition due to its high water solubility (Table S3, Supplement). TM4-ECPL calculates that about 61% of OXL is removed from the atmosphere via wet deposition ($\sim 23 \text{ Tg yr}^{-1}$). Dry deposition has a smaller impact on OXL abundance, removing about 4% of OXL ($\sim 1 \text{ Tg yr}^{-1}$) on the global scale. The resulting wet and dry deposition global OXL turnover times are calculated to be about 5 days and 86 days, respectively. The global mean lifetime of OXL according to both chemical and physical processes in the atmosphere is calculated to be about 3 days.

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4 Oxalate atmospheric concentrations

Figure 1 presents monthly mean cloud LWC (Fig. 1a,b) and aerosol LWC (Fig. 1c,d) for the year 2005. The calculated distributions (S1 simulation) of OXL are presented in Fig. 2 for the lowest (surface) model level and the zonal mean vertical distribution for the Northern Hemisphere (NH) winter (December, January and February: DJF) and NH summer (June July and August: JJA). OXL concentrations reflect their precursor distributions and LWC abundance, being maximum over tropical Africa and the Amazon basin (where abundant biogenic VOC emissions occur). During DJF, OXL calculated concentrations reach $1 \mu\text{g m}^{-3}$ in the tropics over land. During JJA, because of enhanced photochemistry in the NH, the model calculates a secondary OXL concentration maximum ($0.2\text{--}0.4 \mu\text{g m}^{-3}$) in northern mid-latitudes. The summertime OXL peak can be attributed both to higher aqueous phase OH radical concentrations and to higher biogenic VOC emissions, occurring during the warm season. Summertime aqueous phase OH radical concentrations are supported both by higher gas-phase OH concentration, and thus more transfer to the aqueous phase, and by enhanced aqueous phase OH production due to more intense in-cloud H_2O_2 photolysis. Conversely intense wet scavenging during wintertime keeps OXL concentrations low.

The model also calculates significant OXL concentrations in the free troposphere, although almost 5 times lower than the surface concentrations. In the tropics, biogenic hydrocarbons like isoprene are convectively transported to the mid and high troposphere, where cloud LWC is also high (Fig. 1b). Maximum OXL concentrations ($>0.2 \mu\text{g m}^{-3}$) in the tropical free troposphere (up to ~ 300 hPa) are calculated during DJF. The enhanced photochemical production of OXL from the intense biogenic emissions during summertime is reflected on the vertical distribution. During JJA, a second free tropospheric maximum ($>0.1 \mu\text{g m}^{-3}$) is calculated to occur over the mid-latitudes in the NH.

Figure 3a,b depicts the simulated annual mean surface and 500 hPa concentrations of OXL. The contributions of OXL to the SOA mass for the lowest model level as well as

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for 500 hPa, are presented in Fig. 3c,d, respectively. Figure 3c shows that cloud processing is the main source of SOA over the global ocean, where it accounts for 40–50% of the SOA mass (with the exception of the Southern Ocean and South Hemisphere tropical Pacific, where TM4-ECPL predicts a significant contribution of sulfur-containing SOA on total SOA; Myriokefalitakis et al., 2010). At 500 hPa, almost everywhere, but especially in the NH 50% of SOA is calculated to consist of OXL. In Fig. 3e, the OXL concentrations are compared with those of nss-SO_4^{2-} , which is also partly a cloud-processing product. The OXL to nss-SO_4^{2-} mass ratios shown in this figure indicate that nss-SO_4^{2-} dominates in terms of mass in the NH continental polluted regions but not in the tropics, where OXL clearly prevails by up to 50%, over terrestrial biogenic sources (e.g., Amazon Basin and Central Africa). A similar pattern between the OXL concentrations and SO_4^{2-} is also predicted for 500 hPa (Fig. 3f), although with slightly higher OXL to nss-SO_4^{2-} mass ratios over larger extent. This also depicts the different precursor sources of these two aerosol components.

The OXL contribution to the total OC amount is depicted in Fig. 4; about 20% of the total OC over oceanic regions, mainly in the tropical Pacific Ocean, both at surface and the free troposphere (Fig. 4a,b). Zonal mean OXL (expressed in OC) to OC fraction, presents a maximum over the tropics (~20%), where high biogenic emissions and LWC occur. Moreover, a second maximum over the NH is seen (~10%), which depicts the relative importance of OXL formation over anthropogenically influenced areas. Note however, that in the present study the in-cloud OXL formation is calculated to be biogenically driven since potential OXL formation from other pathways like photo-ageing of OA (Eliason et al., 2003) and/or aqueous phase oxidation of longer chain carboxylic acids to shorter diacids (Legrand et al., 2007), which could form OXL, especially over anthropogenically influenced regions (i.e in the NH), are not currently included in the present study.

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5 Comparison with observations

The ability of the model to reproduce the seasonality and levels of OXL is investigated in Fig. 5, which shows the comparison of OXL monthly mean observation in bulk or PM₁₀ aerosol with the TM4-ECPL simulations. OXL observations include measurements at the Finokalia atmospheric monitoring station of the University of Crete (Mihalopoulos et al., 1997) in the Eastern Mediterranean, Amsterdam Island (Sciare et al., 2009), the Southern Indian Ocean, Mace Head Atmospheric Research Station on the west coast of Ireland (Jennings et al., 1997) and the CARBOSOL sites in Europe (Legrand et al., 2007).

TM4-ECPL is able to reasonably simulate OXL concentrations and their seasonal variation for most locations. Computed OXL concentrations show strong seasonal dependence, with the maxima occurring during the warm season. However, TM4-ECPL simulation S1 appears to significantly underestimate winter OXL concentrations, likely due to either (i) missing OXL primary sources (tentatively taken into account in S2), or (ii) deficient parameterization of OXL formation in the aqueous phase (tested in S3), or (iii) missing OXL precursors abundance (tentatively accounted in S4). The high photochemical activity and enhanced precursor emissions during summertime result in more efficient OXL formation in the aqueous phase.

Finokalia, located on the northern coast of Crete, is a site representative for the background atmospheric composition of the Eastern Mediterranean (Mihalopoulos et al., 1997; Kouvarakis et al., 2002). The Eastern Mediterranean is the receptor of transported pollution and subject to intensive photochemistry, but also affected by terrestrial and marine biogenic local emissions. Maximum monthly mean OXL concentrations are observed during summer ($\sim 270 \text{ ng m}^{-3}$ in July; Fig. 5a) and minimum during autumn ($\sim 55 \text{ ng m}^{-3}$ in October; Fig. 5a) in 2005. Koulouri et al. (2008) showed strong correlations between OXL and ammonium (NH_4^+), nitrate (NO_3^-) and non nss- SO_4^{2-} , which indicate secondary heterogeneous formation of OXL in this region. They pointed that the observed significant correlation between OXL and methanesulfonate (MS^-) in this

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region indicates that at least a fraction of OXL originates from marine sources. Such sources could be partly attributed to secondary formation from marine biogenic hydrocarbons (e.g. isoprene) (Liakakou et al., 2007), or photo-oxidation of biogenic fatty acids and longer chain acids (Legrand et al., 2007). In summertime, Finokalia is also influenced by biomass burning (Koulouri et al., 2008; Sciare et al., 2008), known to emit OXL and its precursors in the atmosphere. Biomass burning emissions of OXL are, however, not strong enough to account for the observed OXL levels.

Amsterdam Island, located in the Southern Indian Ocean, is representative of pristine marine conditions, especially during summer when low wind speeds are prevailing (Sciare et al., 2009). OXL presents its maximum ($\sim 17 \text{ ng m}^{-3}$ in September; Fig. 5b) during early spring and minimum ($\sim 55 \text{ ng m}^{-3}$ in May; Fig. 5b) during early autumn (Sciare, 2011). Sciare et al. (2009) observed that both non- MS^- water soluble organic carbon (WSOC) and MS^- increase during summer, which would suggest a similar (secondary) production mechanism for WSOC and MS^- that can be linked to the seasonality in marine productivity. TM4-ECPL (S1) predicts reasonably well the OXL observations at Amsterdam island in both winter and summer periods. In contrast to other sites, the in-cloud photochemical OXL production slightly over predicts the measured concentrations during summer. During wintertime, fossil fuel emitted mainly from South Africa and biomass burning originating from the whole Austral Africa and Madagascar influence Amsterdam Island by long range transport (LRT), that is, however, weak. Simulation S2 accounting for potentially primary combustion sources of OXL, shows that transport of such emissions (e.g. from Africa) does not significantly enhance OXL abundance, whereas when the model accounts for an additional OXL formation in aerosol water (S3), the calculated OXL concentrations are enhanced.

The Mace Head atmospheric research station (Jennings et al., 1997) is located on the west coast of Ireland, about 86 km westward Galway City. The station is westerly exposed to the North Atlantic Ocean, with the Atlantic shipping routes located more than 150 km to the west of the station. The OXL observations depicted in figure 5c were performed from May 1998 to September 1999 (Kleefeld et al., 2002). From

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April to September marine air masses influenced the station, whereas from September to October pollution from Continental Europe and UK was received. OXL (Fig. 5c) shows elevated concentrations from May to September and a decrease during winter (November–December). The model (S1) simulates reasonably well the observations as reported by Kleefeld et al. (2002). However, primary OXL sources (S2) and OXL formation in aerosol water (S3) do not enhance significantly the model OXL concentrations. On the contrary, adoption of an additional source of GLY in the marine environment (S4) significantly improves OXL simulations.

Aveiro, Portugal, is a rural background station located in an area characterized by maritime pine, eucalyptus forests and small-scale agricultural fields used to grow maize in spring and summer (Pio et al., 2007). The maximum OXL monthly mean concentrations are observed in late summer ($\sim 430 \text{ ng m}^{-3}$ in August; Fig. 5d) and the minimum in winter ($\sim 160 \text{ ng m}^{-3}$ in December; Fig. 5d) (Legrand et al., 2007). The observations show a bi-modal seasonality with a secondary maximum in early spring that is not captured by the model. TM4-ECPL significantly under predicts the OXL observations year around. This could be attributed to high removal by precipitation in the model, shortening the atmospheric lifetime of OXL, or more likely to missing or not accurately distributed primary and secondary sources of OXL in the model (as discussed in Sect. 4).

Azores sampling station is representative of the background marine atmosphere over the mid-north Atlantic Ocean, influenced by LRT from North America, Europe and Africa and from local agricultural activities (Pio et al., 2007). Maximum OXL concentrations are observed during summertime ($\sim 100 \text{ ng m}^{-3}$ in June; Fig. 5e) and minimum during early spring ($\sim 20 \text{ ng m}^{-3}$ in March). Legrand et al. (2007) suggested that LRT to Azores enhances organic diacid concentrations. In addition to the transported precursors for the in-cloud formation of OXL, local sources could also play a significant role in OXL abundance. Legrand et al. (2007) found that aerosols in Azores consist of unsaturated fatty acids that are commonly present in phytoplankton, particularly during summer, and have been suggested as OXL precursors (Oliveira et al., 2007). TM4-ECPL

is able to capture the mean levels of OXL with a yearly average OXL concentration of about 45 ng m^{-3} , but cannot simulate the late spring/early summer high OXL observations. As is the case for Mace Head, adoption of an additional source of GLY in the marine environment (S4) significantly improves OXL simulations at Azores.

5 The Schauinsland sampling site is a rural background station situated on a mountain ridge (1205 m a.s.l.) in the Black Forest (Southwestern Germany). The site is surrounded by forests and agricultural fields, and during summer is influenced by LRT polluted air masses from the city of Freiburg in the Rhine valley (Legrand et al., 2007). The maximum OXL concentrations are observed in summer ($\sim 390 \text{ ng m}^{-3}$ in July; Fig. 5f) and the minimum in winter ($\sim 80 \text{ ng m}^{-3}$ in December; Fig. 5f). TM4-ECPL simulations show a summer maximum as observed. Again here the model (S1) fails in reproducing the late spring/summer OXL observed high concentrations, although significant improvement is achieved when accounting for OXL formation in aerosol water. OXL formation during OA ageing (Eliason et al., 2003) might be a candidate to fill in the gap between model results and observations.

15 The Puy de Dome site, located on the top of the Puy de Dome mountain (1450 m a.s.l.) in Central France, is a continental background sampling station, influenced by intensive agriculture and forest management activities, while in winter it is often under free tropospheric conditions (Legrand et al., 2007). The maximum OXL concentrations are observed during early summer ($\sim 265 \text{ ng m}^{-3}$ in June; Fig. 5g) and the minimum during winter ($\sim 40 \text{ ng m}^{-3}$ in December; Fig. 6g). The model (S1) simulates the seasonality of OXL concentrations and lies closer to the low edge of observed values. OXL emissions taken into account by the model (S2) do not seem to considerably enhance the calculated OXL concentrations, although significant changes are computed in S3 that accounts for the additional OXL production in the aerosol water.

25 K-Puszt, a characteristic rural background station, is located in the middle of the Hungarian Plain, surrounded by forests, 60 km southeast from Budapest (Legrand et al., 2007). The maximum concentrations (Fig. 5h) are observed in early spring ($\sim 400 \text{ ng m}^{-3}$ in March) and the minimum in late spring ($\sim 170 \text{ ng m}^{-3}$ in May). Legrand

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et al. (2007) found that the K-Pusztta region is highly influenced by vehicular emissions that represent a plausible source of oxalic acid, either primary or secondary. Vehicular emissions such as toluene and ethene, which are known OXL precursors, enhance its secondary formation. The model (S1, S2) under predicts significantly the observed OXL concentrations during winter, indicating missing potential OXL sources (primary and secondary) or an overestimate of OXL removal by the model. On the contrary, during summer (May to July), high photochemical activity and enhanced precursor emissions result in more efficient OXL formation in the aqueous phase, and OXL concentrations calculated by TM4-ECPL are closer to observations. Here again, OXL production in the aerosol water (S3) shows enhanced levels of OXL, closer to observations.

In Fig. 6, all observations of OXL available in literature are compared with monthly mean predictions for simulation S3. OXL measurements around the world are sparse (Fig. 6a); comparison of the model results with available observations is nevertheless valuable to increase confidence to simulations and evaluate associated uncertainties (Fig. 6b). Due to the relatively low resolution of the global model, the high spatial variability of urban emissions is not resolved by TM4-ECPL, thus classification of the stations as urban, rural and marine can facilitate data interpretation. Comparisons are focusing on locations representative of the regional background. Urban core observations, shown only for completeness, indicate a large underestimate by the model and have to be viewed with caution. Analysis of variance (ANOVA), applied on the data depicted in Fig. 6b, shows that the model successfully represents the observations. Figure 6b shows that the model simulates more realistically the marine (slope=1.03±0.07, $r^2=0.83$, $N=43$, $a=0.05$, $F=202$, $p\text{-value}=1.9\times 10^{-17}$), and rural (marine and rural together: slope=0.83±0.06, $r^2=0.67$, $N=106$; $a=0.05$, $F=217$, $p\text{-value}=3.5\times 10^{-27}$) observations, rather than the urban ones (no correlation). Overall, as can be seen by the slopes of the correlations, the model tends to underestimate OXL observations, which indicates that the model either misses OXL sources (primary and secondary) or possibly overestimates OXL sinks.

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6 Conclusions

The global 3-dimensional chemistry/transport model TM4-ECPL has been adapted to simulate the temporal and spatial OXL distribution. The global OXL net chemical source has been estimated to be between 17 Tg yr^{-1} and 27 Tg yr^{-1} . Primary biomass burning OXL sources of about 0.1 Tg C yr^{-1} ($\sim 0.4 \text{ Tg OXL yr}^{-1}$) have not enhanced much the calculated OXL concentrations, which indicates that further investigations are needed on OXL emissions from combustion processes. The potential OXL formation into aerosol water is predicted to enhance its chemical formation by about 2 Tg yr^{-1} and successfully explains the observed OXL concentrations at NH locations. Isoprene is calculated to be the most important OXL precursor ($\sim 27 \text{ Tg yr}^{-1}$). More than 60% of OXL is removed from the atmosphere via wet deposition. The global tropospheric burden of OXL is calculated to be about $0.24\text{--}0.39 \text{ Tg}$. The computed OXL global mean turnover time against deposition is about 5 days. The composition of cloud droplets and especially cloud water ionic strength is shown to be a critical factor of uncertainty in the calculations of OXL atmospheric chemical production, due to its significant impact on the effective Henry's law constant values and deserves further investigations.

The present global 3-dimensional modeling study underlines the significant contribution of the atmospheric aqueous phase processes to the organic aerosol mass in the atmosphere. According to TM4-ECPL model calculations, OXL increases global tropospheric burden of OA by 13–19%. Near the surface increases of OC of about 10% over oceanic locations are computed due to OXL formation whereas over tropical regions the OC column is enhanced by about 20%. Comparison of calculated OXL concentrations with observations shows that TM4-ECPL underestimates OXL measurements, especially during winter. This indicates that potentially other secondary or primary sources or weaker sinks need to be considered to better describe the global tropospheric OXL abundance.

Further investigations are needed to improve our knowledge on such processes and in particular to properly account for gas-to-aqueous phase organic compounds transfer.

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Aqueous-phase oxidation of longer carboxylic acids and marine unsaturated fatty acids to shorter diacids and carboxylic acid formation during OA photo-ageing processes, which are neglected in the present study, could lead to a further enhancement of OXL and OA in the troposphere.

5 **Supplementary material related to this article is available online at:**
**[http://www.atmos-chem-phys-discuss.net/11/485/2011/
acpd-11-485-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/485/2011/acpd-11-485-2011-supplement.pdf)**

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Table 1. Outline of simulations performed in this study.

Simulation	Description
S1	In-cloud OXL formation taking into account the ionic strength of cloud droplets.
S1.1	As S1, neglecting the ionic strength of cloud droplets.
S1.2	As S1, omitting the temperature dependence of Henry constants.
S1.3	As S1, assuming constant pH values of 4.5 for cloud droplets.
S2	As S1, also taking into account potential primary sources of OXL.
S3	As S2, also taking into account the potential chemical formation of OXL into aerosol water.
S4	As S3, also taking into account GLY oceanic concentrations.

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Table 2. Global oxalate budget analysis.

Simulation	Atmospheric burden (Tg)	Primary source (Tg yr ⁻¹)	Chemical production (Tg yr ⁻¹)	Chemical destruction (Tg yr ⁻¹)	Net chemical production (Tg yr ⁻¹)	Dry deposition (Tg yr ⁻¹)	Wet deposition (Tg yr ⁻¹)
S1	0.34	–	37.3	13.0	24.3	1.5	22.8
S1.1	0.24	–	28.5	11.1	17.4	1.1	16.4
S1.2	0.35	–	38.6	13.5	25.1	1.5	23.5
S1.3	0.28	–	30.6	11.3	19.3	1.2	18.1
S2	0.35	0.4	37.6	13.3	24.3	1.5	23.2
S3	0.38	0.4	39.1 ^a	13.6	25.5	1.7	24.3
S4	0.39	0.4	40.9 ^b	14.1	26.8	1.8	25.4

^a Including 1.9 Tg yr⁻¹ chemical production in aerosol water.

^b Including 2.2 Tg yr⁻¹ chemical production in aerosol water.

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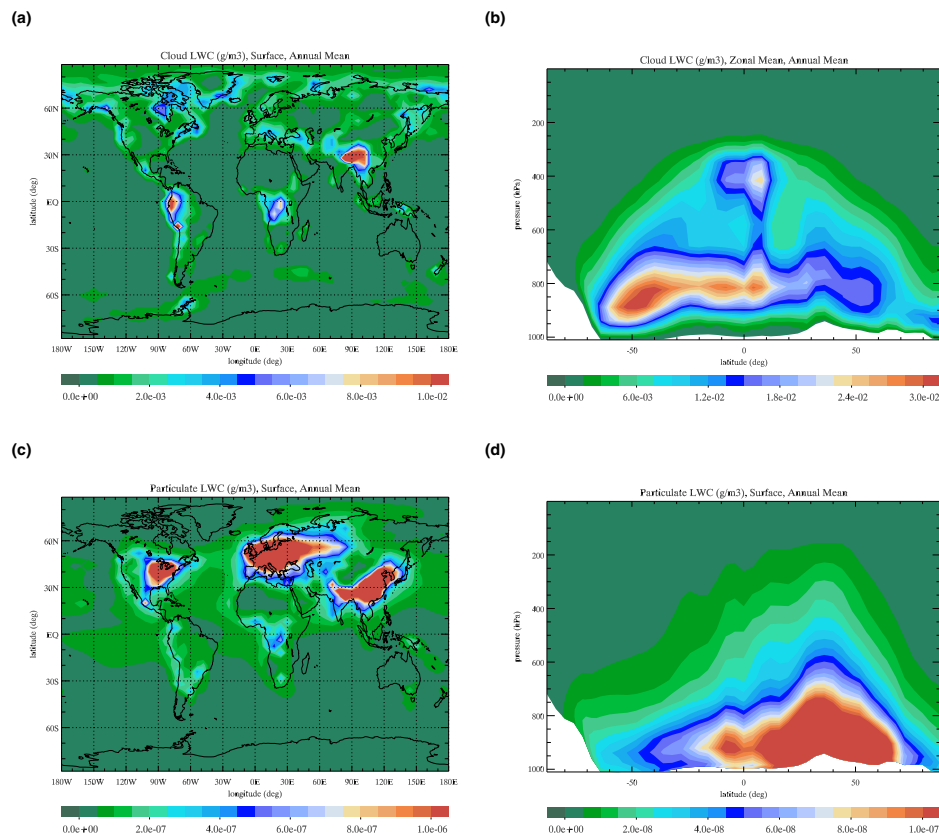


Fig. 1. Annual mean cloud LWC in g m^{-3} for surface (a) and zonal mean concentrations (b) for the year 2005, and calculated aerosol LWC in g m^{-3} (c) for surface (d) and zonal mean concentrations (right panels) for the same period.

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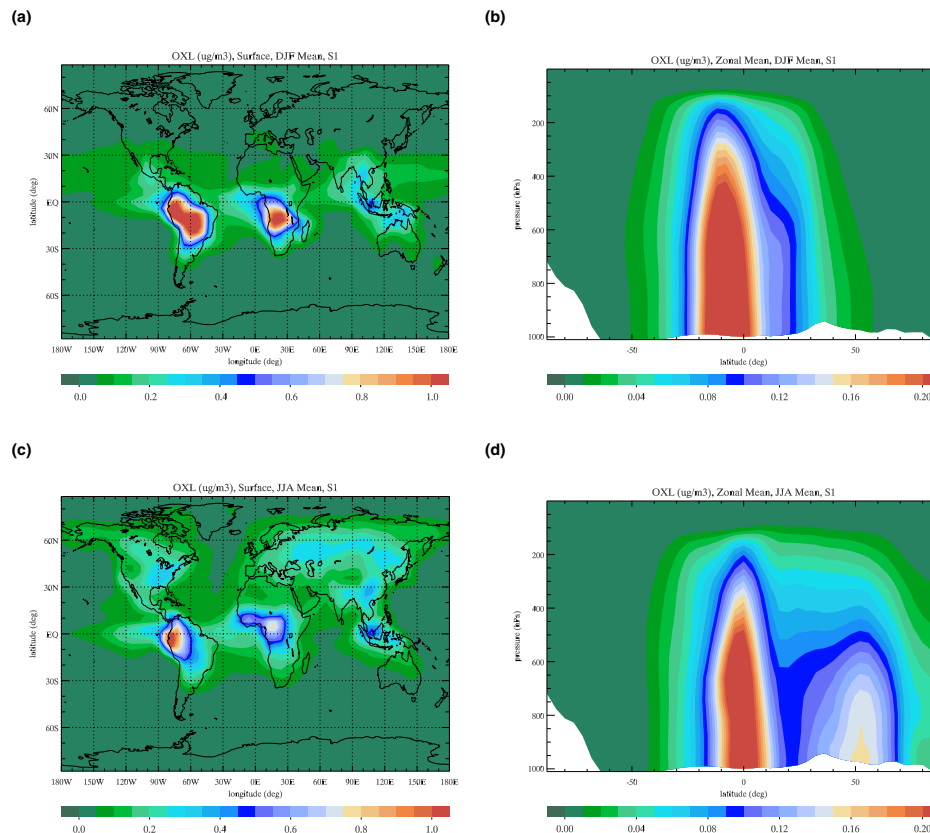


Fig. 2. Calculated OXL surface (a, c) and zonal mean (b, d) concentrations (in $\mu\text{g}\text{m}^{-3}$) for North Hemisphere winter (DJF mean) (a, b) and North Hemisphere summer (JJA mean) (c, d) for S1 ($\mu\text{g}\text{m}^{-3}$).

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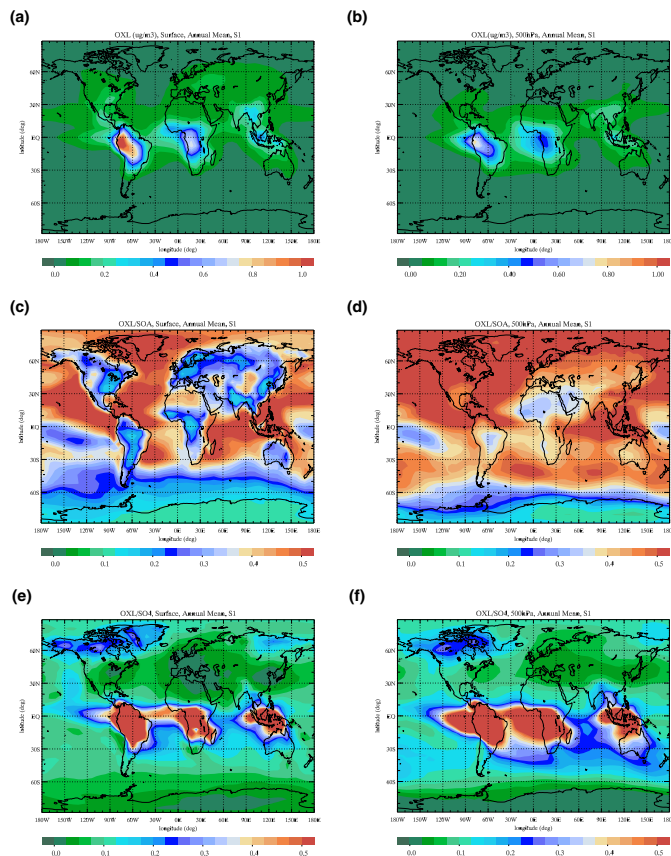


Fig. 3. Calculated annual mean for S1: **(a)** Surface OXL ($\mu\text{g m}^{-3}$) **(b)** OXL ($\mu\text{g m}^{-3}$) at 500 hPa, **(c)** Surface OXL/SOA mass ratio, **(d)** OXL/SOA mass ratio at 500 hPa, **(e)** Surface OXL/nss- SO_4^{2-} mass ratio and **(f)** OXL/nss- SO_4^{2-} mass ratio at 500 hPa.

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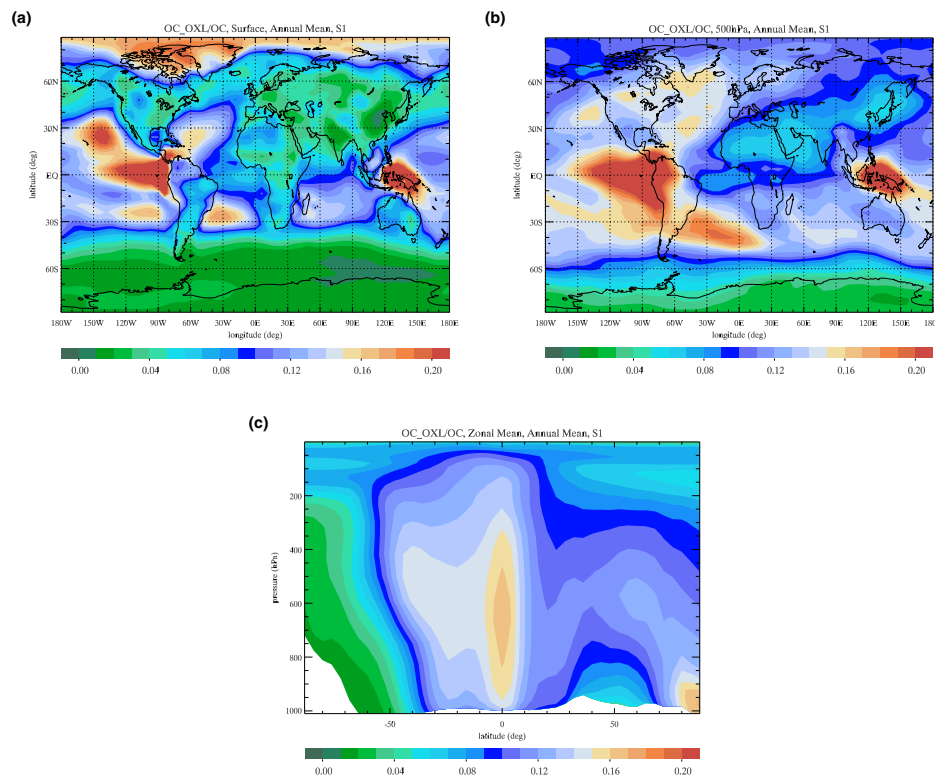


Fig. 4. Annual mean ratios of OXL (expressed in OC; OC_OXL) to total OC (carbon mass ratio) in the model for S1 simulation, **(a)** surface, **(b)** 500 hPa, and **(c)** zonal mean.

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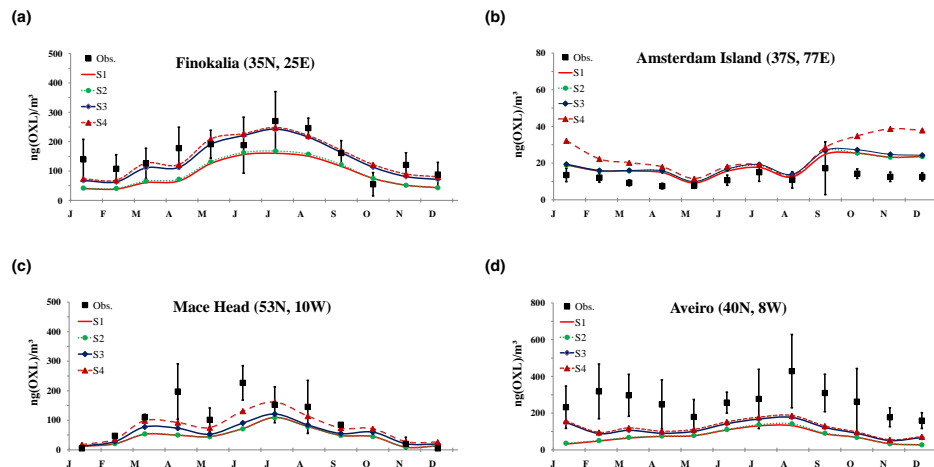


Fig. 5. Comparison of OXL observations black squares (■) in ng m^{-3} with model results from simulations S1 light-red solid line (—), S2 green closed circle dotted line (·-·), S3 blue-diamond solid line (—◆) and S4 (—▲) dark-red triangle dashed line. OXL observations are taken from the Finokalia environmental monitoring station in Eastern Mediterranean (Koulouri et al., 2008; Mihalopoulos, 2011) for the year 2005, Amsterdam Island in the Southern Indian Ocean (Sciare et al., 2009; Sciare, 2011) for the year 2005 and other locations in Europe (CARBOSOL sites from Legrand et al., 2007 and Simpson et al., 2007 for monthly mean measurements for period September 2002–September 2004, Mace Head Atmospheric Research Station on the west coast of Ireland from Kleefeld et al., 2002 for monthly mean measurements for period September 1998–September 1999).

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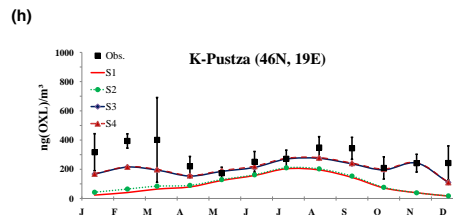
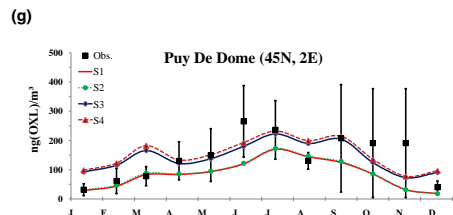
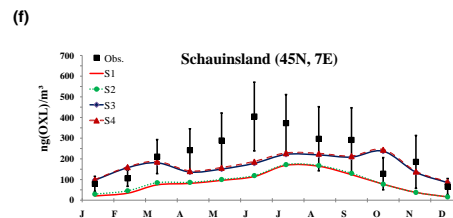
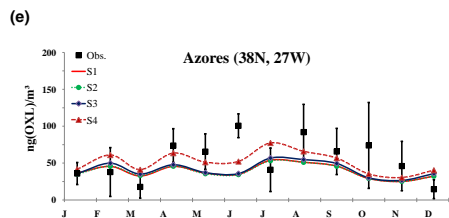


Fig. 5. Continued.

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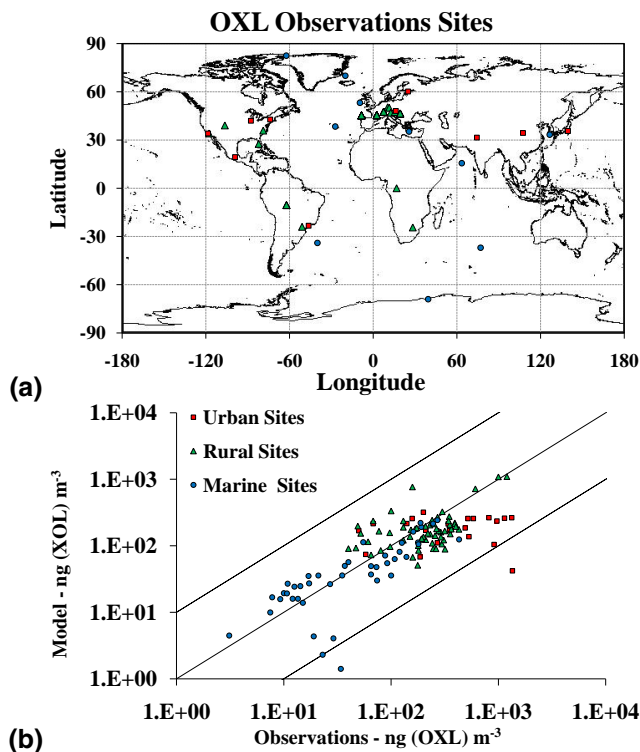


Fig. 6. (a) Location of stations with OXAL observations taken into account for the model validations. (b) Comparison of OXAL observations with TM4-ECPL results. Red squares represent urban sites, green triangles represent rural sites and blue circles marine sites. The solid line shows the 1:1 relationship between model results and observations and the dashed line shows the 1:10 and 10:1 relationship. Observations are taken from: Allen and Miguel (1995); Baboukas et al. (2000); Biswas et al. (2008); Crahan et al. (2004); Falkovich et al. (2005); Fosco and Schmeling (2006); Graham et al. (2002); Grosjean (1988); Kawamura et al. (1985, 1993, 1996, 2004, 2005); Khwaja (1995); Kleefeld et al. (2002); Legrand et al. (2007); Lewandowski et al. (2007); Limbeck et al. (1999, 2005); Mader et al. (2004); Martinelango et al. (2007); Mihalopoulos (2011); Muller et al. (2005); Neuss et al. (2002); Norton et al. (1983); Pauliquevis et al. (2007); Plewka et al. (2006); Puxbaum et al. (2000); Ruellan et al. (1999); Saarnio et al. (2010); Sempere and Kawamura (1994); Sciare (2011); Stone et al. (2010); Talbot et al. (1988, 1992); Topping et al. (2004); Viana et al. (2008); Wang et al. (2010); Wosfy et al. (1992).

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