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INSIGHTS INTO ATMOSPHERIC OXIDATION

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Academic dissertation

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Ditte Mogensen

University of Helsinki, 2015

Abstract

Forests emit biogenic volatile organic compounds (BVOCs) that, together with e.g. sulfuric acid, can operate as aerosol precursor compounds when oxidised. Aerosol particles affect both air visibility, human health and the Earth's radiative budget, thus making the emission inputs and oxidation mechanisms of VOCs absolutely crucial to understand. This thesis discusses the life cycle of compounds in the atmosphere. Specifically, we studied the representations of emission of BVOCs, the atmosphere's oxidation ability along with the sources and sinks of sulfuric acid. The main tool to achieve this was numerical modelling, often compared to field observations. Additionally, we performed computational chemistry simulations in order to calculate transitions in sulfuric acid.

The main findings of this thesis can be summarised into the following: (1) Biological understanding of VOC emission processes needs to be enhanced in order to predict VOC concentrations with a high precision. (2) The unexplained fraction of the total OH reactivity in the boreal forest is larger than the known fraction and known secondary organic oxidation products of primary emitted terpenes cannot explain the missing reactivity. (3) OH is the main oxidation agent of organic compounds in the boreal atmosphere. (4) Criegee Intermediates, produced from unsaturated hydrocarbons, can oxidise SO₂ effectively in order to provide as an essential source of sulfuric acid in areas with high VOC concentrations. (5) Two-photon electronic excitation did not turn out to be a significant sink of gaseous sulfuric acid in the stratosphere.

This thesis closes a large part of the sulfuric acid concentration gap in VOC rich environments. Further, this thesis raises awareness of the fact that we still do not fully comprehend the mechanisms leading to BVOC emissions nor the organic atmospheric chemistry in the boreal forest. Finally, this work encourage to study alternative BVOC emission sources as well as alternative atmospheric oxidants.

Keywords: Scots pine forest, 1D modelling, atmospheric chemistry, volatile organic compounds, sulfuric acid, reactivity, oxidation, photolysis

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List of publications

This thesis consists of an introductory review, followed by five peer-reviewed research articles. In the review, these papers are cited according to their Roman numerals. **Paper I-IV** are reproduced under the Creative Commons Attribution License, while **Paper V** is reproduced with kind permission of Elsevier.

- I** Smolander, S., He, Q., **Mogensen, D.**, Zhou, L., Bäck, J., Ruuskanen, T., Noe, S., Guenther, A., Aaltonen, H., Kulmala, M., and Boy, M. (2014). Comparing three vegetation monoterpene emission models to measured gas concentrations with a model of meteorology, air chemistry and chemical transport. *Biogeosciences*, 11:5425–5443.
- II** **Mogensen, D.**, Smolander, S., Sogachev, A., Zhou, L., Sinha, V., Guenther, A., Williams, J., Nieminen, T., Kajos, M.K., Rinne, J., Kulmala, M., and Boy, M. (2011). Modelling atmospheric OH-reactivity in a boreal forest ecosystem. *Atmos. Chem. Phys.*, 11:9709–9719.
- III** **Mogensen, D.**, Gierens, R., Crowley, J.N., Keronen, P., Smolander, S., Sogachev, A., Nölscher, A.C., Zhou, L., Kulmala, M., Tang, M.J., Williams, J., and Boy, M. (2015). Simulations of atmospheric OH, O₃ and NO₃ reactivities within and above the boreal forest. *Atmos. Chem. Phys.*, 15:3909-3932.
- IV** Boy, M., **Mogensen, D.**, Smolander, S., Zhou, L., Nieminen, T., Paasonen, P., Plass-Dülmer, C., Sipilä, M., Petäjä, T., Mauldin, L., Berresheim, H., and Kulmala, M. (2013). Oxidation of SO₂ by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations. *Atmos. Chem. Phys.*, 13:3865–3879.
- V** **Mogensen, D.**, Mikkelsen, K.V., and Kjaergaard, H.G. (2010). Calculated two-photon electronic transitions in sulfuric acid and its atmospheric relevance. *Chem. Phys. Lett.*, 498:18–21.

1 Introduction

Volatile organic compounds (VOCs) originate from both human activity (including biomass burning), but mostly ($\sim 90\%$) from biological sources such as vegetation and organic matter in oceans (Guenther et al., 2012). After the tropical forests, the boreal forest zone and the temperate forests represent the largest forested areas worldwide (Guenther, 2013). It is estimated that the boreal forest ecosystem accounts for $\sim 5\%$ of the global emission of BVOCs (biological VOCs, Guenther, 2013). The BVOCs are various in their molecular structure, but isoprene (C_5H_8) dominates the global emission spectrum ($\sim 50\%$ of the total emission, Guenther et al., 2012), while monoterpenes ($C_{10}H_{16}$) prevail in the boreal forest ecosystem (Rinne et al., 2007, 2009). In forests, the many different BVOCs are emitted from both the forest soil and litter, tree trunks and branches, but mostly from the tree crown through needles and leaves (Goldstein and Galbally, 2007; Aaltonen et al., 2011; Hakola et al., 2003, 2006; Aalto et al., 2014b). The production and emission of BVOCs depend on both the chemical and physical properties of the VOC of interest, together with both biotic and abiotic factors affecting the individual vegetational species differently. Temperature is one of the drivers of both isoprene and monoterpene emissions (Guenther et al., 1993; Tingey, 1981). It is expected that the temperature in the boreal forest zone, together with the Arctic, will increase more than at any other place on Earth (as much as $\sim 8.5^\circ\text{C}$ by year 2100, IPCC (2014)). This will not only increase the magnitude of the input of VOCs to the atmosphere, but we can also expect a dramatic change in the tree species population, which will also lead to a perturbation of the VOC emissions. **Papers I-IV** deal with the biogenic emission of VOCs from the boreal forest ecosystem.

When emitted to the atmosphere, the VOCs will undergo oxidation. Since individual VOCs consist of different functional groups, the oxidation by a specific oxidant is selective, however, overall the most effective chemical oxidants are OH, NO_3 and O_3 (**Paper III**, Seinfeld and Pandis, 2006). The oxidation of the VOCs generates an alteration of the atmospheric oxidation budget (**Papers I-IV**) and formation of new products with different chemical and physical properties than their parent molecule. These species tend to have lower vapour pressures than their parent molecules which enables them to participate (1) in the formation of new particles (Went, 1960; Andreae and Crutzen, 1997; Claeys et al., 2004; Kiendler-Scharr et al., 2009; Kulmala et al., 2014) and (2) to condense onto already existing particles and thereby contribute to their growth (Ehn et al., 2014; VanReken et al., 2006; Hao et al., 2011; Liao et al., 2014). (1) Organic compounds cannot

alone explain the occurrence of particle formation, instead many studies (e.g. Kulmala et al., 2004; Schobesberger et al., 2013; Weber et al., 1995; Kirkby et al., 2011) suggest that the very hygroscopic sulfuric acid (H_2SO_4) could be a necessary ingredient. Traditionally it is thought that sulfuric acid is formed from OH oxidation of SO_2 , however, recent investigations suggest that unsaturated hydrocarbons that have undergone ozonolysis (Criegee intermediates, CIs) oxidise SO_2 and thereby provide an important channel to produce H_2SO_4 in VOC rich environments (**Paper IV**; Mauldin III et al., 2012; Welz et al., 2012). Above an altitude of 35 km in the atmosphere, the concentration of water is low, thus sulfuric acid is mainly found in a gaseous form (Zhao et al., 1995) and its main sink is instead photolysis (**Paper V**), leading to SO_2 reproduction. (2) If the particles reach the sizes of cloud condensation nuclei (CCN), atmospheric water vapour can use the CCN as seeds and condense onto those. Hereby cloud droplets are formed. Clouds alter the Earth's radiation budget by scattering and absorption of solar light, thus aerosol particles, and their sources (VOCs), directly affect our climate (e.g., Makkonen et al., 2012; Ehn et al., 2014).

In the atmospheric boundary layer, which is the layer studied in **Papers I-IV**, the meteorological mixing is strong, thus the VOCs and aerosols can be transported to the top of the layer within a few minutes, though it can take some hours before compounds are well mixed.

In order to predict climate change, we need to simulate the globe, including the boreal forests, in a perturbed environment. However, in order to do that with less uncertainty, we firstly need to understand the processes that occur in the current climatic state. This thesis aims to gain new insights onto the first part of the biosphere-atmosphere-climate system: biogenic VOC emissions and atmospheric oxidation. A simplified schematics of the biosphere-atmosphere-climate systems and the main focus areas of the papers in this thesis are presented in Fig. 1. The main objectives of this thesis are to:

- 1) identify gaps in our understanding and representation of BVOC emissions and to examine the connection between vegetation emission and ambient gas concentrations.
- 2) investigate whether secondary organic oxidation products can explain the unaccounted OH reactivity in forests.
- 3) determine the relative importance of the individual atmospheric oxidants in the boreal forest.

4) quantify new sources and sinks of atmospheric sulfuric acid.

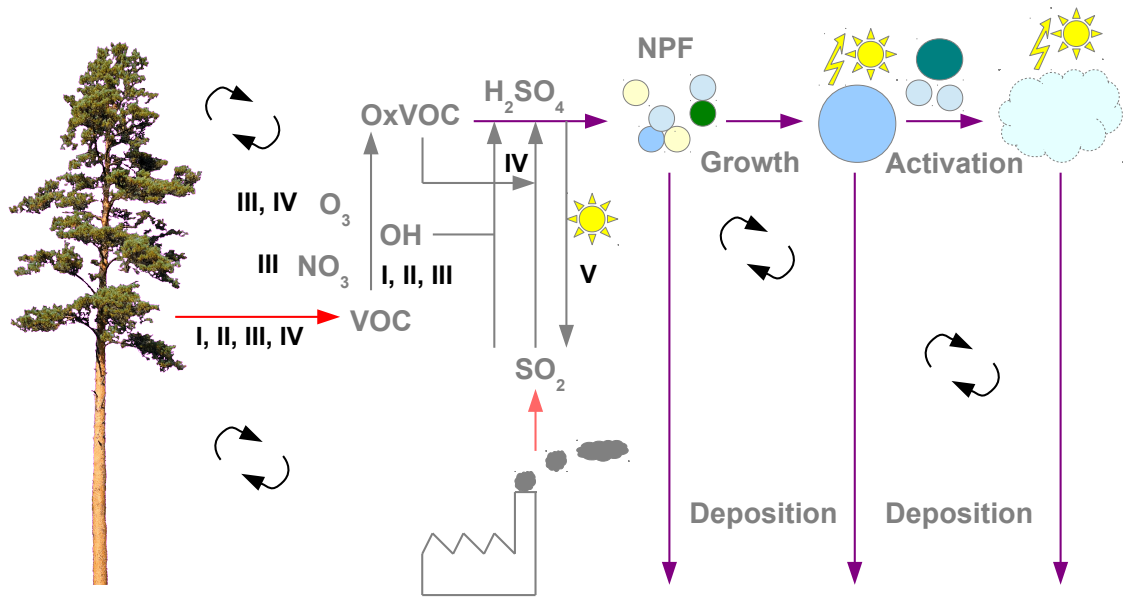


Figure 1: Simplified schematics of the biosphere-atmosphere-climate systems, indicating (in bold Roman numbers) the main themes handled in each paper in this thesis. The red arrows indicate emission (biogenic emission in dark red and anthropogenic emission in light red), the grey arrows symbolise chemical production, the magenta arrows illustrate physical processes, while black circular arrows represent turbulent mixing. The balls represent aerosol particles in different sizes, while NPF is an abbreviation for new particle formation.

2 Scientific background

2.1 Biogenic emission of volatile organic compounds

Forest is one of the main land cover types in most of the northern hemisphere and in Finland, forest land covers 86% of the total land area (Finnish Forest Research Institute, 2012). The forest type is here boreal, thus it is dominated by evergreen conifer that often emit larger amounts of monoterpenes than the globally most emitted BVOC, isoprene (Rinne et al., 2009). Scots pine (*Pinus sylvestris*) forest has been the focus of this thesis, since pine is the dominant tree species in the Finnish boreal forest with $\sim 50\%$ of the total forest inventory volume (Finnish Forest Research Institute, 2012). Interestingly, the Scots pine canopy terpene emission distribution is rather specific for tree individuals, which is caused by differences in inherited properties and has been characterised as chemotypic variation between the trees in a stand (Bäck et al., 2012).

Why do vegetation emit VOCs?

Different tree species can emit large amounts of various chemical compounds. The two main functions for this emission are (1) induced and (2) constitutive (Fineschi and Loreto, 2012). (1) Trees can experience temporary stresses, whereby they will emit VOCs in order to repel the stress or to increase their resistance towards the stress (Niinemets et al., 2013). Such stresses include e.g. herbivory attacks and abiotic stresses (e.g. heat or atmospheric oxidants). For example a rather rapid induction of compounds will follow an attack by insects. These compounds can repel the pests (Fraenkel, 1959; Paré and Tumlinson, 1997; De Moraes et al., 2001; Loivamäki et al., 2008; Dicke and Baldwin, 2010), attract carnivores (Dicke and Baldwin, 2010) and/or signal a warning to other trees, whereby they can launch their own defence mechanisms (Farmer and Ryan, 1990; Baldwin and Schultz, 1983; Engelberth et al., 2004). Trees can also emit VOCs in order to enhance the thermotolerance during periods with heat and light stresses (Sharkey and Singsaas, 1995), and to protect the plant from atmospheric oxidants (Loreto et al., 2001). (2) Trees will also emit VOCs due to "normal" plant metabolism such as growth, transpiration and carbon uptake (Aalto et al., 2014a). This emission does not necessarily serve a specific benefit for the plant, rather it represents a loss of carbon that has been obtained via photosynthesis.

What controls VOC emission?

One needs to keep in mind, that a VOC will not necessarily be emitted directly upon

production due to the physico-chemical properties of the VOC of interest (e.g. volatility). There are many biological and physical factors that influence both the production and emission of VOCs. Especially the biological parameters are difficult to account for, since they cause large variation in emission rates even in similar physical conditions. The different drivers for emission and production are tree species specific and include, among others, herbivore attack, different physico-chemical controls (volatility and diffusion), different physiological controls (substrate availability and enzyme activity) and the circadian clock/phenology. Further, mechanical damage (tree cutting or wind) stress vegetation, whereby VOCs are emitted. Meanwhile, drought stress has been shown to reduce VOC emissions, though the mechanism is currently not understood (Grote et al., 2010). Also the ambient CO₂ concentration has been shown to influence the production of VOCs (see below). Lastly, both production and emission often depend on both temperature and light (see below). Since isoprene is globally the most emitted VOC and monoterpenes are the VOCs in focus in this thesis, I will briefly describe their production and emission: *Isoprene* is produced in plastids and is therefore highly linked to photosynthesis, thus the emission of isoprene increases with an increase in both light and temperature (Silver and Fall, 1991; Guenther et al., 1993). Though CO₂ is required for isoprene production, the emission of this hemiterpenoid decreases when exposed to high levels of CO₂, since high CO₂ levels draw intermediate compounds from the isoprenoid biosynthetic pathway and cause thus a decrease in produced isoprene (Rosenstiel et al., 2003). *Monoterpenes* are synthesised in both cytoplasm and plastids and their emission is dominated by temperature controlled volatilisation from storage pools (mainly resin ducts) inside the needles/leaves, however, a variable part of the emission originates from recently assimilated carbon, i.e. *de novo* (Ghirardo et al., 2010).

Emission models

There exist a variety of emission models, both mechanistic algorithms (Niinemets et al., 2002; Grote et al., 2006; Schurgers et al., 2009) and those that are based on empirical observations (e.g. Guenther et al., 1993, 1995, 2006) and they vary largely in their required input. Two empirical and one process based model were utilised in this thesis. The structure and content of these are described in **Papers I-IV** (and references therein) and here we will only briefly go through how the emission is simulated. In *G95* (Guenther et al., 1995) the emission is calculated as a function based on the emission of a VOC at standard conditions, a correction factor that accounts for emission changes due to non-standard conditions together with a factor that accounts for loss and production within the canopy. *MEGAN 2.04* (Model of Emissions of Gases and Aerosols from Na-

ture, Guenther et al., 2006) is based on G95 but individual VOCs and their individual response to temperature and light are included. Also the correction factor that accounts for emission at non-standard conditions is improved and now accounts for effects of soil moisture, leaf age, leaf area index, light, temperature, humidity and wind. In *SIM-BIM* (Seasonal Isoprenoid synthase Model – Biochemical Isoprenoid biosynthesis Model, Grote et al., 2006) the emission is derived from photosynthetic input of carbon, and this model is thus able to take into account the effects of short- and long-term dynamics of plant activity on emission rates. It accounts for substrate availability, enzyme activity, CO₂ concentration, stomatal conductance, humidity, light and temperature.

The underlying assumption for the use of such empirical models as MEGAN and G95 is that the abiotic affects on the VOC emission prevail the biotic, however, we currently have a limited understanding of the relative importance of biotic versus abiotic driven emission of VOCs. E.g. Gray et al. (2010) suggest that abiotic sources of VOCs from litter are generally less important than the biotic sources and that the relative importance depends strongly on vegetation species and which VOC is considered.

2.2 Atmospheric oxidation

Atmospheric oxidation is the mechanism that drives the entire life cycle of any element emitted to the atmosphere: Elements are emitted in a reduced form into the atmosphere in different configurations of compounds. During their stay in the atmosphere, the elements will undergo various steps of oxidation, which enables their ability to condense onto aerosol particles and following deposit out of the atmosphere either due to gravitation or wet deposition. The elements will then undergo reduction in e.g. the biosphere, hydrosphere or lithosphere, whereby they can be re-emitted. Oxidation is therefore considered as the cleaning procedure of the layer above ground. Oxidation can be viewed as a process where at least one electron is lost. It will happen simultaneously with a reduction process, where the same amount of electrons are gained. Oxidants are strongly electronegative and the most important agents in the atmosphere are OH, NO₃ and O₃ (**Paper III**). The OH radical is considered the main atmospheric cleaning agent, since it is capable of fast reactions with most functional groups. Due to its large photolytic source, OH has a distinct daily profile with a daytime peak, and is only present at low concentrations during night. Oppositely, light is a large sink of the NO₃ radical, thus the oxidative importance of NO₃ dominates during night. While O₃ generally has no clear daily pattern in the

boreal forest, it is always present in abundance (tens of ppb_v), however, it is usually less reactive than OH and NO₃. **Papers I-IV** focus on the boundary layer oxidation. As most biogenically and anthropogenically emitted trace gases are oxidised within the Earth's boundary layer, the oxidising capacity of this layer may be considered to be approximately that of the atmosphere.

Criegee Intermediate as an alternative oxidant

Recently Criegee Intermediates (CIs) have also been suggested as important atmospheric oxidants (Welz et al., 2012; Mauldin III et al., 2012). They are formed via ozonolysis of unsaturated hydrocarbons (originating e.g. from vegetation), whereby a 5-membered ring (POZ, primary ozonide) is produced (see Fig. 2).

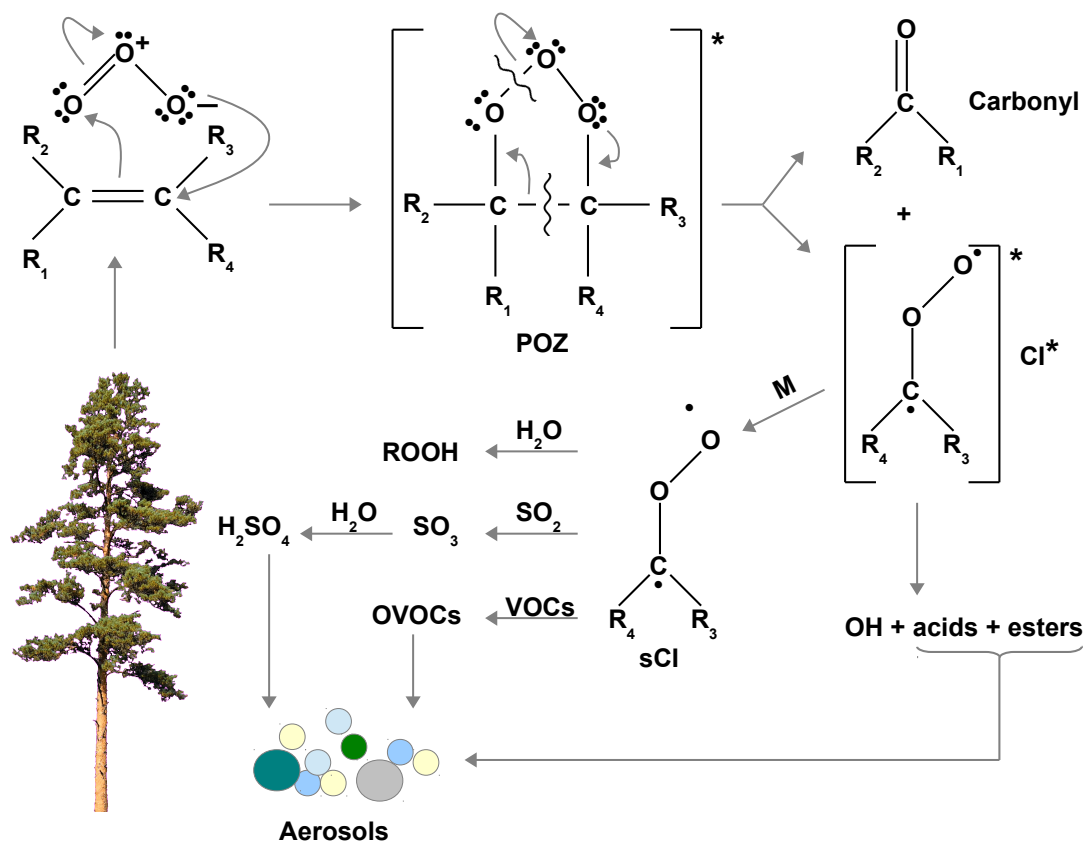


Figure 2: Schematic diagram of the formation of Criegee Intermediates and their following destiny in the atmosphere. (R₁₋₄ can be different carbon groups or H).

This POZ possesses excess energy, thus it decomposes instantaneously by cleaving an O-O and a C-C bond in the ring, and thereby forms a carbonyl compound and the

exited biradical; the Criegee intermediate. The Criegee intermediate will now either undergo a unimolecular reaction by decomposition into different products (esters and acids) including OH, or collisionally stabilise to form the stabilised Criegee intermediate (sCI, the CI without excess energy). The sCI can then react with various atmospheric compounds, particularly with H₂O to form hydrogenperoxide (ROOH), with VOCs to form oxygenated VOCs (OVOCs), and finally with SO₂ to form sulfuric acid.

The CI was discovered in the liquid phase already back in the 1940's (Criegee and Wenner, 1949). During the 80's it was investigated whether the CI would be an important atmospheric oxidant of SO₂, however, it was found that the reaction rate was too slow (Hatakeyama et al., 1986). Very recently, researchers have revisited the rate of reaction of different CIs with SO₂ and the atmospherically abundant water vapour, both in the lab, field and using theoretical calculations (Welz et al., 2012; Mauldin III et al., 2012; Kurtén et al., 2011). These new studies propose that the rate for the reaction of SO₂ and various CIs are orders of magnitude faster than previously suggested. However, still many parameters related to the CI chemistry are vitiated due to various uncertainties, on e.g. the chemical mechanisms, pathways, products, stabilisations and yields, thermal lifetimes, pressure dependency and reaction rate coefficients. A short summary and discussion of those are provided in **Paper IV**. In **Paper IV** we further tested how large a fraction of sulfuric acid in forested regions are produced by the conventional pathway (OH + SO₂) and how large a fraction is due to the CI path using the most recently obtained reaction rates.

Instantaneous and steady state reactivity

The total reactivity (R_{OX}) of an oxidant (OX) is defined as its total loss rate from the atmosphere, thus it is the inverse of the lifetime (τ) of the oxidant:

$$R_{OX} = \frac{1}{\tau} \quad (1)$$

One should, however, differentiate between *instantaneous* reactivity (R_{inst}) and the reactivity that defines the *turnover lifetime* of the radical out of steady state (R_{ss}). The reactivity related to a single reaction is calculated by multiplying the reaction rate coefficient (between the oxidant and reactant (Y)) by the concentration of the reactant ([Y]). The total instantaneous reactivity is then the sum of all these terms, which means all sink reactions have been taken into account regardless whether these reactions lead to reformation of the radical or not:

$$R_{inst} = \sum_{\text{Reactions}} k_{OX+Y} \times [Y] \quad (2)$$

where $k_{\text{OX+Y}}$ is the bimolecular reaction rate coefficient for the chemical reaction between the oxidant and the chemical species. The instantaneous lifetime is distinct from the turnover lifetime (τ_{ss}) derived from steady state analysis of e.g. measured radical concentrations ($[\text{radical}]$) and known production (P_{net}) terms:

$$R_{\text{ss}} = \frac{P_{\text{net}}}{[\text{radical}]} = \frac{1}{\tau_{\text{ss}}} \quad (3)$$

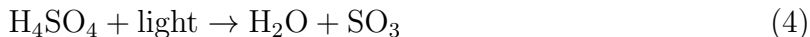
As the steady state lifetime deals with net production and loss terms, it takes into account the reformation of e.g. OH or NO_3 .

The instantaneous reactivity of OH has been measured in both urban (e.g., Ren et al., 2003; Lou et al., 2010) and remote and forested environments (e.g., Kovacs et al., 2003; Nölscher et al., 2012b; Sinha et al., 2010). A great unexplained part of the reactivity persists in all investigations, with the largest fraction missing in studies of forested areas. OH is therefore lost due to unaccounted processes that is most often attributed to unmeasured and unidentified compounds either originating from direct emission or formed via oxidation processes (e.g., Mount and Eisele, 1992; Di Carlo et al., 2004; Sinha et al., 2010). In **Paper II** we further speculate that part of the missing OH reactivity could be explained by uncertainties in rate coefficients.

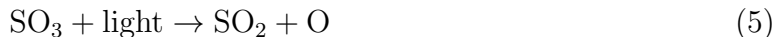
The reactivity of NO_3 has never been directly measured and there exists only a few recent studies that have addressed the reactivity of O_3 (Park et al., 2013; Matsumoto, 2014). We present the first simulated O_3 and NO_3 reactivities in **Paper III**.

2.3 Photodissociation

Photochemistry includes the absorption of a photon by a molecule, whereby the molecule reaches an excited state. The excited molecule can release its excess energy either by e.g. quenching, ionisation, luminescence or by cleaving a bond (dissociation). One example of atmospheric photolysis is sulfuric acid that decomposes to water and SO_3 (Burkholder et al., 2000):



Sulfur trioxide (SO_3) can then be further photolysed to SO_2 (Burkholder and McKeen, 1997):



In order for the molecule to photodissociate, the energy of the absorbed photon(s) need(s) to at least equal the energy of the bond that will be broken. We refer to this as the dissociation energy (D_0). The transition(s) involved is/are either (1) vibrational overtone transitions or (2) electronic excitation.

(1) Vibrational overtone dissociation

While the fundamental vibrational frequency of a molecule corresponds to the transition from $v = 0$ to $v = 1$ (where v indicates the vibrational state), vibrational overtone transitions can occur when a vibrational mode is excited more than $\Delta v = +1$ (e.g. $v = 0 \rightarrow v = 2$ and $v = 0 \rightarrow v = 3$, see Fig. 3a). If one supplies more vibrational energy than D_0 into a molecule, the molecule can break a bond. E.g. it has been suggested that the photodissociation of sulfuric acid could happen via near-infrared and visible vibrational OH stretching overtone transitions (Lane and Kjaergaard, 2008). A schematic of the intermolecular vibrational energy exchange leading to the dissociation of sulfuric acid is presented in Fig. 3b.

(2) Electronic excitation

In an electronic transition, a molecule is excited from the ground vibrational state of the electronic ground state (GS), to a range of vibrational states of the electronically excited state (ES, see Fig. 3a). This process can occur by absorption of one or several photons. E.g. two-photon electronic excitation consists of a molecule absorbing two photons within a infinitesimally short time frame and thereby gets excited from one state to a higher electronic states, going through an imaginary intermediate state. The photons can be of equivalent as well as of non-equivalent frequency, however, the total energy absorbed by the molecule will equal the sum of the energy of the two photons (**Paper V**, see Fig. 3a).

It has also been suggested that the mechanism for photolysis of sulfuric acid could be by electronic excitation in the UV region (Zhao et al., 1995; Rinsland et al., 1995), or by vacuum UV electronic transition in the wavelength region around Lyman- α radiation (121.6nm, 10.2 eV) (Mills et al., 2005a,b; Lane and Kjaergaard, 2008). In **Paper V** we tested the probability of two-photon excitation as the mechanism for photodissociation of sulfuric acid in the atmosphere.

Rate of photolysis

Photolysis is a crucial process in the atmosphere, since it provides as a source and sink of many compounds and is the only source of some compounds. The main focal point of **Paper V** is photolysis, but photodissociation is also covered in **Papers I-IV**. The rate

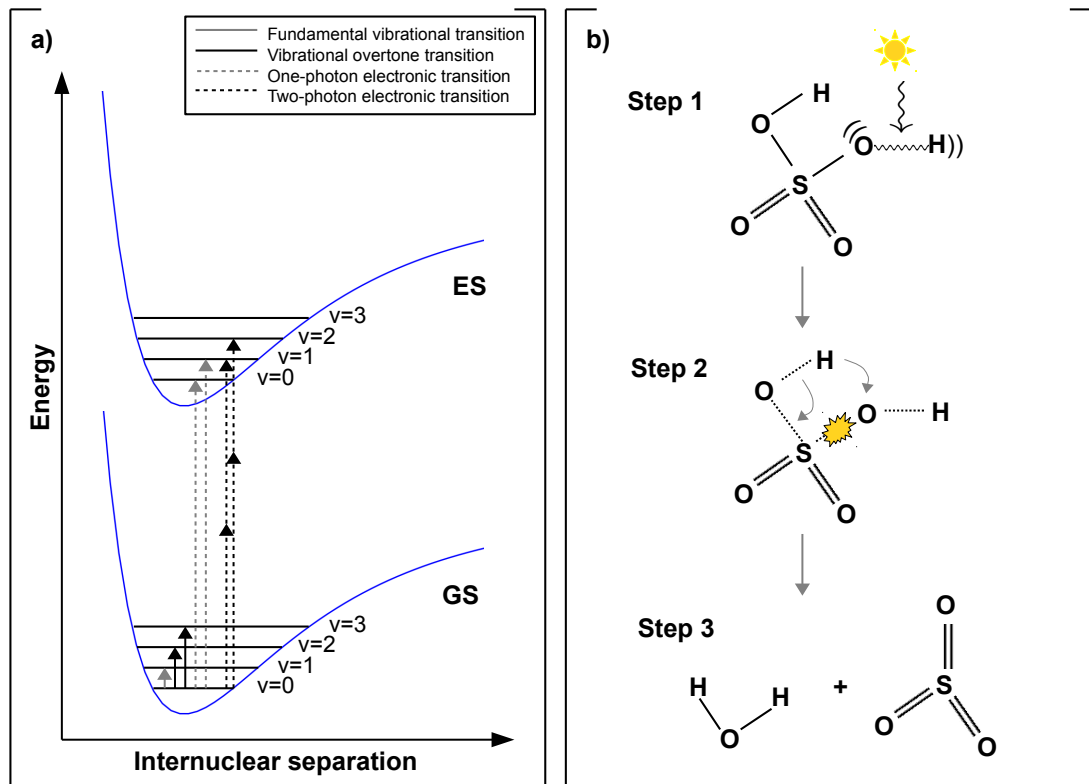


Figure 3: (a) Schematic diagram of the potential energy of a diatomic molecule including examples of vibrational (v) and electronic excitations in the electronic ground state (GS) and the first excited electronic state (ES). (b) Suggested mechanism for photodissociation of sulfuric acid by vibrational OH stretching overtone transitions.

of photolysis can be expressed by the J-value, equivalent to the rate coefficient (k) for a chemical reaction. The J-value is well established for traditional excitation, but in **Paper V** we formulated the photolysis rate when two photons with the wavelengths of λ_1 and λ_2 are absorbed:

$$J = \int \int \sigma(\lambda_1, \lambda_2) F(\lambda_1) F(\lambda_2) \phi(\lambda_1, \lambda_2) d\lambda_1 d\lambda_2 \quad (6)$$

In both the traditional formulation and in the equation for two photon excitation, the J-value depends on (1) the molecular cross section (σ , wavelength dependent), (2) the molecular quantum yield (ϕ , wavelength dependent) that describes the probability of the

dissociation when all criteria for photolysis are fulfilled, and (3) the solar actinic flux (F, wavelength and altitude dependent). Photodissociation of a compound will only take place if there is an overlap of both the cross section, quantum yield and actinic flux. While the molecular cross section can be estimated both experimentally and theoretically, the quantum yield is assessed empirically. Often the actinic flux, which is the photon flux from all directions, is not observed, but instead converted from measured irradiance. In **Paper III** we developed a simple empirical parametrisation for conversion of measured spectral irradiance into actinic flux.

2.4 Boundary layer meteorology

Except for **Paper V** that investigates mechanisms in the stratosphere and mesosphere, all other papers in this thesis (**Papers I-IV**) operate in the atmospheric boundary layer (ABL). The ABL, which is the lowest part of the atmosphere, found below the free troposphere, is directly and highly influenced by the presence of the surface of Earth, thus it responds to surface forcing within maximum an hour. The concentration of any quantity usually underlies a gradient. E.g. not all parts of the forest canopy (e.g. soil, trunk, crown) emit even amounts and composition of chemical compounds, thus the vertical input is different. This generates a concentration gradient that mixing (e.g. by turbulence) will try to even out, creating transport and flux. Mogensen and Boy (2015) already pointed out, as a comment on the publication by Hens et al. (2014), that it is crucial to consider the vertical dimension of the ABL when assessing atmospheric chemistry. When studying chemical concentrations and reactivity in the ABL, one needs to gain information on (1) transport and mixing and (2) the dilution volume.

(1) Transport and turbulent mixing

Generally there are three different forces that drive atmospheric boundary layer mixing: (1) molecular diffusion, (2) advection, and (3) turbulence. (1) Molecular diffusion is transport of molecules due to random motion (Brownian motion). It is a consequence of concentration gradients and only important within the first few millimetres above any surface. (2) Transport via horizontal advection is the result of large-scale uniform motion and is neglected in horizontally homogeneous situations. (3) Turbulence is small-scale, random motion that vary in speed and direction (three-dimensional). Mixing as well as transport of heat, momentum and all compounds in the ABL proceeds mainly by turbulence. Turbulence is generated either mechanically by strong wind shear or wakes,

or thermally by convection. The meteorology in the stratosphere and mesosphere is very different from that in the boundary layer, with much less turbulent mixing.

(2) Dilution volume

Due to thermal mixing, the height of the ABL peaks during daytime ($\sim 1500 - 2500$ m) and decreases during the cold nights (to a few hundred meters or even lower). This generates a smaller ABL air volume during night time, thus e.g. chemical concentrations increase if their daytime and night time sources and sinks are identical. It is critical to consider the dilution volume when operating with e.g. emissions and concentrations of compounds with lifetimes longer than some tens of minutes. E.g. if the emission of some species predominates during the day and the lifetime of that compound is very short (sec-min), then the daily concentration trend will be similar as the emission trend. However, if the lifetime is longer, the emission and concentration trends will not necessarily follow each other and vertical transport has to be considered (**Paper II-III**).

3 Methods: measurements & numerical simulations

In this thesis, we utilised atmospheric field measurement data (Sec. 3.1) together with the methods of process modelling (Sec. 3.2) and computational chemistry (Sec. 3.3). In the sections below, we briefly go through the main aspects of these methods together with short descriptions of the central instrumentation from which we have used data.

3.1 Atmospheric field measurements

Papers I-IV contain field measurements from the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations, Sec. 3.1.1, **Papers I-IV**) and the Meteorological Observatory Hohenpeissenberg (Sec. 3.1.2, **Paper IV**). **Paper I** makes use of data from the entire year 2007 and the first half of year 2009, while **Paper II** uses campaign data from the BFROM campaign (Boreal Forest OH Reactivity Measurements, Sinha et al., 2010) during August 2008. Both **Papers III-IV** investigate the HUMPPA-COPEC-10 campaign (Hyytiälä United Measurement of Photochemistry and Particles – Comprehensive Organic Particle and Environmental Chemistry 2010, Williams et al., 2011) during July – August, 2010. Finally, **Paper IV** also includes a few days of data from the HAFEX campaign (the Hohenpeissenberg Aerosol Formation EXperiment, Birmili et al., 2003) during January – August, 2000.

Several instruments to measure the concentration of a variety of atmospheric trace gases are covered in **Papers I-IV**. The most essential measurement instruments for this thesis are the Proton Transfer Reaction – Mass Spectrometer (PTR-MS, Sec. 3.1.3, **Papers I-II, IV**) that detects the protonated mass of several VOCs, and the Comparative Reactivity Method (CRM, Sec. 3.1.4, **Papers II-III**) that measures the instantaneous reactivity of OH.

3.1.1 SMEAR II

The SMEAR II station (61°51'N, 24°17'E), Hyytiälä, southern Finland (Hari and Kulmala, 2005; Vesala et al., 1998; Kulmala et al., 2001a) plays a central role in this thesis. SMEAR II is located in the southern boreal vegetation zone in Finland, in a rather homogeneous Scots pine (*Pinus sylvestris*) forest sown in 1962. With time, other species have made an

appearance due to airborne transfer of seeds. These species include mostly Norway spruce (*Picea abies*), trembling aspen (*Populus tremula*) and silver birch (*Betula pubescens*). In an area of 1600 km² around the station, forests dominated by spruce trees cover $\sim 26\%$, those with pine trees $\sim 23\%$, and those with both spruce and pine $\sim 21\%$, water bodies 13%, agriculture $\sim 10\%$, while the remaining land is made up by open land, deciduous forest, clear cuts, wetlands and buildings (Haapanala et al., 2007). Due to a lack of detailed emission measurements on the other tree species than pine, we have assumed a 100% Scots pine forest throughout this thesis. This is a reasonable assumption for the model, although strictly valid only near the measurement station. Further, we have assumed that the forest is homogeneous with a canopy height of ~ 18.5 m, a canopy depth of ~ 9 m, a total leaf area index (LAI) of 5.8 and a biomass of 0.0538 g/cm².

3.1.2 Hohenpeissenberg

The Meteorological Observatory Hohenpeissenberg (47°48'N, 11°0'E), southern Germany (Birmili et al., 2003) is located atop the Hohenpeissenberg (985 m a.s.l.) which reaches ~ 300 m above the surrounding terrain, which consists mainly of agricultural land and forest. Especially spruces and beeches grow on the slopes of the mountain in most directions. The canopy was ~ 10 m at the time of the measurements. The site is rural with anthropogenic influences e.g. from Munich which is located ~ 60 km from the station. During night, the boundary layer is often found below the measurement station itself, thus emissions do not reach the site.

3.1.3 PTR-MS and concentration measurements of VOCs

A Proton Transfer Reaction – Mass Spectrometer is an online instrument that measures the concentration of various VOCs in air (Hansel et al., 1995; Lindinger et al., 1998; Lindinger and Jordan, 1998). A PTR-MS measures continuously atmospheric concentrations of several VOCs from several heights inside and above the canopy at the SMEAR II station (Taipale et al., 2008) and those are the measurements used in this thesis. The method consists of the following steps: (1) Hydronium ions (H₃O⁺) are produced from ionisation of water vapour. (2) Air containing VOCs are sucked into the system and the VOCs are chemically ionised by proton transfer from the hydronium ions. (3) The positively charged VOCs are affected by an electric field (generated by a quadrupole) and

detected based on their mass-to-charge ratio (m/z). The soft ionisation method ensures low fragmentation and the dominant fraction of the parent VOC is found at the VOC mass plus one. Since the concept of the method uses protonation, and water as the proton source, it is crucial that the compounds of interest have a proton affinity that is greater than that of water and that the proton thereby favours the VOC and not water.

The general uncertainty on the measurement is estimated to be 15% (Taipale et al., 2008). If the proton affinity of the compound of interest (e.g. formaldehyde, 712.9 kJ/mol) is greater, but close to that of water (691 kJ/mol), the uncertainty on the measurement exceeds the general uncertainty. The detection limit is individual for the various compounds, but e.g. in case of the monoterpenes, it is 0.01 ppb_v.

The instrumental time and mass resolution can be increased by inserting a reflectron Time-Of-Flight Mass spectrometer (TOF-MS) after the protonation (Blake et al., 2004, 2009). These improvements are retrieved by a very fast measurement and that all masses are detected simultaneously in the TOF-MS system, whereas the individual unit masses are detected consecutively in the PTR-MS quadrupole system. A disadvantage of the PTR-MS system (including the PTR-TOF-MS) is its incapability to distinguish different compounds with identical mass. This is a problem, e.g. in case of the monoterpenes where only the total monoterpene concentration can be obtained.

Another technique to measure the concentration of various VOCs is by Gas Chromatography – Mass Spectrometry (GC-MS). This method includes the use of liquid gas chromatography where molecules are retained by a capillary column. The compounds of interest will spend different time travelling the column due to differences in the chemical properties between the different compounds of interest in the mixture and their relative affinity for the stationary phase of the column. The separated compounds can then be detected by the MS. This technique enables the separation and detection of molecules with identical mass, providing an advantage over the PTR-MS. The measurement can be conducted both in situ and offline, but both are slower measurements than the PTR-MS. We have used GC-MS obtained data in **Paper IV**.

3.1.4 CRM and measurements of OH reactivity

The Comparative Reactivity Method (CRM, Sinha et al. (2008, 2010); Nölscher et al. (2012b)) measures the instantaneous OH reactivity. The instrument is online and the

setup consists of a glass reactor coupled to a PTR-MS as illustrated in Fig. 4a. The measurement is an in situ competitive kinetics approach, where the idea behind the technique is depicted in Fig. 4b. The method consists of the following steps: (1) pyrrole molecules are injected into the reactor and the concentration (C_1) is detected by the PTR-MS. (2) Synthetically generated OH radicals are then introduced into the reactor at a constant rate. OH and pyrrole will react and the concentration of pyrrole will decrease to C_2 . (3) Finally, ambient air that contains OH reactive compounds is added. The OH reactive species compete with pyrrole for the OH, which increases the pyrrole concentration to C_3 .

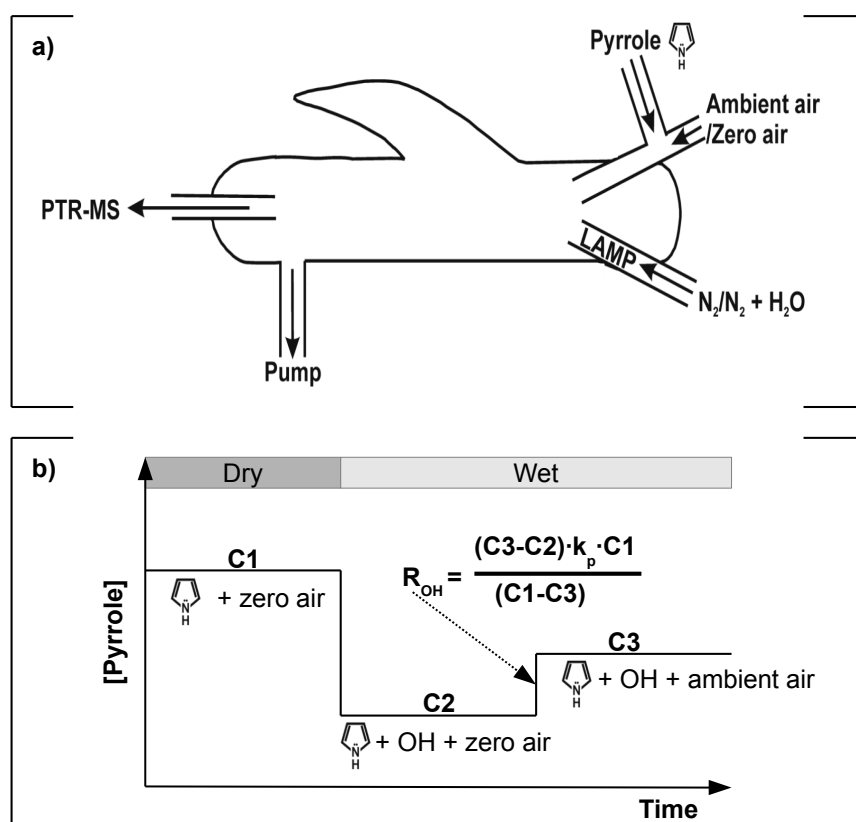


Figure 4: (a) The setup of the CRM consists of a glass reactor and a detector (PTR-MS). (b) Schematic illustration of the steps of the CRM method.

The total OH reactivity (R_{OH}) of the ambient air can then be determined using the three obtained concentrations of pyrrole (C_1 - C_3) and the rate coefficient for the reaction of OH with pyrrole (k_p) (Sinha et al., 2008):

$$R_{\text{OH}} = \frac{(C3 - C2)}{(C1 - C3)} \times k_p \times C1 \quad (7)$$

The detection limit for the measurement is $\sim 3 \text{ s}^{-1}$, the overall uncertainty $\sim 16 - 20\%$, while the time resolution is 10 s (Sinha et al., 2008; Nölscher et al., 2012b).

In principle one could operate with another compound than pyrrole, though the chosen molecule should not be found in the atmosphere, the rate coefficient for reaction with OH should be suitable and well established, and the protonaffinity be larger than that of water if a PTR-MS is used as detector.

Another detector than the rather expensive PTR-MS could also serve. E.g. Nölscher et al. (2012a) connected the CRM to a much cheaper detector; a Gas Chromatographic Photoionization Detector (GC-PID). Though the time resolution, sensitivity and overall uncertainty were somewhat poorer than compared to measurements with a PTR-MS as detector, the performance was still satisfying.

The CRM is, however, not the only technique to measure the reactivity of OH. Currently there exists two other methods that both utilise Laser-Induced Fluorescence (LIF) as the detector. Those include (1) the "pump-and-probe" technique where artificially high OH concentrations are produced by photolysis of ozone using a pump laser. The OH concentration will decay due to reaction with OH reactive compounds. This decay is detected by the LIF and used to derive the atmospheric OH lifetime (Sadanaga et al., 2004; Lou et al., 2010). The other technique includes (2) a discharge flow tube where high OH concentration levels are produced in a movable inlet and injected into a large flow tube. The decay of OH is monitored by the LIF at different inlet positions, which generate different reaction times, whereby the overall loss rate of OH can be determined (Kovacs and Brune, 2001; Mao et al., 2010). The main advantage of the two LIF based systems over the CRM method is the low detection limit ($\sim 1 \text{ s}^{-1}$). While the instrumental uncertainties are comparable to the CRM method, the LIF based methods are slower; the time resolutions are 30-180 s for the "pump-and-probe" technique and 210 s for the flow tube.

Currently there exists no direct measurement of the NO_3 reactivity. However, some recent studies have addressed the reactivity of O_3 (Park et al., 2013; Matsumoto, 2014). Matsumoto (2014) measured the O_3 reactivity in the lab, though the detection limit of the used method is so high that ambient measurements are impossible. Park et al. (2013) has

developed the new method ORMS (Ozone Reactivity Measurement System) and tested this in ambient conditions during the SOAS (Southeast Oxidant and Aerosol Study) campaign in summer 2013. These measurements suggest that the ambient reactivity of O_3 is several orders of magnitude lower than that of OH. Also, it seems that a large fraction of the reactivity of O_3 cannot be explained (this is concluded after personal communication with Jeong-Hoo Park).

3.2 Process based modelling

While measurements are used to observe the world, modelling is used to understand what is observed. The main method of this thesis is therefore numerical simulation with an emphasis on the one dimensional chemistry–transport model SOSAA (model to Simulate Organic vapours, Sulphuric Acid and Aerosols, Sec. 3.2.1, **Papers I-IV**).

What is process based modelling?

Process based models are mathematical descriptions of known (or proposed) mechanisms. Process models therefore include some (better or worse justified) understanding of a mechanism together with the dependencies of the process on driving factors (and identification of these factors). This enables testing of the performance of the model in different environments. If all processes are fully understood, the results should be identical with those measured if no uncertainties are connected to the measurement. E.g. if the prediction of some variable in Helsinki depends on certain parameters, then the prediction of the same variable in Hyytiälä will depend on the very same parameters in an identical way. We aim to have mostly process based modules in our models, since they reflect our scientific knowledge. However, sometimes we need to account for some crucial effects and if we do not know the processes behind or we lack the necessary input data, then we use an empirical approach (e.g. the Guenther algorithms for BVOC emission). Empirical models are based on statistical analysis of observed data, thus they might only be valid under the same conditions which the observations were made.

Models of different scale

As measurements are carried out in different locations using various instrumentation, one can also choose a variety of models that differ in both spatial and temporal scale. Starting from the smallest, we find the box model (e.g. Wang et al., 2013; Hermansson et al., 2014). This type of model excludes a spatial dimension, whereby transport is excluded. When applied to the ambient atmosphere one can think that only one spatial

point in the atmosphere, or e.g. 1 cm^3 is represented. Box models can also be used to simulate smog chamber experiments with well mixed air (e.g. Liao et al., 2014; Roldin et al., 2014), where the box will have the same dimensions as the chamber. In this case, one has to take the chamber walls and their potential losses/sources into account (e.g. deposition and evaporation of compounds, Liao et al. (2014)). It is naturally not necessary to account for wall losses when simulating the atmosphere, however, deposition onto surfaces (e.g. onto needles) still has to be considered. One advantage of the box model type is its cheap cost. By this follows that it can be executed on a laptop, the run time is fast and many detailed processes can be simulated. Another advantage is that one is capable of isolating specific atmospheric processes. E.g. the complicated effects due to meteorology are removed and one has the capability to restrain the model by more measurements if such are available. E.g. in **Paper IV** we aimed at investigating the CI chemistry at the Hohenpeissenberg station. Since the station is located on a mountain, the surrounding area is very heterogeneous and the meteorology very complicated. A box model was therefore the most suitable method for our purpose, since it was connected to less uncertainties. Also, the studied chemical mechanisms were much faster than the time scale of the transport.

1D models (Saylor, 2013, and references therein) add the vertical dimension of the boundary layer to the box model. One can think that a column is placed on a 1 m^2 surface on the ground or that the 1D model consists of many box models that are stacked on top of each other. The benefit of this type of model is that it is capable of describing both the sources of compounds (let it be from e.g. forested or urban areas), the chemical degradation and production of gaseous species and aerosol particles and how these are vertically transported. The vertical aspect is important, since one is not able to conduct the same measurement at many heights throughout the ABL. E.g. in **Paper II** we discovered that there is a large discrepancy between the canopy/ground OH reactivity ratio during night and day. This information is important e.g. when assessing the sinks of OH and in the prediction of the OH concentration. 1D models are relatively computationally cheap. Often the most expensive calculations are the chemical differential equations. If one chooses a smaller chemical subset (e.g. a few hundred of reactions) and a simulation time of some days, it is possible to execute the code on a laptop (e.g. Boy et al., 2006; Gierens et al., 2014). If one desires thousands of chemical reactions and long simulation times (months–years), there is a need to parallelise especially the chemical concentrations calculation, but also the aerosol dynamics, in the different layers of the model and the code will then be executed on a computer cluster. The main drawback of the 1D model

is that description of horizontal transport is in theory impossible, though in practice, the effects of horizontal transport can be accounted for in some variables, by constraining the model by measured quantities. For this reason one should only simulate areas that are horizontally homogeneous.

The horizontal dimensions are achieved by 3D regional and global models. Whereas the regional model type simulates the boundary layer in the local region (with a resolution of a few km to a few tens of km, (e.g. Sofiev et al., 2006)), global models (e.g. Stier et al., 2005) simulates the entire surface of Earth with a resolution that varies from ~ 100 to $200 - 300$ km. Global models do often not only consider the atmosphere, but also the interactions with other spheres, e.g. the biosphere and hydrosphere. The main convenience of such comprehensive models is the ability to investigate how some specific mechanism can perturb the Earth system and climate. Among the potential problems are the expense and large amounts of written code. The numerics are coded by many researchers, thus the user cannot know the entire code by themselves. Such aspect could generate errors. Process based models (both box and 1D models) should test theories and pinpoint which processes are important. Then those processes should be simplified and parametrised and implemented into a larger scale model (e.g. a global model) where the response on the Earth system due to these processes are investigated.

Independent of the type of model, all should maintain the mass balance. There exist more types of models than listed here, e.g. two-box model systems, puff models, "running" 1D models and lagrangian models. The right model for a particular study depends highly on the research question. In this study we only utilised a box- and a 1D model.

3.2.1 SOSA/SOSAA

The 1D atmospheric chemistry-transport model SOSAA (Boy et al., 2011) was employed for studies of various aspects of atmospheric-biosphere interactions in **Papers I-IV**. The content of the model has been described repeatedly in **Papers I-IV**, Boy et al. (2011) and Zhou et al. (2014), while the modular structure is depicted in Fig. 5.

SOSAA is programmed in Fortran 90 and consists of four modules. (1) The atmospheric boundary layer meteorology and turbulent mixing is described by a 1D version of the coupled plant-atmosphere boundary layer model SCADIS (Boy et al., 2011, **Paper III**, and references therein). The module consists of prognostic equations for temperature, hori-

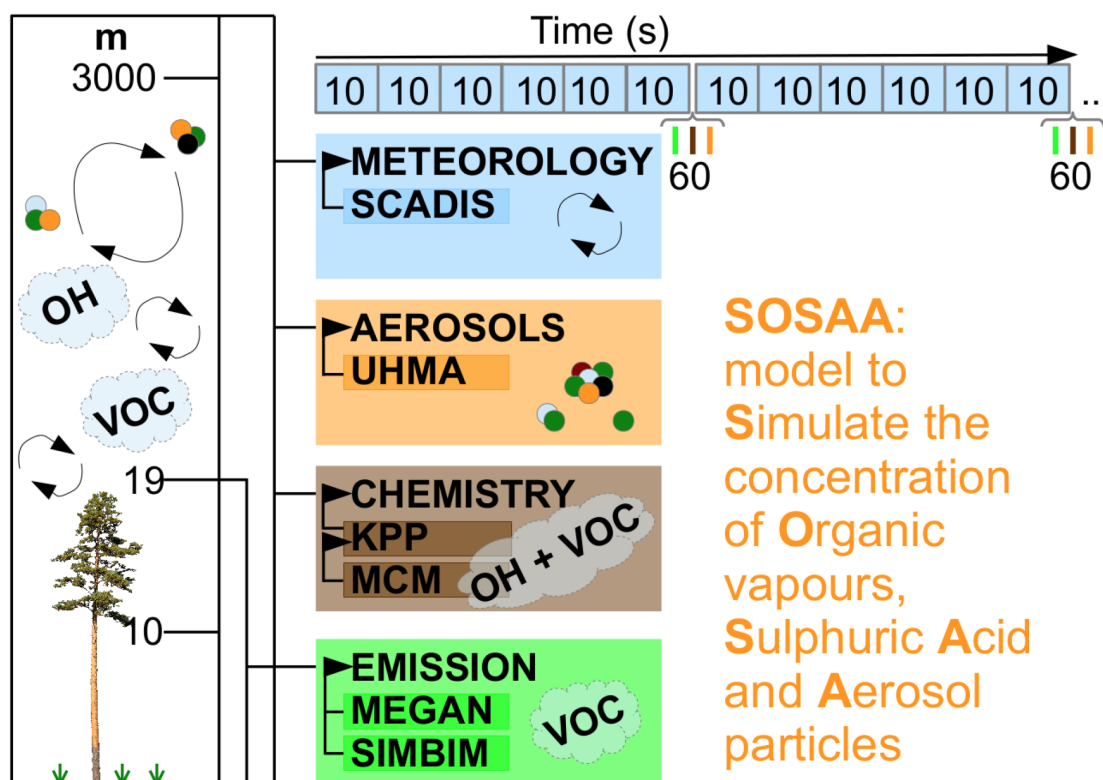


Figure 5: Schematic illustration of SOSAA (model to Simulate Organic vapours, Sulphuric Acid and Aerosols). The meteorological mixing is simulated by SCADIS (SCAlar DIStribution). The emission of biogenic volatile organic compounds is predicted by either MEGAN (Model of Emissions of Gases and Aerosols from Nature) or SIM-BIM (Seasonal Isoprenoid synthase Model – Biochemical Isoprenoid biosynthesis Model). Chemical reactions are chosen from MCM (Master Chemical Mechanism), while the chemical concentrations are calculated by KPP (Kinetic PreProcessor). Lastly, aerosol dynamics is solved by UHMA (University of Helsinki Multicomponent Aerosol model). The figure is originally from **Paper III**.

zonal wind speed, humidity, turbulent kinetic energy (TKE) and the specific dissipation rate of TKE (ω). Nudging is applied in order to force temperature, horizontal wind speed and humidity towards the observations. Turbulent fluxes are solved by a TKE – ω type closure scheme (two–equation closure) (Sogachev, 2009). The domain reaches from the surface to 3000 meters with a flexible amount of logarithmically distributed horizontally

orientated layers. (2) Biogenic tree emissions of several volatile organic compounds are predicted by MEGAN or SIM-BIM as described in Sec. 2.1. (3) Gas phase chemical reactions are chosen from the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997, 2012; Saunders et al., 2003) via website <http://mcm.leeds.ac.uk/MCM/>, while the concentrations of the included compounds are calculated by the Kinetic PreProcessor (KPP) (Damian et al., 2002) and its included solver DLSODE (Radhakrishnan and Hindmarsh, 1993). Photochemical reactions from MCM and a few additions from Atkinson et al. (2004) are also included. Measured spectral irradiance (Boy and Kulmala, 2002) is used as input and converted to actinic flux using the measured photolysis rates of NO_2 and O_3 (to form O^1D) as according to **Paper III**. (4) Aerosol dynamics is based on UHMA (University of Helsinki Multicomponent Aerosol model, Korhonen et al. (2004)) and is an extension (Zhou et al., 2014) to the original model SOSA (model to Simulate Organic vapours and Sulphuric Acid). It includes equations for nucleation, condensation, evaporation, coagulation and deposition. This module was not used in this thesis. The chemistry (3) and aerosol (4) modules utilises parallel computing and the model is executed on a computer cluster.

MALTE-BOX

In **Paper IV** we also utilised MALTE-BOX which is a zero dimensional version of the 1D atmospheric chemistry-transport model MALTE (Model to predict new Aerosol formation in the Lower Troposphere, **Paper IV**; Boy et al., 2006; Lauros et al., 2011; Gierens et al., 2014). There is a possibility to generate/emit BVOCs in the model if no measurements are available, however in **Paper IV** we constrained the model by measured observables. MALTE-BOX also includes gas phase chemistry and aerosol dynamics which are handled in a similar manner as in SOSAA though the modules are not parallelised.

3.3 Computational chemistry

Computational chemistry is the method of choice in **Paper V**. By solving the Schrödinger equation, molecular properties can be calculated. Unfortunately, the wave function can only be solved exactly for a few one-electron systems, thus one have to approximate it by some functional form. This is done by assuming the nuclei to be stationary (Born and Oppenheimer, 1927), and then approximate a solution for the wave function of the electrons alone. There exists a variety of methods to retrieve this. We have used two methods. (1) *ab Initio* (no inclusion of experimental data) coupled-cluster (CC) meth-

ods (Bartlett, 1989) that corrects for the explicit Coulomb electron-electron repulsion to different degrees. Within CC there exists various methods that differ in the amount of included terms used in order to describe the electron correlation. When more terms are included, the result asymptotes to the exact result, however the computational cost also increases. CC is in general very expensive and it is only possible to perform calculations on smaller molecules. (2) In Density Functional Theory (DFT, Hohenberg and Kohn (1964)) the total energy is expressed in terms of the total electron density/electron cloud, rather than the wave function. It treats the electrons as though they make up a uniform gas that under certain conditions will bond atoms together. DFT is much cheaper than CC, enabling the simulations of large molecular systems. As in CC, there are also different methods to choose from, however, in principle there is no way to know which method will perform the best without comparing the results to those obtained from CC simulations.

The program used in **Paper V** in order to conduct the two-photon excitation calculations is DALTON 2.0 (<http://www.kjemi.uio.no/software/dalton/dalton.html>). Though Dalton is not particularly user friendly, it is still the program that is capable of providing the most precise result.

4 Overview of key results

4.1 Gaps in BVOC emission representations and how these affect ambient gaseous concentrations

When BVOCs are emitted into the atmosphere, they are influenced by meteorological mixing and chemical degradation. In **Paper I**, three emission models (Guenther et al., 1995, 2006; Grote et al., 2006) were implemented into SOSAA (Boy et al., 2011), whereby both effects were accounted for. While concentration measurements provide a snapshot from a given moment, highly influenced by the close local environment, the model aims to represent a horizontally homogeneous area, thus we observe that the discrepancy between modelled and measured VOC concentrations in the canopy air is larger than the simulated and observed flux above the canopy.

We discovered that the ambient concentration of monoterpenes and the reactivity of OH were both very sensitive to the variations in the monoterpene emission spectrum, due to the reactivity difference of the terpenes. Since the boundary layer mixing volume is smallest during night (**Paper II**), the summer time monoterpene concentrations also peak during the dark hours, thus the discrepancy in both the OH reactivity ($\sim 30\%$ bias) and the monoterpene concentration due to the chosen chemotype, is also found to be largest during night.

The monthly concentration of the sum of monoterpenes predicted by the three emission models, together with the measured concentration, are presented in Fig. 6. The process model captures the spring better than the empirical models (G95, MEGAN) that underestimate the concentrations. This underestimation is expected due to the lack of inclusion of phenological responses such as e.g. budding and flowering (Aalto et al., 2014a) but also decomposition of autumn litter that appears upon snow-melt. The summertime high emissions are captured well by all models. During the early autumn, all emission models, and especially the empirical algorithms, underestimate the monoterpene concentration greatly. During this period, the trees loose leaves and needles, however, degradation of litter leading to VOC emissions are usually not accounted for in emission models. We included measured forest floor VOC emissions, however, only from January till June due to limited data. We found that this extra source could not fully account for the high spring time monoterpene concentrations. Overall all models predict a somewhat reasonable concentration, however, it is clear that at times, there are necessary processes that

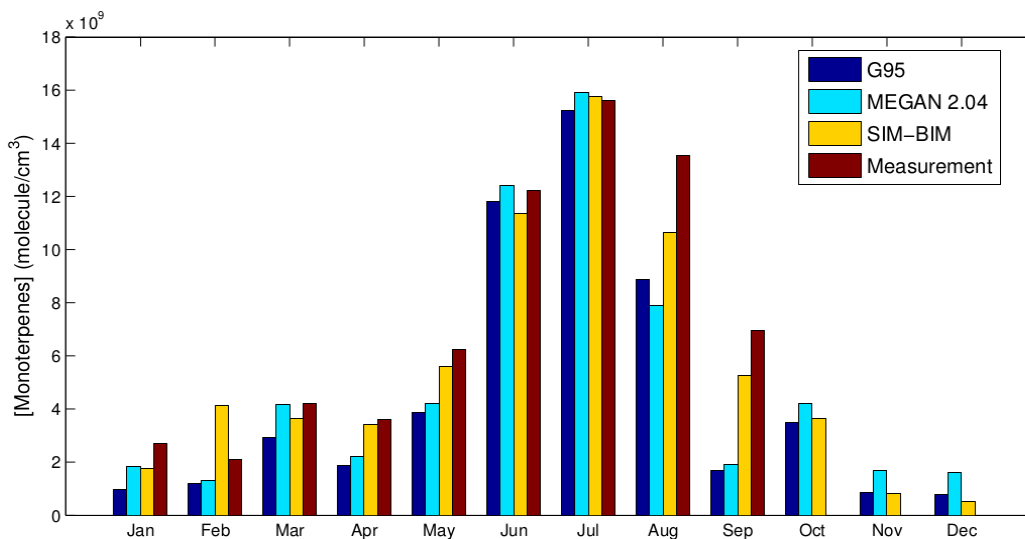


Figure 6: Comparison of modelled (G95, MEGAN 2.04, SIM-BIM) and measured (at the SMEAR II station) average monthly monoterpene concentrations at 4 m height for the year 2007. The figure is found in **Paper I** as Fig. 4.

we have not included. This result is expected due to the limited understanding of BVOC emission mechanisms and the influence of biotic factors that have not been accounted for.

4.2 Known secondary organic oxidation products cannot explain the missing OH reactivity

While the total OH reactivity has been measured in several forested environments (e.g., Kovacs et al., 2003; Nölscher et al., 2012b; Sinha et al., 2010), researchers have tried to account for the reactivity using the simultaneously measured concentrations of OH reactive gases (e.g., Nölscher et al., 2012b; Sinha et al., 2010). While the amount of available measurements can be limited, the obtained gases are either inorganic or directly emitted organic compounds. Organic oxidation products are mostly not measured, since they often are more reactive and have a lower vapour pressure than their parent molecule, thus they are not accounted for in the calculated OH reactivity.

The hypothesis in **Paper II** was that the missing OH reactivity could be accounted for by organic reaction products represented in a near-explicit chemical mechanism (MCM).

However, we underestimated the measured OH reactivity by 50 – 70% and found that the organic oxidation products account for a similar fraction of the OH reactivity as the primary emitted monoterpenes (see Fig. 7). The contribution to the OH reactivity was also investigated in **Paper III**. Here it was found that emitted monoterpenes contributed significantly less than the oxidised biogenic volatile organic compounds to the OH reactivity (see also Sec. 4.3). This difference arises due to several changes made in the later study (**Paper III**), the most important being the updated chemistry scheme. In **Paper II** we used reactions from the MCM v3.1, which included 415 other organic compounds than monoterpenes, isoprene and methane in our simulations. MCM v3.2, which included 1071 other organic compounds was available for the study made in **Paper III**. Furthermore, the temperature was significantly higher during the campaign described in **Paper III**, which increases not only the emission, but also alters the reaction speeds.

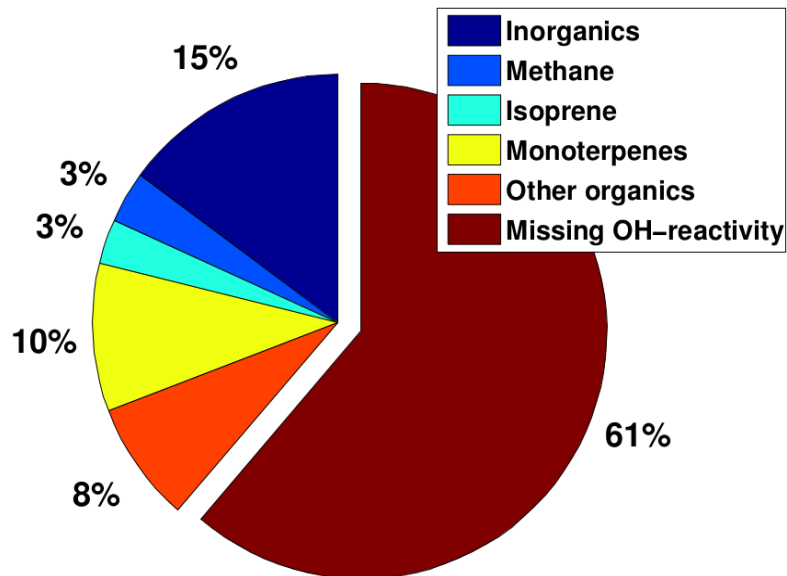


Figure 7: Calculated contributions to the OH reactivity during summertime. The figure is found in **Paper II** as Fig. 3.

The known secondary organic oxidation products could therefore not explain the missing OH reactivity in either study, however, as more oxidation products are included, the gap becomes smaller. We therefore assume that the missing reactivity is at least partly due to unmeasured unknown BVOCs. However, as illustrated in **Paper I** (and in Sec. 4.1),

the predicted OH reactivity highly depends on the assumption made on the chemotype of the tree, thus the choice of chemotype can also explain part of the missing reactivity. Since BVOC emissions peak during warm, sunny times (**Paper I**), we expect that the missing OH reactivity is highest during summer.

4.3 Relative oxidation strength of the atmospheric cleaning agents

The OH radical is considered the main atmospheric cleaning agent and consequently, it has received a lot of attention (**Papers I-IV**; Levy, 1971; Mount and Eisele, 1992; Lelieveld et al, 2008). However, due to its missing photolytic source during dark hours, the concentration of OH decreases. During night various compounds are still present in the atmosphere, thus in **Paper III** we searched for other oxidants that could be important players in the atmospheric oxidation capacity. For the very first time, we present the modelled instantaneous reactivity of O_3 and NO_3 . Below I will compare the importance of atmospheric oxidants depending on different criteria.

Seasonal, vertical and daily importance of OH, NO_3 and O_3

We found that the simulated total OH reactivity peaks in summer (**Paper II**). The main OH sink is then BVOCs, whereas the main wintertime sink consists of inorganic compounds. The summertime accounted OH radical sinks are inorganic compounds ($\sim 40\%$, mainly due to reaction with CO), emitted monoterpenes ($\sim 15\%$) and oxidised biogenic volatile organic compounds ($\sim 45\%$, **Paper III**). However, since the missing reactivity is large and expected to be due to unknown BVOCs (Sec. 4.2), the true main sink of OH is not expected to be inorganic compounds. NO_3 reacts mainly with primary emitted monoterpenes ($\sim 60\%$) and inorganic compounds ($\sim 37\%$, including NO_2 , **Paper III**). O_3 almost exclusively reacts with inorganic compounds ($\sim 91\%$, mainly NO, but also NO_2 during night) and less with primary emitted sesquiterpenes ($\sim 6\%$) and monoterpenes ($\sim 3\%$, **Paper III**). Since the main sink of both OH and NO_3 are biogenic species, their reactivity peaks during summer nights, when the emission is still persisting and the boundary layer is shallow. Since O_3 mainly perish due to inorganic compounds, the O_3 reactivity is highest during daytime. Due to their chemical sources, both the OH and the NO_3 reactivities are larger within the canopy crown, whereas the reactivity of O_3 is larger above the canopy, since the inorganic compounds do not have many local sources and instead are transported to the site. The largest difference between in-canopy and

above-canopy reactivity, when considering the full day and canopy is $\sim 15\%$ in case of OH, $\sim 50\%$ for NO_3 and about a factor of three in case of O_3 .

Relative oxidation strength

We find that OH is the most reactive oxidant ($R \sim 3 \text{ s}^{-1}$) followed by NO_3 ($R \sim 0.07 \text{ s}^{-1}$) and O_3 ($R \sim 2 \times 10^{-5} \text{ s}^{-1}$). When considering the importance of an oxidant, one should not only focus on its reactivity, but also consider its concentration and with what it reacts. In **Paper III** we introduced an *oxidation strength* (OS, or rate of removal) of the oxidant (OX) by multiplying its concentration ($[\text{OX}]$) with its reactivity (R_{OX});

$$\text{OS}_{\text{OX}} = R_{\text{OX}} \times [\text{OX}] \quad (8)$$

The time dependent oxidant strength of each of the oxidants considered is illustrated in Fig. 8.

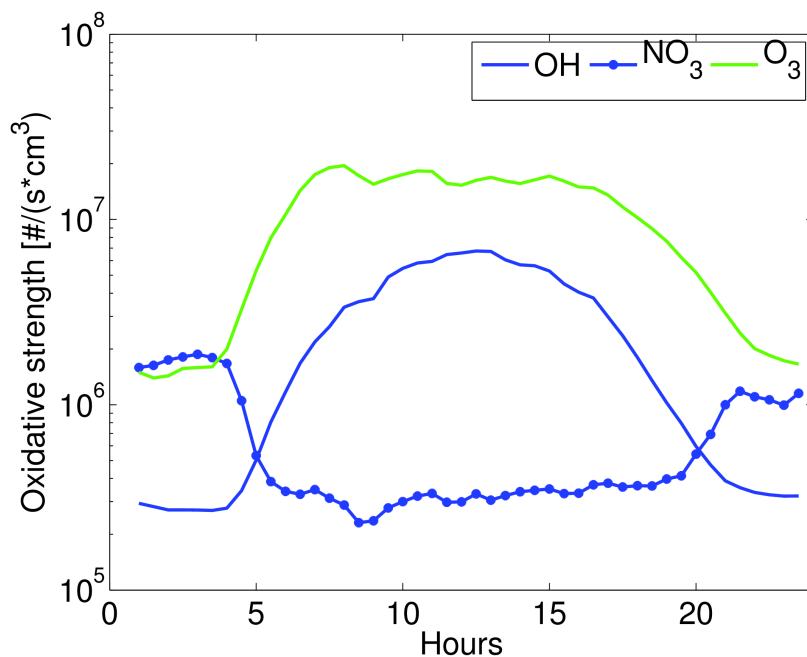


Figure 8: The daily averaged total oxidation strength of OH (blue line), O_3 (green line) and NO_3 (blue line with dots) at 18 m. Please note the log scale on the y-axis.

While the day time oxidant strength of NO_3 is similar to the night time oxidant strength of OH, O_3 is capable of removing compounds from the atmosphere fastest during daytime, and O_3 and NO_3 are competing during night time. However, NO_3 , and especially OH,

are capable of reacting with a much larger diversity of compounds than O_3 - notably compounds of organic origin. Traditionally, it has been thought that the main role of O_3 in the atmosphere is to keep the inorganic chemistry chain alive (e.g. by production of OH and NO_3) and not to clean it of carbon. With respect to organic chemistry, O_3 is mostly thought to only participate in the first oxidation step of primary emitted organic compounds (especially sesquiterpenes). However, Ehn et al. (2014) very recently showed that alkenes can undergo H-shifts after ozonolysis whereby compounds with extremely low volatility are formed. While the inorganic reactivity of NO_3 influences the partitioning between NO_X and NO_Y at night, NO_3 also oxidises directly emitted monoterpenes (first oxidation step). Though NO_3 reacts with many organic compounds, the oxidation is not fast and cannot compete with OH. NO_3 can remove carbon from the atmosphere by oxidation of terpenes to soluble nitrates which can then be washed out. The OH radical can oxidise organic compounds until the species have such a low vapour pressure that they go into the particle phase and then later can deposit out of the atmosphere. OH is therefore the main atmospheric cleaning agent in the boreal forest.

4.4 New insights into atmospheric sulfuric acid chemistry

Since sulfuric acid is a crucial molecule for new particle formation, it is essential that we can predict its concentration. This is only achieved if all its sources and sinks are recognised. We studied a new formation mechanism of sulfuric acid in the boundary layer in **Paper IV** and a potential photolysis sink in the stratosphere in **Paper V**.

Criegee Intermediates are important oxidants for formation of H_2SO_4 in VOC rich environments

Traditionally the production of sulfuric acid has been thought to occur through OH oxidation of SO_2 , while the dominant removal process is assumed to be by condensation onto aerosol particles. Unfortunately, it seems that models are repeatedly underestimating the measured H_2SO_4 concentration in environments with high VOC levels (**Paper IV**, Zhou et al., 2014). In **Paper IV**, where we study a VOC rich site, we find that the measured concentration is underestimated by a factor of two. Even when the sizable uncertainty on the concentration measurement is considered (30 – 60%, Plass-Dülmer et al., 2011), it still seems that either the sink of sulfuric acid is overestimated or the source term is underestimated. Sulfuric acid condensation (CS) onto pre-existing aerosols is calculated based on measured particle number concentrations from the smallest sizes at around 3

nm up to several μm (Kulmala et al., 2001b). However, in order to determine the CS, one needs to make assumptions on the hygroscopic growth behaviour. Undoubtedly, this adds uncertainties to the sink term.

In **Paper IV** we addressed the source of H_2SO_4 , by considering Criegee Intermediate oxidation of SO_2 to form sulfuric acid. We found that this path can explain up to 33–46% of the total sulfuric acid concentration at our VOC rich sites. Though the rate for reaction of SO_2 with CI, where the CI originates from a monoterpene, is slower than when the CI emerge from isoprene, the combination of formation and stabilisation rates of the CI from isoprene is smaller. Since the emission in the studied environments are further dominated by monoterpenes, Criegee Intermediates derived from monoterpenes, influence the sulfuric acid production mostly. We found that the CI pathway to sulfuric acid production dominated at night when the OH concentration was low, while the contribution by CIs was less during day, though it still persisted (Fig. 9a).

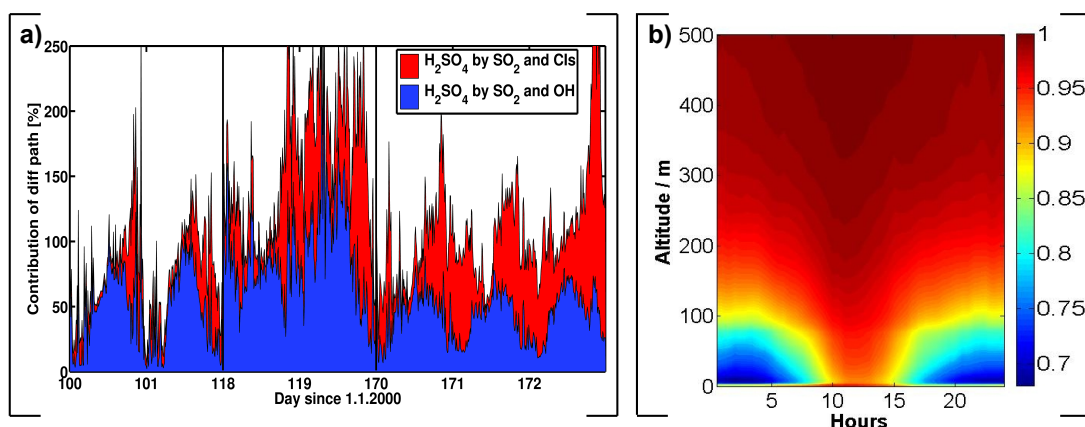


Figure 9: (a) Percentage contribution of the traditional (SO_2+OH) and the CI ($\text{SO}_2\text{-CIs}$) pathways to the sulfuric acid concentration at the Hohenpeissenberg station. The figure is a modification of Fig. 9 in **Paper IV**. (b) Yearly averaged sulfuric acid concentration ratio at SMEAR II. The ratio is given as the sulfuric acid concentration when only production via SO_2+OH is considered, divided by the sulfuric acid concentration when formation via both SO_2+OH and SO_2+CI is included. If H_2SO_4 is only produced from OH, the ratio will be one, while the ratio will be zero, if H_2SO_4 is formed purely by CIs. The figure is a modification of Fig. 11 in **Paper IV**. Both (a) and (b) are based on model results.

Due to the absence of light (less OH) and a shallow boundary layer (accumulation of VOCs), the CI path is, on a seasonal scale, most crucial during wintertime (by $\sim 50\%$).

The importance of this chemical path is found to be predominant close to the VOC emission source, though it still influences the H_2SO_4 concentration at higher altitudes (up to 100 m, Fig. 9b).

Two-photon electronic excitation is not an important mechanism for photodissociation of sulfuric acid in the atmosphere

The current knowledge of atmospheric sulfuric acid suggests that its sink term is altitude dependent. Below ~ 35 km, sulfuric acid condenses, whereas it undergoes photolysis in the layers above. Until 70 km the dominant photodissociation mechanism is proposed to be due to absorption in the visible region by OH stretching overtone transitions, whereas above 70 km, the prevailing path is thought to be through absorption of Lyman- α radiation by high energy Rydberg excited states (Lane and Kjaergaard, 2008). In **Paper V** we investigated another mechanism of photodissociation of sulfuric acid; by electronic transitions due to absorption of two photons. The J-value at two heights (30 and 100 km) was calculated and compared to the photolysis rate obtained when the mechanism of interest was overtone transitions, highly excited and low lying electronic states. We found that the J-value due to the two-photon path was many orders of magnitude less than the other three paths. We therefore concluded that electronic excitation of sulfuric acid by the use of two photons is not an effective path to photolyse sulfuric acid in the upper atmosphere.

5 Review of papers and the author's contribution

I am solely responsible for the introductory part of this thesis.

Paper I evaluates three canopy emission models and the response of emitted VOCs on gaseous chemistry using a 1D model. We found a larger discrepancy in canopy VOC concentrations than in the fluxes. We determined that the chosen chemotype highly affects the predicted OH reactivity. Finally, we conclude that the inclusion of litter cannot explain the missing spring time monoterpene concentration and that inclusion of phenology in general improves the concentration prediction. I did the necessary model development and contributed to writing of the paper.

Paper II presents the first modelled vertical OH reactivity in a boreal forest during a full year and tries to pinpoint the sources of the reactivity using SOSA. OH is found to mainly react with inorganic compounds during winter time, while the reactivity is dominated by biogenic organic compounds during summer time. It was found that the missing fraction of the OH reactivity was larger than the known and that known secondary organic oxidation products can only explain about 10% of the total reactivity. I did parts of the needed model development, ran the simulations, conducted the data analysis and wrote most of the paper.

Paper III investigates the vertical reactivity of OH, O₃ and NO₃ in a boreal forest during summer time using the 1D model SOSAA. We found OH to be most reactive, while O₃ was least reactive. When considering both the oxidant concentration and reactivity, O₃ was found to be the oxidant that can remove the largest total concentration of compounds from the boreal atmosphere, though its capability to remove carbon from the atmosphere is limited. We also distinguished between instantaneous and steady state reactivity and found that the steady state reactivity of NO₃ was about 6–7 times less than the instantaneous reactivity of NO₃. Also in this study the missing OH reactivity was found to be great. I did the model development, simulations and data analysis related to the chemistry, and I wrote most of the paper.

Paper IV addresses the unexplainable large sulfuric acid concentration in the atmospheric boundary layer. Oxidation of SO₂ by biradicals (CI) originating from ozonolysis of unsaturated hydrocarbons to produce sulfuric acid has previously been suggested, but very recent experiments showed that the reaction rates were underestimated. We tested these new rates using measurements from two VOC rich field sites together with a box and

a column model (SOSA). We showed that this pathway could be very important, since it contributed with as much as 33 – 46% to the sulfuric acid concentration at our sites. I am responsible for everything in the paper concerning SOSA (development, simulations, description/text, figures and table) and I wrote the section on the CI uncertainties (Sec. 5).

Paper V tests a new photolysis mechanism of sulfuric acid in the upper atmosphere. The mechanism is electronic photodissociation by absorption of two photons. We conclude that the mechanism cannot explain photolysis of sulfuric acid in the atmosphere. In order to reach this conclusion, we performed both coupled-cluster and Density Functional Theory calculations and suggested a formulation for calculation of the J-value for two-photon electronic excitation. I created all input for DALTON, performed all simulations and calculations and wrote most of the paper.

6 Conclusions and future directions

The motivation for this thesis was to gain information on various aspects of the boreal forest boundary layer oxidation and further to investigate new chemical and photochemical mechanisms in the atmosphere. This work utilised field measurements alongside various numerical approaches. The main conclusion of this thesis are the following:

1) We investigated our lack in understanding of BVOC emissions by comparing measured monoterpene concentrations with concentrations obtained by using both empirical and process based emission modules in a chemistry-transport model. We conclude that existing emission models do not include the necessary representation of biotic influences, and possibly all potential abiotic effects, thus field obtained VOC concentrations cannot be predicted with high accuracy. This problem seems to be largest at smaller scales (canopy scale), but decreases when the footprint area is considered. It is important to raise the question "does this discrepancy matter?". The answer is "yes", since we observe a significant alteration in both the OH reactivity and the monoterpene concentration. Both will highly influence predicted aerosol yields. Our future tasks include to gain a better understanding of the biological process, whereby our representation can be improved. Further, we need to consider other sources than leaves/needles, e.g. trunks, branches and the forest floor and the variation within species has to be investigated further. Lastly, there is a great demand for development of parametrisations based on field data and not just laboratory experiments.

2) Using a 1D chemistry-transport model, we presented the first vertical OH reactivity profiles. We found that the missing fraction of the total reactivity in the boreal forest is larger than the known fraction. We conclude that known secondary organic oxidation products cannot explain the missing OH reactivity and that these oxidation products account for about the same reactivity as the primary emitted monoterpenes or up to about three times more. The OH reactivity measurements have been more common during the past years. Since the majority of measurements conducted in forested areas report a large missing reactivity, we need to take a new approach in order to uncover the missing reactivity. This must be considered crucial in order to make predictions for the future. Perhaps it is not necessary to know the specific compounds, but instead their sources (e.g. directly emitted or oxidation products), the factors affecting their sources (e.g. temperature and light) and their chemical nature (e.g. volatility).

3) We quantified the relative importance of three atmospheric oxidants in the boreal

boundary layer atmosphere using field measurements and the 1D chemistry-transport model SOSAA. We conclude that OH is the main cleaning agent of organic compounds in the atmosphere. We find that OH is approximately one order of magnitude more reactive than NO_3 and five orders of magnitude more reactive than O_3 when considering the total reactivity. We discovered that O_3 is overall the oxidant that is fastest in removing compounds from the boreal atmosphere, however, O_3 does not have the ability to directly remove carbon. Though OH is the most important oxidant, the remaining oxidising agents also have their own functions. The future path must therefore be to develop techniques that can capture the reactivity of other oxidants in addition to OH, and to determine the missing reactivity of those so that we are able to account for their true reactivity.

4) We discovered that oxidation of SO_2 by stabilised Criegee Intermediate biradicals can be an important source for tropospheric sulfuric acid in VOC rich environments. Thereby we closed part of the sulfuric acid concentration gap. This finding was reached by the use of field data and process models. The remaining work includes to decrease the uncertainties combined with the CI chemistry, whereby our conclusion becomes more certain. Using both coupled-cluster and Density Functional Theory calculations, we further conclude that two-photon electronic excitation is not a significant sink of gaseous sulfuric acid in the stratosphere, thus it will not impact the production of SO_2 in the upper atmosphere.

This thesis shed light on alternative atmospheric oxidants in the boreal forest. It pinpoints specific lacks in our understanding of the biosphere-atmosphere system and hopefully it will serve as a springboard to investigate these unknowns. The paths that should be followed include investigation on how much details matter. For example, within the subject of BVOC emissions, we should aim to pinpoint what specific information is needed in order to predict VOC emissions with a satisfying precision. We should also aim to close the gap in the comprehension of the forest OH reactivity and as we should also investigate the role of other oxidants than OH in the atmosphere. These future aims will hopefully help enlighten aspects of the feedbacks between the boreal forest and climate change.

References

- Aalto, J., Kolari, P., Hari, P., Kerminen, V.-M., Schiestl-Aalto, P., Aaltonen, H., Levula, J., Siivola, E., Kulmala, M., and Bäck, J. (2014a). New foliage growth is a significant, unaccounted source for volatiles in boreal evergreen forests. *Biogeosciences*, 11:1331–1344.
- Aalto, J., Rantala, P., Vanhatalo, A., Kajos, M.K., Schallhart, S., Aaltonen, H., Barreira, L., Bhutto, S., Chen, Y., Bäck, J., and Rinne, J. (2014b). From chamber measurements to ecosystem level – the first stand level comparison of monoterpene measurements on different scales. *Report Series in Aerosol Science*, 157:153–157.
- Aaltonen, H., Pumpanen, J., Pihlatie, M., Hakola, H., Hellén, H., Kulmala, L., Vesala, T., and Bäck, J. (2011). Boreal pine forest floor biogenic volatile organic compound emissions peak in early summer and autumn. *Agr. Forest Meteorol.*, 151:682–691.
- Andreae, M.O. and Crutzen, P.J. (1997). Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry. *Science*, 276:1052–1058.
- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., and Troe, J. (2004). Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I – gas phase reactions of O_x, HO_x, NO_x and SO_x species. *Atmos. Chem. Phys.*, 4:1461–1738.
- Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy M. (2012). Chemodiversity of a Scots pine stand and implications for terpene air concentrations. *Biogeosciences*, 9:689–702.
- Baldwin, I.T. and Schultz, J.C. (1983). Rapid changes in tree leaf chemistry induced by damage: Evidence for communication between plants. *Science*, 221:277–279.
- Bartlett, R.J. (1989). Coupled-cluster approach to molecular structure and spectra: A step toward predictive quantum chemistry. *J. Phys. Chem.*, 93:1697–1708.
- Blake, R.S., Whyte, C., Hughes, C.O., Ellis, A.M., and Monks, P.S. (2004). Demonstration of proton-transfer reaction time-of-flight mass spectrometry for real-time analysis of trace volatile organic compounds. *Anal. Chem.*, 76:3841–3845.
- Blake, R.S., Monks, P.S., and Ellis, A.M. (2009). Proton-transfer reaction mass spectrometry. *Chem. Rev.*, 109:861–896.

- Birmili, W., Berresheim, H., Plass-Dülmer, C., Elste, T., Gilge, S., Wiedensohler, A., and Uhrner, U. (2003). The Hohenpeissenberg aerosol formation experiment (HAFEX): A long-term study including size-resolved aerosol, H₂SO₄, OH, and monoterpenes measurements. *Atmos. Chem. Phys.*, 3:361–376.
- Born, M. and Oppenheimer, J.R. (1927). Zur Quantentheorie der Molekeln. *Ann. Phys.*, 389:457–484.
- Boy, M. and Kulmala, M. (2002). The part of the solar spectrum with the highest influence on the formation of SOA in the continental boundary layer. *Atmos. Chem. Phys.*, 2:375–386.
- Boy, M., Hellmuth, O., Korhonen, H., Nilsson, E.D., ReVelle, D., Turnipseed, A., Arnold, F., and Kulmala, M. (2006). MALTE – model to predict new aerosol formation in the lower troposphere. *Atmos. Chem. Phys.*, 6:4499–4517.
- Boy, M., Sogachev, A., Lauros, J., Zhou, L., Guenther, A., and Smolander, S. (2011). SOSA – a new model to simulate the concentrations of organic vapours and sulphuric acid inside the ABL – Part I: Model description and initial evaluation. *Atmos. Chem. Phys.*, 11:43–51.
- Burkholder, J.B. and McKeen, S. (1997). UV absorption cross sections for SO₃. *Geophys. Res. Lett.*, 24:3201–3204.
- Burkholder, J.B., Mills, M., and McKeen, S. (2000). Upper limit for the UV absorption cross sections of H₂SO₄. *Geophys. Res. Lett.*, 27:2493–2496.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., and Maenhaut, W. (2004). Formation of secondary organic aerosols through photooxidation of isoprene. *Science*, 303:1173–1176.
- Criegee, R. and Wnner, G. (1949). Die Ozonisierung des 9-10-Oktalins. *Liebigs Ann. Chem.*, 564:9–16.
- Damian, V., Sandu, A., Damian, M., Potra, F., and Carmichael, G.R. (2002). The kinetic preprocessor KPP – a software environment for solving chemical kinetics. *Comput. Chem. Eng.*, 26:1567–1579.
- De Moraes, C.M., Mescher, M.C., and Tumlinson, J.H. (2001). Caterpillar-induced nocturnal plant volatiles repel nonspecific females. *Nature*, 410:577–580.

- Di Carlo, P., Brune, W.H., Martinez, M., Harder, H., Leshner, R., Ren, X., Thornberry, T., Carroll, M.A., Young, V., Shepson, P.B., Riemer, D., Apel, E., and Campbell, C. (2004). Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs. *Science*, 304:722–725.
- Dicke, M. and Baldwin, I.T. (2010). The evolutionary context for herbivore-induced plant volatiles: beyond the "cry for help". *Trends Plant Sci.*, 15:167–175.
- Ehn, M., Thornton, J.A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L.B., Jorgensen, S., Kjaergaard, H.G., Canagaratna, M., Dal Maso, M., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D.R., Wildt, J., and Mentel, T.F. (2014). A large source of low-volatility secondary organic aerosol. *Nature*, 506:476–479.
- Engelberth, J., Alborn, H.T., Schmelz, E.A., and Tumlinson, J.H. (2004). Airborne signals prime plants against insect herbivore attack. *Proc. Natl. Acad. Sci. USA*, 101:1781–1785.
- Farmer, E.E. and Ryan, C. (1990). Interplant communication: Airborne methyl jasmonate induces synthesis of proteinase inhibitors in plant leaves. *Proc. Natl. Acad. Sci. USA*, 87:7713–7716.
- Finnish Forest Research Institute. Statistical Yearbook of Forestry 2012.
- Fineschi, S. and Loreto, F. (2012). Leaf volatile isoprenoids: an important defensive armament in forest tree species. *iForest*, 5:13–17.
- Fraenkel, G.S. (1959). The raison d'Être of secondary plant substances. *Science*, 129:1466–1470.
- Ghirardo, A., Koch, K., Taipale, R., Zimmer, I., Schnitzler, J.-P., and Rinne, J. (2010). Determination of *de novo* and pool emissions of terpenes from four common boreal/alpine trees by ¹³CO₂ labelling and PTR-MS analysis. *Plant, Cell Environ.*, 33:781–792.
- Gierens, R.T., Laakso, L., Mogensen, D., Vakkari, V., Beukes, J.P., Van Zyl, P.G., Hakola, H., Guenther, A., Jacobus, P.J., and Boy, M. (2014). Modelling new particle formation events in South African savannah. *S. Afr. J. Sci.*, 110, No 5/6.

- Goldstein, A.H. and Galbally, I.E. (2007). Known and unexplored organic constituents in the Earth's atmosphere. *Envir. Sci. Techn.*, 41:1514–1521.
- Gray, C.M., Monson, R.K., and Fierer, N. (2010). Emissions of volatile organic compounds during the decomposition of plant litter. *J. Geophys. Res.*, 115:G03015.
- Grote, R., Mayrhofer, S., Fischbach, R.J., Steinbrecher, R., Staudt, M., and Schnitzler, J.-P. (2006). Process-based modelling of isoprenoid emissions from evergreen leaves of *Quercus ilex* (L.). *Atmos. Environ.*, 40:S152–S165.
- Grote, R., Keenan, T., Lavoie, A.-V., and Staudt, M. (2010). Process-based simulation of seasonality and drought stress in monoterpene emission models. *Biogeosciences*, 7:257–274.
- Guenther, A., Zimmerman, P.R., Harley, P.C., Monson, R.K., and Fall, R. (1993). Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analysis. *J. Geophys. Res.*, 98:12609–12617.
- Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P. (1995). A global model of natural volatile organic compound emissions. *J. Geophys. Res.*, 100:8873–8892.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., and Geron, C. (2006). Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.*, 6:3181–3210.
- Guenther, A.B., Jiang, X., Heald, C.L., Sakulyanontvittaya, T., Duhl, T., Emmons, L.K., and Wang, X. (2012). The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): An extended and updated framework for modeling biogenic emissions. *Geosci. Model Dev.*, 5:1471–1492.
- Guenther, A. (2013). Biological and chemical diversity of biogenic volatile organic emissions into the atmosphere. *ISRN Atmospheric Sciences*, Article ID 786290.
- Haapanala, S., Rinne, J., Hakola, H., Hellén, H., Laakso, L., Lihavainen, H., Janson, R., O'Dowd, C., and Kulmala, M. (2007). Boundary layer concentrations and landscape scale emissions of volatile organic compounds in early spring. *Atmos. Chem. Phys.*, 7:1869–1878.

- Hakola, H., Tarvainen, V., Laurila, T., Hiltunen, V., Hellén, H., and Keronen, P. (2003). Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.*, 37:1623–1634.
- Hakola, H., Tarvainen, V., Bäck, J., Ranta, H., Bonn, B., Rinne, J., and Kulmala, M. (2006). Seasonal variation of mono- and sesquiterpene emission rates of Scots pine. *Biogeosciences*, 3:93–101.
- Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W. (1995). Proton transfer reaction mass spectrometry: On-line trace gas analysis at the ppb level. *Int. J. Mass Spectrom.*, 150:609–619.
- Hao, L.Q., Romakkaniemi, S., Yli-Pirilä, P., Joutsensaari, J., Kortelainen, A., Kroll, J.H., Miettinen, P., Vaattovaara, P., Tiitta, P., Jaatinen, A., Kajos, M.K., Holopainen, J.K., Heijari, J., Rinne, J., Kulmala, M., Worsnop, D.R., Smith, J.N., and Laaksonen, A. (2011). Mass yields of secondary organic aerosols from the oxidation of α -pinene and real plant emissions. *Atmos. Chem. Phys.*, 11:1367–1378.
- Hari, P. and Kulmala, M. (2005). Station for measuring ecosystem-atmosphere relations (SMEAR II). *Boreal Env. Res.*, 10:315–322.
- Hatakeyama, S., Kobayashi, H., Lin, Z.-Y., Takagi, H., and Akimoto, H. (1986). Mechanism for the Reaction of CH_2OO with SO_2 . *J. Phys. Chem.*, 90:4131–4135.
- Hens, K., Novelli, A., Martinez, M., Auld, J., Axinte, R., Bohn, B., Fischer, H., Keronen, P., Kubistin, D., Nölscher, A.C., Oswald, R., Paasonen, P., Petäjä, T., Regelin, E., Sander, R., Sinha, V., Sipilä, M., Taraborrelli, D., Tatum Ernest, C., Williams, J., Lelieveld, J., and Harder, H. (2014). Observation and modelling of HO_x radicals in a boreal forest. *Atmos. Chem. Phys.*, 14:8723–8747.
- Hermansson, E., Roldin, P., Rusanen, A., Mogensen, D., Kivekäs, N., Boy, M., and Swietlicki, E. (2014). Biogenic SOA formation through gas-phase oxidation and gas-to-particle partitioning – Comparison between process models of varying complexity. *Atmos. Chem. Phys.*, 14:11853–11869.
- Hohenberg, P. and Kohn, W. (1964). Inhomogeneous electron gas. *Phys. Rev.*, 136:B864–B871.

- IPCC (the Intergovernmental Panel on Climate Change). (2014). Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part B: Regional Aspects. Available online at <http://www.ipcc.ch/report/ar5/wg2/>. IPCC secretariat, Geneva, Switzerland.
- Jenkin, M.E., Saunders, S.M., and Pilling, M.J. (1997). The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmos. Environ.*, 31:81–104.
- Jenkin, M.E., Wyche, K.P., Evans, C.J., Carr, T., Monks, P.S., Alfarra, M.R., Barley, M.H., McFiggans, G.B., Young, J.C., and Rickard, A.R. (2012). Development and chamber evaluation of the MCM v3.2 degradation scheme for β -caryophyllene. *Atmos. Chem. Phys.*, 12:5275–5308.
- Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, T.F., Tillmann, R., Uerlings, R., Schurr, U., and Wahner, A. (2009). New particle formation in forests inhibited by isoprene emissions. *Nature*, 461:381–384.
- Kirkby, J., Curtius, J., Almeida, J., Dunne, E., Duplissy, J., Ehrhart, S., Franchin, A., Gagné, S., Ickes, L., Kürten, A., Kupc, A., Metzger, A., Riccobono, F., Rondo, L., Schobesberger, S., Tsagkogeorgas, G., Wimmer, D., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Downard, A., Ehn, M., Flagan, R.C., Haider, S., Hansel, A., Hauser, D., Jud, W., Junninen, H., Kreissl, F., Kvashin, A., Laaksonen, A., Lehtipalo, K., Lima, J., Lovejoy, E.R., Makhmutov, V., Mathot, S., Mikkilä, J., Minginette, P., Mogo, S., Nieminen, T., Onnela, A., Pereira, P., Petäjä, T., Schnitzhofer, R., Seinfeld, J.H., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Vanhanen, J., Viisanen, Y., Vrtala, A., Wagner, P.E., Walther, H., Weingartner, E., Wex, H., Winkler, P.M., Carslaw, K.S., Worsnop, D.R., Baltensperger, U., and Kulmala, M. (2011). Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature*, 476:429–433.
- Korhonen, H., Lehtinen, K.E.J., and Kulmala, M. (2004). Multicomponent aerosol dynamics model UHMA: model development and validation. *Atmos. Chem. Phys.*, 4:757–771.
- Kovacs, T.A. and Brune, W. (2001). Total OH loss rate measurement. *J. Atmos. Chem.*, 39:105–122.
- Kovacs, T.A., Brune, W.H., Harder, H., Martinez, M., Simpas, J.B., Frost, G.J., Williams, E., Jobson, T., Stroud, C., Young, V., Friede, A., and Werte, B. (2003). Direct mea-

- surements of urban OH reactivity during Nashville SOS in summer 1999. *J. Environ. Monit.*, 5:68–74.
- Kulmala, M., Hämeri, K., Aalto, P.P., Mäkelä, J.M., Pirjola, L., Nilsson, E.D., Buzorius, G., Rannik, Ü., Dal Maso, M., Seidl, W., Hoffman, T., Janson, R., Hansson, H.-C., Viisanen, Y., Laaksonen, A., and O’Dowd, C.D. (2001a). Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus*, 53B:324–343.
- Kulmala, M., Dal Maso, M., Mäkelä, J.M., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K., and O’Dowd, C.D. (2001b). On the formation, growth and composition of nucleation mode particles. *Tellus*, 53B:479–490.
- Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., A. Lauri, A., Kerminen, V.-M., Birmili, W., McMurry, P.H. (2004). Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.*, 35:143–176.
- Kulmala, M., Petäjä, T., Ehn, M., Thornton, J., Sipilä, M., Worsnop, D.R., and Kerminen, V.-M. (2014). Chemistry of atmospheric nucleation: On the recent advances on precursor characterization and atmospheric cluster composition in connection with atmospheric new particle formation. *Annu. Rev. Phys. Chem.*, 65:21–37.
- Kurtén, T., Lane, J.R., Jørgensen, S., and Kjaergaard, H.G. (2011). A computational study of the oxidation of SO₂ to SO₃ by gas-phase organic oxidants. *J. Phys. Chem. A*, 115:8669–8681.
- Lane, J.R. and Kjaergaard, H.G. (2008). Calculated electronic transitions in sulfuric acid and implications for its photodissociation in the atmosphere. *J. Phys. Chem. A*, 112:4958–4964.
- Lauros, J., Sogachev, A., Smolander, S., Vuollekoski, H., Sihto, S.-L., Mammarella, I., Laakso, L., Rannik, Ü., and Boy, M. (2011). Particle concentration and flux dynamics in the atmospheric boundary layer as the indicator of formation mechanism. *Atmos. Chem. Phys.*, 11:5591–5601.
- Lelieveld, J., Butler, T.M., Crowley, J.N., Dillon, T.J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.G., Martinez, M., Taraborrelli, D., and Williams, J. (2008). Atmospheric oxidation capacity sustained by a tropical forest. *Nature*, 452:737–740.

- Levy II., H. (1971). Normal atmosphere: Large radical and formaldehyde concentrations predicted. *Science*, 173:141–143.
- Liao, L., Dal Maso, M., Mogensen, D., Roldin, P., Rusanen, A., Kerminen, V.-M., Mentel, T.F., Wildt, J., Kleist, E., Kiendler-Scharr, A., Tillmann, R., Ehn, M., Kulmala, M., and Boy, M. (2014). Modelling the contribution of biogenic VOCs to new particle formation in the Jülich Plant Atmosphere Chamber. *Atmos. Chem. Phys. Discuss.*, 14:27973–28018.
- Lindinger, W. and Jordan, A. (1998). Proton-transfer-reaction mass spectrometry (PTR-MS): On-line monitoring of volatile organic compounds at pptv levels. *Chem. Soc. Rev.*, 27:347–375.
- Lindinger, W., Hansel, A., and Jordan, A. (1998). On-line monitoring of volatile organic compounds at pptv levels by means of proton-transfer-reaction mass spectrometry (PTR-MS) – medical applications, food control and environmental research. *Int. J. Mass Spectrom.*, 173:191–241.
- Loivamäki, M., Mumm, R., Dicke, M., Schnitzler, J.-P. (2008). Isoprene interferes with the attraction of bodyguards by herbaceous plants. *Proc. Nat. Acad. Sci. USA*, 105:17430–17435.
- Loreto, F., Mannozi, M., Maris, C., Nascetti, P., Ferranti, F., and Pasqualini, S. (2001). Ozone quenching properties of isoprene and its antioxidant role in leaves. *Plant Physiol.*, 126:993–1000.
- Lou, S., Holland, F., Rohrer, F., Lu, K., Bohn, B., Brauers, T., Chang, C.C., Fuchs, H., Häsel, R., Kita, K., Kondo, Y., Li, X., Shao, M., Zeng, L., Wahner, A., Zhang, Y., Wang, W., and Hofzumahaus, A. (2010). Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results. *Atmos. Chem. Phys.*, 10:11243–11260.
- Makkonen, R., Asmi, A., Kerminen, V.-M., Boy, M., Arneth, A., Guenther, A., and Kulmala, M. (2012). BVOC–aerosol–climate interactions in the global aerosol–climate model ECHAM5.5–HAM2. *Atmos. Chem. Phys.*, 12:10077–10096.
- Mao, J., Ren, X., Chen, S., Brune, W., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J., and Leuchner, M. (2010). Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies. *Atmos. Environ.*, 44:4107–4115.

- Matsumoto, J. (2014). Measuring biogenic volatile organic compounds (BVOCs) from vegetation in terms of ozone reactivity. *Aerosol. Air Qual. Res.*, 14:197–206.
- Mauldin III, R.L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M. (2012). A new atmospherically relevant oxidant. *Nature*, 488:193–196.
- Mills, M.J., Toon, O.B., and Thomas, G.E. (2005a). Mesospheric sulfate aerosol layer. *J. Geophys. Res.*, 110:D24208.
- Mills, M.J., Toon, O.B., Vaida, V., Hintze, P.E., Kjaergaard, H.G., Schofield, D.P., and Robinson, T.W. (2005b). Photolysis of sulfuric acid vapor by visible light as a source of the polar stratospheric CN layer. *J. Geophys. Res.*, 110:D08201.
- Mogensen, D. and Boy M. (2015). Comment on "Observation and modelling of HO_x radicals in a boreal forest" by Hens et al. (2014). *Atmos. Chem. Phys. Discuss.*, 15:853–856.
- Mount, G.H. and Eisele, F.L. (1992). An intercomparison of tropospheric OH measurements at Fritz Peak Observatory, Colorado. *Science*, 256:1187–1190.
- Niinemets, Ü., Seufert, G., Steinbrecher, R., and Tenhunen, J.D. (2002). A model coupling foliar monoterpene emissions to leaf photosynthetic characteristics in Mediterranean evergreen *Quercus* species. *New Phytol.*, 153:257–276.
- Niinemets, Ü., Kännaste, A., and Copolovici, L. (2013). Quantitative patterns between plant volatile emissions induced by biotic stresses and the degree of damage. *Front. Plant Sci.*, 4:262.
- Nölscher, A.C., Sinha, V., Bockisch, S., Klüpfel, T., and Williams, J. (2012a). Total OH reactivity measurements using a new fast Gas Chromatographic Photo-Ionization Detector (GC-PID). *Atmos. Meas. Tech.*, 5:2981–2992.
- Nölscher, A.C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A.M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J.N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H.G., Vilá-Guerau de Arellano, J., and Lelieveld J. (2012b). Summertime total OH reactivity measurements from boreal forest during HUMPPA–COPEC 2010. *Atmos. Chem. Phys.*, 12:8257–8270.

- Paré, P.W. and Tumlinson, J.H. (1997). Induced synthesis of plant volatiles. *Nature*, 385:30–31.
- Park J.-H., Guenther A., and Helmig D. (2013). Ozone reactivity of biogenic volatile organic compound (BVOC) emissions during the Southeast Oxidant and Aerosol Study (SOAS). *AGU Fall Meeting*, San Francisco, Dec. 9–13, Abstract A13A–0172.
- Plass-Dülmer, C., Elste, T., Paasonen, P., and Petäjä, T. (2011). Sulphuric acid measurements by CIMS – uncertainties and consistency between various data sets. *EGU General Assembly 2011*. Geophysical Research Abstracts Vol. 13, EGU2011-11691, available at <http://meetingorganizer.copernicus.org/EGU2011/EGU2011-11691.pdf>
- Radhakrishnan, K. and Hindmarsh, A.C. (1993). Description and use of LSODE, the Livermore Solver for Ordinary Differential Equations. *LLNL report*, UCRL-ID-113855.
- Ren, X.R., Harder, H., Martinez, M., Leshner, R.L., Oligier, A., Shirley, Y., Adams, J., Simpas, J.B., and Brune, W.H. (2003). HO_x concentrations and OH reactivity observations in New York city during PMTACS–NY2001. *Atmos. Environ.*, 37:3627–3637.
- Rinne, J., Taipale, R., Markkanen, T., Ruuskanen, T.M., Hellén, H., Kajos, M.K., Vesala, T., and Kulmala, M. (2007) Hydrocarbon fluxes above a Scots pine forest canopy: measurements and modeling. *Atmos. Chem. Phys.*, 7:3361–3372.
- Rinne, J., Bäck, J., and Hakola, H. (2009). Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions. *Boreal Env. Res.*, 14:807–826.
- Rinsland, C.P., Gunson, M.R., Ko, M.K.W., Weisenstein, D.W., Zander, R., Abrams, M.C., Goldman, A., Sze, N.D., and Yue, G.K. (1995). H₂SO₄ photolysis: A source of sulfur dioxide in the upper stratosphere. *Geophys. Res. Lett.*, 22:1109–1112.
- Roldin, P., Eriksson, A.C., Nordin, E.Z., Hermansson, E., Mogensen, D., Rusanen, A., Boy, M., Swietlicki, E., Svenningsson, B., Zelenyuk, A., and Pagels, J. (2014). Modelling non-equilibrium secondary organic aerosol formation and evaporation with the aerosol dynamics, gas- and particle-phase chemistry kinetic multi-layer model ADCHAM. *Atmos. Chem. Phys.*, 14:7953–7993.
- Rosenstiel, T.N., Potosnak, M.J., Griffin, K.L., Fall, R., and Monson, R.K. (2003). Increased CO₂ uncouples growth from isoprene emission in an agriforest ecosystem. *Nature*, 421:256–259.

- Sadanaga, Y., Yoshino, A., Watanabe, K., Yoshioka, A., Wakazono, Y., Kanaya, Y., and Kajii, Y. (2004). Development of a measurement system of OH reactivity in the atmosphere by using a laser-induced pump and probe technique. *Rev. Sci. Instrum.*, 75:2648-2655.
- Saunders, S.M., Jenkin, M.E., Derwent, R.G., and Pilling, M.J. (2003). Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds. *Atmos. Chem. Phys.*, 3:161–180.
- Saylor, R.D. (2013). The Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS): model description and application to a temperate deciduous forest canopy. *Atmos. Chem. Phys.*, 13:693–715.
- Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I.K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A.J., Dunne, E.M., Flagan, R.C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A.P., Rondo, L., Santos, F.D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K.S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N.M., and Worsnop, D.R. (2013). Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules. *Proc. Natl. Acad. Sci. USA*, 110:17223–17228.
- Schurgers, G., Arneth, A., Holzinger, R., and Goldstein, A.H. (2009). Process-based modelling of biogenic monoterpene emissions combining production and release from storage. *Atmos. Chem. Phys.*, 9:3409–3423.
- Seinfeld, J.H. and Pandis, S.N. (2006). *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. John Wiley & Sons, Inc., New York.
- Sharkey, T.D. and Singaas, E.L. (1995). Why plants emit isoprene. *Nature*, 374:769–769.
- Silver, G.M. and Fall, R. (1991). Enzymatic synthesis of isoprene from dimethylallyl diphosphate in aspen leaf extracts. *Plant Physiol.*, 97:1588–1591.
- Sinha, V., Williams, J., Crowley, J.N., and Lelieveld, J. (2008). The comparative reactivity method – a new tool to measure total OH reactivity in ambient air. *Atmos. Chem. Phys.*, 8:2213–2227.

- Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T.M., Kajos, M.K., Patokoski, J., Hellén, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M. (2010). OH reactivity measurements within a boreal forest: Evidence for unknown reactive emissions. *Environ. Sci. Technol.*, 44:6614–6620.
- Sofiev, M., Siljamo, P., Valkama, I., Ilvonen, M., and Kukkonen, J. (2006). A dispersion modelling system SILAM and its evaluation against ETEX data. *Atmos. Environ.*, 40:674–685.
- Sogachev, A. (2009). A note on two-equation closure modelling of canopy flow. *Bound.-Lay. Meteorol.*, 130:423–435.
- Stier, P., Feichter, J., Kinne, S., Kloster, S., Vignati, E., Wilson, J., Ganzeveld, L., Tegen, I., Werner, M., Balkanski, Y., Schulz, M., Boucher, O., Minikin, A., and Petzold, A. (2005). The aerosol-climate model ECHAM5-HAM. *Atmos. Chem. Phys.*, 5:1125–1156.
- Taipale, R., Ruuskanen, T.M., Rinne, J., Kajos, M.K., Hakola, H., Pohja, T., and Kulmala, M. (2008). Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS – measurement, calibration, and volume mixing ratio calculation methods. *Atmos. Chem. Phys.*, 8:6681–6698.
- Tingey, D. (1981). The effect of environmental factors on the emission of biogenic hydrocarbons from live oak and slash pine, in *Atmospheric Biogenic Hydrocarbons*, edited by J. Bufalini and R. Arnts. Ann Arbor Science, Ann Arbor, pp. 53–72.
- VanReken, T.M., Greenberg, J.P., Harley, P.C., Guenther, A.B., and Smith, J.N. (2006). Direct measurement of particle formation and growth from the oxidation of biogenic emissions. *Atmos. Chem. Phys.*, 6:4403–4413.
- Vesala, T., Haataja, J., Aalto, P., Altimir, N., Buzorius, G., Garam, E., Hämeri, K., Ilvesniemi, H., Jokinen, V., Keronen, P., Lahti, T., Markkanen, T., Mäkelä, J.M., Nikinmaa, E., Palmroth, S., Palva, L., Pohja, T., Pumpanen, J., Rannik, Ü., Siivola, E., Ylitalo, H., Hari, P., and Kulmala, M. (1998). Long-term field measurements of atmospheric-surface interactions in boreal forest combining forest ecology, micrometeorology, aerosol physics and atmospheric chemistry. *Trends in Heat, Mass and Momentum Transfer*, 4:17–35.
- Wang, Z.B., Hu, M., Mogensen, D., Yue, D.L., Zheng, J., Zhang, R.Y., Liu, Y., Yuan, B., Li, X., Shao, M., Zhou, L., Wu, Z.J., Wiedensohler, A., and Boy, M. (2013).

- The simulations of sulfuric acid concentration and new particle formation in an urban atmosphere in China. *Atmos. Chem. Phys.*, 13:11157–11167.
- Weber, R.J., McMurry, P.H., Eisele, F.L., and Tanner, D.J. (1995). Measurements of expected nucleation precursor species and 3-500-nm diameter particles at Mauna Loa observatory, Hawaii. *J. Atmos. Sci.*, 52:2242–2257.
- Welz, O., Savee, J.D., Osborn, D.L., Vasu, S.S., Percival, C.J., Shallcross, D.E., and Taatjes, C.A. (2012). Direct kinetic measurements of Criegee Intermediate (CH_2OO) formed by reaction of CH_2I with O_2 . *Science*, 335:204–207.
- Went, F.W. (1960). Blue hazes in the atmosphere. *Nature*, 187:641–643.
- Williams, J., Crowley, J., Fischer, H., Harder, H., Martinez, M., Petäjä, T., Rinne, J., Bäck, J., Boy, M., Dal Maso, M., Hakala, J., Kajos, M., Keronen, P., Rantala, P., Aalto, J., Aaltonen, H., Paatero, J., Vesala, T., Hakola, H., Levula, J., Pohja, T., Herrmann, F., Auld, J., Mesarchaki, E., Song, W., Yassaa, N., Nölscher, A., Johnson, A.M., Custer, T., Sinha, V., Thieser, J., Pouvesle, N., Taraborrelli, D., Tang, M.J., Bozem, H., Hosaynali-Beygi, Z., Axinte, R., Oswald, R., Novelli, A., Kubistin, D., Hens, K., Javed, U., Trawny, K., Breitenberger, C., Hidalgo, P.J., Ebben, C.J., Geiger, F.M., Corrigan, A.L., Russell, L.M., Ouwersloot, H.G., Vila-Guerau de Arellano, J., Ganzeveld, L., Vogel, A., Beck, M., Bayerle, A., Kampf, C.J., Bertelmann, M., Köllner, F., Hoffmann, T., Valverde, J., Gonzalez, D., Riekkola, M.-L., Kulmala, M., and Lelieveld, L. (2011). The summertime boreal forest field measurement intensive (HUMPPA-COPEC-2010): an overview of meteorological and chemical influences. *Atmos. Chem. Phys.*, 11:10599–10618.
- Zhao, J.X., Toon, O.B., and Turco, R.P. (1995). Origin of condensation nuclei in the springtime polar stratosphere. *J. Geophys. Res.*, 100:5215–5227.
- Zhou, L., Nieminen, T., Mogensen, D., Smolander, S., Rusanen, A., Kulmala, M., and Boy, M. (2014). SOSAA – A new model to simulate the concentrations of organic vapours, sulphuric acid and aerosols inside the ABL – Part 2: Aerosol dynamics and one case study at a boreal forest site. *Boreal Env. Res.*, 19B:237–256.