Dissertationes Forestales 310

O_3 and NO_x interactions with foliage: processes and compounds at the needle-air interface

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Academic dissertation

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Ozone (O_3) and nitrogen oxides (NO_x: nitrogen monoxide NO and nitrogen dioxide NO_2) are reactive gases with an important role in atmospheric chemistry. Terpenes are a reactive subgroup of BVOCs (biogenic volatile organic compounds) emitted by plants. Needle or leaf surfaces are the first point of contact between the atmosphere and a plant. Boreal forests represent a significant portion of the global land area available for atmosphere-biosphere interactions.

The aim was to develop methods for observing the exchange of NOx in field conditions and to explore the roles of terpenes on needle surfaces and nitrate fertilization on the fate of O_3 and NOx in plant-soil-atmosphere interfaces. The methods included whole-canopy measurements, shoot-scale chamber measurements, needle sampling and laboratory analyses, utilizing both continuous observations and experimental setups.

In the studied low- NO_x environment, the shoot-level NO_x fluxes were too small to be monitored accurately in field conditions with an automated dynamic chamber. In addition to interference, the signal to noise ratio was low, and a significant proportion of the observed fluxes were to/from chamber walls. No clear NO_x fluxes from Scots pine foliage were detected, and there was no effect of nitrogen fertilization on the observed fluxes. It seems unlikely that a fertilization treatment could cause significant NO_x emission from boreal pine forests. The fluxes reported in our earlier studies included compounds other than NO_x.

Shoot terpene emissions and needle wax extracts were both dominated by monoterpenes. There was variation in the terpene spectra of both emissions and wax extracts. The proportion of sesquiterpenes was higher in the epicuticular waxes than emissions, and the observed sesquiterpene compounds were for the most part different in the emissions and wax extracts. The role of direct transport through the cuticle from sites of terpene synthesis may be more important than has been assumed.

Keywords: NO_x flux, dynamic chamber, chamber blank, nitrate fertilization, terpene, epicuticular wax

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The beginning of my thesis project may have been slightly uncontroversial. My supervisor-to be contacted me with an offer of a PhD position, something I thought was a possibility that was unrevokably past. She told me about the topic, and I had to protest: I knew nothing about it. Her reply was undeniable: “No-one does. That’s why this is called top-notch science.” Ten years later, I feel I still know very little about the topic, but quite a bit about what I don’t know about it. I have been told that is called expertise. I know that is too strong a word for my academic years, but maybe I now have an idea what it’s about.

First I want to thank my supervisors and all the members of the guidance group. Professor Jaana Bäck dedicated to this thesis much of her precious and scarce time, and never seemed in a hurry even when the opposite was evident. She has been a true rock to lean on and quite probably the best boss I have ever had. Maarit Raivonen has been the patient, understanding and encouraging main supervisor of this thesis. During our regular meetings her comments and ideas on the work and life in general were valuable, sincere and often fun. Nuria Altimir did not let physical kilometers, sometimes thousands of them, stop her from guiding me through the parts that required her expertise. Timo Vesala helped me see the beauty of physics, chemistry and biology coming together in all things alive (or dead); he is probably to blame for my (latest) career turn into teaching physics. Pasi Kolari taught me very nearly everything I know about dynamic shoot cuvettes and coding, and without Petri Keronen I would have been terminally lost in the fine technical detail of the magnificent piece of science that is SMEAR II. Juho Aalto, Anni Vanhatalo and Hermanni Aaltonen have never been too busy to answer my questions, ponder my problems or show how something works.

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I owe my curiosity towards all things breathing (or not) to my parents Eila and Erkki and their patience with chaotic bedrooms, overdue library books and earthworms as pets. Thank you Jussi, for not only sticking by my side for over two decades, but for respecting my decision to start this project and giving your unwavering support. And finally, a special thank you hug is in order to my bright, fun and wonderful children Maija & Oskari, who have played soccer in the Hyytiälä mud, hiked Siikaneva in a thunderstorm and been amazingly understanding through the whole process. Finally, the day has come to see the completion of the Iisakinkirkko (Saint Isaac's Cathedral, built for 40 years) that is my thesis.

LIST OF ORIGINAL ARTICLES

The thesis is based on the following articles, which are referred to in the text by their Roman numerals. The articles are reprinted with the kind permission of the publishers.

I Raivonen M., Joensuu J., Keronen P., Altimir N., Kolari, P. (2014). Assessment of field monitoring of plant fluxes of oxidized nitrogen with two types of detectors. Boreal Environment Research 19, suppl. B: 20-34.
www.borenv.net

II Joensuu J., Raivonen M., Kieloaho A.-J., Altimir N., Kolari P., Sarjala T., Bäck. J. (2015). Does nitrate fertilization induce NO_x emission from Scots pine (P. sylvestris) shoots? Plant and Soil 388: 283-295.
https://doi.org/10.1007/s11104-014-2328-x

III Joensuu J., Altimir N., Hakola H., Rostás M., Raivonen M., Vestenius M., Riederer M., Bäck J. (2016). Role of needle surface waxes in dynamic exchange of mono- and sesquiterpenes. Atmospheric Chemistry and Physics 16: 7813–7823.
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Author´s contribution:
Johanna Joensuu is responsible for the summary part of this thesis. She is the main author of articles II and III and second author of article I. In study I, she participated in planning and carrying out the experiments, performed the calculations and data handling and participated in writing the article. In study II, she planned, prepared and carried out the fertilization experiments, analyzed and interpreted the data and wrote the article with the help of co-authors. In study III, the doctoral candidate planned, prepared and carried out the BVOC experiments (apart from some laboratory analyses), analyzed and interpreted the data and wrote the article with the help of co-authors. The ideas and setups for the work presented in these articles are the result of teamwork by the respective authors.

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ABBREVIATIONS

BVOC	Biogenic volatile organic compounds
HNO_3	Nitric acid
HONO	Nitrous acid
$HOONO_2$	Peroxynitric acid
NMHC	Non-methane hydrocarbons
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
$\cdot NO_3$	Nitrate radical
N_2O_5	Dinitrogen pentoxide
NO_x	Nitrogen oxides (NO + NO_2)
NO_y	Reactive nitrogen species, including NO_x and their oxidation products
O	Atomic oxygen
O_3	Ozone
$\cdot OH$	Hydroxyl radical
PAN	Peroxyacetyl nitrate
PAR	Photosynthetically active radiation
$RONO_2$	Alkyl nitrates
$ROONO_2$	Peroxyalkyl nitrates
SO_2	Sulfur dioxide
SO_2^{4-}	Sulfate
UVA	Type A ultraviolet radiation, wavelength 315-400 nm
UVB	Type B ultraviolet radiation, wavelength 280-315 nm

INTRODUCTION

Like animals, plants depend on the atmosphere for their survival. At the same time, they actively shape and change the environment they live in. Plants absorb, transmit and release water, oxygen and carbon in both simple and complex forms, varying in amount and reactivity. In addition to their metabolic activity, plants provide a variety of surfaces for adsorption, absorption, desorption and various reactions of chemical compounds either produced by the plant or transported from elsewhere. The vast variety and interplay of these interactions poses a formidable challenge to research on processes, mechanisms and interactions of plants and their surroundings. This challenge brings together physics, chemistry and the biological sciences and is further complicated by the fact that the environment of the plant is itself, for a large part, alive. Any changes in the inorganic environment change the balance of this complex system, and research into details of these changes helps us understand how the system's different parts and the system as a whole will react to changes like the climate change or anthropogenic nitrogen load.

A noteworthy part of this puzzle, ozone (O_3) and nitrogen oxides (NO_x, here: nitric oxide NO and nitrogen dioxide NO_2) are reactive trace gases; they are present in the troposphere in the range of parts per billion (ppb). Despite the small concentrations, because of their reactivity O_3 and NO_x are key elements in atmospheric chemistry, for example in reactions of the OH radical, as discussed below. Some of their reactions, especially in the free atmosphere, have been relatively well known for years, but especially their various roles in both normal and pathological plant physiology and at the plant-atmosphere boundary are a topic of constant discovery (Seinfeld and Pandis 1998; Fowler et al. 2009; Ganzeveld et al. 2015).

The reactivity of both O_3 and NO_x applies not only to atmospheric reactions but also to the interactions of these gases with any matter, living or dead. Thus, both O_3 and NO_x can be harmful to all living organisms, with detrimental effects on both human health and plant productivity (WHO 2006; Felzer et al. 2007; Kampa and Castanas 2008). They are pollutant gases, with natural sources accounting for only a small portion of the concentrations found in urban atmospheres (Table 1, Lelieveld and Dentener 2000). In addition, tropospheric O_3 is a greenhouse gas, with direct effects on the climate change. Their key role in atmospheric chemistry combined with their effects on plant and animal health make O_3 and NO_x a matter of relevance in many fields of research and decision-making (e.g. IPCS 2017).

All forms of nitrogen deposition on soils and plants contribute to eutrophication, an increase in the nitrogen content of ecosystems. This can have positive effects on growth but also leads to changes in species composition, algal blooms and O_2 deficiency in some aquatic ecosystems (Sponseller et al. 2016). In addition to the atmospheric effects, NO_x thus have another way of influencing climate change: through their effects on plant growth and therefore the carbon cycle (Magnani et al. 2007; Gruber and Galloway 2008). HNO_3 deposition is also acidic. The tightened regulation of acid rain precursor emissions (NO_x and SO_2) has decreased their atmospheric conditions in Europe and North America, but despite downward trends in NO_3^- and SO_2^{4-} deposition, the pH of rainwater has increased (Burns et al. 2016).

Table 1. Global O_3 precursor emissions 1993 (Lelieveld and Dentener 2000). (O_3 = ozone, NO_x = nitgogen oxides, CO = carbon monoxide, NMHC = non-methane hydrocarbons)

		NO_x TgN/yr	**CO TgC/yr**	**NMHC Tg/yr**
Natural	Lightning	5		
	Vegetation and Soils	3	115	403
	Fire	0.8	46	4
	Stratospheric injection	0.6		
	Total	8	161	407
Anthropogenic	Agricultural soils	2.2		
	Energy use	26.2	195	95
	Industrial processes	1.5	15	56
	Biomass burning (incl. fires)	6.4	214	39
	Total	36.3	424	190
Total		44.3	585	597

Needle or leaf surfaces are the first point of contact between the atmosphere and a plant. Boreal forests are the world’s largest biome, covering some 15 million km^2. Despite being often located in areas of low atmospheric concentrations of both O_3 and NO_x, these forests represent a significant portion of the surface area available for atmosphere-biosphere interactions. Even minor changes in these interactions can therefore have significant implications.

O_3 and NO_x in the troposphere

O_3 and NO_x enter the troposphere in various ways. O_3 is introduced into the troposphere mostly through photochemical reactions (Table 1, Figure 1), and the tropospheric O_3 concentrations are strongly affected by the emissions of the precursors in these reactions, including NO_x but also carbon monoxide (CO) and non-methane hydrocarbons (NMHC) (Lelieveld and Dentener 2000; Table 1). These emissions, in turn, are heavily influenced by human activities (Table 1). There is also a contribution from the stratosphere (some 10 %), where O_3 concentration is higher than in the troposphere (Lelieveld and Dentener 2000; Collins et al. 2000).

The main natural inputs of NO_x into the atmosphere are lightning strikes and soils (Lelieveld and Dentener 2000; Table 1). In soils, NO is either produced or consumed in various processes, for the most part involving nitrification/denitrification and resulting in net emission of NO from the soil (Fowler et al. 2009). Increased substrate availability through nitrogen fertilization can increase emission (Fowler et al. 2009; Kesik et al. 2006). There is also a small input from the stratosphere. Anthropogenic sources include biomass burning and fuel combustion (Lelieveld and Dentener 2000; Table 1); total anthropogenic emissions are roughly fourfold compared with natural emissions. NO_x enters the atmosphere mostly as NO, but it oxidizes into NO_2 so easily that in the normal troposphere, NO_2 is more abundant than NO.

Because the atmospheric O_3-NO_x chemistry is dependent on radiation and also anthropogenic emissions, O_3 and NO_x concentrations show a clear annual and diurnal pattern. In clean-air boreal areas, such as the site of this study, O_3 concentration is usually highest in the spring and early summer, with a daily maximum in the early afternoon (Rummukainen et al. 1996). NO_x concentrations are highest in the wintertime, when emissions from heating and traffic are highest.

The atmospheric ozone concentration at the Earth's surface has more than doubled in Europe since late 19th century (1 to 5 ppb per decade since the 1970s) (IPCC 2014). In the recent decades, the emissions of precursor gases, most notably NO_x, has leveled off or decreased in Europe and North America, but in Asia the trend is still upwards (IPCC 2014). This is reflected in regional and local O_3 concentrations. Typical daytime concentrations in Southern Finland range from 30 to 50 ppb in the summer and 20 to 30 ppb in the winter for O_3 (Rannik et al. 2012). Ambient NO_x concentrations are generally around 1 ppb (Kulmala et al. 2000).

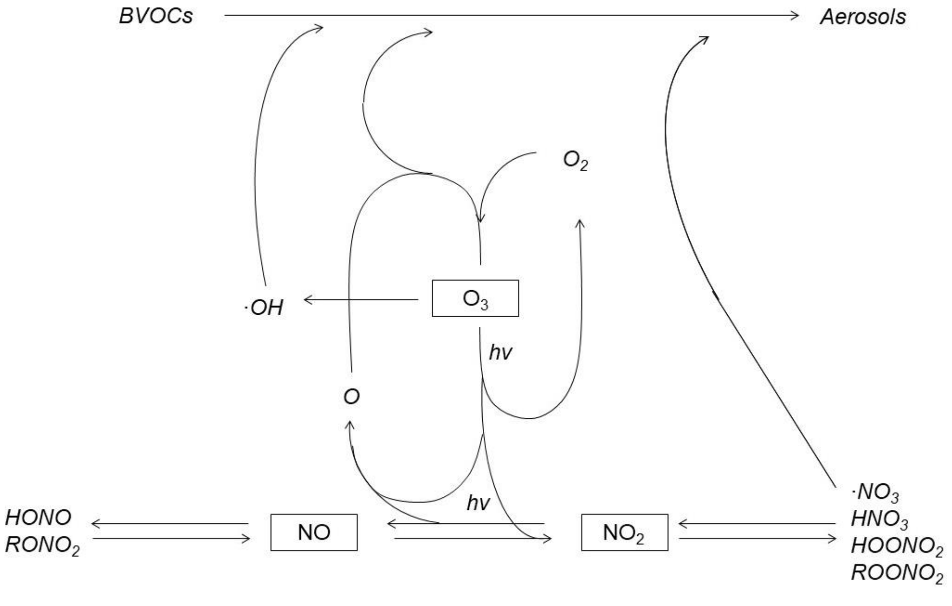

Figure 1. O_3-NO_x-reactions in the troposphere. (BVOCs = biogenic volatile organic compounds, O_3 = ozone, O = atomic oxygen, NO_x = nitrogen oxides, NO = nitrogen monoxide, NO_2 = nitrogen dioxide, hv = photon (light), ·OH = hydroxyl radical, HONO = nitrous acid, $RONO_2$ = alkyl nitrates, $·NO_3$ = nitrate radical, HNO_3 = nitric acid, $HOONO_2$ = peroxynitric acid, $ROONO_2$ = peroxyalkyl nitrates)

In the atmosphere, O_3 and NO_x create a chemical “triangle” of interacting reactions (Figure 1). O_3 oxidizes NO into NO_2, which in the presence of UV radiation photolyzes into NO and an oxygen radical that creates a new molecule of O_3 when it reacts with oxygen (O_2). O_3 is a greenhouse gas but also a precursor of the ·OH radical, the major atmospheric oxidant which governs the lifetime of many gases in the atmosphere, including methane, a more powerful greenhouse gas (Finlayson-Pitts and Pitts 1997; Monks et al. 2009). NO_x affect the concentrations and reactions of O_3 in the atmosphere, as well as those of the ·OH radical. In addition, O_3 and NO_x affect the formation of secondary biogenic aerosols that have a cooling effect (Kurpius and Goldstein 2003; Bonn and Moortgat 2003; Kulmala et al. 2004; Tunved et al. 2006).

In addition to the abovementioned chemistry, O_3 and NO_x are involved in a multitude of possible other reactions. O_3 reacts, for example, with volatile organic compounds (VOCs, hydrocarbons that are volatile at room temperature and normal atmospheric pressure) emitted from both anthropogenic and natural sources (Guenther et al. 1995; Goldstein and Galbally 2007). Biogenic VOCs (BVOCs) are important reaction partners for ·OH (Monks et al. 2009). O_3-BVOC reactions affect aerosol formation (Kurpius and Goldstein 2003; Bonn and Moortgat 2003; Kulmala et al. 2004). In current climate change estimates, processes related to aerosols are still a major source of uncertainty (IPCC 2014). Atmospheric NO_x, on the other hand, gets oxidized further into nitric acid (HNO_3), nitrous acid (HONO), the nitrate radical (·NO_3), dinitrogen pentoxide (N_2O_5) and organic nitrogenous compounds such as PANs (peroxyacyl nitrates) (Figure 1). Together with NO_x this group is often referred to as NO_y. In remote areas, the relative proportion of NO_y species more stable than NO_x, facilitating long-range transport, increases compared to locations near anthropogenic sources (Moxim et al. 1996). Because of the chemistry described above, the concentrations of O_3 and NO_x vary significantly in time and space according to changing conditions and concentrations of the different compounds.

In many of these reactions, the net result depends both on the reactivities and on the relative concentrations of the compounds involved. In rural areas an increase in NO_x typically increases O_3 production, but in urban areas the opposite may happen (Seinfeld and Pandis 1998; Monks 2005). The tropospheric chemistry of O_3 and NO_x has been reviewed in e.g. Finlayson-Pitts and Pitts (1997), Monks (2005) and Monks et al (2009); the chemical properties of major BVOCs are reviewed in Atkinson and Arey (2003).

In addition to the atmospheric reactions discussed above, O_3 and NO_x are removed from the atmosphere through deposition on surfaces. NO_x are removed from the atmosphere mostly as wet or dry deposition of one of their oxidation products, HNO_3, or particulate nitrate (Newland et al. 2017). O_3 deposition on surfaces is governed by both environmental conditions and surface properties (Fowler et al. 2009). In living plants, O_3 and NO_x can also gain access into the plant interior through open stomata. The conditions inside a forest canopy and especially very close to a plant surface can be very different from those in the free atmosphere in terms of wind speed, turbulence, temperature, humidity and concentrations of various compounds. Thus, there is a wide range of reaction sites, types and partners available to O_3 and NO_x molecules in the atmosphere (Figure 2).

O_3 and NO_x at the plant-atmosphere boundary

Both O_3 and NO_x can be harmful to all living organisms, including humans, due to their reactive nature (WHO 2006; Felzer et al. 2007; Kampa and Castanas 2008). It is worth noting that plant-emitted compounds significantly change the composition of the air very close to the plant surface, both on the outside and inside (intercellular air space) (Figure 2). Stomatal deposition is affected by the factors regulating stomatal closure, most importantly phenology, light and humidity (Altimir et al. 2006).

Ozone

The type of damage caused by O_3 depends on both the O_3 concentration and the duration of exposure, but also plant species and the site of O_3-plant tissue contact (Figure 2). Atmospheric ozone is taken up by plants in a non-constant but irreversible manner. The removal rate depends on numerous factors: type of vegetation, phenology, the plant's physiological status, temperature, past and present humidity all play a role in determining how fast ozone is deposited onto and into plants (e.g. Rannik et al. 2012; Ganzeveld et al. 2015). During the active growing period, especially in dry and sunny conditions, O_3 removal is dominated by what is known as stomatal deposition (Altimir et al. 2004, 2006; Clifton et al. 2020 and references therein). O_3 enters the interior of leaves and needles through stomata that are open to allow the gas exchange necessary for plant metabolism (CO_2, H_2O and O_2). There are various possible reaction sites available for O_3 on this route (Figure 2): the O_3 molecule may react in the air space with plant-emitted compounds (such as biogenic volatile organic compounds, BVOCs), with the guard cells of the stoma, with compounds in the liquid apoplast (e.g. ascorbic acid) that covers the internal surfaces of the substomatal cavity or with components of cell walls (Altimir et al. 2008).

The primary mechanisms of ozone damage are related to reaction cascades triggered by O_3 reaching the plant interior and reacting with components of living tissue anywhere it makes contact, first and foremost in the apoplast. These cascades result in production of reactive oxygen species (ROS), with oxidative capacity of their own but also with a role in the internal signaling plants use in their response to e.g. pathogens, leading to premature aging and senescence (for a review, see Ainsworth et al. 2012 and Vainonen and Kangasjärvi 2015). Plants produce antioxidants, reactive components of their own, that scavenge reactive compounds reaching the plant interior, reducing the damage. One of the best-known antioxidants is ascorbic acid that has a demonstrated effect on both O_3 and NO_x (Conklin and Barth 2004; Teklemariam and Sparks 2006).

In addition to stomatal deposition, a varying but non-negligible amount of O_3 is deposited on outer plant surfaces (and any other available surfaces) (Figure 2). The proportion of this non-stomatal deposition can be 50-60% of the total removal (Altimir et al. 2004; Altimir et al. 2006; Clifton et al. 2020 and references therein), but depends on a given surface on environmental factors like temperature (thermal decomposition, Coyle et al. 2009), solar radiation (photolysis, Coyle et al. 2009), BVOCs (Hogg et al. 2007) and surface wetness (Coyle et al. 2009; Altimir et al. 2006). Past humidity is even more important than humidity at the moment (Altimir et al. 2006). It has been suggested that water films, gradually developing on surfaces in high humidity, enhance O_3 deposition and that chemical compounds in or on those water films may change the reaction rate of O_3 with the surface (Burkhardt and Eiden 1994; Neinhuis and Barthlott 1997; Burkhardt and Hunsche 2013). It has been shown that especially as a needle ages, these water films can actually reach through the stomata into the substomatal cavity, effectively creating a continuous path for diffusive transport of water-soluble compounds (Burkhardt et al. 2012). In the synthesis by Clifton et al. (2020), aqueous heterogeneous reactions are deemed the primary mechanism controlling non-stomatal O_3 deposition on leaves.

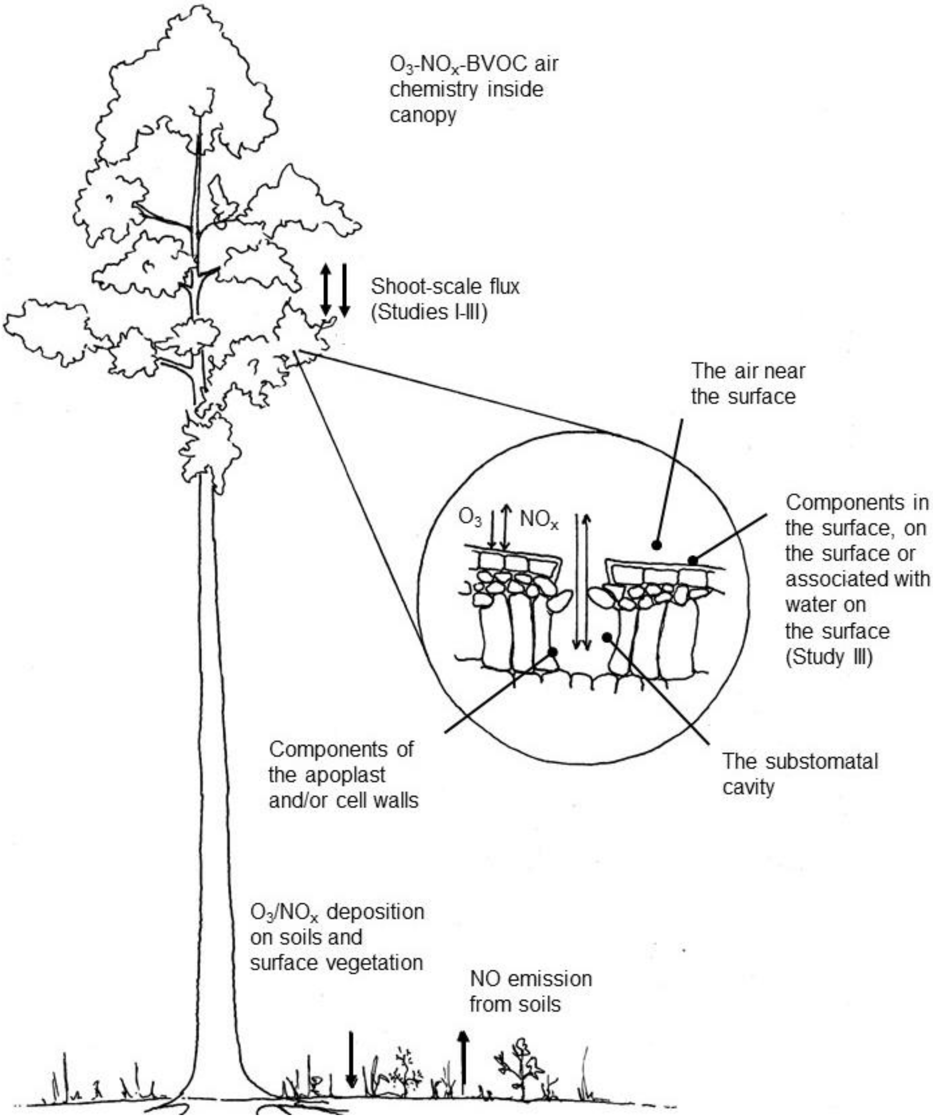

Figure 2. O_3/NO_x interactions inside a forest. This thesis concentrates mostly on the shoot-scale fluxes. The blowup shows possible reaction sites/partners near and at needle surfaces. Study I focused on measuring technology of the total NO_x fluxes. Study II was aimed at capturing possible (stomatal) NO_x emissions from the shoot. Study III explored the needle surface to assess the influence of BVOC compounds bound onto/into the surface on the (nonstomatal) O_3 flux.

On epicuticular surfaces, O_3 damage can impair the protective function of the epicuticulum, leading to increased permeability and wettability (Barnes and Brown 1990). This may have a pronounced role for evergreen plants that do not renew their foliage every year, and the rate of needle surface degeneration has been linked with O_3 pollution (Bytnerowicz and Turunen 1994).

Because of the fast reactions, O_3 is virtually undetectable in the apoplast (Laisk et al. 1989). Separating the total O_3 removal into stomatal and non-stomatal components is not an easy task, because in addition to the challenging measurements, the controlling factors are to a large extent the same or closely linked (Altimir et al. 2004, 2006; Clifton et al. 2020). The measurements of shoot-scale O_3 deposition are thus based on gas exchange measurements close to the shoot. Also transport speed controls O_3 and NO_x chemistry as the reaction rate is in part dependent on the availability of the reaction partners. In the free atmosphere, transport mainly happens as turbulent transport, but very close to a plant's surface transport happens through molecular diffusion.

Biogenic volatile compounds (BVOCs)

A factor influencing both the stomatal and non-stomatal component of O_3 deposition are reactive compounds produced by the plant itself. BVOCs are a group of such compounds, emitted by different plant species in different amounts and proportions (Guenther et al. 2012). Terpenes (monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$)) are a reactive subgroup of BVOCs. Plants emit them constantly, but especially during certain physiological stages such as flowering and senescence. BVOCs are also used to communicate with other plants or in response to both biotic and abiotic stresses like herbivory or heat (Holopainen and Gershenzon 2010; Loreto and Schnitzler 2010; Pichersky and Raduso 2018). The physicochemical properties (e.g. water-solubility, volatility, reactivity) of plant-produced terpenes are highly variable (Atkinson and Arey 2003; Niinemets and Reichstein 2003).

Some of these terpenes react with O_3 in the free atmosphere after they are emitted and produce a significant sink of O_3 (Atkinson and Arey 2003; Wolfe et al. 2011), but reactions are likely to happen also at and near needle surfaces, influencing non-stomatal O_3 deposition (Goldstein et al. 2004; Altimir et al. 2006; Bouvier-Brown et al. 2009) (Figure 2). The possible O_3-terpene reactions very close or even inside a leaf or a needle are very difficult to measure, and little is known on this topic. However, as the concentration of terpenes, emitted through stomata, is highest close to the emission site, it is easy to assume that these reactions must take place at a significant rate, and the terpene emission measured from the plant only represents the fraction that actually reaches the free atmosphere. It has also been suggested that terpenes, produced by the plant or transported from elsewhere, might get bound onto or into the waxy layer covering leaves and needles, providing additional protection against oxidants, pathogens or herbivory (Sabljic et al. 1990; Welke et al. 1998; Widhalm et al. 2015), or affect O_3 deposition by enhancing formation of water films on leaf surfaces (Rudich et al. 2000; Sumner et al. 2004).

The possible reactions of BVOCs in the atmosphere include photolysis, reaction with the hydroxyl radical $\cdot OH$, reaction with O_3 and reaction with the nitrate radical $\cdot NO_3$ (Atkinson and Arey 2003). BVOCs can also be removed through wet or dry deposition onto surfaces. $\cdot OH$ is produced by photolysis of O_3 during the day, but can be produced in O_3-BVOC reactions even at night (Atkinson and Arey 2003). $\cdot NO_3$ is produced in NO_x-O_3 reactions, but because of fast photolysis, its concentration is measurable only at night (Atkinson and Arey 2003). In low-NO_x environments, BVOC oxidation by ozone reduces ozone concentration in the atmosphere (Lerdau and Slobodkin 2002) and the role of OH and NO_3 reactions is more pronounced. The BVOC-OH reactions can lead to formation of secondary organic aerosols (Seinfeld and Pandis 1998). These aerosols have a cooling effect on the climate, which makes BVOCs a key element in climate change (Paasonen et al. 2013).

Nitrogen oxides

Atmospheric NO_y reach plants mostly as HNO_3 or NO_3 deposition, but also as atmospheric NO and NO_2 molecules that come in contact with external or internal plant surfaces in a similar way with O_3 (Figure 2). The direct interactions of NO_x between plants and the atmosphere are still a controversial topic. At high ambient concentrations, NO_x are taken up by plants (e.g. Sparks et al. 2001, Teklemariam and Sparks 2006), but it is less clear what happens at low ambient conditions (~1 ppb) typical of remote areas, common in the boreal region (Kulmala et al. 2000). Sometimes emission has been observed (e.g. Thoene et al. 1996; Sparks et al. 2001; Hereid and Monson 2001; Teklemariam and Sparks 2006), other times not (e.g. Johansson 1987; Rondón and Granat 1994; Breuninger et al. 2013). There are results suggesting that plants emit NO_x at low ambient conditions with a threshold value, a compensation point, depending on species and conditions (e.g. Thoene et al. 1996; Gessler et al. 2000; Sparks et al. 2001; Teklemariam and Sparks 2006; Raivonen et al. 2009) (Table 2). However, some studies report NO_x deposition even at very low ambient concentrations (Chaparro-Suarez et al. 2011; Delaria et al. 2020). Because of varying measurement techniques these results are not always directly comparable. In addition, the separation of stomatal and non-stomatal fluxes is extremely challenging due to measurement uncertainty (Ganzeveld et al. 2015) and, in low-NO_x environments, often low signal to noise ratio (Raivonen et al. 2003). In addition to the physiological processes discussed earlier, suggested mechanisms for NO_x emission include photochemical surface reactions (Raivonen et al. 2006). Most of the NO_x uptake apparently happens through stomata (e.g. Thoene et al. 1991; Gessler et al. 2000), but in a similar way to O_3, deposition may be enhanced by water films on plant surfaces (e.g. Burkhard and Eiden 1994). NO fluxes between plants and the atmosphere are small compared to NO_2 (Rondón et al. 1993; Hereid and Monson 2001).

Although NO_x can be toxic to plants, nitrogen in itself is the most important plant nutrient. Plants need nitrogen in all protein synthesis, and the scarcity often limits growth (Reich et al. 2006; Lebauer and Treseder 2008). Plants take up easily available inorganic nitrogen, ammonium (NH_4^+) or nitrate (NO_3^-), but also amino acids from soils (e.g. Kielland et al. 2007). In boreal forests plants usually take up efficiently the small amounts of available inorganic nitrogen (Korhonen et al. 2013). Also atmospheric nitrogen deposited onto plant leaves is taken up and used in protein synthesis. Plants are known to uptake inorganic nitrogen in several forms, including NH_4^+, NO_3^- and HONO, but also organic nitrates and peroxyacetyl nitrate (e.g. Gessler et al. 2002; Teklemariam and Sparks 2004; Schimang et al. 2006; Lockwood et al. 2008; Wuyts et al. 2015). The canopy uptake can constitute a significant proportion of the total N uptake of a forest; estimates vary from 0 to 50 % of N demand (Harrison et al. 2000).

Table 2. Studies of shoot-scale NOx fluxes on conifers. DC = Dynamic chamber, PLC = Photolytic conversion, FeSo = Ferrous Sulphate conversion, Mo = Molybdenum conversion, CLD = Chemiluminescence detection, LIF = Laser-induced fluorescence.

Authors	**Year**	**Species**	**Methods**	**Lab/field**	**NOx compensation point**
Johansson	1983	*P. sylvestris*	DC, FeSo + CLD	Field	1–2 ppb (NO_2)
Thoene et al.	1991	*P. abies*	DC, Mo + CLD	Lab	possible (NO_2)
Rondón & Granat	1994	*P. Sylvestris*, *P. abies*	DC, FeSo + CLD	Lab/field	<0.1–0.3 ppb (NO_2)
Thoene et al.	1996	*P. abies*	DC, Mo + CLD	Lab	1.6 ppb (NO_2)
Raivonen et al.	2001	*P. sylvestris*	DC, Mo + CLD	Field	1–3 ppb (NOy)
Geßler et al.	2002	*P. abies*	DC	Field	1.7 ppb (NO_2)
Raivonen et al.	2009	*P. sylvestris*	DC, Mo + CLD	Field	2–3 ppb (NOy)
Chaparro-Suarez et al.	2011	*P. sylvestris*	DC, PLC + CLD	Lab	– (NO_2)
Delaria et al.	2020	*P. sabiniana*, *P. ponderosa*, *P. contorta*, *P. menziesii*, *C. decurrens*, *S. sempervirens*	LIF	Lab	– (NO_2)
Breuninger et al.	2012	*P. abies*	DC, PLC + CLD	Lab/field	–

Before utilization, nitrate needs to be reduced to ammonium in a reaction catalyzed by the enzyme nitrate reductase either in the roots or in the leaves (Andrews 1986, Lambers et al. 2008). In Scots pine this reduction mostly happens in the roots (Pietiläinen and Lähdesmäki 1988), but when the soil temperature is low or if there is abundant nitrate fertilization, the enzyme activity in the needles increases (Pietiläinen and Lähdesmäki 1988; Sarjala 1991). It has been suggested that nitrite accumulation in the needles could lead to NO production and even emission. There are also results from laboratory conditions supporting this hypothesis (Wildt et al. 1997; Rockel et al. 2002; Chen et al. 2012). NO is also produced in many key plant processes related to, among other things, germination, root development, stomatal closure and internal signaling via the ROS cascades mentioned above (Besson-Bard et al. 2008; Kulik et al. 2015). Production of NO from nitrite (NO_2^-) is catalyzed by a nitrate reductase enzyme (NR) and possibly in another pathway by an enzyme analogous to nitric oxide synthase (NOS) in animals (Kulik et al. 2015). Any excess created in these processes could, in principle, result in NO emission. Such emission has indeed been observed from plants lacking the nitrate reductase enzyme (Morot-Gaudry-Talarmain et al. 2002).

OBJECTIVES OF THE STUDY

Despite recent advances in forest-atmosphere interaction science, there are still unknown processes influencing the fluxes and reactions of reactive gases like O_3, NO_x and BVOCs (e.g. Rinne et al. 2009; Rohrer et al. 2014). Because of their significance in atmospheric reactions in both rural and urban areas and role in plant internal signaling, it is necessary to elucidate their exchange between atmosphere and ecosystems both to accurately model the atmosphere and atmospheric changes and to estimate and predict the potentially detrimental effect of O_3 and NO_x on plants and animals (Rohrer et al. 2014; Ganzeveld et al. 2015; Clifton et al. 2020). Therefore, this study focused on developing methods for observing the exchange of NOx in field conditions and on experimenting where and how molecules of NO_x and O_3 are processed in the plant-soil-atmosphere interfaces (Figure 2).

The specific aims were

- to evaluate the performance of two different NO_y/NO_x measurement systems to detail the changes in accuracy and behavior of the system, in order to estimate if the more recent NO_x measurement system could yield more detailed information on the NO_y emissions observed in previous studies and to correctly compare new results with the older ones
- to probe the role of anthropogenic nitrogen load (as wet or dry N deposition) on atmospheric NO_x-O_3-BVOC chemistry in boreal regions by testing whether nitrate fertilization of Scots pine (*Pinus sylvestris* L.) plants leads to accumulation of NO_3^- or NO_2^- in the needles and subsequent NO_x emission from the shoot
- to explore the role of BVOCs produced by the plant in heterogeneous O_3-BVOC surface reactions on needle surfaces by determining whether terpenes can be found on the epicuticles of Scots pine and, if so, to compare the spectra of the terpenes with those found in shoot emissions and estimate their possible role in O_3 deposition.

MATERIALS AND METHODS

The methods used in the studies included in this thesis span across several spatial scales from individual needles (III) to a whole canopy (I), but they all addressed the interactions of Scots pine shoots with the atmosphere, measured in field conditions (Table 4). Some of the data used was from the continuous observations at the SMEAR II station, some was experimental. This approach permitted selecting a suitable setup for each study question and flexible use of existing technology and measurements where possible. Furthermore, I could access and join in the expertise and cooperation of researchers in different aspects of the field within or close to the research group.

Study site and experimental setup

Studies I-III were all carried out at the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, Southern Finland (61°N, 24°E, 180 m asl). The annual mean temperature is 3.5 °C and precipitation 711 mm (Pirinen et al. 2012). The station is located in a managed stand of mostly Scots pine (*Pinus sylvestris* L.), sown in 1962, with some Silver and Downy birch (*Betula pendula* Roth and *Betula pubescens* Ehrh.) and

Common aspen (*Populus tremula* L.). The soil is mostly haplic podzol, and the understorey consists mostly of woody shrubs. A scaffolding tower provides access to the canopy of a few trees. The location is rural, with summertime ambient O_3 concentrations generally in the range 25-40 ppb and NO_x concentrations around 1 ppb (Table 3; Kulmala et al. 2000; Raivonen et al. 2014). The station is described in more detail in Hari and Kulmala (2005).

The range of continuous measurements and experiments conducted at the station over the past decades created an exceptional framework for such a varied set of studies. For study I, I utilized results from the automated continuous measurement cycle for shoot NO_x/NO_y fluxes, set up in the scaffolding tower, together with corresponding measurements from a 73 m mast, to evaluate the performance of the automated measurement system. In study II I connected my own experiment setup into the automated measurement cycle, which ensured a reliable method of measuring the NO_x fluxes of pine seedlings with varying nitrogen treatment. To facilitate this, the experiment was set up in the measurement tower. For study III, to explore the role of BVOCs in O_3 deposition, a chamber setup created for earlier BVOC experiments was used. The BVOC flux measurements were then done separately from the automated system and with a different type of chamber. For easy access and handling (for example darkening), the experiment was done in an open area near the station.

Table 3. Hourly ozone and NO_x concentrations at the study site during Studies I-III (SMEARII mast, height 16.8 m).

		O_3 **Mean**	 **Max**	**NO_x** **Mean**	 **Max**
2005	May	39.6	59.2	1.2	4.1
	June	32.8	46.7	1.4	6.4
	July	31.3	53.3	1.3	3.9
	August	25.7	57.5	1.4	7.5
2006	May	44.2	73.2	1.6	5.9
	June	38.2	79.1	1.2	5.2
	July	35.1	76.3	1.1	3.2
	August	33.9	51.5	1.2	3.3
2007	May	35.7	56.6	0.6	5.1
	June	34.0	59.7	0.4	6.4
	July	27.7	45.4	0.4	2.0
	August	31.1	55.3	0.5	4.5
2008	May	44.4	63.3	0.4	2.0
	June	36.6	67.4	0.5	4.0
	July	31.3	47.2	0.4	2.0
	August	24.5	46.2	0.6	5.2
2012	May	39.2	55.9	0.4	4.7
	June	31.8	52.6	0.4	2.3
	July	31.3	49.5	0.3	1.5
	August	32.1	50.8	0.4	3.9
2013	May	37.9	56.4	0.3	3.9
	June	33.6	55.6	0.3	3.7
	July	28.1	53.0	0.2	2.6
	August	29.4	49.5	0.3	2.7

For studies II and III, an experimental setup with grafted Scots pine seedlings was created. Grafted seedlings, genetically identical from stump level up, were chosen to reduce variation in the results (Bäck et al. 2012). To create variable conditions in terms of available nitrogen (in amount and form), in study II the seedlings were fertilized with either ammonium sulphate $(NH_4)_2SO_4$ or potassium nitrate KNO_3 or left without nitrogen fertilization. Soil application (rather than aerial) was used to separate the effects of foliar and root uptake, but also for technical simplicity, since a fumigation system was not readily available. To compensate for the fertilizing effect of potassium in the nitrate fertilizer, the ammonium and control treatments received the same amount of potassium as potassium sulphate K_2SO_4.

Chamber measurements

NO_x flux measurements with dynamic shoot chambers (studies I and II)

Dynamic chambers are an often-used method to measure gas fluxes between vegetation and the atmosphere. Different types of chambers have been developed for different research needs, and each chamber setup has its advantages and disadvantages. In the studies included in this thesis, NO_x fluxes were measured at the shoot level with a highly automated setup that is an integral part of the SMEAR II system. The setup is optimized for long-term measurements aiming at detecting patterns or responses in time, rather than space; only a few shoots are measured simultaneously at any given time, but each shoot is followed for a long period (two to three years for pine, one summer for aspen). This necessitates debudding the shoot each year to prevent growth. The setup for study II differed from the usual in that several seedlings were measured for a short period (without debudding), but the study still utilized the automated gas flux measurement system.

The shoot selected for measurement was fitted with a UV-transparent 1 L chamber (40mm x 125 mm 200 mm) made of methacrylate plastic, with a roof made of quartz glass and an inner coating of fluorinated ethylene propylene (FEP) film (Figure 4). When not in measurement, the chamber was open to the surrounding atmosphere via ventilation holes in the bottom. At the start of a measurement, the chamber closed by closing of the ventilation holes. During the one-minute closure sample air was pulled from the chamber to the analyzers, located in a building near the measurement tower, at a rate of 4 $dm^3 min^{-1}$. The 70 m long sample tubing was made of PTFE, darkened to prevent light reactions and heated to minimize condensation. Residence time in the tubing was approximately 37 seconds. The sample flow was replaced with ambient air flowing into the chamber, not so airtight as to prevent the flow. The chamber setup is described in more detail in Altimir et al. (2002) and Raivonen et al. (2003).

Table 4. Scales and measurements used in the separate papers of this study.

Scale of measurement		**I**	**II**	**III**
Stand		x		
Shoot		x	x	x
Needle			x	x
Measurement	**Instrument/method**			
Shoot scale NO_x flux	Chamber, chemiluminescence analyzer (TEI 42CTL, Thermo Environmental Instruments, USA)	x	x	
Shoot scale NO_y flux	Chamber, chemiluminescence analyzer (TEI 42S, Thermo Environmental Instruments, USA) with Molybdenum converter	x		
Shoot scale NO flux	Chamber, chemiluminescence analyzer (TEI 42CTL, Thermo Environmental Instruments, USA)	x	x	
Shoot scale BVOC flux	Chamber, adsorbent tubes (Tenax-TA and Carbopack-B), thermal desorber (Perkin-Elmer TurboMatrix 650 ATD, PerkinElmer, USA), gas chromatograph-mass spectrometer (Perkin-Elmer Clarus 600, PerkinElmer, USA)			x
Shoot scale CO_2 and H_2O fluxes	Chamber, infrared gas analyzer (URAS 4, Hartmann and Braun, Germany)	x	x	
Canopy NOx flux	Chemiluminescence analyzer (TEI 42CTL, Thermo Environmental Instruments, USA)	x		
Canopy NO flux	Chemiluminescence analyzer (TEI 42CTL, Thermo Environmental Instruments, USA)	x		
Soil and needle inorganic nitrogen, nitrate, nitrite and ammonium	Colorimetric microplate assay (Hood-Nowotny et al. 2008)		x	
Total dissolved nitrogen	Total organic carbon analyzer (TOC-V cph/cpn TNM-1, Shimadzu Corporation, Japan)		x	
Epicuticular terpenoids	Dichloromethane solvent, gas chromatograph (Agilent 6890N, Agilent, USA) with a mass spectrometric detector (Agilent 5973, Agilent, USA)			x
chamber temperature	Thermistor (Philips KTY 80/110)		x	x

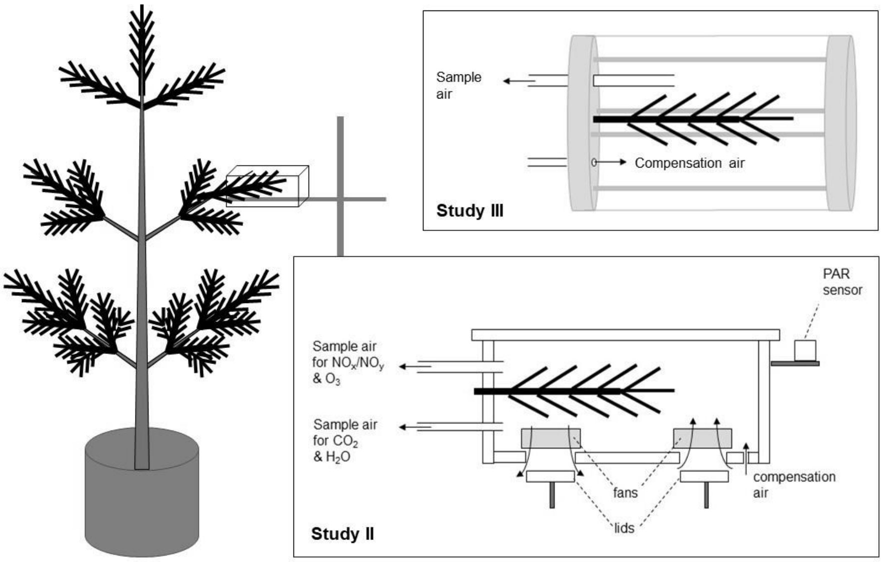

Figure 4. Measurement setup for Studies II and III.

Gas concentrations in the sample air were measured every 5 seconds. Until July 2006, the system measured NO_y/NO_x with a chemiluminescence analyzer (TEI 42S, Thermo Environmental Instruments, USA) equipped with heated molybdenum conversion for NO_2. In July 2007, this was replaced with another model (TEI 42CTL) from the same company with more accurate blue light photolytic NO_2 conversion (Droplet Measurement Technologies, USA). The purpose of the NO_2 conversion is to turn all NO_2 molecules into NO for total NO_x measurement. The molybdenum converter is known to be rather unspecific: it converts other nitrogenous species, such as HONO, organic nitrates and nitrites alongside with NO_2. Thus, prior to the analyzer replacement the measured quantity was NO_y flux, after that NO_x flux. Study I was aimed at evaluating the performance of the new chamber setup compared with the old one.

From the development of the concentration of each gas during a single measurement (Figure 5), the flux was calculated using a mass balance differential equation that takes into account all processes that change the concentration inside the chamber: the sample flow q_s ($m^3\ s^{-1}$), inflow of ambient air q_c ($m^3\ s^{-1}$) and the flux J created by sinks and/or sources inside the chamber (mol s^{-1}):

$$\frac{VdC(t)}{dt} = q_c C_a - q_s C(t) + J \qquad (1)$$

Where V is the volume of the chamber (m^3), C(t) is the measured concentration at moment t (mol m^{-3}) and C_a is the concentration in ambient (inflowing) air (mol m^{-3}). The possible sinks and sources creating the flux J include the shoot and the measurement chamber. Since

q_c and q_s are equal, Equation 1 can be solved for C(t), the measured quantity. The flux J can then be found by fitting the solved equation to the measured concentrations. The equation is described in more detail in Raivonen et al (2003) for NO_x. The data processing and quality were also discussed in Study I.

It is well-known that in shoot chamber gas exchange field measurements of reactive gases, some of the flux is created by the chamber walls, not the shoot itself (Thoene et al. 1996; Altimir et al. 2002; Raivonen et al. 2003). Additionally, the flux to/from the chamber walls depends on environmental conditions, especially humidity (Thoene et al. 1996; Altimir et al. 2006) and, in the case of NO_y, UV radiation and age of the chamber lining (e.g. Raivonen et al. 2003). Ideally, this additional flux should be taken into account in the data analysis. Typically this is done by measuring a separate empty chamber alongside the shoot chambers (Thoene et al. 1991; Geßler et al. 2002; Chaparro-Suarez et al. 2011) or measuring the shoot chamber empty before or after the experiment (Rondón and Granat 1994; Teklemariam and Sparks 2006). The first mentioned protocol was followed in Study I (Figure 5), using one chamber with a shoot and an identical empty chamber for reference. This approach solves the problem only partially, because Raivonen et al. (2003) observed considerable differences in the NO_y fluxes between empty chambers. Variable fluxes to/from empty chambers are also reported by Rondón and Granat (1994). In a laboratory study with controlled conditions, Chaparro-Suarez et al. (2011) measured negligible chamber wall effects for both a reference chamber and a shoot chamber measured empty. Similarly, Breuninger et al. (2012) observed no emission from an empty chamber in a laboratory setup. Most studies, however, do not report the behavior of the empty chambers. In Study II, an empty chamber was measured alongside the chambers with a shoot, and an additional measurement of empty chambers was done after the main experiment.

In flux measurements the main interest is usually in concentration changes, not absolute concentrations of the target gases. Therefore, a systematic error in all concentration readings is not necessarily a fatal issue. In some uses however, like when trying to pinpoint a deposition/emission threshold concentration for a gas, the absolute concentration is of interest. Accurate concentration measurements are also needed to study the dependency of the observed fluxes on ambient concentrations; at SMEAR II, these measurements are performed separately in a measurement mast. To evaluate the accuracy of our shoot chamber concentration measurements, in study I the NO, NO_x and NO_y concentrations measured in the shoot chambers while they were open (nearly ambient air) were compared with those measured simultaneously at approximately the same level inside the canopy in the SMEAR II measurement mast, some 50 m away, with similar analyzers. The main difference between the concentration measurements was the measurement of background luminescence in the analyzer; in the shoot measurements this was done manually once a week to facilitate fast measurements. The correction was later interpolated for the days between calibration measurements and taken into account in data processing (described in Study I). In the mast measurements, with a longer time between individual measurements, the background correction (zero correction) was made automatically before each measurement.

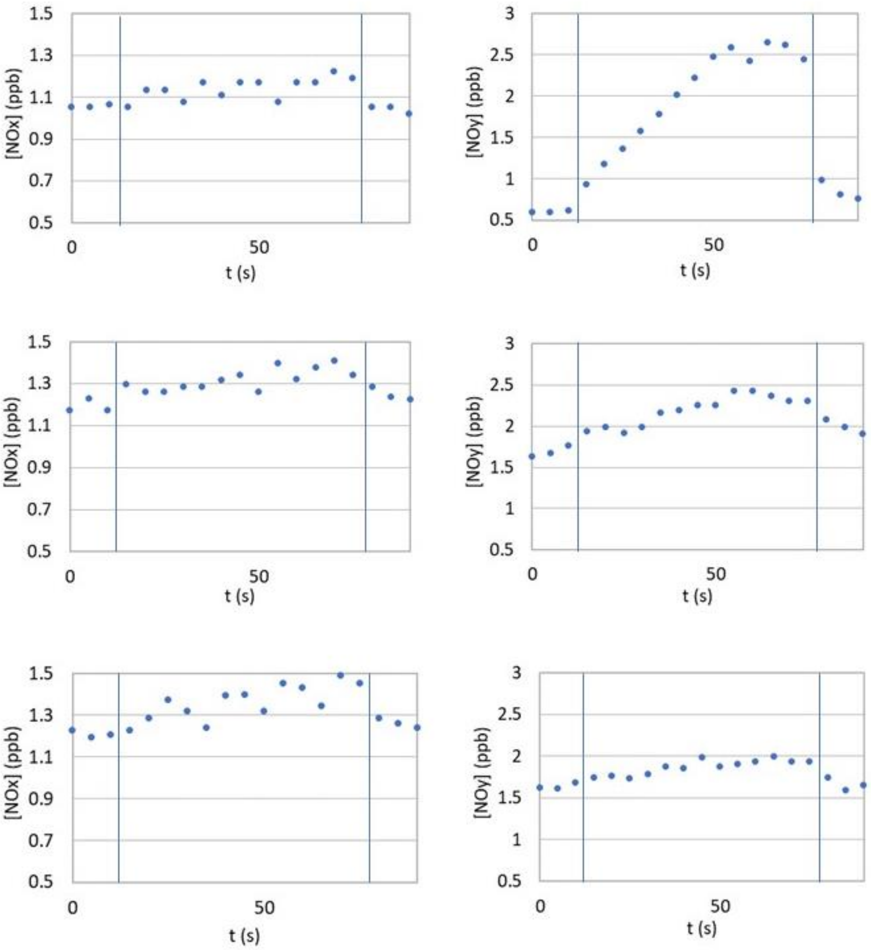

Figure 5. The development of NO_x and NO_y concentration during a measurement close to noon in May 2006 in a chamber with a shoot (top row), the same chamber + shoot two days later, with a new FEP lining (middle) and an empty chamber (with fresh FEP lining) on the latter date (bottom). Chamber closure and opening is marked with vertical bars. Note the different scale for NO_x and NO_y.

BVOC emissions (Study III)

In study III the aim was to estimate the role of plant-produced BVOCs (specifically terpenes) on needle surfaces in O_3 deposition to trees. To compare the compounds found on needle surfaces with those in the more studied shoot emissions, BVOC emissions of four grafted pine seedlings were measured with a dynamic chamber, consisting of a PTFE-coated steel frame and a FEP bag supported by the frame (Figure 3). The diameter of the chamber was 14 cm and length 30 cm, giving a chamber volume of 4600 cm^3 (4.6 l). An external pump, with an active carbon filter and an ozone scrubber, pushed air through the chamber (2.5

l/min). The chamber system is described in more detail in Hakola et al. (2006). A sample flow was directed through adsorbent tubes (Tenax-TA and Carbopack-B) attached to the inlet and outlet tubes. The resin filling of the tube adsorbed BVOCs, which were later desorbed and analyzed at the Finnish Meteorological Institute with a thermal desorber (Perkin-Elmer TurboMatrix 650 ATD) connected to a gas chromatograph – mass spectrometer (Perkin-Elmer Clarus 600). The measured compounds were identified using authentic standards and the NIST library.

The observed emission rate (E, µg m^{-2} h^{-1}) was calculated for each compound as

$$E = \frac{(C_2 - C_1)}{A} F \qquad (2)$$

Where C_2 is the concentration in the outlet air (µg m^{-3}), C_1 is the concentration in the inlet air (µg m^{-3}), F is the flow rate into the enclosure (m^3 h^{-1}) and A is the needle area of the shoot (m^2). From E, I obtained the spectra of emitted compounds (% of total emissions).

After each emission measurement, the chamber was removed from around the shoot. The seedling was transported into a darkened room and left to settle for 30 minutes, after which time stomata were assumed to be closed. Three separate needle samples (20 needle pairs each) were then collected and stored in a liquid nitrogen dry shipper until analysis (two weeks later).

Laboratory analyses

Nitrogen content (Study II)

In order to determine the fertilization effect in Study II, the needles and soil were sampled before the treatments and in the end of the experiment. From soil samples, pH_{H2O} and gravimetric soil water content were determined and the rest of the sample was extracted with 1 M potassium chloride (KCl) for exchangeable inorganic and organic nitrogen. The needle samples were ground at -196 °C and extracted using a modification of the method introduced by Sarjala (1991).

The inorganic nitrogen, nitrate, nitrite and ammonium analysis was performed using colorimetric microplate assay methods introduced by Hood-Nowotny et al. (2008). The colorimetric assay for NH_4^+ was a modified indolphenol method based on the Barthelot reaction (Kandeler and Gerber 1988); a modified acidic Griess reaction was used for NO_2^- and NO_3^-. Absorbance values were measured with a microplate reader (Infinite M200, Tecan Group Ltd., Swizerland, Männedorf). Dissolved organic nitrogen content was calculated by subtracting the sum of inorganic nitrogen species from total dissolved nitrogen. Total dissolved nitrogen was determined by a total organic carbon analyzer equipped with a total nitrogen unit (TOC-Vcph/cpn TNM-1, Shimadzu Corporation, Japan, Kyoto).

Terpenes in epicuticular waxes (Study III)

In study III, I wanted to estimate the possible role of terpenes (a key category of BVOCs produced by trees) stored in or on the epicuticular surfaces in O_3 deposition on needle surfaces. To detect the presence of terpenes associated to the epicuticular surfaces, the waxy material from the needle surfaces was collected for subsequent analysis by dipping the needles in dichloromethane. The obtained extract was evaporated to 1 ml volume with pure nitrogen gas. The reduced extract was then analyzed with a gas chromatograph (Agilent 6890N) with a mass spectrometric detector (Agilent 5973) to identify terpenes. A JandW DB-5MS column (30 m, i.d. 0.25 mm) and a 5 m pre-column (Agilent FS) were used for the chromatography. The analysis method is described in more detail in Vestenius et al. (2011). The measured compounds were identified using authentic standards and the NIST library. The compounds to be identified were not predetermined, and hence calibration standards were not available for all of them. Some of the compounds were therefore identified and quantified only tentatively, using the NIST library and reference from another compound. For quantification reference, a known sesquiterpene with a closely matching mass spectrum was chosen.

RESULTS AND DISCUSSION

The feasibility of monitoring shoot-scale NO_x fluxes in low-NO_x environments (Studies I and II)

Study I was the latest chapter in our strive to evaluate and improve the performance of the measurement system for shoot-scale NO_x/NO_y fluxes at SMEAR II. In terms of absolute NO_x/NO_y concentrations, the NO and NO_2 concentrations from the chamber system were consistently higher than those measured from the mast (assumed to be accurate); the mean difference was 0.2–0.45 ppb. In contrast, the NOy concentrations measured from the chambers were usually lower than from the mast (mean difference 0.2 ppb). Ambient concentrations during the study were 0–3 ppb (NO), 0–13 ppb (NO_2) and 0–18 ppb (NO_y). The accuracy of the NO_x analyzer (with blue light conversion) was slightly lower than the NO_y analyzer (with a heated molybdenum converter). On the other hand, the information gained on shoot-level NO_x fluxes was improved by the higher selectivity for the compounds of interest (NO and NO_x) of the blue-light conversion. It has to be noted, however, that even NO_x measurements are known to be susceptible to interference caused by other nitrogenous compounds (like HONO) or VOCs (Ryerson et al. 2000; Villena et al. 2012). The NO_x measurements in Study I were found to be more sensitive than NO_y to variation in sample air properties, like concentrations of other atmospheric gases like BVOCs. It is therefore not clear that even the NO_x fluxes measured using blue-light conversion consisted purely of NO and NO_2.

Results from running the two analyzers side by side (Study I) confirmed the suspicions that the NO_y fluxes reported in our earlier studies (Hari et al. 2003; Raivonen et al. 2006) often, if not always, included compounds other than NO_x (likely at least HONO and PAN). Those from Study I are the only published results directly comparing shoot-level NO_y and NO_x measurements, but similar results have been reported in other types of studies in rural areas (Steinbacher et al. 2007; Xu e tal. 2013). Zhou et al. (2011) observed HONO production in a forest canopy, correlating with leaf surface nitrate load and nitrate photolysis rate. Nitrate or HNO_3 photolysis was proposed as the source of the observed shoot NO_y emissions also in Raivonen et al. (2006).

Both the NO_y and the NO_x fluxes in the chamber with a shoot showed a diurnal pattern with UV-related emissions, but with lower values for NO_x emissions (-1–2 pmol/s) than NOy emissions (0–18 pmol/s). The emissions were related to the age of the chamber or chamber lining. Replacing an old chamber with a new one (around the same shoot) resulted in a drop in both NO_y and NO_x emissions to levels comparable with an empty chamber (0–2 pmol/s, no significant difference between NO_x and NO_y fluxes), although the drop in NO_y emissions was more dramatic. In contrast, in study II no relation could be found between the measured NO or NO_x fluxes, the CO_2 flux (a measure of plant activity), temperature or UV radiation. At least a partial explanation is that at the start of Study II, all chambers were clean and the FEP coating was new. To rephrase, an empty chamber showed NO_x emissions that were comparable in magnitude to those from a chamber with a shoot.

Study II gave an interesting indication on the origin of the empty chamber fluxes: After the shoots had been removed, the NO/NO_x emissions from the now empty chambers continued (at a rate of -2–4 pmol/s), showing a marked difference to the chamber that had been kept empty for the whole experiment (-2–1 pmol/s). The NO_x emissions assumed a clear diurnal pattern peaking at midday, suggesting photochemical reactions as reported e.g. in Raivonen et al. (2006), while NO emission occurred at high relative humidity. The always empty chamber, measured alongside, showed no emissions. The emissions were then likely to originate from nitrogenous compounds, released by the trees or possibly micro-organisms on the shoot/needle surfaces, that had accumulated on the chamber walls during the experiment. Regardless of the fertilization treatment it seems that the pine shoots emitted one or more compound that accumulated on chamber walls and was/were subsequently released as NO or NO_x (=$NO+NO_2$). Some of these reactions were photochemical by nature, as indicated by their diurnal pattern, but the humidity-related NO emissions had another source or mechanism. The nature and significance of these emissions remains unknown and present an interesting, but potentially extremely challenging, question for future research. A combined laboratory and field experiment, possibly involving an analysis of active compounds and/or micro-organisms on needle surfaces, could yield valuable results.

As a part of study II, I calculated the possible significance of O_3-NO_x-reactions in the tubing of the measurement system, but found it to be negligible. Breuninger et al. (2012) reached a similar conclusion for a very similar setup. In addition, they propose a tool for estimating the role of photochemical reactions happening in the chamber during the measurement. An early attempt at modeling the atmospheric NOx-O_3-BVOC chemistry during a cuvette measurement was made by Kulmala et al. (1999). To some extent, this has been taken into account by using an empty reference chamber, but since – as the results show – the chambers are not identical, also the photochemistry might differ, as suggested also by Breuninger et al. (2012).

Effect of nitrate fertilization on NO_x fluxes (Study II)

Nitrates (NO_3^-) are not themselves active parties in atmospheric photochemistry but rather end products that are deposited on plants, soils and other surfaces. In theory they could re-enter the atmosphere if after uptake and metabolism plants released them in a reactive form, like NO_x or NO (Wildt et al. 1997; Chen et al. 2012). Nitrogen deposited on plants and soils is effectively taken up by plants, and the metabolic route involves reactive nitrogen compounds, making the theory feasible. This theory was tested in Study II.

I found no effect of nitrogen fertilization of pine seedlings with either ammonium sulphate $(NH_4)_2SO_4$ or potassium nitrate KNO3 on the observed NO_x or NO fluxes (that were on average deposition). The NO_x flux in the empty chamber behaved very similarly with the fluxes in shoot chambers, and there was no diurnal pattern. The NO flux, however, behaved differently. Often the flux was practically zero in all chambers. Sometimes clear NO emission was observed during the experiment from all chambers, while at other times the emission from chambers with a shoot (irrelative to the treatment) was clearly higher than from the empty one. The highest emissions, reaching 2.55 pmol/s, happened during high humidity, peaking on rainy nights, but there was no clear daily pattern. The results suggested plant-derived non-NO_x compounds, probably nitrogenous, accumulating on chamber surfaces and their subsequent release. Rondón and Granat (1994) also propose such a process as an explanation for NO_2 emissions from an empty chamber.

Thus it seems unlikely that a fertilization treatment could cause significant NO_x emission from boreal Scots pine forests. This finding was contradictory to the laboratory experiments by Wildt et al. (1997) and Chen et al. (2012). One of the reasons for this may be soil chemistry and biology, changing the total and relative amounts in the living forest soil (e.g. Figueiredo et al. 2016 and references therein). In the laboratory experiments, the NO emissions were the result of sudden, drastic changes in the nutrient concentrations of the growth medium, unrealistic in natural soils. A longer experiment, covering also the annual variation in the trees' enzymatic activity, could yield more detailed information on the effects of fertilization or atmospheric N deposition on the NO_x exchange of forest trees.

Terpenes in shoot emissions and epicuticular waxes (Study III)

As the first point of contact between the atmosphere and pine shoots, needle surfaces and their properties are crucial both in terms of surface chemistry and the effects the atmosphere has on the tree (e.g. Burkhardt and Eiden 1994; Altimir et al. 2006; Clifton et al. 2020). BVOCs emitted by vegetation scavenge O_3 molecules before they ever reach plant surfaces, but any terpenes stored on or near needle surfaces could provide another point of ozonolysis (Loreto and Velikova 2001; Altimir et al. 2008). The near-simultaneous measurements of shoot terpene emissions and terpenes in epicuticular waxes in Study III not only revealed similarities and differences in the terpene spectra, but also suggested a pathway of the terpenes from synthesis site to needle surface.

The shoot emissions as well as the wax extracts were clearly dominated by monoterpenes, with α-pinene the most abundant compound. In the emissions, the three most abundant monoterpenes included also myrcene and carene, while in the waxes the other two most abundant compounds were carene and limonene. The composition of terpene emissions from pine shoots was in line with earlier results (e.g. Hakola et al. 2006; Bäck et al. 2012). Interestingly, notable variation was observed in the terpene spectra of both emissions and wax extracts between tree individuals and, for the wax extracts, even samples from the same individual, despite the fact that the seedlings were grafted. Since the terpene synthesis apparatus of grafted seedlings shares the same DNA (the only genetic differences are belowground), any differences in terpene synthesis should be the result of differences in environmental conditions and life histories, as the variation in terpene production is assumed to be genetically determined (Muona et al. 1986). In addition to variation in e.g. light conditions inside the canopy, insect bites, pathogens and the like can induce terpene synthesis and emissions in both systemic and local scales (Heijari et al. 2011). There is reason to suspect that the observed high emission peaks were to some extent induced by shoot handling during the experiment. Handling is known to increase emissions, and the emitted terpenes can adsorb on chamber walls, to be released over several days (Ruuskanen et al. 2005). The same chamber was used to measure all seedlings, so some contamination cannot be ruled out.

The proportion of sesquiterpenes was higher in the epicuticular waxes (5–21 % of total) than in the emissions (0–2 %). The observed sesquiterpene compounds were different in the emissions and wax extracts with the exception of α-humulene. The different proportion of sesquiterpenes together with the observed differences in the terpene spectra of the emissions and the waxes supported the hypothesis of terpenes associated to the epicuticular waxes. The result is supported by Despland et al. (2016), who detected corresponding monoterpene profiles in different proportions in spruce epicuticular waxes and needles. In addition to the preselected compounds, with standards available, the analysis of the epicuticular waxes found six unidentified sesquiterpenes (unidentified compounds were not looked for in the emission analysis). This group was likely to include cadinene, cubebene and muurolene. This result highlights the need for more detailed studies of sesquiterpene production in conifers.

The experiment was performed also with 5-year-old seedlings of Siberian larch (*Larix Sibirica* (*Lebed*.), not grafted), but due to the soft and small needles the wax extraction was unsuccessful, and the results were excluded from further analysis and the published article. In larch emissions, the most abundant monoterpenes were α-pinene, carene, limonene and myrcene, followed by β-pinene and p-cymene (Figure 5). Total monoterpene emissions were twice those from pine (1287 vs 639 ng/g/h). The highest sesquiterpene emissions were seen for alloaromadendrene/farnesene, bornylacetate and β-caryophyllene (Figure 5). Total sesquiterpene emissions from larch were only roughly one third of those from pine (3.4 vs 11.7 ng/g/h). It has to be noted, though, that the high average emission seen for pine were caused by one tree with extremely high longifolene emissions. In general, sesquiterpenes were seen in the pines more frequently than the larches. The results are relevant, because despite the widespread distribution of the species, measurements of Siberian larch terpene fluxes are scarce (Ruuskanen et al. 2007; Rinne et al. 2009).

The relative abundance of the most reactive and also most lipophilic compounds (like α-humulene and β-caryophyllene) in the epicuticular waxes suggested that the role of direct transport through the cuticle from the sites of terpene synthesis may be more important than has been assumed. This finding is supported by Widhalm et al. (2015), who proposed a mechanism for active BVOC through cell membranes. Based on the relative proportions of sesquiterpenes in the emissions and the wax extracts in Study III, redeposition after emission seems to be of minor importance as a transport route. This conclusion is supported by Cape et al. (2009), but contradicted by others (e.g. Himanen et al. 2010; Li and Blande 2015; Camacho-Coronel et al. 2020). The third pathway for terpenes to reach the epicuticular surface, diffusive transport in an aqueous layer extending from the substomatal cavity through the stoma onto the outer needle surface (Burkhardt and Hunsche 2013), is by nature more readily available to the more water-soluble terpenes. In Study III, these were present in the epicuticular waxes in smaller proportions than in the shoot emissions.

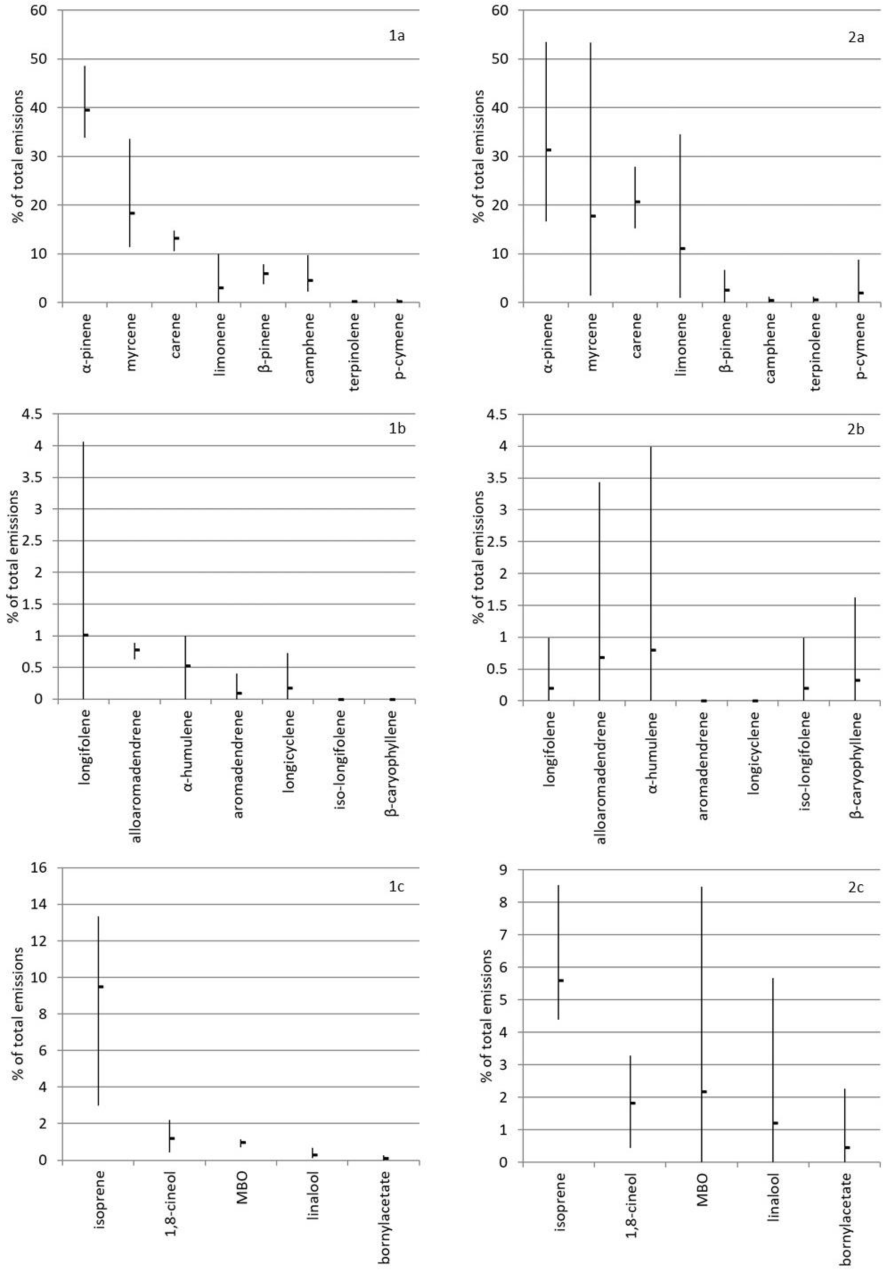

Figure 5. *The shoot-scale BVOC emissions from pine (1) and larch (2), mean ± SD. a: monoterpenes, b: sesquiterpenes, c: others.*

The atmospheric significance of any terpenes bound in or on the surface depends on the rate that any reaction partner, such as ozone, NO_x or OH, reaches the terpene, and the rate at which the terpene pool in the waxes is replenished. The latter is a product of synthesis rate and transport rate, whatever the transport pathway is. The existence of reactive terpenes in the wax extracts indicated that the pool is renewed at least at a comparable rate to the reaction partners reaching the pool. A rough calculation in the ambient conditions showed that the terpenes found on the needle surfaces could in theory react with 5 hours of non-stomatal O_3 deposition. The role of the terpene pool associated with the epicuticular waxes would ultimately depend also on the exact location of the terpene molecules. If they are on or very close to the surface, they are likely to be short-lived and transported either by redeposition or aqueous diffusion on the needle surface. On the other hand, terpene molecules embedded deeper in the wax layer may survive longer but are more unlikely to partake in any surface chemistry with O_3. Instead, they might contribute to plant defense against pathogens or herbivores.

The role of (plant) surfaces in tree-atmosphere fluxes of reactive trace gases (Studies I-III)

Processes and compounds on the needle surface, but also on any equipment surfaces, bring together the measurements and experiments of this thesis and O_3, NO_x and BVOC reactions. In study I, the conclusion was (albeit as a “best guess”) that not only some non-NO_x nitrogenous compounds (like HONO) but VOCs affect the NO_x analyzer. In study II, NO/NO_x emissions from the chambers continued after the shoots had been removed, showing a relation with both UV radiation (NO_x emissions) and humidity (NO emission). In study III, the presence of a considerable amount and number of reactive compounds on or near needle surfaces was detected.

In a shoot chamber there are two types of surfaces: the shoot surfaces (needle and twig) and the chamber surfaces. The chamber was manufactured to minimize any reactions on its surfaces and cleaned regularly for the same purpose, but results (from these and earlier experiments) showed that over time compounds accumulate on the surfaces nevertheless. Similar accumulation happens on the shoot surfaces, if they are not washed by rain. Unlike the chamber, the shoot is a living thing actively interacting with its surroundings, releasing compounds that can then accumulate on surfaces and possibly be released later. In addition to chemical compounds, the shoot surfaces are inhabited by various organisms like fungi and bacteria. These organisms have their own metabolisms and life cycles, contributing to the total shoot fluxes and their development over time (see Vorholt 2012 for a review).

In addition to reactive compounds present at a site on or near a surface (O_3, NO_x, BVOC etc., originating from the atmosphere, the surface or plant/microbiota processes), properties of the environment (humidity, pH, temperature, UV radiation) affect the outcome. In Study I, both the NO_x and NO_y emissions (originating mostly from the chamber) correlated with UVA radiation, indicating photolytic reactions. Correlations with UVB radiation were not tested. In our earlier studies with a similar setup (Raivonen et al. 2003) identified UVA radiation as the primary driver of the emissions. In Study II, the NO_x emissions from the post-experiment empty chambers assumed a clear diurnal pattern peaking at midday, also suggesting photochemical reactions. Zhou et al. (2011) observed HONO production in a forest canopy, correlating with leaf surface nitrate load and nitrate photolysis rate. Nitrate or HNO_3 photolysis was proposed as the source of the observed shoot NO_y emissions also in Raivonen et al. (2006).

Photochemistry plays a role also in BVOC reactions. In study III, the emphasis was on the possible role of terpenes on or near needle surfaces on O_3 deposition. BVOCs, however, react also with NO_x or their reaction products at least in polluted environments (Villena et al. 2012). Another interesting possibility is the reactions of terpenes with the OH radical (product of O_3 photolysis) very close to or on plant surfaces. BVOCs are known to react with ·OH (Atkinson and Arey 2003), but OH is also created in O_3-BVOC reactions (Paulson and Orlando 1996). Current measurements and models do not agree well on ·OH: there is an unknown ·OH sink in the atmosphere-biosphere system, often assumed to result from unmeasured BVOC or non-hydrocarbon emissions (e.g. Sinha et al. 2010; Yang et al. 2016; Praplan et al. 2019). It may be that some of the reactions of known compounds happen too close to the emission source to be measured. Any reactions on needle surfaces would certainly fall into this category. Study III also indicated that there may well be compounds that currently go totally unnoticed, a notion supported by Goldstein and Galbally (2007) and Praplan et al. (2019).

Another environmental variable with a major role in surface chemistry is humidity. High relative humidity can theoretically decrease the signal of NO_x analyzers (Gerboles et al. 2003), although in Study I no signal quenching was found. A more relevant phenomenon to the results at hand can be the change in HONO/NO_x ratio produced in HNO_3 photolysis when water and organic compounds are present (Zhou et al. 2003) – conditions that are most definitely met in our studies. On wet surfaces, HONO can be produced for example in the hydrolysis of NO_2 with water or the reaction of NO with HNO_3 (Sumner et al. 2004). Water is adsorbed even onto hydrophobic surfaces, certainly plant surfaces but even FEP films, if they have sufficient surface roughness (Sumner et al. 2004). This water uptake is RH dependent (Sumner et al. 2004); at high humidity, deposition in the water film and heterogeneous reactions are thus possible also on FEP film surfaces. In Study II, the NO emission occurred at high relative humidity. During the experiment, the highest NO emissions happened during high humidity, peaking on rainy nights.

Also the nonstomatal shoot-scale deposition of O_3 at the study site is known to be highest on humid nights (Altimir et al. 2006). Liquid films on surfaces enhance BVOC deposition (Burkhardt and Eiden 1994), and particles or compounds deposited earlier can dissolve in the film, possibly making them potential reaction partners to trace gases. As noted earlier, the properties of the surface affect liquid film formation (Rudich et al. 2000). In a study by Potier et al. (2017), a major portion of the nonstomatal O_3 deposition was accounted to organic compounds detected in water used to wash fresh leaves, concluding that these compounds leach out of the leaf into the liquid on the leaf surface. The chemical composition of leaf surface water was also found to differ significantly from rainwater. Pine shoot BVOC emissions have a clear diurnal pattern, peaking in the early afternoon and close to zero emissions at nighttime (Aalto et al. 2014). The enhanced O_3 deposition on humid nights can therefore not result from O_3-BVOC reactions in the air. Reactions in surface liquid films, with varying chemical composition, are a more plausible explanation, as suggested by Potier et al (2017) and Sun et al. (2016). A role for surface liquid films has also been suggested in nonstomatal NO_x deposition (Chaparro-Suarez et al. 2011, Teklemariam and Sparks 2006).

BVOC emissions from plant leaves are known to have an antioxidant function, protecting the plant from ozone damage: O_3 exposure stimulates BVOC synthesis (Loreto et al. 2004; Holopainen et al. 2018). Terpenes also inhibit the growth of airborne bacteria, preventing their establishment on needles (Gao et al. 2005). There are few studies on the impact of elevated nitrogen load on tree BVOC emissions, and the results are varied. Both Kivimäenpää et al. (2016) and Tiiva et al. (2018) report higher BVOC emissions from Scots pine after nitrogen fertilization; Carriero et al. (2016) have similar results for silver birch (*Betula pendula* Roth). The effects of elevated O_3 and nitrogen seem to be additive (Kivimäenpää et al. 2016; Carriero et al. 2016). Huang et al. (2020) however report an increase in total BVOC emissions from Masson's pine (*Pinus massoniana* Lambert) after foliar application of nitrogen, but not after soil application and a decrease from *Schima superba* Gardner and Champion regardless of treatment. The responses seem to vary between tree species. In addition, in nature nitrogen deposition happens both directly on tree foliage and on soils (with soil chemistry affecting the nitrogen available to trees); the total effect on BVOC emissions requires therefore further enquiry.

Although VOCs are known to be taken up by epicuticular waxes (e.g. Welke et al. 1998), the role of BVOCs on epicuticular surfaces in plant defenses has been questioned. Their transport has been assumed to happen as passive diffusion; for most compounds the direct pathway from sites of synthesis to the epicuticular surface would be too slow for BVOCs to reach the surface in significant amounts, and any emitted reactive compounds would react ;before they reach the surface (Niinemets and Reichstein 2003; Camacho-Coronel et al. 2020). Widhalm et al. (2015), however, propose active transport of BVOCs through membranes, making continuous renewal of the BVOC pool associated with surfaces plausible. There is gathering evidence to support this theory (Tissier et al. 2017 and references therein). Some monoterpenes may absorb into the waxes as they diffuse out through the stomata (Müller and Riederer 2005). On the other hand, the emission-redeposition scheme is also supported by research evidence. Camacho-Coronel et al. (2020) and Mofikoya et al. (2017) showed that emitted BVOCs not only were sequestered by epicuticular wax layers but also provided defense against fungal infection and herbivory.

CONCLUDING REMARKS

The observations made in Studies I and II led to the conclusion that there is no clear evidence of plant-related NO_x emissions at the SMEAR II station that would be measurable with the measurement system described above, optimized for automatic long-term measurements. Despite improved accuracy, the NO_x analyzer was very likely subject to interference. Recent advances in measurement technology, like laser-induced fluorescence (Thornton e al. 2000) and cavity ring-down spectrometry (Fuchs et al. 2009; Li et al. 2019) are specific to NO_2 and might prove valuable also in long-term measurements. In addition to specificity issues, the signal to noise ratio was low, and a significant proportion of the observed fluxes were to/from chamber walls. Reports on empty chamber fluxes in field conditions are practically nonexistent. In laboratory conditions, Rondón and Granat (1994) evidenced both NO_2 emission and deposition from an empty chamber, depending mostly on ambient NO_2 concentration, while in the study by Chaparro-Suarez et al. (2011) wall effects were deemed negligible. Following these findings, the continuous automated measurements of NO_x at SMEAR II were discontinued. To my knowledge, there are no other ongoing long-term shoot-scale NO_x/NO_y measurements either.

In the studied low-NO_x environment, the shoot-level NO_x fluxes were too small to be monitored accurately in field conditions over extended time periods using an automated dynamic chamber. In my studies, no clear NO_x fluxes from Scots pine foliage could be detected. Instead of automated monitoring, experiments would better be targeted at specific phenomena or processes proposed to play a role in these fluxes, like the nitrogen status of the plant and photochemistry or heterogenous chemistry on plant surfaces.

One such experiment was performed in Study II on the effects of nitrate fertilization on observed shoot-level NO_x fluxes. Although no fluxes were detected during the experiment, the study suggested plant-derived non-NO_x nitrogenous compounds accumulating on chamber surfaces. Targeted flux measurements of other nitrogenous compounds than NO_x/NO_y, such as HONO, could provide valuable insight into how trees interact with the atmosphere.

The terpene experiment (Study III) showed that not only are terpenes present on needle surfaces, but that the composition of the mixture can differ from that of the emissions. An extended version of the experiment, with a longer study period, several different grafts (possibly with different life histories) and a more diverse list of analyzed compounds would shed light on the true diversity of terpenes in needles and emissions. Also the fertilization experiment (Study II) would benefit from a longer study period, giving soil chemistry and plant physiological processes time to stabilize.

Overall, estimating the fluxes of reactive trace gases remains a major challenge. The processes governing the atmospheric concentrations and reactions of gases like O_3 and NO_x in rural areas, with relatively low ambient conditions, play a key role in global atmospheric chemistry and modeling. The terpene emission dynamics affect both O_3 and NO_x chemistry and fluxes, and the vast areas covered by boreal forest add weight to studies in these ecosystems. The remaining challenges also demonstrate the continuing need for multiscale studies. For best results, field measurements and monitoring, providing natural conditions, need to be combined with targeted laboratory and field experiments that work better in revealing details of studied processes but can never capture the variety of conditions present in nature. Field measurements should include both long-term measurements of key variables and shorter measurement campaigns addressing interesting questions that arise from more targeted studies. On the other hand, continuous field measurements can suggest phenomena and processes that need to be studied in more detail. Ideally, both types of facilities would be located close to each other and work in close collaboration.

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