Atmospheric degradation of reactive biogenic VOCs and their role in aerosol formation: Modelling activities, laboratory experiments and field studies in different vegetation zones

Dissertation

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Abstract

Atmospheric aerosols influence the earth's climate through absorbing or scattering solar radiation. Furthermore, they can act as cloud condensation nuclei and affect human health (Fuzzi *et al.*, 2006). The terrestrial biosphere is a continuous and major source of atmospheric aerosol, mainly of particulate organic matter from which a significant fraction is formed by oxidation of biogenic precursors (Kleindienst *et al.*, 2007; Hu *et al.*, 2008). In large forested areas secondary organic aerosol (SOA) can even increase to the major part of the fine aerosol mode (Kanakidou *et al.*, 2005; Martin *et al.*, 2010).

This work investigated the role of high reactive volatile organic compounds emitted by terrestrial vegetation in formation of secondary organic aerosol. After optimizing the sample preparation, synthesizing reference compounds for quantification, conducting reaction chamber experiments and performing simulation model runs to improve and enlarge the knowledge about the degradation mechanism of β-caryophyllene, the role of terpene oxidation products in secondary organic aerosol formation over different vegetation zones was investigated.

Aerosol samples representative for a boreal forest environment were analysed for their major carboxylic terpene oxidation products. The monoterpene oxidation products were the dominating species in the collected aerosol. The calculated contribution of terpene SOA to the total ambient organic aerosol mass reached values up to 29 %. The wind speed influenced the composition of the particulate phase, probably by affecting the residence times of the air masses over forested areas leading to changes in concentration of terpene oxidation products and their oxidation state. Furthermore, influences of forest fires, which occured during the field campaign, on the aerosol composition were detected due to long range transport.

Aerosol samples representative for a tropical rainforest environment were analysed for their major carboxylic terpene oxidation products. Although monoterpene oxidation products were also the dominating species in the collected aerosol, sesquiterpene oxidation products played a more important role in SOA formation than in the boreal forest environment. Generally, terpene SOA contributed to a substantial higher extend (with calculated maximum values of 63 %) to the total ambient organic

aerosol, indicating that biogenic emissions play a major role in fine particulate matter formation over tropical rainforest. Again, the wind speed influenced the aerosol composition over the tropical rainforest.

Aerosol samples collected at a temperate rural site in Germany throughout one year were analysed for the major carboxylic terpene oxidation products. The monoterpene oxidation products were much more abundant in ambient aerosol than the sesquiterpene oxidation products. Generally, the terpene oxidation products showed about tenfold (in case of monoterpenes) or even about hundredfold (in case of sesquiterpenes) decreased concentrations in ambient aerosol compared to aerosol samples from the boreal or tropical forest. Also the calculated contribution of terpene SOA to ambient organic aerosol with a maximum value of 7 % was quite low, indicating that this area is probably much more influenced by anthropogenic instead of biogenic emissions. Nonetheless, the terpene oxidation products showed a significant annual pattern with a strong increase during late spring and also the oxidation state of the products varied throughout one year due to annual ozone and hydroxyl radical cycles.

However, although the monoterpene oxidation products were the dominating terpene species in the collected aerosol from all three vegetation zones, the concentration of sesquiterpene oxidation products in ambient secondary organic aerosol increased significantly under special conditions, reaching maximum values of up to 10 % (temperate mixed coniferous forest), 17 % (boreal coniferous forest) or even 26 % (tropical rainforest) of the total monoterpene oxidation product concentration.

Zusammenfassung

Atmosphärische Aerosole beeinflussen die Energiebilanz der Erde durch Absorption und Streuung der einfallenden Sonnenstrahlung. Des Weiteren können sie sowohl als Wolkenkondensationskeime fungieren, als auch die menschliche Gesundheit beeinträchtigen (Fuzzi *et al.*, 2006). Die Biosphäre ist eine permanente, große Quelle an atmosphärischem Aerosol. Sie produziert überwiegend organische Partikel, welche zu einem großen Teil durch oxidative Umwandlung der emittierten Vorläufersubstanzen entstehen (Kleindienst *et al.*, 2007; Hu *et al.,* 2008). In großen Waldgebieten kann auf diese Weise gebildetes sekundäres organisches Aerosol sogar den Hauptbestandteil der feinen Partikelmasse ausmachen (Kanakidou *et al.*, 2005; Martin *et al.*, 2010).

In dieser Arbeit wurde die Rolle der hochreaktiven biogenen flüchtigen organischen Kohlenwasserstoffe in der Aerosolbildung untersucht. Nach einer erfolgreichen Optimierung der Probenaufarbeitung, der Synthese von Referenzsubstanzen zur Quantifizierung, der Durchführung mehrere Atmosphären-Simulationsexperimente und Modellrechnungen zur Aufklärung des atmosphärischen Abbaus von β-Caryophyllen, wurde die Rolle von Terpenoxidationsprodukten bei der Bildung von sekundärem organischem Aerosol in verschiedenen Vegetationszonen untersucht.

Über dem borealen Nadelwald gesammelte Aerosolproben wurden auf saure Terpenoxidationsprodukte untersucht. Die Monoterpenoxidationsprodukte wiesen die höchste Konzentration auf. Es wurde ein maximaler Beitrag der Terpene von 29 % zum gesamten organischen Aerosol abgeschätzt. Die Aerosolzusammensetzung wurde durch die Windgeschwindigkeit und durch die daraus resultierende Aufenthaltsdauer der Luftmassen über bewaldeten Gebieten sowie durch das Alter der gesammelten Luftmassen beeinflusst. Des Weiteren wurde ein Einfluss von Waldbränden auf die Aerosolzusammensetzung beobachtet.

Über dem tropischen Regenwald gesammelte Aerosolproben wurden ebenfalls auf saure Terpenoxidationsprodukte untersucht. Obwohl auch hier die Monoterpenoxidationsprodukte den Hauptanteil ausmachten, war jedoch der Einfluß von Sesquiterpenoxidationsprodukten wesentlich höher als bei den Aerosolproben des borealen Nadelwaldes. Ebenfalls der abgeschätzte Beirag von Terpenen zum

organischen Aerosol (mit Werten bis zu 63 %) war stark erhöht. Dies deutet auf eine überwiegend biogene Herkunft der feinen Partikel über dem tropischen Regenwald hin. Auch hier wurden Einflüsse der Windgeschwindigkeit auf die Aerosolzusammensetzung beobachtet.

Schließlich wurden Aerosolproben aus einem gemischten Laub- und Nadelwald der gemäßigten Zone auf saure Terpenoxidationsprodukte untersucht. Die Monoterpenoxidationsprodukte wiesen eine wesentlich höhere Konzentration auf als die Sesquiterpenprodukte. Generell war der Beitrag biogener Vorläufer zum atmosphärischen feinen Aerosol jedoch gering. Der abgeschätze prozentuale Anteil der Terpene am organischen Aerosol betrug maximal 7 %. Dies deutet auf einen hohen anthropogenen und nur geringen biogenen Beitrag zur regionalen Aerosolbildung hin. Dennoch zeigten die sauren Terpenoxidationsprodukte stark ausgeprägte Jahresverläufe, welche abhängig von der jeweiligen Vorläufersubstanz deutlich voneinander variierten. Auch der Oxidationszustand der Terpenprodukte unterlag einem Jahreszyklus aufgrund der ebenfalls durch die Jahreszeiten variierenden Ozon und Hydroxylradikal Konzentrationen.

Trotz der dominierenden Rolle der Monoterpenoxidationsprodukte in den Aerosolproben aller drei Vegetationszonen, stieg die Konzentration der Sesquiterpenoxidationsprodukte im sekundären organischen Aerosol unter bestimmten Bedingungen signifikant an und erreichte Maximalwerte von bis zu 10 % (gemischter Laub- und Nadelwald der gemäßigten Zone), 17 % (borealer Nadelwald) oder sogar 26 % (tropischer Regenwald) der totalen Konzentration der Monoterpenoxidationsprodukte.

Contents

1 Introduction

1.1 The Atmosphere – A life sustaining protective shield

Compared to the earth-radius the atmosphere is just a very thin layer surrounding the surface of our planet, but nevertheless it is essential for life on earth (Seinfeld and Pandis, 2006). It protects the earth's surface from harmful solar radiation but is transparent for life sustaining sunlight as energy source for all living organisms. It preserves our planet from overheating and likewise from hypothermia and is involved in all essential element cycles. The atmosphere is divided into five horizontal layers: Troposphere, stratosphere, mesosphere, thermosphere and exosphere (Dörnbrack, 2012). The vertical structure of the atmosphere is shown in Figure 1.

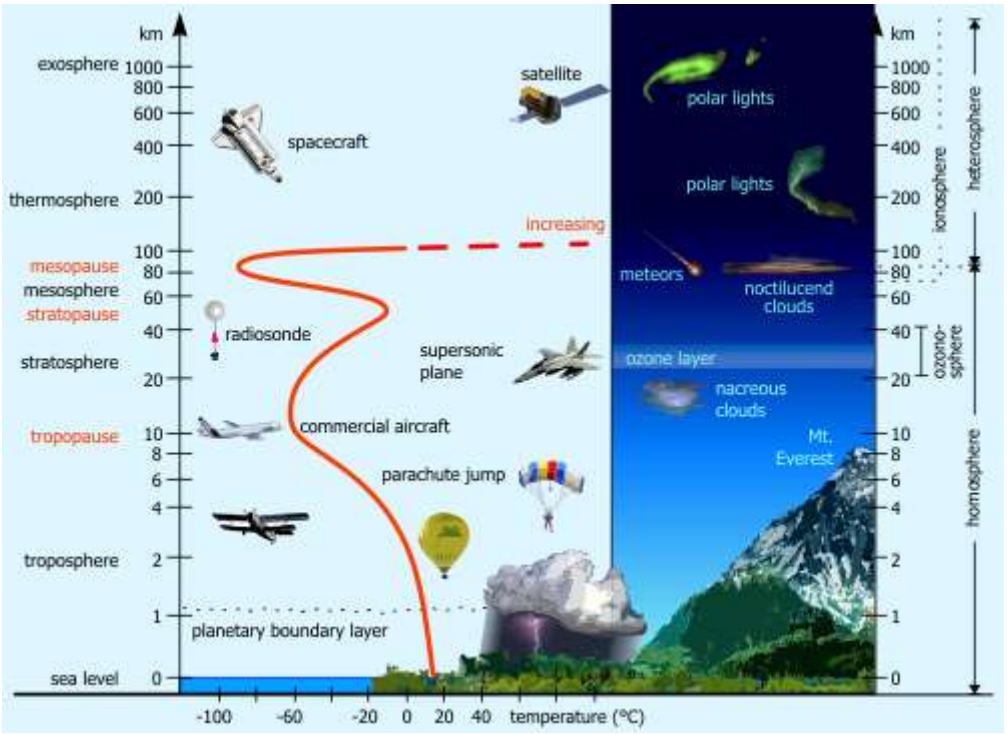


Figure 1: Vertical structure of the atmosphere (Figure from Köhne and Wössner, 2013)

Life takes place in the bottom layer, the troposphere. It bears 80 % of the total atmospheric mass and 99 % of the atmospheric water vapour (Dörnbrack, 2012).

Furthermore cloud formation and all other weather events take place in this layer. The troposphere extends to 10-15 km altitude, depending on season and latitude and is divided into the boundary layer at the bottom with a thickness of about 1 km and the upper free troposphere (Seinfeld and Pandis, 2006). The atmosphere is mainly composed of nitrogen, oxygen, argon and water, minor components are trace gases and particulate matter (Schlager, Grewe and Roiger, 2012). Although being present in minute quantities the trace gases and particulate matter have a severe influence on atmospheric processes, air quality and human health (Schlager, Grewe and Roiger, 2012). The atmosphere is a dynamic system which bidirectional interacts with vegetation, ocean, soils and biological organisms by an exchange of heat, moisture, gases and aerosols (Piekle *et al.*, 1998). Hence, the emissions from the earth's surface in turn influence the earth climate, air quality and global biodiversity (Fowler *et al.*, 2009). To be able to assess to what extend human activities influence the atmosphere as a whole, a complete understanding of the atmospheric cycles of trace gases, their sources and sinks as well as their role in aerosol formation and growth is essential.

1.2 Biogenic volatile organic compounds

The biosphere plays a major role in trace gas exchange between the earth's surface and the atmosphere. The organic atmospheric trace gases other than CO_2 and CO emitted from vegetation, also called volatile organic compounds (Kesselmeier and Staudt, 1999) are crucially involved in the global carbon cycle and hence in tropospheric chemistry (Guenther, 1995). Estimated 1.1 Gt carbon are emitted as volatile organic compounds (VOCs) from biogenic sources each year, with forests being the most productive sources, whereas anthropogenic emissions constitute the minor part with just 0.15 Gt carbon emitted annually as VOCs (Steinbrecher and Koppmann, 2007). The emitted VOCs differ significantly in their reactivity depending on their sources. Biogenic volatile organic compounds (BVOCs) consist mainly (about 60 %) of isoprenoids and thus are very reactive, on the contrary most anthropogenic VOCs like e.g. alkanes are less reactive (Seinfeld and Pandis, 2006; Steinbrecher and Koppmann, 2007) and hence influence the oxidative capacity and chemistry of the atmosphere to a lesser attend and much slower than BVOCs. Nevertheless, on local scale the

anthropogenic contribution to VOC emission can increase significantly and in densely populated areas even exceed the biogenic emission. Many hundreds of different VOCs are emitted by terrestrial vegetation which vary in structure and functional groups (Kesselmeier and Staudt, 1999; Dore *et al.*, 2003). The largest part is made up by the isoprenoids. On global scale the strongest isoprenoid emissions were registered for isoprene (Guenther *et al.*, 2000; Guenther *et al.*, 2006), followed by the group of monoterpenes (Fowler *et al.*, 2009). Sesquiterpenes as well as oxygenated compounds like alcohols, aldehydes and ketones are emitted in much smaller quantities (Heiden *et al.*, 2003; Seco, Peñuelas and Filella, 2007). The physiological role of isoprenoids is not completely understood yet. However, their emission can attract pollinating insects (Knudsen, Tollsten and Bergström, 1993; Dobson and Bergström, 2000), enable inter- and intraplant communication as well as allelopathy (Heil and Kost, 2006), and attract insectivores (Turlings *et al.*, 1995; Paré and Tumlinson, 1999; Theis and Lerdau, 2003). Furthermore several studies proved, that increasing ambient temperatures, radiation strength and ozone concentrations can favor enhanced isoprenoid emission (Schuh *et al.*, 1997; Staudt *et al.,* 1997; Seufert, 2003; Helmig *et al*., 2006; Holzinger *et al.,* 2006; Hansen and Helmig *et al.*, 2007; Bourtsoukidis *et al*., 2012; Kivimäenpää *et al.*, 2013). The emission of biogenic volatile compounds from plants is not only correlated to light, temperature, abiotic and biotic stresses, it also shows a distinct annual pattern. These annual changes of the emission strength can be attributed to strong annual cycles of foliar biomass in the temperate zone, but also to seasonal changes in plant metabolism (Holzke *et al.*, 2006a; Holzke *et al.*, 2006b) as well as to different leaf development states. Once released into the atmosphere the trace gases get photochemically or chemically oxidized by ozone as well as hydroxyl and nitrate radicals. Depending on their reactivity the atmospheric lifetimes of the emitted compounds range between a few seconds and many years (Seinfeld and Pandis, 2006). The atmospheric degradation of reactive BVOCs plays a major role in tropospheric greenhouse gas generation, mainly ozone (Atkinson, 2000; Seinfeld and Pandis, 2006; Steinbrecher and Koppmann, 2007), and secondary organic aerosol (SOA) formation (see scheme in Figure 2).

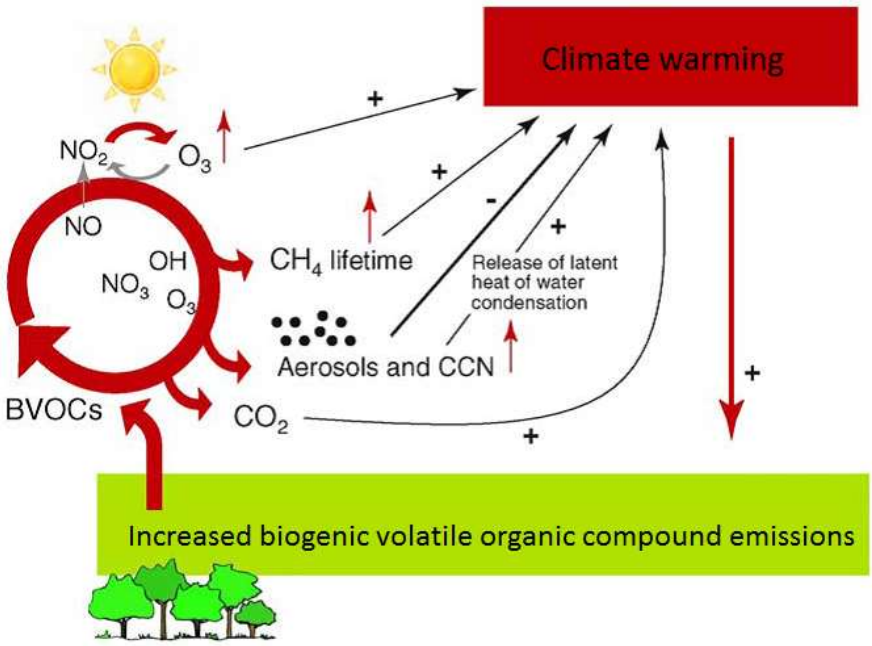


Figure 2: Schematic figure of coupling of BVOC emissions and atmospheric chemistry and climatic changes (Figure from Peñuelas and Staudt, 2009)

The low volatile isoprenoid oxidation products can condense on existing aerosol particles or small aerosol clusters and hence promote their growth (Hoffmann *et al.*, 1997). Monoterpene oxidation products are assumed, to increase the particle growth rate significantly, especially during nucleation events (Janson *et al*., 2001; Lyubovtseva *et al*., 2005; Rissanen *et al.,* 2006; Asmi *et al*., 2011), although they are not the nucleating species (Janson *et al.,* 2001; Kulmala *et al*., 2001). Recent studies indicate that also sesquiterpenes play an important role in SOA formation (Hallquist *et al.*, 2009) due to the high reactivity of many sesquiterpenes towards O_3 (Shu and Atkinson, 1995; Kesselmeier and Staudt, 1999) and the low volatility of their oxygenated products (Bonn and Moortgat, 2003; Jaoui, Leungsakul and Kamens, 2003; Lee *et al.*, 2006a; Nguyen *et al.*, 2009).

However, through formation of secondary organic aerosol and greenhouse gases the oxidation of BVOCs influences significantly the earth's radiative budget. Furthermore, their impact radius is enlarged from regional to global scale due to the longer atmospheric lifetime of the aerosol particles.

1.3 Atmospheric aerosol – A complex and dynamic mixture

The atmosphere contains particulate matter with maximum concentrations of 10^7-10^8 cm^{-3} (Seinfeld and Pandis, 2006). These atmospheric particles differ widely in size, origin, chemical composition, age, optical properties and hygroscopicity. They influence the earth's climate through absorbing or scattering sunlight (Fuzzi *et al.*, 2006). While SOA, nitrate and sulphate aerosols are mainly scattering the solar radiation, black carbon generally absorbs sunlight (Unger, 2012). However, the global net effect of aerosols is a global cooling (Forster *et al.*, 2007). Furthermore, aerosols can act as cloud condensation nuclei. They modify the size and number concentration of cloud droplets, and hence change their reflecting and absorbing properties as well as their lifetime. Through increasing the number concentration and decreasing the size of cloud droplets a bigger optical thickness and hence a better reflection of sunlight is obtained (Twomey, 1991). Due to the smaller size of the droplets the precipitation formation is inhibited and hence the atmospheric lifetime of the cloud is increased as well as its horizontal and vertical extension (Albrecht, 1989). Another important function of particulate matter is the provision of a surface where atmospheric reactions can take place. In addition, atmospheric aerosols can affect human health (Fuzzi *et al.*, 2006). Through inhaling particles allergic and infectious diseases may be caused or toxic aerosol ingredient may be absorbed by the human body (Fuzzi *et al.*, 2006). The terrestrial biosphere is a continuous and major source of atmospheric aerosol, mainly of particulate organic matter. It emits primary organic aerosols (POA), particles which are directly released into the atmosphere without any chemical transformation like pollen, spores and microorganisms and is involved in secondary organic aerosol formation through the emission of reactive trace gases (Carslaw *et al.*, 2010). On average, due to its smaller aerodynamic diameter, SOA has a longer atmospheric lifetime compared to POA ranging from days to weeks and hence a broader impact radius (Seinfeld and Pandis, 2006). SOA contributes significantly to ambient fine particulate matter (particles with a smaller aerodynamic diameter than 1 µm (Jacob, 1999)) and organic carbon concentrations (Seinfeld and Pandis, 2006; Hallquist *et al.*, 2009). Annual SOA formation is estimated to be around 12-70 Tg (Kanakidou, 2005). However, Goldstein and Galbally (2007) as well as

Hallquist *et al.* (2009) assume that this value is still one order of magnitude too small. SOA production from BVOCs is estimated to range between 2.5 and 44.5 Tg per year (Tsigaridis and Kanakidou, 2003). But due to the limited understanding of the formation mechanisms as well as the precursor trace gases involved in the formation processes and their global emission strength the actual biogenic and anthropogenic contribution to atmospheric secondary organic aerosol remains highly uncertain.

2 The Aim of the Work

Particulate organic matter constitutes a large fraction, typically 20-60 % of the fine mode atmospheric aerosol (Kanakidou *et al.*, 2005; Docherty *et al.*, 2008; Carlton, Wiedinmyer and Kroll, 2009) which can increase in large forested areas like the tropics to almost 90 % (Kanakidou *et al.*, 2005; Martin *et al.*, 2010). Secondary organic aerosol formed from biogenic precursors is known to contribute significantly to ambient particulate organic matter (Kleindienst *et al.*, 2007; Hu *et al.*, 2008). It consists of a complex mixture of several hundreds or even more of organic compounds (Seinfeld and Pandis, 2006) from which currently just a minute fraction is identified. Especially the role of sesquiterpene oxidation products in aerosol formation as well as their emission strength and influence on the oxidative capacity and chemistry of the atmosphere is highly uncertain. Some studies indicate that sesquiterpene emission can be as high as 30 or 40 % of the total monoterpene emission or even exceed it (Hakola *et al.*, 2003; Tarvainen *et al.*, 2005; Helmig *et al.*, 2007). However, due to the high reactivity of most sesquiterpenes and the resulting short atmospheric lifetimes (Shu and Atkinson, 1995; Kesselmeier and Staudt, 1999) their measurement in ambient air is quite challenging. One possibility is the measurement of these compounds through branch enclosure, but it is difficult to avoid reactive surfaces causing unwanted reactions and chemical shifts leading to analyte losses. In addition, branch enclosure measurements are usually performed on a small number of trees and hence less suited to determine their emission strength from a whole environment or ecosystem. Another approach is the determination of their oxidation products in particulate matter which additionally provides information about their role in aerosol formation and growth.

The aim of this work is the identification and quantification of carboxylic monoterpene and sesquiterpene oxidation products in secondary organic aerosol:

- By synthesizing reference compounds through oxidation of several monoterpene and sesquiterpene precursors in order to enable a reliable

quantification of terpene SOA tracers and an exact assignment of the oxidation products to their precursor compounds

- By optimizing sample preparation and chromatographical separation to gain a representative and reproductive method for the quantification of terpene oxidation products in biogenic SOA filter samples
- By conduction of atmospheric simulation experiments in a reaction chamber to determine the major oxidation products of β-caryophyllene by ozonolysis as well as their product yields. By application of the atmospheric chemistry box model CAABA/MECCA expected product yields are compared to experimental determined values in order to reveal possible gaps in the assumed degradation pathway of β-caryophyllene.
- By analyzing aerosol samples collected over a boreal forest and a tropical rainforest environment for their major carboxylic terpene oxidation products. The impact of various meteorological parameters on the aerosol composition is investigated and the contribution of terpene SOA to the total organic matter is estimated.
- By analyzing aerosol samples collected over a rural countryside in Germany in different seasons throughout one year for their major carboxylic terpene oxidation products. The impact of various factors like temperature, global radiation, atmospheric oxidant concentrations as well as seasonal vegetation changes on the aerosol composition is determined and the contribution of terpene SOA the total organic matter is estimated.

3 Experimental Part

3.1 Instrumental setup

3.1.1 GC-MS-measurements

Derivatization:

25 µL of the solution were mixed with 5 µL pyridine (≥ 99+ %, Acros organics) and 25 µL BSTFA + TMS 99:1 (Supelco) and stirred vigorously for 30 seconds. The reaction mixture was heated to 343 K for 30 minutes and afterwards cooled to room temperature.

Measurement:

1 µL of this solution was injected into the gas chromatograph (Agilent, 6850) coupled to an electron ionization quadrupol mass spectrometer (Agilent, 5973). A FS-Supreme-5ms column (30 m x 0.25 mm x 0.25 µm; CS Chromatographie, Langerwehe, Germany) was used for separation. The temperature program was as follows: The starting temperature of 343 K was held for 2 minutes and was than increased with a rate of 13 K min^{-1} to the final temperature of 573 K which was held for 2 minutes. Helium (5.0, Westfalen, Germany) was used as carrier gas with a flow rate of 1 mL min^{-1}. The injector temperature was 523 K and the temperature of the transfer line was 573 K. The MS was operated at 70 eV ionization energy and the spectra were measured in full scan mode (m/z 45-450).

3.1.2 HPLC-MS-measurements

20 µL of the filter sample extracts and 10 µL of the calibration standard solutions were injected into a HPLC-system (Agilent 1100 series, auto sampler, gradient pump and degasser) coupled with an electrospray ionization ion trap mass spectrometer (Bruker-Daltonics GmbH, Bremen, Germany). A Pursuit XRs 3 C8 column (150 mm x 2.0 mm, 3 µm particle size; Varian, Germany) was used. The eluents were HPLC grade water

(Milli-Q water system, Millipore, Bedford, USA) with 0.04 % formic acid and 2 % acetonitrile (eluent A) and acetonitrile with 2 % HPLC grade water (eluent B). The flow rate of the mobile phase was 0.2 mL min^{-1}. The gradient of the mobile phase was as follows: The starting ratio was 1 % eluent B and 99 % eluent A. Eluent B was increased to 99 % within 30 minutes and this ratio was held for 5 minutes. The eluent B was then decreased to 1 % within 5 minutes and this ratio was held for 20 minutes. The MS was operated with a nebuliser pressure of 30 psi, a dry gas flow of 10 L min^{-1}, a dry gas temperature of 573 K and a spray voltage of 5000 V. The MS was operated in the negative ion mode.

3.1.3 NMR-measurements

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer and signals were referred to the residual solvent signal ($CDCl_3$: δ_H = 7.26 ppm) (Gottlieb, Kotlyar and Nudelman 1997). 10 mg of each synthesized compound were dissolved in 1 mL $CDCl_3$ (99.8 %, VWR).

3.1.4 On-line-APCI-MS-measurements

The on-line-APCI-MS-measurements were performed with an atmospheric pressure chemical ionization ion trap mass spectrometer (LCQ classic, Finnigan MAT, USA). A modified inlet allows a direct introduction of the aerosol particles into the ion source (Kückelmann, Warscheid and Hoffmann, 2000; Hoffmann *et al*., 2002). Helium (5.0, Westfalen, Germany) was used as collision gas. The MS was operated with a discharge current of 3 µA, a vaporizer temperature of 623 K, a capillary temperature of 473 K, a capillary voltage of - 8 V and a lens voltage of 15 V.

3.1.5 UHPLC-MS-measurements

20 µL of the filter sample extracts and 10 µL of the calibration standard solutions were injected into an UHPLC-system (Dionex UltiMate 3000 series, auto sampler, gradient pump and degasser) coupled with a Q Exactive electrospray ionization Orbitrap mass spectrometer (Thermo Scientific). A Hypersil Gold column (50mm x 2.1 mm, 1.9 µm particle size, 175 Å pore size; Thermo Scientific) was used. The eluents were HPLC grade water (Milli-Q water system, Millipore, Bedford, USA) with 0.01 % formic acid and 2 % acetonitrile (eluent A) and acetonitrile with 2 % HPLC grade water (eluent B). The flow rate of the mobile phase was 0.5 mL min^{-1}. The gradient of the mobile phase was as follows: The starting ratio was 1 % eluent B and 99 % eluent A. This ratio was held for 30 seconds. Eluent B was increased to 20 % within 90 seconds and this ratio was held for 60 seconds. Eluent B was then increased to 30 % within 60 seconds, then to 50 % within 180 seconds and finally to 99 % within 30 seconds. This ratio was held for 90 seconds. Eluent B was then decreased to 1 % within 6 seconds, this ratio was held for 120 seconds. The column was held on a constant temperature of 298 K in the column oven. The MS was operated with an aux gas flow rate of 15 (arbitrary units of the instrument used), a sheath gas flow rate of 30 (arbitrary units of the instrument used), a capillary temperature of 623 K and a spray voltage of 3000 V. The MS was operated in the negative ion mode, the resolution was 70000 and the measured mass range was m/z 80-350.

3.2 Synthesis and quantification

3.2.1 Synthesis on preparative scale

Caryophyllonic acid:

This reaction was performed according to the method of Parshintsev and coworkers (Parshintsev *et al.*, 2008) and Walborsky and coworkers (Walborsky, Davis and Howton, 1951). 3.5 g β-Caryophyllene (≥80 %, Sigma Aldrich) were dissolved in 300 mL dichloromethane (≥ 99.9 %, Roth). The solution was cooled to 195 K and stirred vigorously. Ozone was bubbled trough the solution with a flow rate of 2 g O_3 h^{-1} for

560 minutes. The solvent was evaporated and the residue was dissolved in 60 mL ethanol (≥ 99.9 %, VWR) and a solution of 3.36 g silver nitrate (≥ 99.9 %, Roth) in 150 mL ethanol was added. The mixture was kept under a gentle nitrogen flow and stirred vigorously. A solution of 2.44 g sodium hydroxide (≥ 99 %, Roth) in 13 mL water was added dropwise. The solution was stirred overnight and the silver precipitate was removed by filtration. The solvent was evaporated and the residue was resolved in 150 mL ethyl acetate (≥ 99.5 %, Sigma Aldrich). 150 mL water were added and the mixture was acidified with hydrochloric acid (≥ 37 %, Fluka). The organic layer was separated and the water layer was extracted twice with ethyl acetate. The organic layers were dried and the solvent was evaporated. The product was purified by flash chromatography (silica gel 0.060-0.200 mm 60 Å (Acros Organics); hexane (98.9 %, VWR)/ ethyl acetate, 2:3). A yellowish viscous oil was received. The yield of caryophyllonic acid was 60.1 % (2.08 g).

βCA198 and nocaryophyllonic acid:

This reaction was performed according to the method of Parshintsev and coworkers (Parshintsev *et al*., 2008). 1.8 g Caryophyllonic acid was dissolved in 150 mL dichloromethane (≥ 99.9 %, Roth). The solution was cooled to 195 K and stirred vigorously. Ozone was bubbled trough the solution with a flow rate of 2.8 g O_3 h^{-1} for 96 minutes. The solvent was evaporated and the product was purified with flash chromatography (silica gel 0.060-0.200 mm 60 Å (Acros Organics); hexane (98.9 %, VWR)/ ethyl acetate (≥ 99.5 %, Sigma Aldrich), 2:3).

A yellowish viscous oil was received. Conversion of caryophyllonic acid to nocaryophyllonic acid: 89.3 % (1.57 g).

Conversion of caryophyllonic acid to βCA198: 10.7 % (115 mg).

Caryophyllinic acid:

This reaction was performed following the description of Porter *et al*. (1991).

2 g Caryophyllonic acid were dissolved in 40 mL 1,4-dioxane (≥ 99.5 %, Sigma Aldrich), stirred vigorously and cooled to 273 K. 10 g sodium hydroxide (≥ 99 %, Roth) in 10 mL water were added dropwise. A solution of 8.3 g iodine (≥ 99.8 %, Roth) and 16 g potassium iodide (≥ 99.5 %, Sigma Aldrich) in 80 mL water was added dropwise. The

reaction mixture was stirred overnight and heated under reflux for 2 h. A solution of sodium metabisulfite (analytical reagent grade, Fisher Scientific) was added until the reddish color of the iodine disappeared. The reaction mixture was acidified with hydrochloric acid (≥ 37 %, Fluka) and extracted twice with ethyl acetate. The organic layers were washed with water twice, dried and the solvent was evaporated. The product was purified with flash chromatography (silica gel 0.060-0.200 mm 60 Å (Acros Organics); hexane (98.9 %, VWR)/ ethyl acetate (≥ 99.5 %, Sigma Aldrich), 1:1).

A yellowish viscous oil was received. Conversion of caryophyllonic acid to caryophyllinic acid: 24.3 % (490 mg).

βCA200:

This reaction was performed according to the method of Parshintsev *et al*. (2008).

0.5 g Caryophyllinic acid was dissolved in 40 mL dichloromethane (≥ 99.9 %, Roth). The solution was cooled to 195 K and was stirred vigorously. Ozone was bubbled trough the solution with a flow rate of 2.8 g O_3 h^{-1} for 45 minutes. The solvent was evaporated and the product was purified with flash chromatography (silica gel 0.060-0.200 mm, 60 Å (Acros Organics); hexane (98.9 %, VWR)/ ethyl acetate (≥ 99.5 %, Sigma Aldrich), 2:3).

A yellowish viscous oil was received. Conversion of caryophyllinic acid to βCA200: 48.3 % (190 mg).

3.2.2 Synthesis on non-preparative scale

100 µL of the terpene was dissolved in 5 mL dichloromethane (≥99.9 %, Roth). The solution was cooled to 195 K and ozone was bubbled through the solution with a flow rate of 2 g O_3 h^{-1} for several minutes.

Every 2 minutes an aliquot was taken out and the formed oxidation products were analyzed with GC-MS. This procedure was repeated until the desired carboxylic oxidation products were formed.

The used terpenes as well as the duration of the ozonolysis are shown in Table 1.

Table1: Duration of the ozonolysis of the different terpenes

Terpene	*Seller and purity*	*Duration of ozonolysis*
(-)-α-pinene	Fluka, ≥99 %	10 minutes
(-)-β-pinene	Aldrich, 99 %	10 minutes
R-(+)-limonene	Aldrich, 97 %	10 minutes
(+)-Δ-3-carene	Fluka, ≥ 98.5 %	10 minutes
Myrcene	Fluka	2 minutes
Sabinene	Roth	10 minutes
(-)-trans-caryophyllene	Sigma, ≥ 98.5 %	6 minutes
α-humulene	Fluka, ≥98 %	2 minutes
(-)-α-cedrene	Fluka, ≥ 99%	6 minutes
β-farnesene	Wako, ≥ 85 %	2 minutes
(-)-isolongifolene	Fluka, ≥98 %	76 minutes
Aromadendrene	Fluka, ≥ 97 %	26 minutes

Upon completion of the ozonolysis reaction 100 µL of the solution was evaporated in an evaporation unit (Reacti Vap 1; Fisher Scientific) with a gentle nitrogen flow at room temperature and the residue was resolved in 100 µL of a HPLC grade water/acetonitrile mixture (8:2).

3.2.3 Quantification

The quantification of the monoterpene oxidation products was made by calibration with pinic acid (Sigma Aldrich), cis-pinonic acid (98 %, Aldrich) and tricarballylic acid (≥ 99 %, SAFC).

The quantification of the sesquiterpene oxidation products was made by calibration with the synthesized standard compounds of β-caryophyllene.

3.3 Filter extraction

3.3.1 Optimization of extraction procedure

One filter half (TFE coated borosilicate glass fibre filters; PALLFLEX, T60A20, Pall Life Science, USA) was spiked with 500 ng (Experiment Nr. 1-16) or 100 ng (Experiment Nr. 17-44) of each analyte (carballylic acid, pinonic acid, pinic acid, βCA198, βCA200, caryophyllonic acid, caryophyllinic acid and nocaryophyllonic acid), cut into small pieces, placed in a glass extraction vessel and covered with 2 mL extraction solvent. The vial was placed in a sonication bath for 30 minutes at room temperature. The extraction solution was sucked out with a syringe and was filtered through a syringe filter. This procedure was repeated twice. The filter extracts were concentrated in an evaporation unit (Reacti Vap 1; Fisher Scientific) with a gentle nitrogen flow at room temperature and the residue was resolved in 100 µL of a HPLC grade water/acetonitrile mixture (8:2). The performed experiments are listet in detail in Table 2.

Table 2: Parameters of extraction efficiency experiments

Experiment Nr.	***Extraction Solvent***	***Syringe Filter Diameter***	***Syringe Filter Pore Size***	***Glass Extraction Vessel***	***Syringe Material***
1-4	EtOH	8 mm	0.45 µm	Non-silylated	Multi-Way Glass
5-8	MeOH	8 mm	0.45 µm	Non-silylated	Multi-Way Glass
9-12	ACN	8 mm	0.45 µm	Non-silylated	Multi-Way Glass
13-16	DCM	8 mm	0.45 µm	Non-silylated	Multi-Way Glass
17-20	ACN	8 mm	0.45 µm	Non-silylated	Multi-Way Glass
21-24	ACN	15 mm	0.45 µm	Non-silylated	Multi-Way Glass
25-28	ACN	25 mm	0.45 µm	Non-silylated	Multi-Way Glass
29-32	ACN	15 mm	0.2 µm	Non-silylated	Multi-Way Glass
33-36	ACN	15 mm	0.45 µm	Non-silylated	Multi-Way Glass
37-40	ACN	15 mm	0.45 µm	Silylated	Multi-Way Glass
41-44	ACN	15 mm	0.45 µm	Silylated	One-Way PE-PP

3.3.2 Silylation

The glass vessels were rinsed with HPLC grade water and dried at 393 K for 60 minutes. The hot glass vessels were dipped into a 5 % solution of dimethyldichlorosilane in hexane for 1 minute. The vessels were rinsed with methanol, dried at 333 K and rinsed with acetonitrile.

3.3.3 Reaction chamber experiment filter samples

One half of the filter was cut into small pieces, placed in a glass vial and covered with 2 mL acetonitrile (≥ 99.9 %; Sigma Aldrich). The vial was placed in a sonication bath for 30 minutes at room temperature. The extraction solution was sucked out with a glass syringe and was filtered through a syringe filter (Satorius Minisart SRP 4, PTFE membrane 0.45 µm). This procedure was repeated twice. The filter extracts were concentrated with an evaporation unit (Reacti Vap 1; Fisher Scientific) with a gentle nitrogen flow at room temperature and the residue was resolved in 100 µL (ambient air samples) or 200 µL (samples from reaction chamber experiments) acetonitrile (≥ 99.9 %; Sigma Aldrich).

3.3.4 Ambient air filter samples

One half of the filter was cut into small pieces, placed in a silylated glass vial and coated with 2 mL acetonitrile (≥ 99.9 %; Sigma Aldrich). The vial was placed in a sonication bath for 30 minutes at room temperature. The extraction solution was sucked out with a PE-PP single-use syringe (Norm-Ject, 1mL, HSW, Germany) and filtered through a syringe filter (PTFE membrane, 0.45 µm pore size, 15 mm diameter, Roth, Germany). This procedure was repeated twice. The filter extracts were evaporated in an evaporation unit (Reacti Vap 1; Fisher Scientific) with a gentle nitrogen flow at room temperature and the residue was resolved in 100 µL of a HPLC grade water (Milli-Q water system, Millipore, Bedford, USA) / acetonitrile (≥ 99.9 %; Sigma Aldrich) mixture (8:2).

3.4 Reaction chamber experiments and box modelling

3.4.1 β-Caryophyllene/ozone reaction chamber experiments

100 µL β-Caryophyllene (≥98.5 %, Sigma Aldrich) were filled in a GC vial which was placed in a heated test gas source at 343 K (Hoffmann, 1995; Thorenz *et al.*, 2012). The evaporated β-caryophyllene was released into a nitrogen flow (5.0, Westfalen, Germany) of 190 mL min^{-1} and transported into the 100 L dark reaction chamber. An additional synthetic air flow was blown into the chamber with a flow rate of 2400 mL min^{-1}. A particle counter (CPC, TSI, 3022A) was connected to the chamber and air from the reaction chamber was sucked out through an activated carbon diffusion denuder with a flow rate of 2000 mL min^{-1} into the ion source of the APCI-IT-MS. The temperature inside the reaction chamber was 291 ± 1 K and the relative humidity 19 ± 1 %. Excess air was passed out of the chamber through a teflon tube to obtain a constant pressure. After 2 hours equilibration time a constant mixing ratio of β-caryophyllene of 51 ppbv (± 10 %) was achieved in the reaction chamber. The synthetic air stream was reduced to 1200 mL min^{-1} and ozone-containing synthetic air (generated by irradiating the synthetic air with an UV lamp) was blown into the chamber with a flow rate of 1200 mL min^{-1}. The ozone concentration in the chamber was measured with an ozone analyzer (model 1008-RS; Dasibi Environmental Corp., Glendale CA, USA). The ozone mixing ratio in the chamber after approximately 2-3 h equilibration time when no terpene was injected into the reaction chamber was adjusted to be either 1 ppmv (± 10 %) or 200 ppbv (± 10 %). In the presence of β-caryophyllene, the ozone concentration under steady state conditions (several hours) reached concentrations of about 920 ppbv (± 10 %) or 130 ppbv (± 10 %) respectively. The first 2.5 h of the reaction were monitored by APCI-IT-MS. Afterwards the APCI-IT-MS was disconnected from the chamber system and replaced by a filter holder. The air from the chamber was then sucked through an activated carbon diffusion denuder with a flow rate of 2000 mL min^{-1} into the filter head and the sampling time was 17 h. TFE coated borosilicate glass fibre filters (PALLFLEX, T60A20, Pall Life Science, USA) were used for sampling. After sampling the filters were stored at 253 K until extraction.

3.4.2 Estimation of the yields of β-caryophyllene oxidation products

An additional heated test gas source at 298 K with a GC vial filled with 100 µL α-terpinene (≥95 %, Sigma Aldrich) was connected to the chamber. The evaporated α-terpinene was released into a nitrogen flow (5.0, Westfalen, Germany) of 190 mL min^{-1} and transported into the 100 L reaction chamber. After 2 hours equilibration time a constant mixing ratio of 51 ppbv (± 10 %) β-caryophyllene and 104 ppbv (± 10 %) α-terpinene was achieved in the reaction chamber. The ozone mixing ratio in the chamber after approximately 2-3 h equilibration time when no terpene was injected into the reaction chamber was adjusted to 1 ppmv (± 10 %). In the presence of β-caryophyllene and α-terpinene after approximately 2-3 h reaction time an ozone concentration at steady state of about 820 ppbv (± 10 %) was measured.

3.4.3 Box modelling

To compare the results of the reaction chamber experiments with theoretical predictions, the box model CAABA/MECCA (Sander *et al.*, 2011) was used. In its base configuration CAABA/MECCA simulates the chemistry of an atmospheric air parcel. For this study, however, it was adapted to the conditions of the reaction chamber: Photolysis reactions were switched off and input fluxes were adjusted to the conditions described in section 2.3 and 2.4 (mixing ratios of 51 ppbv β-caryophyllene and 104 ppbv α-terpinene). Only gas-phase reactions were considered. The chemistry mechanism was extended to calculate the product yields of different oxidation products of β-caryophyllene. Reactions and rate coefficients were taken from the Master Chemical Mechanism v3.2 (MCM, Jenkin *et al.*, 1997; Saunders *et al.*, 2003; http://mcm.leeds.ac.uk/MCM). A few reactions were included in addition to those from the MCM: Individual chemical equations for the OH radical consumption and production through the ozonolysis of α-terpinene were taken from Aschmann, Arey and Atkinson (2002) and chemical equations for the formation of βCA200 were added according to the formation of a similar oxidation product (ßCA198) within the MCM

v3.2 (MCM, Jenkin *et al.*, 1997; Saunders *et al.*, 2003; http://mcm.leeds.ac.uk/MCM). A complete list of these changes is presented in Table 3.

Table 3: Added and modified equations to the reaction mechanism extracted from the MCM

	Equation	***Rate constant (cm^3 $molecule^{-1}$ s^{-1})***	***Literature***
1	C137CO2H + O3 = C1211CO2H + CH2OOF	1.10E-16*0.330	MCM, Jenkin *et al.*
2	C137CO2H + O3 = C1137OOA + HCHO	1.10E-16*0.670	1997, Saunders *et*
3	C1137OOA = C1137OO	KDEC*0.5	*al.* 2003,
4	C1137OO + CO = C1211CO2H	1.20E-15	http://mcm.leeds.a
5	C1137OO = C1211CO2H + H2O2	1.40E-17*C(H2O)	c.uk/MCM
6	C1137OOA = C1137O2 + OH	KDEC*0.5	
7	C1137O2 + HO2 = C1137OOH	KRO2HO2*0.968	
8	C1137OOH + OH = C1137CO + OH	3.41E-11	
9	C1137CO + OH = C1111CO3 + HCOCH2CO2H	1.55E-11	
10	C1111CO3 + HO2 = C1111CO2H + O3	KAPHO2*0.15	
11	C1111CO3 + HO2 = C1111CO3H	KAPHO2*0.41	
12	C1111CO3H + OH = C1111CO3	1.45E-11	
13	C1111CO3 + HO2 = C1111O2 + OH	KAPHO2*0.44	
14	C1111CO3 = C1111CO2H[1]	1.00E-11*RO2*0.3	
15	C1111CO3 = C1111O2	1.00E-11*RO2*0.7	
16	C1137O = C1111CO3 + HCOCH2CO2H	KDEC	
17	C1137O2 = C1137CO	8.80E-13*RO2*0.2	
18	C1137O2 = C1137O	8.80E-13*RO2*0.6	
19	C1137O2 = C1137OH	8.80E-13*RO2*0.2	
20	C1137OH + OH = C1137CO + HO2	2.19E-11	
21	C1111CO2H + OH = C1111O2	1.14E-11	
22	ATERPINENE + O3 = 0.38 OH + 0.03 CH3COCH3 + 0.023 DIACID186 + 0.6 ATERPINOO	2.1E-14	Aschmann, Arey and Atkinson, 2002
23	ATERPINENE + OH = 0.1 CH3COCH3	3.4E-10	
24	ATERPINOO = ATERPINAL	2E-16*C(H2O)	

[1]C1111CO2H is βCA200

3.5 Ambient air samples

3.5.1 HUMPPA-COPEC campaign

Filter samples were taken during the HUMPPA-COPEC campaign summer 2010 at the SMEAR II station in Hyytiälä, Southern Finland. PM 2.5 was sampled with a flow rate of 2.3 m^3 h^{-1} (Warnke, Bandur and Hoffmann, 2006) on the radiation tower at a height of 16 m above ground level. For sampling TFE coated borosilicate glass fibre filters (PALLFLEX, T60A20, Pall Life Science, USA) were used. The sampling time of the filters ranged between 19 h and 27 h. The filter samples were stored at 255 K until extraction. The description of the site as well as the performed measurements and meteorological conditions during the HUMPPA-COPEC campaign can be found at Williams *et al.* (2011).

3.5.2 ATTO-IOP2 campaign

Filter samples were taken during the ATTO-IOP 2 campaign November 2012 (transition period from dry to wet season) at a remote site in the Amazon rainforest, 150 km NE of Manaus, Brazil (Amazonian Tall Tower Observatory (ATTO) site). PM 2.5 was sampled with a flow rate of 2.3 m^3 h^{-1} on an INSTANT tower at a height of 42 m above ground level. For sampling TFE coated borosilicate glass fibre filters (PALLFLEX, T60A20, Pall Life Science, USA) were used. The sampling time of the filters was 12 h. The filter samples were stored at 255 K until extraction.

Estimation of the vapour pressure:

The vapour pressure of monoterpene and sesquiterpene oxidation products identified in the aerosol samples collected during the ATTO-IOP2 campaign was estimated with the model SIMPOL1 developed by Pankow and Asher (2008). The estimated vapour pressure of the terpene oxidation products is listed in Table 4.

Table 4: Classification of terpene oxidation products according to their estimated vapour pressure

Name	*Estimated vapour pressure (in Pa)*
Intermediate volatile organic compounds (IVOC) (vapour pressure >1*10^{-3})	
Pinonic acid	2.99* 10^{-3}
Caronic acid	2.99* 10^{-3}
Norketolimononic acid	1.01 * 10^{-3}
βCA198	1.09* 10^{-3}
Semi volatile organic compounds (SVOC) (1*10^{-3} > vapour pressure > 1*10^{-6})	
Ketolimononic acid	3.68* 10^{-4}
Norpinic acid	1.35* 10^{-4}
Norcarenic acid	1.35* 10^{-4}
Pinic acid	4.92* 10^{-5}
Sabinic acid	4.92* 10^{-5}
βCA200	1.80* 10^{-5}
Hydroxy pinonic acid	1.75* 10^{-5}
Hydroxy caronic acid	1.75* 10^{-5}
Hydroxy sabinonic acid	1.75* 10^{-5}
Nocaryophyllonic acid	2.33* 10^{-6}
Low volatile organic compounds (LVOC) (1*10^{-6} > vapour pressure > 1*10^{-9})	
Norcedrinic acid	8.54* 10^{-7}
Noraromadendrinic acid	8.54* 10^{-7}
Aromadendrinic acid	3.12* 10^{-7}
Cedrinic acid	3.12* 10^{-7}
Caryophyllinic acid	2.51* 10^{-7}
Hydroxy caryophyllonic	8,92* 10^{-8}
TCA	3.65* 10^{-8}
Hydroxy nocaryophyllonic acid	1.37* 10^{-8}
Hydroxy aromadendrinic acid	1.83* 10^{-9}
Hydroxy cedrinic acid	1.83* 10^{-9}

The terpene oxidation products were summarized according to their estimated vapour pressure to LVOC, SVOC and IVOC (Donahue *et al.*, 2012).

3.5.3 Hohenpeissenberg campaign

Filter samples were taken from the 28th of February 2012 till the 24th of April 2013 at the Meteorological Observatory in Hohenpeissenberg. PM 2.5 was sampled with a flow rate of 2.3 m^3 h^{-1} on a tower at a height of approximately 20 m above ground level. For sampling TFE coated borosilicate glass fibre filters (PALLFLEX, T60A20, Pall Life Science, USA) were used. The sampling time was 24 h ± 4 h. The filter samples were stored at 255 K until extraction. Further site descriptions can be found at Birmili *et al.* (2003).

4 Results and Discussion

4.1 Sythesis of reference compounds

4.1.1 Sythesis of reference compounds on preparative scale

A method was developed to synthesize caryophyllonic acid (I), nocaryophyllonic acid (III), caryophyllinic acid (IV) and two acids with molecular masses of 198 g mol^{-1} (II) and 200 g mol^{-1} (V) in a preparative scale. Starting from β-caryophyllene, five different oxidation products were synthesized. The ring opening was carried out through ozonolysis to give a mixture of caryophyllene aldehyde and caryophyllonic acid. The generated by-product β-caryophyllene aldehyde was oxidized with silver nitrate to caryophyllonic acid. This acid was processed in different ways to obtain three other oxidation products. The oxidation of the exocyclic double bond was carried out with ozone to furnish nocaryophyllonic acid and as a by-product 3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid (βCA198). The oxidation of the ketone functional group with an iodoform reaction yielded caryophyllinic acid as a major product. The latter compound was oxidized with ozone to 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid (βCA200). Figure 3 shows schematically the individual reaction steps.

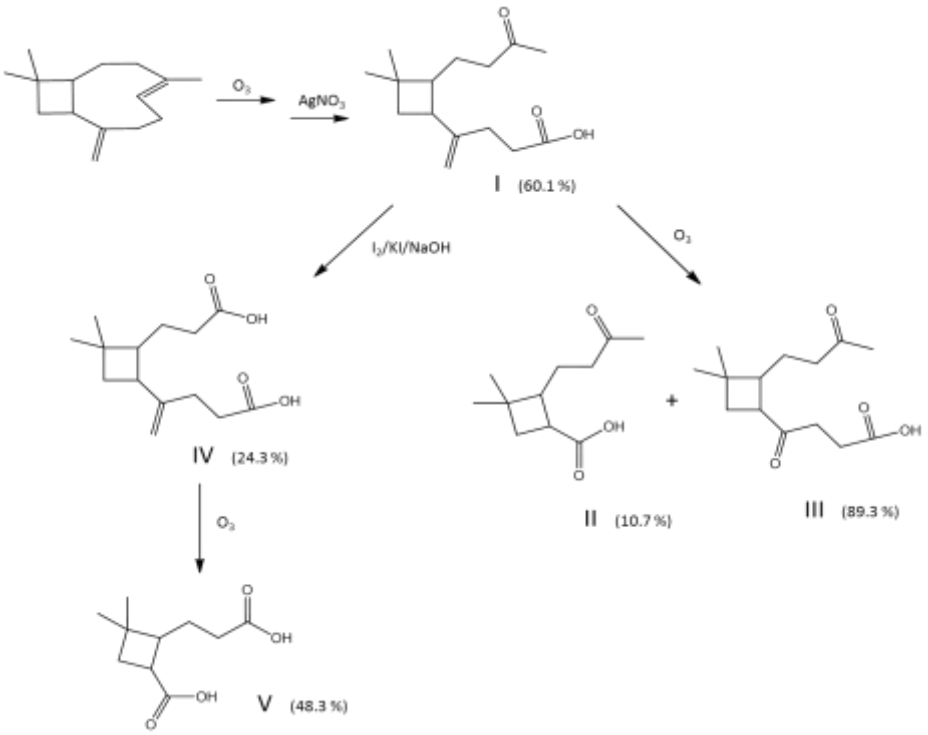


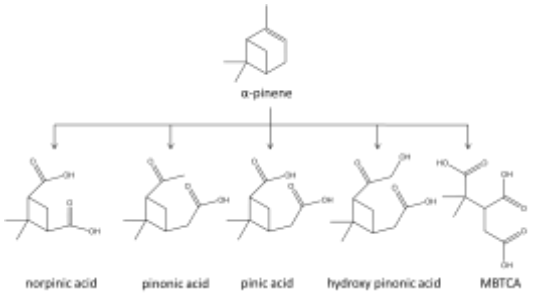
Figure 3: Schematic diagram of the reaction steps and individual yields of the products

The structures of the products were determined by ^{1}H-NMR, ^{13}C-NMR and two-dimensional NMR. The synthesized compounds were characterized with GC-MS to obtain EI spectra of the silylated compounds. The NMR data and EI spectra of the synthesized compounds are shown in Figure A1-A11 of the appendix.

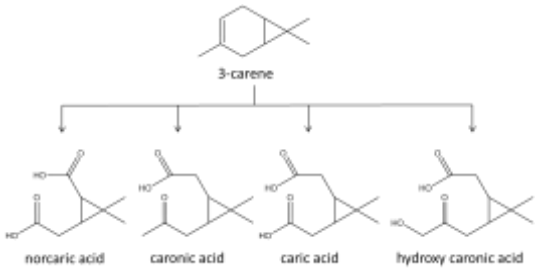
4.1.2 Sythesis of reference compounds on non-preparative scale

Six monoterpenes were analyzed for their major carboxylic acid oxidation products. Through ozonolysis of the monoterpenes in the liquid phase the carboxylic acids formed from these precursors by oxidation were determined. The suggested structure of the oxidation products was estimated through their molecular mass, their retention time at UHPLC-MS measurements and comparison to former literature suggestions.
The formed oxidation products of α-pinene are shown in Figure 4. These oxidation products were also identified as α-pinene oxidation products through ozonolysis in the gas phase from α-pinene (Jang and Kamens, 1999; Yu *et al.*, 1999; Müller *et al.*, 2012).

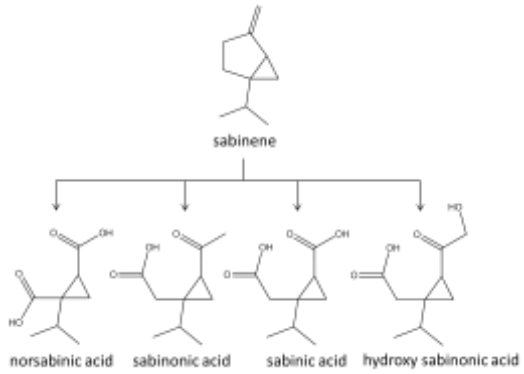
Ozonolysis of α-pinene:



Ozonolysis of Δ-3-carene:



Ozonolysis of sabinene:



Ozonolysis of limonene:

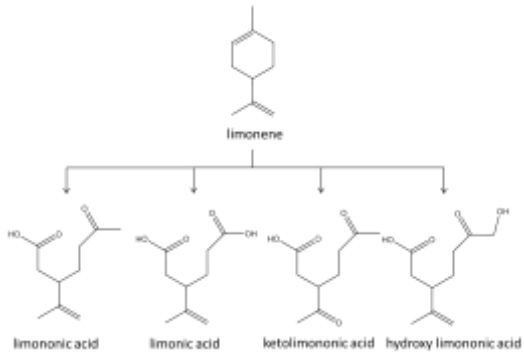
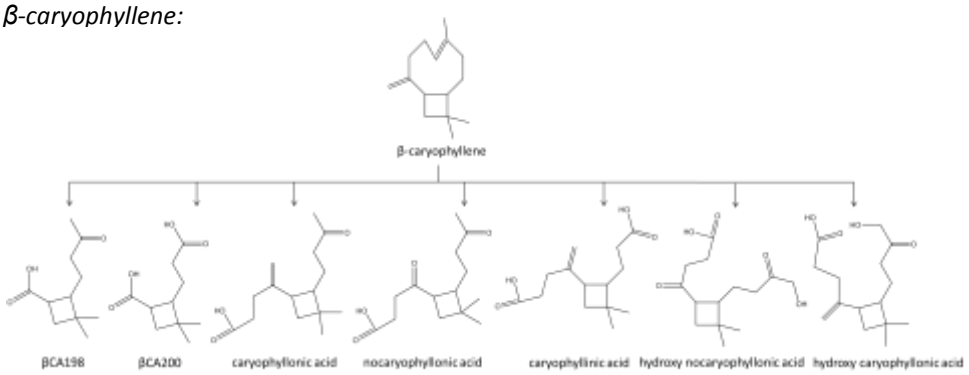
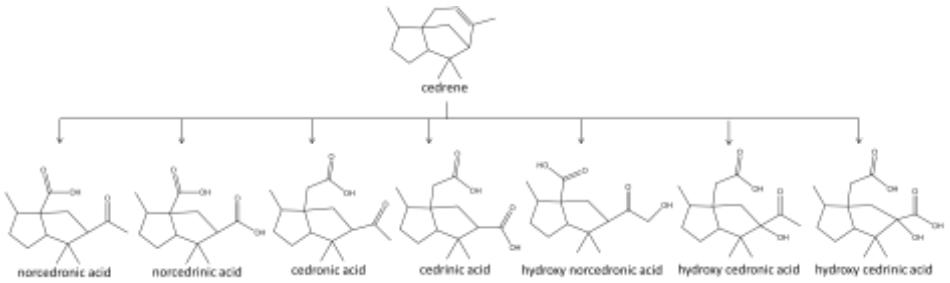


Figure 4: Oxidation products of α-pinene, Δ-3-carene, sabinene and limonene formed through ozonolysis in the liquid phase

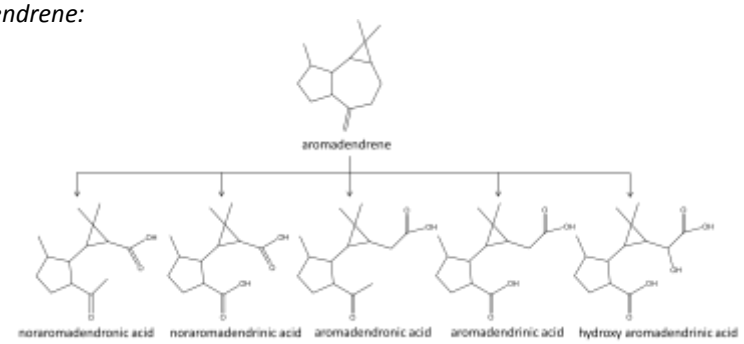
Ozonolysis of β-caryophyllene:



Ozonolysis of cedrene:



Ozonolysis of aromadendrene:



Ozonolysis of isolongifolene:

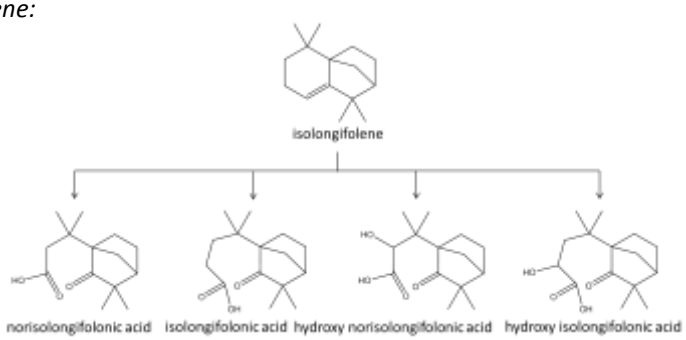


Figure 5: Oxidation products of β-caryophyllene, cedrene, aromadendrene and isolongifolene formed through ozonolysis in the liquid phase

The formed carboxylic acids from α-pinene had the same masses and retention times as the oxidation products generated by ozonolysis in the liquid phase from β-pinene, so they are listed subsequently together as pinene oxidation products.

The formed oxidation products of Δ-3-carene, sabinene and limonene ozonolysis are also listed in Figure 4. Yu *et al.* (1999) and Warscheid and Hoffmann (2001) identified the same Δ-3-carene and sabinene oxidation products and Larsen *et al.* (2001) and Warscheid and Hoffmann (2001) the same limonene oxidation products at reaction chamber experiments.

The formed oxidation products of myrcene through ozonolysis in the liquid phase were small chain acids with six or less carbon atoms. These carboxylic acids were regarded to be too unspecific to enable an exact precursor determination in ambient air samples, because the formed carboxylic acids are known to be formed by oxidation of several other hydrocarbons present in the atmosphere as well. Therefore they are not mentioned here.

Furthermore six sesquiterpenes were analyzed for their major carboxylic acid oxidation products. Through ozonolysis of the sesquiterpenes in the liquid phase the carboxylic acids formed from these precursors by oxidation were determined. The suggested structure of the oxidation products was estimated through their molecular mass, their retention time at UHPLC-MS measurements and comparison to former literature suggestions. To ensure that in the liquid phase the same oxidation products are formed through ozonolysis as in the gas phase, reaction chamber experiments with β-caryophyllene/ozone were performed to compare the generated carboxylic acids. The seven generated oxidation products of β-caryophyllene in the liquid phase were also formed in the reaction chamber experiment. On the basis of the consistency of the ozonolysis products of β-caryophyllene in the gas and liquid phase it was assumed that this consistency also relates for the other monoterenes and sesquiterpenes analyzed.

The formed oxidation products of β-caryophyllene are shown in Figure 5. Some of these oxidation products were also identified as β-caryophyllene oxidation products through ozonolysis in the gas phase from β-caryophyllene (Jaoui, Leungsakul and Kamens, 2003).

The formed oxidation products of cedrene, aromadendrene and isolongifolene are also listed in Figure 5. Jaoui, Sexton and Kamens (2004) identified four of these cedrene oxidation products at reaction chamber experiments but the remaining three cedrene oxidation products as well as the suggested structures of aromadendrene and isolongifolene oxidation products are not recorded in literature yet. Anyhow, for aromadendrene and isolongifolene there are no carboxylic oxidation product recorded in literature yet.

The formed oxidation products of α-humulene and β-farnesene through ozonolysis in the liquid phase were small chain acids with six or less carbon atoms. These carboxylic acids were regarded to be too unspecific to enable an exact precursor determination in ambient air samples, because the formed carboxylic acids are known to be formed by oxidation of several other hydrocarbons present in the atmosphere as well. Therefore they are not mentioned here.

4.2 Improvement of sample preparation

The sample preparation was optimized in order to gain a reproductive and well suited method for quantification of carboxylic terpene oxidation products in biogenic SOA filter samples. The filter extraction was performed following the description of Warnke, Bandur and Hoffmann (2006), Müller *et al.* (2008) and Reinnig *et al.* (2008). In order to avoid possible analyte losses due to long evaporation times water was precluded as extraction solvent. Furthermore three extraction steps were performed instead of two to ensure an optimum extraction rate. Four different solvents were tested as extraction solvent: Methanol, ethanol, acetonitrile and dichloromethane. Furthermore the influence of different diameters and pore sizes of the syringe filter as well as non-silylated and silylated glass extraction vessels and syringe materials on the extraction efficiency was determined.

4.2.1 Influence of extraction solvent

Four solvents were tested for extraction. Methanol and acetonitrile showed the best extraction efficiencies as can be seen in Figure 6.

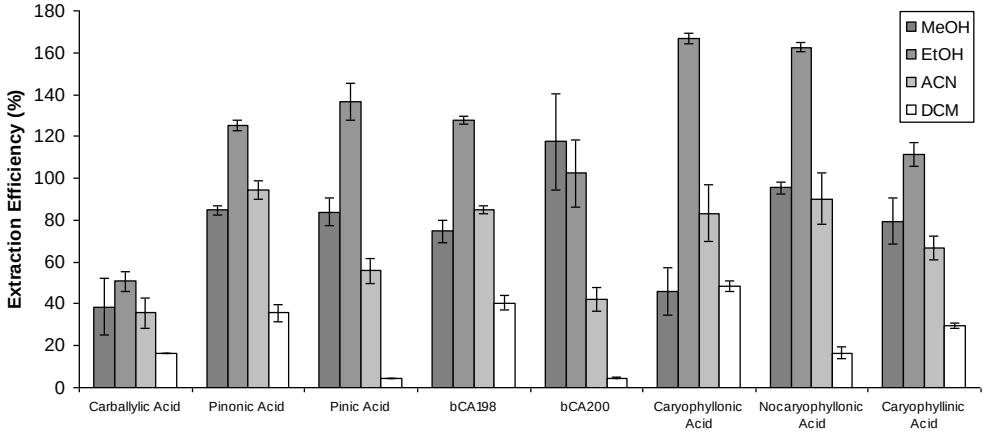


Figure 6: Influence of the extraction solvent on the extraction efficiency

Polar dicarboxylic terpene oxidation products showed high extraction efficiencies by use of methanol, whereas less polar monocarboxylic terpene oxidation products were extracted to a larger extend with acetonitrile. Ethanol showed extraction efficiencies

for some terpene oxidation products exceeding 100 %, probably due to impurities leading to a high baseline and hence high blank values. Dichloromethan showed very low extraction efficiencies of less than 50 % for each terpene oxidation product. However, the use of acetonitrile as extraction solvent in all further experiments was preferred due to its low toxicity compared to methanol and the advantage that in acetonitrile dissolved samples can be used for further GC-MS measurement without any additional evaporation and resolving of the analytes. Furthermore methanol showed high blank values for βCA198, hence leading to false and overpredicted values for this analyte. The extraction efficiency of the analytes at lower concentrations at the same order of magnitude as atmospheric air samples was tested with acetonitrile as solvent. The lower concentration of the analytes led to a drastic decrease of extraction efficiency as can be seen in Figure 7. Especially the dicarboxylic acids pinic acid, βCA200 and caryophyllinic acid showed high losses during sample preparation with extraction efficiencies about or even lower than 10 %. The decrease of the extraction efficiency is caused by the fact that with smaller concentrations small losses are more effective and severe than by use of high concentrations. One possible loss mechanism represents the use of a syringe filter, therefore in the following several diameters and pore sizes of syringe filters were tested to reduce the possible loss to a minimum.

4.2.2 Influence of syringe filter size and pore size

Three syringe filter diameter sizes were tested. The smallest syringe filter diameter of 8 mm showed the lowest extraction efficiencies due to losses during the sample preparation caused by frequent but not reproducible blockages of the syringe filter during filtering leading to leaking of the extraction solution at the plunger side at high pressures. The extraction efficiencies by use of different syringe filter diameters are presented in Figure 7.

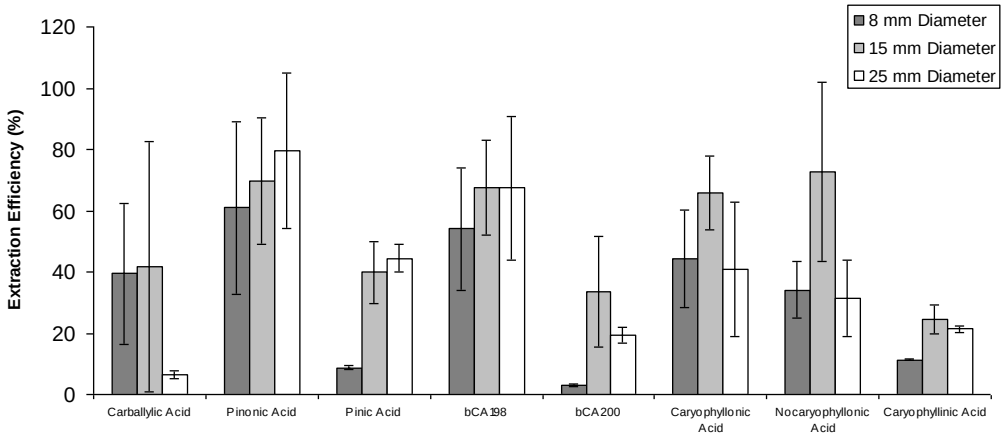


Figure 7: Influence of the syringe filter diameter on the extraction efficiency

By increasing the syringe filter surface to a diameter of 15 mm these blockages were avoided leading to higher extraction efficiencies of the analytes. By a further increase of the syringe filter diameter to 25 mm the extraction efficiencies decreased again, suggesting that possible analyte losses occur in the higher void volume of the syringe filter. With regard to the pore size of the syringe filter, a bigger pore size proved a more efficient extraction as can be seen in Figure 8. The higher extraction efficiency gained by use of a bigger pore size is again attributed to analyte losses due to syringe filter blockages at small pore sizes. Hence, the middle syringe size with a diameter of 15 mm and a pore size of 0.45 µm were chosen for further extraction. Although there has been an improvement of extraction efficiencies to almost 70 % for most of the analytes, the extraction efficieny of polycarboxylic acids still remains quite low, with values less than 50 %. Furthermore an insufficient reproducibility was achieved, represented in high standard deviations ranging between 20 and almost 100 % of the extraction efficiency itself.

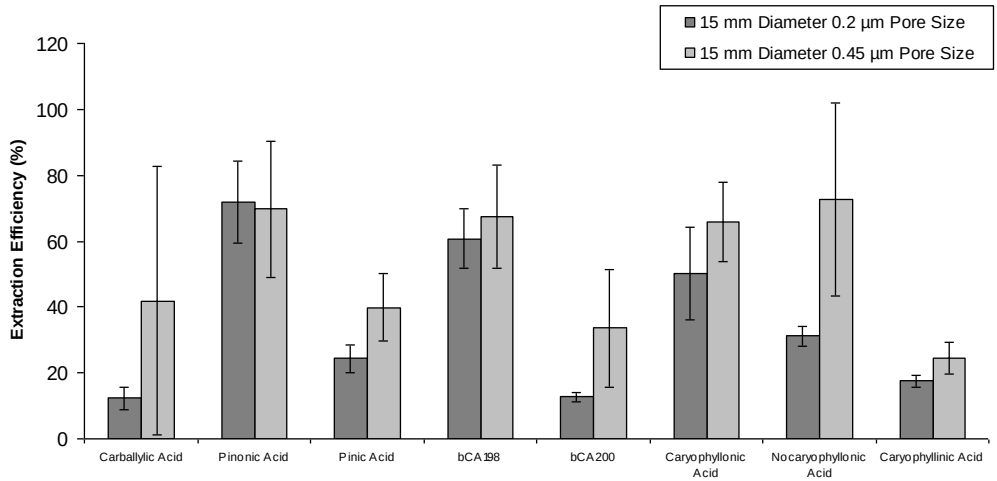


Figure 8: Influence of the syringe filter pore size on the extraction efficiency

The next step was to determine the influence of activated glass surfaces of the extraction vessel and of the syringe on the extraction efficiency.

4.2.3 Influence of the glass surfaces of the extraction vessel and the syringe

Silylation of the glass surface of the extraction vessels led to a significant increase of extraction efficiency as can be seen in Figure 9.

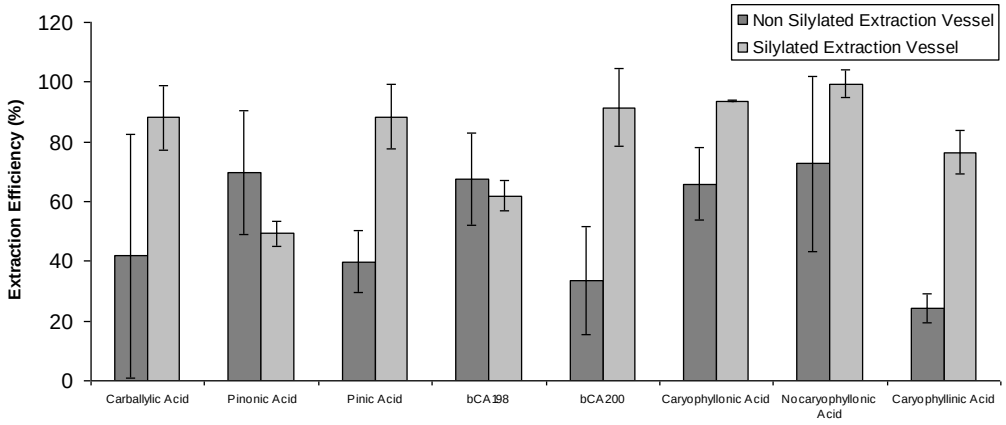


Figure 9: Influence of the extraction vessel glass surface on the extraction efficiency

Especially the extraction efficiency of the polycarboxylic terpene oxidation products increased to a high extend indicating that especially the more polar analytes are adsorbed at the activated glass surfaces leading to an insufficient extraction efficiency. Through silylation of the activated glass surface of the extraction vessel the losses of analytes are reduced drastically and the extraction procedure becomes more reproducible. Furthermore the influence of the glass surface of the syringe was determined. The extraction efficiency depending on the syringe material is shown in Figure 10.

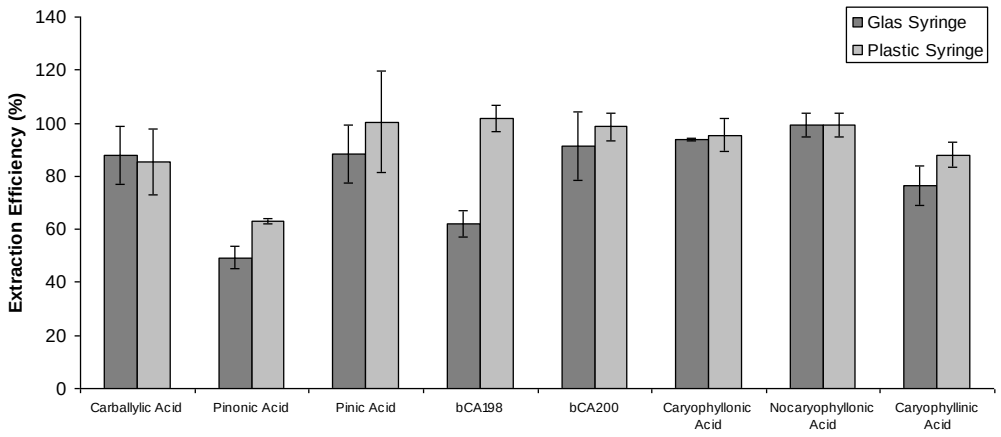


Figure 10: Influence of the syringe material on the extraction efficiency

Due to possible acitivated glass areas in the glass syringe small fractions of the analytes are adsorbed by the glass surface of the syringe. By use of a one way plastic (PE-PP) syringe the extraction efficiency of the analytes is increased because no adsorption of analytes occurs. Except from pinonic acid, a maximum extraction efficiency of all terpene oxidation products of almost 100 % is achieved and the standard deviation is decreased to less than 5 % for all analytes except from carballylic acid and pinic acid. To avoid losses due to analyte adsorption on activated glass surfaces silylated glass extraction vessels were preferred. Furthermore the use of a one-way PE-PP syringe was chosen because of better extraction efficiencies and an easier and timesaving handling. The final extraction efficiencies and standard deviations for the analytes are listed in Table 5.

Table 5: Final extraction efficiencies for terpene oxidation products

Compound	*Extraction Efficiency (%)*	*Standard Deviation (%)*
Carballylic Acid	85	12
Pinonic Acid	63	1
Pinic Acid	100	19
βCA198	100	5
βCA200	99	5
Caryophyllonic Acid	96	6
Nocaryophyllonic Acid	99	4
Caryophyllinic Acid	88	5

4.3 Reaction chamber experiments and estimation of product yields

Due to the high aerosol formation potential of sesquiterpenes (Griffin *et al.*, 1999; Jaoui, Leungsakul and Kamens, 2003; Lee *et al.*, 2006a; Lee *et al.*, 2006b; Ng *et al.*, 2006; Winterhalter *et al.*, 2009; Li *et al.*, 2011) they are assumed to play an important role in formation of secondary organic aerosol (Hallquist *et al.*, 2009). The number of studies investigating sesquiterpene oxidation mechanisms, especially the one from β-caryophyllene (Jaoui, Leungsakul and Kamens, 2003; Nguyen *et al.*, 2009; Winterhalter *et al.*, 2009) as well as the products formed through ozonolysis (Grosjean *et al.*, 1993; Calogirou, Kotzias and Kettrup, 1997; Dekermenjian *et al.*, 1999; Jaoui, Leungsakul and Kamens, 2003; Lee *et al.*, 2006b; Kanawati *et al.*, 2008; Chan *et al.*, 2011; Li *et al.*, 2011) increased significantly in the last decades. But none the less the product distribution from the ozonolysis of β-caryophyllene as well as the quantification of the oxidation products and thus the degradation mechanism of β-caryophyllene are still fraught with uncertainty.

Reaction chamber experiments of β-caryophyllene oxidation were performed at two different ozone concentrations (steady state ozone concentration when no terpene was injected into the reaction chamber was adjusted to be about 1 ppmv and 200 ppbv). The temporal evolution of the individual signal intensities measured by APCI-MS at these two concentrations is shown in Figure 11a. In both cases the signal at m/z 253, which refers to the deprotonated caryophyllinic acid or nocaryophyllonic acid or a mixture of both, shows the highest intensity at a later stage of the experiment (> 1h). For the experiment with the lower ozone mixing ratio the signal at m/z 251, which refers to the deprotonated caryophyllonic acid, represents the second highest peak, whereas in the experiment with the higher ozone mixing ratio m/z 269, which probably refers to the deprotonated hydroxy nocaryophyllonic acid (Jaoui, Leungsakul and Kamens, 2003), is the second highest signal. This observation can easily be explained since at the higher ozone concentration the equilibrium concentration of the higher oxidized products (e.g. second or third generation products) are expected to be higher. Figure 12 shows the chemical structures of some of the products, including the suggested compound hydroxy nocaryophyllonic acid.

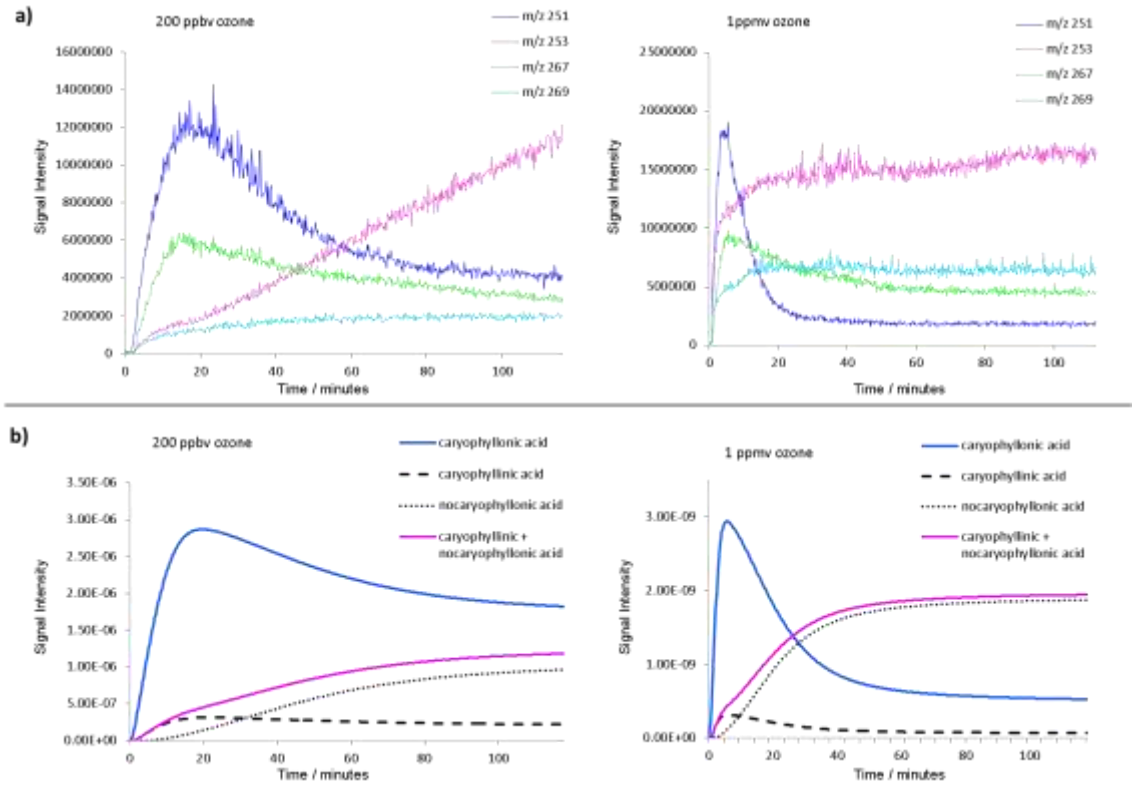


Figure 11: Temporal evolution of the main mass traces during the ozonolysis of ß-caryophyllene from the on-line-APCI-measurements (a) and evaluations from the box model CAABA/MECCA (b)

Figure 11a shows some other interesting features of the β-caryophyllene oxidation. The first compound formed is caryophyllonic acid, clearly indicated by the rapid increase of m/z 251 ($[M-H]^-$). This compound is an unsaturated and still relatively low oxidized product, which is believed to be formed as a major first generation oxidation product of β-caryophyllene. After about 20 minutes at 200 ppbv ozone or 6 minutes at 1 ppmv ozone the amount of caryophyllonic acid starts to decrease due to the further reaction to higher generation products, obviously mainly to the acid with a molecular mass of 254 g mol^{-1} (mass trace m/z 253). As mentioned above two acids (caryophyllinic and nocaryophyllonic acid) possess this molecular mass.

The same temporal behaviour can be observed in case of the acid with a molecular weight of 268 g mol^{-1} (mass trace m/z 267), which probably refers to hydroxy caryophyllonic acid. The concentration of this acid increases within the first 20 minutes (200 ppbv ozone) or 6 minutes (1 ppmv ozone) and decreases afterwards, whereas the acid with a molecular mass of 270 g mol^{-1} (mass trace m/z 269) steadily increases in concentration and slowly approaches an almost constant concentration at a later stage

of the experiment at both ozone concentrations. This indicates that the acid with a molecular weight of 270 g mol^{-1} is an oxidation product (i.e. higher generation oxidation product) of the acid with a molecular weight of 268 g mol^{-1}. Figure 12 shows the structural formula of the suggested compound hydroxy caryophyllonic acid.

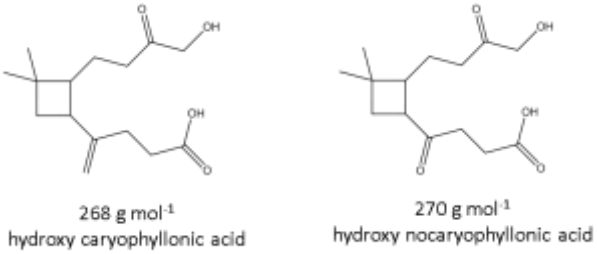


Figure 12: Structural formula of the suggested compounds with a molecular mass of 268 g mol^{-1} and 270 g mol^{-1}

With regard to the different ozone concentrations it can be observed, that with a low ozone/β-caryophyllene ratio the oxidation proceeds much slower than with a high ozone/β-caryophyllene ratio. However, the major oxidation products are the same.
Consequently, it can be pointed out, that regardless of the ozone concentration the main oxidation products from the oxidation of β-caryophyllene with ozone in the particulate phase are acids with a molecular mass of 252 g mol^{-1}, 254 g mol^{-1}, 268 g mol^{-1} and 270 g mol^{-1}. The acid with a molecular mass of 252 g mol^{-1} can be clearly identified as caryophyllonic acid. The acid with a molecular weight of 254 g mol^{-1} cannot clearly be identified since two acids can lead to the observed signal.
In Figure 11b the temporal behaviour of the acids responsible for the main mass traces at m/z 251 and m/z 253 in the APCI-MS-measurements are shown, which were calculated with the box model CAABA/MECCA. The calculated time curves of caryophyllonic acid and the sum of nocaryophyllonic acid and caryophyllinic acid show a good agreement with the on-line measured APCI-MS data. In addition, the signal at the molecular mass of 254 g mol^{-1} (the sum of nocaryophyllonic acid and caryophyllinic acid) from the box model is split up into nocaryophyllonic acid and caryophyllinic acid and reveals that the model predicts that the main compound responsible for the signal at m/z 253 is made up by nocaryophyllonic acid.

To verify the data provided by the box model calculations and to clarify which of the two acids really leads to the high measured APCI-MS signal, the filter extracts taken during the reaction chamber experiments were analyzed with HPLC-MS and compared to the synthesized standard compounds. The retention time window 19 to 27 minutes of the chromatogram of an experiment with an ozone mixing ratio of 1 ppmv is shown in Figure 13.

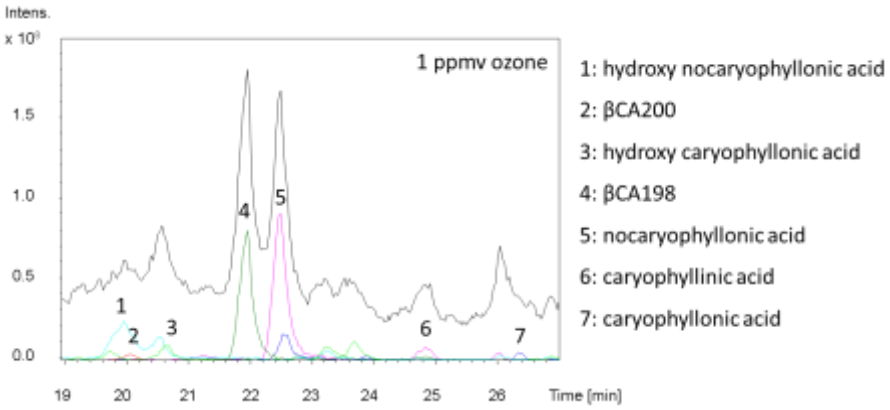


Figure 13: Chromatogram of the filter extract from a reaction chamber experiment of β-caryophyllene with 1 ppmv ozone (black line: TIC; turquoise line: EIC m/z 269; red line: EIC m/z 199; light green line: EIC m/z 267; dark green line: EIC m/z 197; purple line: EIC m/z 253; blue line: EIC m/z 251)

The black line of the TIC (total ion current) shows two major products, one with a retention time of 21.9 minutes and one with a retention time of 22.4 minutes. The dark green line shows the EIC (extracted ion chromatogram) of m/z 197. Both, the retention time and the mass-to-charge ratio of the first peak, perfectly fit with the synthesized reference compound βCA198. The purple line in Figure 13 shows the EIC of m/z 253, which represents the major mass of the chromatographic peak at 22.4 min. In this case the retention time perfectly matches with the retention time of the synthesized nocaryophyllonic acid, a result that suggests that also the mass trace at m/z 253 in the APCI-MS-measurements is caused by this compound.

The results from the HPLC-MS measurements indicate that nocaryophyllonic acid and βCA198 are the major carboxylic acid oxidation products formed during the reaction chamber experiment, however, also the compound with a molecular weight of 270 g mol^{-1}, which probably refers to hydroxy nocaryophyllonic acid and 268 g mol^{-1}, which probably refers to hydroxy caryophyllonic acid can be identified. These results fit well with the APCI-MS-measurement where three of these acids where detected as

major carboxylic acid oxidation products of β-caryophyllene at an ozone mixing ratio of 1 ppmv. However, some differences were observed concerning the masses 198 g mol^{-1} and 252 g mol^{-1}. The mass 198 g mol^{-1} which is detected in the filter extract as second highest signal was measured by the APCI-MS just in very low concentrations, whereas caryophyllonic acid which was detected by HPLC-MS in very low concentrations shows quite high abundances in the APCI-MS-measurements.

The product yields of the seven acids as estimated from the reaction chamber experiments and the estimated product yields from the box model are listed in Table 6.

Table 6: Product yields of the five synthesized acids and the acids of a molecular weight of 268 g mol^{-1} and 270 g mol^{-1} in the filter extract of a reaction chamber experiment with β-caryophyllene and α-terpinene at an ozone mixing ratio of 1 ppmv and from the box model

	Reaction chamber experiment	***Box Model*** *original MCM*	*modified MCM*
caryophyllonic acid	0.45 ± 0.08 %	0.91 %	0.91 %
nocaryophyllonic acid	6.01 ± 0.18 %	3.62 %	3.61 %
caryophyllinic acid	0.40 ± 0.10 %	0.60 %	0.17 %
βCA198	2.79 ± 0.37 %	0.77 %	0.76 %
βCA200	1.79 ± 0.13 %	-	0.04 %
m/z 267[1]	1.18 ± 0.14 %	-	-
m/z 269[2]	2.60 ± 0.23 %	-	-
Sum	**15.22 ± 1.23 %**	**5.9 %**	**5.49 %**

[1] quantified with caryophyllonic acid standard

[2] quantified with nocaryophyllonic acid standard

The product yields from the reaction chamber experiments were obtained by calculating the ratio between the amount of the different acids found in the collected aerosol and the amount of reacted β-caryophyllene in the chamber. However, for product yield calculations from reaction chamber experiments the yield has to be corrected for product losses at the chamber walls. This correction was done using α-terpinene and its carboxylic acid oxidation product with a m/z ratio of 185 (a ketocarboxylic acid) as a reference standard. This product is known to be formed in an individual product yield of 2.3 % (Lee *et al.*, 2006b) and can be assumed to show a similar physico-chemical behavior as the sesquiterpene products.

The product yields from the box model are net yields. The net yield represents the total amount of the acid which is formed during the experiment minus the amount of

acid which is lost due to further reactions. The major oxidation products regardless of the ozone concentration during the chamber experiment are nocaryophyllonic acid with a product yield of 6.01 % and βCA198 with a product yield of 2.79 % and the acid with a molecular mass of 270 g mol^{-1} with a product yield of 2.60 %. Caryophyllonic acid, caryophyllinic acid and βCA200 and the acid with a molecular mass of 268 g mol^{-1} show product yields of less than 2 %.

Comparing the product yields obtained from the experiments and from the box model with the original MCM mechanism, it can be noted, that the acids βCA200, hydroxy caryophyllonic acid and hydroxy nocaryophyllonic acid are missing in the box model. The product yields of βCA198 and nocaryophyllonic acid are underpredicted by the model, whereas the product yields of caryophyllonic acid and caryophyllinic acid are slightly overpredicted. After adding the formation of βCA200 to the mechanism the product yield of caryophyllinic acid decreases and is now also slightly underpredicted. However, the formation of βCA200 is highly underpredicted and the formation of hydroxy caryophyllonic acid and hydroxy nocaryophyllonic acid is missing in the box model. Further changes to the mechanism are needed to fit the predicted results with the experimental ones.

According to these results the acids nocaryophyllonic acid, βCA198, hydroxy nocaryophyllonic acid and βCA200 are also important carboxylic acid oxidation products of β-caryophyllene which can be used as tracers for β-caryophyllene secondary organic aerosol formation. This especially holds true for nocaryophyllonic acid because this compound shows a particular high product yield in the reaction chamber experiments, which is more than a factor of ten higher than the one from caryophyllinic acid, which is often used in previous studies as β-caryophyllene oxidation tracer (Jaoui *et al.*, 2007; Kleindienst *et al.*, 2007; Hu *et al.*, 2008; Lewandowski *et al.*, 2008; Fu *et al.,* 2009; Ding, Wang and Zheng, 2011).

4.4 Biogenic tracer compounds in boreal forest SOA

Northern boreal coniferous forest is one of the largest vegetation zones in the world and covers about 15.8 million km^2 (Archibold, 1995). It is characterized by a short vegetation time of 3-6 month, a low species diversity and large annual variations in temperature (Pott, 2005). It covers huge areas of the northern hemisphere and is an important source of BVOCs. The flora of the boreal coniferous forest is dominated by different pine and spruce species (Pott, 2005), prevalently the Scots pine which is the most widely distributed pine in the world (Critchfield and Little, 1966). The emission profile of boreal forest is often dominated by monoterpenes (Tarvainen *et al*., 2007; Rinne, Bäck and Hakola, 2009). It was found, that increasing terpene concentrations lead to a growth of atmospheric particles and that terpenes play an important role in particle growth during nucleation events in the boreal environment (Janson *et al*., 2001; Lyubovtseva *et al*., 2005; Rissanen *et al.,* 2006; Asmi *et al*., 2011), although they are not the nucleating species (Janson *et al.,* 2001; Kulmala *et al*., 2001).

Although several studies report the aerosol composition above boreal forest (Spanke *et al.*, 2001; Anttila *et al*., 2005; Kourtchev *et al*., 2006; Rissanen *et al*., 2006; Parshintsev *et al*., 2008), data about sesquiterpene oxidation products as well as monoterpene oxidation products (other than those of α- and β-pinene) in the particle phase are still rare. Because of the huge dimension of the boreal forest it is of great interest to determine the chemical composition of the formed aerosol over this vegetation zone and to clarify to which extent the aerosol composition is affected by meteorological parameters.

4.4.1 Concentrations and precursors

Fifteen different carboxylic acid monoterpene oxidation products were detected in the ambient aerosol collected during the HUMPPA-COPEC campaign 2010.

The total concentration of the monoterpene oxidation products ranged from 11 ng m^{-3} to 177 ng m^{-3}. The monoterpene oxidation products detected in the SOA collected during the field campaign are listed in Table 7.

Table 7: Monoterpene oxidation products detected in the ambient aerosol samples from Hyytiälä, Finland

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of α- and β-pinene		
Hydroxy pinonic acid[2]	200	0.16 – 8.89
MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)[3]	204	0.17 – 130.77
Norpinic acid[1]	172	0.37 – 7.00
Pinic acid	186	0.31 – 7.37
Pinonic acid	184	4.65
Sum of all acidic pinene oxidation products		***5.50 – 151.73***
Oxidation products of Δ-3-carene		
Caronic acid[2]	184	0.004 – 1.75
Caric acid[1]	186	0.05 – 7.04
Hydroxy caronic acid[2]	200	0.02 – 7.77
Norcaric acid[1]	172	0.30 – 2.59
Sum of all acidic Δ-3-carene oxidation products		***1.17 – 17.40***
Oxidation products of sabinene		
Hydroxy sabinonic acid[2]	200	0.05 – 2.94
Norsabinic acid[1]	172	0.12 – 1.68
Sabinic acid[1]	186	0.20 – 3.03
Sabinonic acid[2]	184	0.06 – 3.40
Sum of all acidic sabinene oxidation products		***0.92 – 7.65***
Oxidation products of limonene		
Ketolimonic acid[2]	186	0.67 – 2.89
Norketolimononic acid[2]	172	0.74 – 0.91
Sum of all acidic limonene oxidation products		***0.67 – 2.89***
Sum of all acidic monoterpene oxidation products		***11.30 – 177.19***

[1]quantified with pinic acid
[2]quantified with pinonic acid
[3]quantified with carballylic acid

The pinene oxidation products were most abundant in the sampled aerosols. Five pinene oxidation products were identified and their total concentration maximum was 152 ng m^{-3}. The Δ-3-carene oxidation products showed the second highest concentration of all monoterpene oxidation products, the sum of the four identified Δ-3-carene oxidation products reached concentrations up to 17 ng m^{-3}, followed by the sum of the four detected sabinene oxidation products with concentrations up to

8 ng m^{-3}.The lowest concentration in ambient aerosol was measured for the two limonene oxidation products with concentrations up to 3 ng m^{-3}. MBTCA (3-methyl-1,2,3-butanetricarboxylic acid) was the most abundant monoterpene oxidation product with concentrations of up to 130.8 ng m^{-3}. The "hydroxy monoterpenonic acids" showed the second highest concentrations, the concentration of the individual acids reached up to 8.9 ng m^{-3}, followed by the "monoterpic acids" for which the concentrations of the individual acids reached 7.4 ng m^{-3}. "Normonoterpic acid" concentrations reached a maximum of 7.0 ng m^{-3}. The lowest concentrations in the ambient aerosols were measured for the "monoterpenonic acids" with concentrations of the individual acids of up to 4.7 ng m^{-3}. These acids were detected only for a small number of days during the field campaign.

The concentrations of the monoterpene oxidation products summarized according to their precursor terpenes during the campaign are shown in Figure 14.

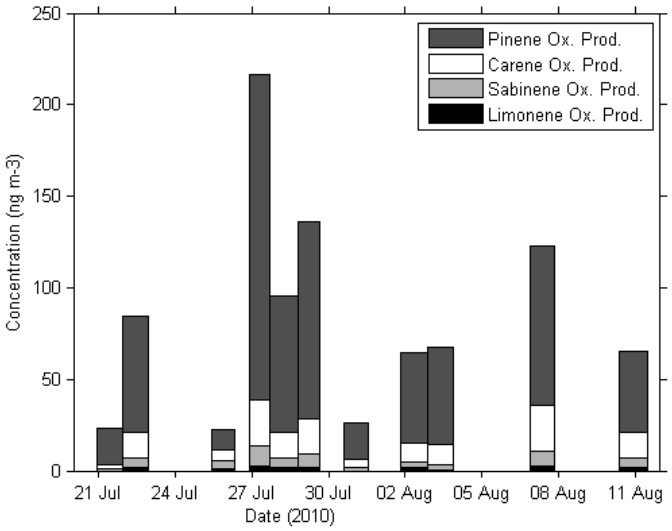


Figure 14: Concentration of the quantified monoterpene oxidation products during the field campaign summarized according to their precursor terpene

α-Pinene, β-pinene and Δ-3-carene were the most abundant VOCs measured above the canopy during the field campaign. Together they contributed more than 50 % to the total monoterpene mixing ratio (Yassa *et al.*, 2012). These observations are in agreement with the observed distribution of the monoterpene oxidation products in the particle phase. Also here the pinene and Δ-3-carene oxidation products were the most abundant monoterpene oxidation products in the particulate phase. The pinene

oxidation products were observed to be the most abundant monoterpene oxidation products in the collected aerosol, they contributed on average about 76 % to the monoterpene oxidation products. Δ-3-Carene oxidation products were the second most abundant species in the collected aerosols, contributing on average about 14 % to the total monoterpene oxidation products. Together, the oxidation products of these 3 precursor terpenes (α-pinene, β-pinene and Δ-3-carene) contributed on average about 90 % to the total monoterpene oxidation products.

Branch enclosure measurements of Scots pine and Norway spruce at the site revealed that also limonene and sabinene were emitted by vegetation, but in much smaller quantities (Yassa *et al.*, 2012). Their oxidation products could also be detected in the particulate phase but in much lower amounts than the pinene and Δ-3-carene oxidation products.

Compared to previous aerosol measurements at the SMEAR II station in Hyytiälä, Finland, the amount of pinic acid of 0.31-7.37 ng m^{-3} measured in the ambient aerosol in this study is located in the same order of magnitude as previous literature values (1-4 ng m^{-3} (Spanke *et al.*, 2001); 0.2-1.5 ng m^{-3} (Anttila *et al.*, 2005); 7-8 ng m^{-3} (Kourtchev *et al.*, 2006)). Pinonic acid was detected in just one sample of the collected aerosol during the HUMPPA-COPEC campaign 2010, but nevertheless this one value of 4.65 ng m^{-3} is also located in the same order of magnitude as values from former measurements of boreal forest SOA (1-4 ng m^{-3} (Spanke *et al.*, 2001); 0.5-3.7 ng m^{-3} (Anttila *et al.*, 2005)). With regard to norpinic acid which was measured in concentrations of 0.37-7 ng m^{-3} during the HUMPPA-COPEC campaign it should be noted that these concentrations are lower than the concentrations of 22-23 ng m^{-3} measured by Kourtchev *et al.* (2006) in SOA above the boreal forest.

Twenty sesquiterpene oxidation products were detected in the collected ambient aerosol during the HUMPPA-COPEC campaign 2010. Ten of these sesquiterpene oxidation products were present in concentrations below the limit of quantification (<0.1 pg m^{-3}): Norisolongifolonic acid, hydroxy norisolongifolonic acid, norcedronic acid, noraromadendronic acid, hydroxy cedronic acid, hydroxy norcedronic acid, hydroxy caryophyllonic acid, cedronic acid, caryophyllonic acid and aromadendronic acid. The twenty detected sesquiterpene oxidation products are listed in Table 8.

Table 8: Sesquiterpene oxidation products detected in the ambient aerosol samples from Hyytiälä, Finland

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of β-caryophyllene		
β-CA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid)	198	0.40 – 4.45
β-CA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid)	200	0.27 – 3.06
Caryophyllinic acid	254	0.02 – 0.44
Caryophyllonic acid	252	BLQ
Hydroxy caryophyllonic acid[1]	268	BLQ
Hydroxy nocaryophyllonic acid[3]	270	0.12 – 2.14
Nocaryophyllonic acid	254	0.01 – 0.63
Sum of all acidic β-caryophyllene oxidation products		***0.99 – 7.16***
Oxidation products of aromadendrene		
Aromadendrinic acid[2]	254	0.04 – 0.16
Aromadendronic acid[1]	252	BLQ
Hydroxy aromadendrinic acid[2]	270	0.05 – 2.62
Noraromadendrinic acid[2]	240	0.01
Noraromadendronic acid[1]	238	BLQ
Sum of all acidic aromadendrene oxidation products		***0.13 – 2.72***
Oxidation products of α-cedrene		
Cedrinic acid[2]	254	0.01 – 0.03
Cedronic acid[1]	252	BLQ
Hydroxy cedronic acid[3]	268	BLQ
Hydroxy norcedronic acid[3]	254	BLQ
Norcedrinic acid[2]	240	BLQ – 0.05
Norcedronic acid[1]	238	BLQ
Sum of all acidic cedrene oxidation products		***0.01 – 0.08***
Oxidation products of isolongifolene		
Hydroxy norisolongifolonic acid[3]	254	BLQ
Norisolongifolonic acid[1]	238	BLQ
Sum of all acidic sesquiterpene oxidation products		***1.24 – 9.95***

[1]quantified with caryophyllonic acid
[2]quantified with caryophyllinic acid
[3]quantified with nocaryophyllonic acid
BLQ : Below limit of quantification

The total concentration of all detected sesquiterpene oxidation products ranged from 1 ng m^{-3} to 10 ng m^{-3} in ambient air. The β-caryophyllene oxidation products showed the highest concentration of the sesquiterpene oxidation products, with total

concentrations of up to 7 ng m^{-3}. Seven β-caryophyllene oxidation products were identified. The aromadendrene oxidation products were the second most abundant sesquiterpene oxidation products. Five aromadendrene oxidation products were identified in the sampled aerosols, with a maximum total concentration of 3 ng m^{-3}. Six oxidation products of cedrene and two of isolongifolene were detected in the ambient aerosol. Their concentration was below 1 ng m^{-3} and in case of isolongifolene, the oxidation products were even too low concentrated to be quantified. The concentrations of sesquiterpene oxidation products summarized with regard to their precursor terpenes during the campaign are shown in Figure 15.

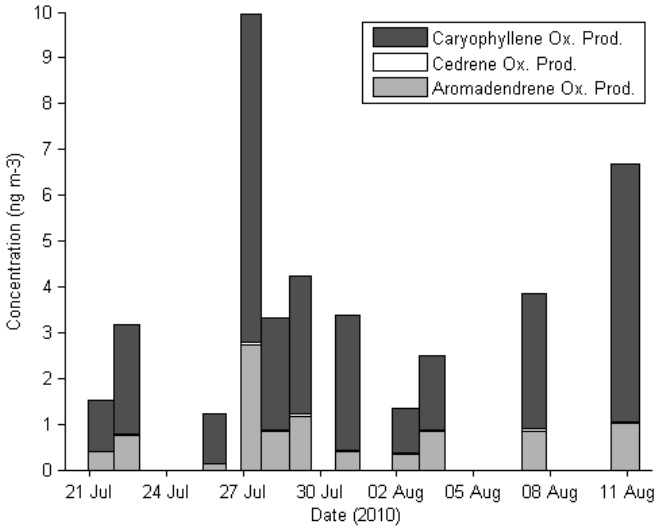


Figure 15: Concentration of the quantified sesquiterpene oxidation products summarized according to their precursor terpene during the field campaign

βCA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid) was the most abundant sesquiterpene oxidation product with concentrations of up to 4.5 ng m^{-3}. βCA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid) showed the second highest concentration, reaching a maximum of 3 ng m^{-3}. The third most abundant sesquiterpene oxidation products were the “hydroxy sesquiterpenic acids” (including hydroxy nocaryophyllonic acid) with concentrations of the individual acids of up to 2.62 ng m^{-3}, followed by the “sesquiterpenic acids” (including nocaryophyllonic acid) with concentrations of the individual acids of up to 0.63 ng m^{-3}. The lowest concentrations showed the “norsesquiterpenic acids”, with concentrations of the individual acids of up to 0.05 ng m^{-3}.

Compared to previous aerosol measurements at the SMEAR II station in Hyytiälä, Finland, the amount of caryophyllinic acid of 0.02-0.44 ng m^{-3} measured in the ambient aerosol in this study is about a factor of 100 lower than previous literature values (42-102 ng m^{-3} (Parshintsev *et al.*, 2010)).

The amount of sesquiterpene oxidation products measured in the collected aerosol from the field campaign constitutes on average 7 % and at its maximum 17 % of the mass of the monoterpene oxidation products, whereas the parent sesquiterpene mixing ratios accounted for only 1 % of the non-oxidized monoterpene mixing ratios during the time of filter sampling at the HUMPPA COPEC campaign 2010 as measured by on-line-PTR-MS. This suggests that sesquiterpene oxidation products may play a more important role in the atmospheric particulate phase than indicated by on-line-PTRMS measurements during the field campaign. Although the ratio between gas-phase monoterpenes and sesquiterpenes is quite high, this ratio is lowered by about a factor of ten with regard to their oxidation products in the particulate phase. This can be attributed to the high reactivity of most sesquiterpenes (Shu and Atkinson, 1994). They react very fast with ozone and the majority of the formed oxidation products has a low vapor pressure, so most of the oxidation products are assumed to partition mainly to the particle phase.

4.4.2 Contribution of terpenes to organic particulate matter

The contribution of the total detected monoterpene oxidation products to the total organic aerosol mass measured by the AMS ranged from 0.17 to 2.64 %.

In a previous study by Kourtchev *et al*. (2006) the sum of the α- and β-pinene oxidation products measured at the SMEAR II station in Hyytiälä, Finland, accounted for 1.4-1.5 % of the organic aerosol mass. These results are in generell agreement with the data from the HUMPPA-COPEC campaign 2010, where the sum of pinene oxidation products accounted for 0.08-2.26 % of the total organic matter.

The total contribution of monoterpene SOA to the ambient organic matter was estimated using a tracer based method proposed by Kleindienst *et al.* (2007). The tracer mass fraction factor f_{SOA} of 0.168 for α-pinene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from pinene, sabinene,

Δ-3-carene and limonene. The tracer mass fraction factor f_{SOA} is determined as the ratio of the total tracer compound concentration to the total aerosol mass formed from the precursor. From the nine α-pinene tracers used by Kleindienst *et al.* (2007) to experimentally determine the mass fraction factor f_{SOA} just pinic acid and pinonic acid were detected in this study. Since the other seven α-pinene tracer compounds were not detected in the collected aerosol, the additional tracers listed in Table 7 were used for the estimation of pinene SOA contribution. Taking into account that for each monoterpene precursor two to five oxidation products were identified in this study and used as tracer compounds whereas Kleindienst *et al.* (2007) used nine oxidation products to determine the mass fraction factor f_{SOA} for α-pinene it cannot be excluded that the estimated contribution of the monoterpene SOA in this study is partially underestimated due to missing tracer compounds. However, the estimated contribution of the monoterpene SOA of pinene, Δ-3-carene, sabinene and limonene to the total organic aerosol mass ranged between 1 and 16 % for this study.

The total concentration of all sesquiterpene oxidation products contributed 0.02 to 0.19 % to the total organic aerosol mass measured by the AMS.

The total contribution of sesquiterpenes to organic matter was also estimated using the tracer based method proposed by Kleindienst *et al.* (2007). The tracer mass fraction factor f_{SOA} of 0.0109 for β-caryophyllene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from β-caryophyllene, cedrene and aromadendrene. However, taking into account that for each sesquiterpene precursor two to five oxidation products were quantified in this study and used as tracer compounds whereas Kleindienst *et al.* (2007) just used caryophyllinic acid to determine the mass fraction factor f_{SOA} for β-caryophyllene it cannot be excluded that the estimated contribution of the sesquiterpenes to SOA in this study might be overestimated due to the additional tracer compounds. The estimated contribution of the sesquiterpene SOA of β-caryophyllene, aromadendrene and cedrene to the total organic aerosol mass ranged between 2 and 17 % and hence is on the same order of magnitude as the contribution of the monoterpene precursors.

4.4.3 Influences of forest fires in Russia and clean air masses

On the 26th-27th of July, 28th-30th of July and on the 7th-9th of August 2010 the air masses arriving in Hyytiälä came from the southeastern direction, blowing over the landmass of Russia on their way. On these days high concentrations of acetonitrile, carbon monoxide and sulfurdioxid were measured at the SMEAR II station (Williams *et al.*, 2011). These high concentrations of wood combustion markers indicated, that the air masses were influenced by forest fires which occured during that time in the Nizhny-Novgorod region of Russia. Three filter samples were taken during these events: on the 26th-27th of July, on the 28th-29th of July and on the 06th-07th of August 2010. As can been seen in Figure 14 the concentration of the monoterpene oxidation products increased significantly during these days. The concentrations measured on the 26th-27th of July and for the 28th-29th of July exceeded the ones measured on 06th-7th of August, which probably is caused by additional high temperatures during that time (a temperature maximum of 299 K and 305 K were measured during the filter sampling periods 26th-27th of July and 28th-29th of July). Also the concentration of the measured sesquiterpene oxidation products was influenced by the forest fires in Russia. The aerosol collected on the 26th-27th of July showed the biggest increase of sesquiterpene oxidation products, whereas for the filter samples taken on the 28th-29th of July and 06th-7th of August only a slight increase of sesquiterpene oxidation products was observed (see Figure 15).

However, monoterpene oxidation product and sequiterpene oxidation product concentrations were elevated in ambient aerosol influenced by forest fires. Through fire and high temperatures plant material and tree barks get destroyed and the resin containing compartments of the inner part of the plants and trees get exposed to ambient air. Therefore, high amounts of monoterpenes, sesquiterpenes and other volatile organic compounds are released into the air, where they are oxidized and partly partition into the particle phase.

On the 23rd of July 2010 a nucleation event took place at the sampling site and two days later, on the 25th of July 2010, the air masses arriving in Hyytiälä were still very clean and the ambient temperature comparably low (Williams *et. al.,* 2011). In addition, the ozone concentration on these days was low leading to a reduction of the

oxidation rate. This is also reflected by the strongly reduced amounts of monoterpene and sesquiterpene oxidation products detected in the collected aerosol from the 25th-26th of July. However, the “monoterpenonic acids”, norketolimononic acid and βCA198 constitute an exception. These five acids were measured in higher concentrations on the 25th-26th of July, indicating that these less oxidized acids are formed faster and can be found in the particle phase before the higher generation products are formed in the clean and cool air which was mainly free from secondary organic aerosol.

4.4.4 Influences of aerosol age

To investigate the influence of aerosol age on the composition of the particulate phase, the time for which the sampled air masses dwelled over land was estimated. Using the NOAA HYSPLIT model (http://www.arl.noaa.gov/ready.php) 36 hour backward trajectories were generated (see Figure B1 of the appendix) and the wind speed as well as the percentage of the trajectories over land was estimated. The trajectories stayed between 50 m and 150 m above ground level. The amount of several compounds in the aerosol phase increased significantly with the time a sampled air mass spent over land (see Figure 16). The longer the air masses dwell over land, the more terpene oxidation products accumulate in the particulate phase. Especially compounds with higher degree of oxidation and therefore with a lower vapor pressure accumulate in the particle phase, like e.g. “monoterpic acids”, “hydroxy monoterpenonic acids”, hydroxy aromadendrinic acid, hydroxy nocaryophyllonic acid and MBTCA.

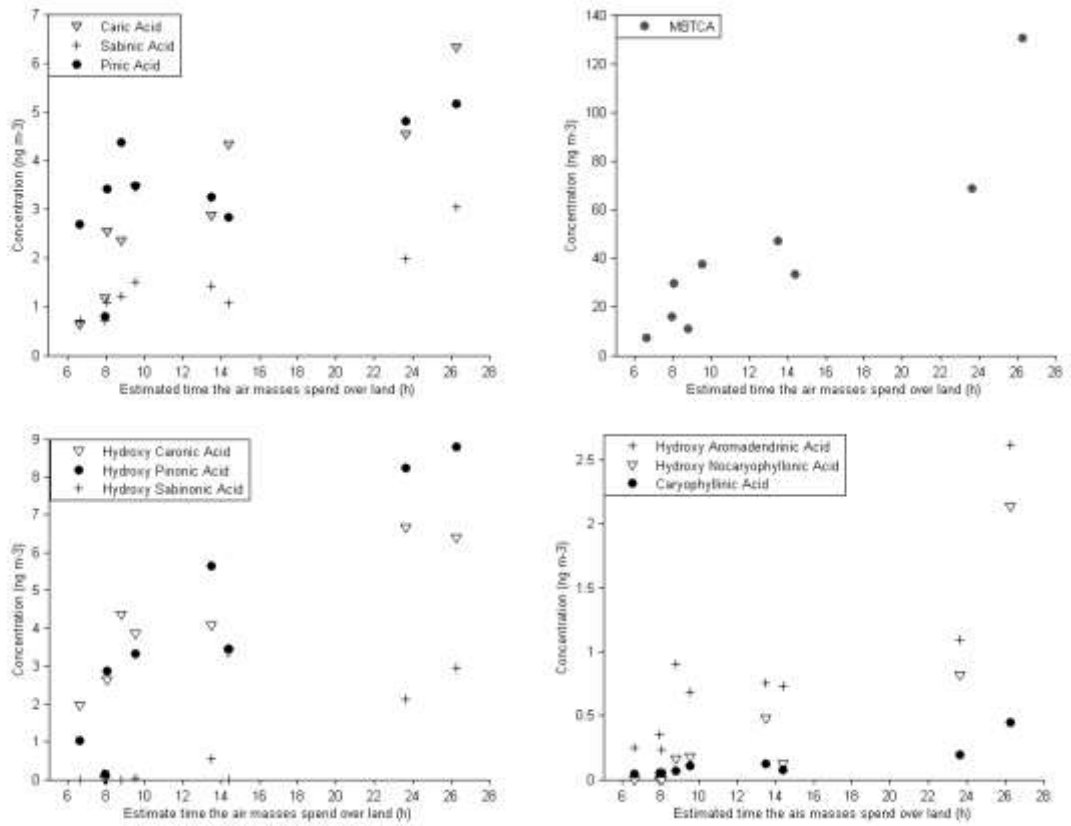


Figure 16: Concentrations of linear dicarboxylic acids and terpene oxidation products correlated with the estimated time the collected aerosol spent over land.

This is also reflected by a slight increase of the oxygen to carbon ratio of the terpene oxidation products with increasing time the traveling air masses spent over land. The oxygen to carbon ratio of monoterpene and sesquiterpene oxidation products in the particulate phase for different dwelling times of the air masses over land is shown in Figure 17.

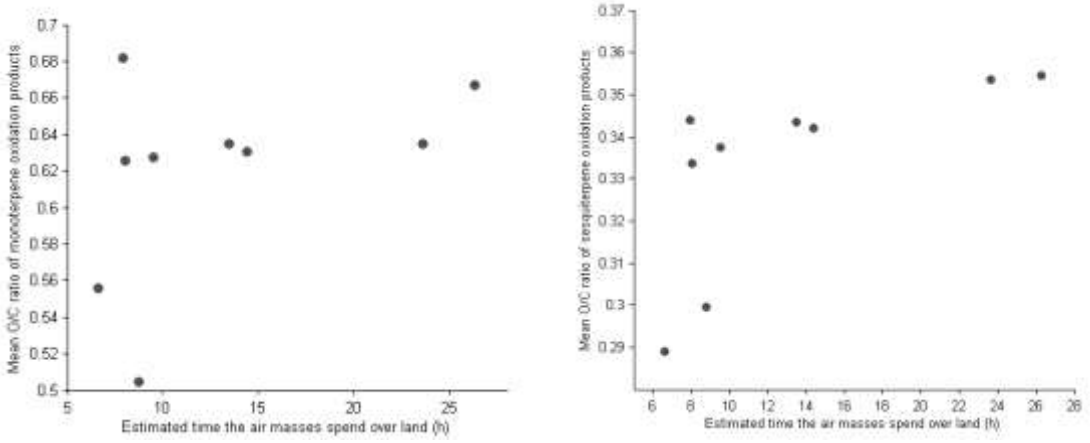


Figure 17: Oxygen to carbon ratio of mono- and sesquiterpenes correlated with the estimated time the collected aerosol spent over land.

The boreal forest represents a permanent source of terpenes and terpene oxidation products. On their way over land the air masses continuously get into contact with freshly emitted terpenes or freshly formed terpene oxidation products in the gas phase above the canopy. These compounds can partition into the particulate phase transported by the air masses. In this way, the terpene oxidation products accumulate in the particulate phase of the air masses during their transport. Volatile oxidation products present in the aerosol phase get oxidized and form low volatility compounds during transport. As a result, especially the higher oxidized compounds accumulate in the particle phase. In addition, oxidation products with lower vapor pressures reside in the particle phase in higher fractions and therefore are less prone to degradation processes like photolysis or further oxidation. However, the oxidation state of the terpene oxidation products increases slightly but not excessively, potentially due to the fact that the oxygen to carbon ratio is in general already quite high in the collected boreal forest aerosol so that the compounds present in ambient aerosol are already in a high oxidation state and hence not so susceptible for further oxidation.

4.5 Biogenic tracer compounds in Amazon rainforest SOA

The Amazon rainforest is the largest neotropical rainforest in the world and covers about seven million square kilometers (Saiter *et al.,* 2009). It is characterized by constant high temperatures and a high humidity (Archibold, 1995). The tropical rainforest is a complex ecosystem with a high diversity of plants and animals. The number of different tree species ranges between 20 and more than 200 per hectare (Pott, 2005) and it provides habitat to more than 100000 floristic species, which approximately make up 40 % of the world`s flora (Archibold, 1995). The evergreen vegetation is highly productive and therefore strongly involved into the global atmospheric chemistry (Sampaio *et al.*, 2007). Previous aerosol measurements at the Amazon rainforest revealed that the aerosol was composed to a large extent of organic carbon (Martin *et al.*, 2010). The coarse particle mode was mainly composed of primary biogenic particles (Gilardoni *et al.*, 2011; Pauliquevis *et al.*, 2012) and the fine particle mode was dominated by biogenic aerosol during wet season and by biomass burning products during dry season (Guyon *et al.*, 2004; Gilardoni *et al.*, 2011; Pauliquevis *et al.*, 2012). Measurements of the chemical composition of aerosol over the Amazon rainforest are rare. Levoglucosan (Schkolnik *et al.*, 2005; Fuzzi *et al.*, 2007; Claeys *et al.*, 2010), several mono- di- and polycarboxylic acids (Mayol-Bracero *et al.*, 2002; Falkovich *et al.*, 2005; Claeys *et al.*, 2010), as well as isoprene tracer compounds (Claeys *et al.*, 2010) were identified in the aerosol phase, whereas the contribution of high reactive compounds as monoterpenes and sesquiterpenes to SOA in this area is still unknown.

4.5.1 Concentrations and precursors

Twelve oxidation products of monoterpenes were detected in the collected aerosol from the Amazon rainforest. The total concentration of these monoterpene oxidation products ranged from 23 ng m^{-3} to 146 ng m^{-3}. The oxidation products were assigned to four precursors: pinene, limonene, sabinene and Δ-3-carene. Their concentration in ambient air during the field campaign is shown in Figure 18.

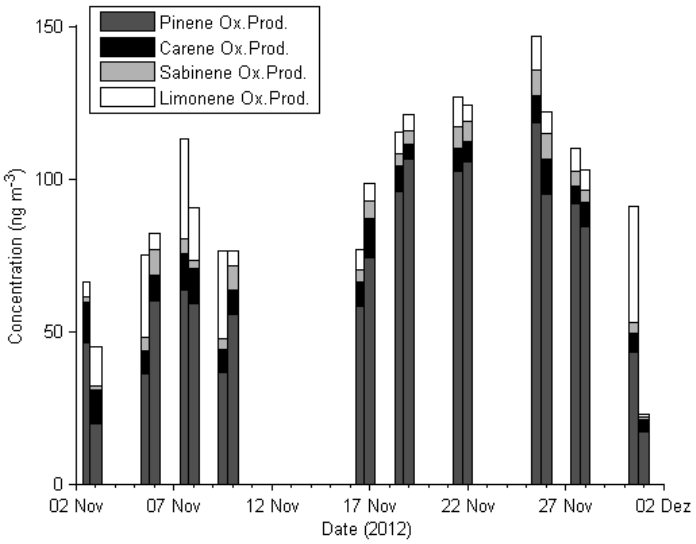


Figure 18: Concentration of monoterpene oxidation products summed according to their precursor terpene

The pinene oxidation products were most abundant in the sampled aerosols, but on some days also the concentration of limonene oxidation products was strongly increased. MBTCA (3-methyl-1,2,3-butanetricarboxylic acid) was the most abundant monoterpene oxidation product with concentrations of up to 73 ng m^{-3}, followed by pinonic acid with a maximum concentration of 46 ng m^{-3} and norpinic acid with concentrations of up to 32 ng m^{-3}. In general, the "normonoterpic acids" showed the highest concentration, followed by the "monoterponic acids" and "monoterpic acids". The lowest concentrations in the ambient aerosols were measured for "hydroxy monoterponic acids". The concentrations of all monoterpene oxidation products are listed in Table 9.

Table 9: Monoterpene oxidation products detected in the ambient aerosol samples from the Amazon rainforest, Brazil

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of α- and β-pinene		
Hydroxy pinonic acid[2]	200	0.63 – 10.24
MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)[3]	204	0.50 – 72.61
Norpinic acid[1]	172	3.72 – 31.82
Pinic acid	186	0.50 – 7.76
Pinonic acid	184	2.50 – 45.94
Sum of all acidic pinene oxidation products		***17.13 – 118.41***

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of Δ-3-carene		
Caronic acid[2]	184	0.26 – 8.81
Hydroxy caronic acid[2]	200	0.65 – 2.44
Norcaric acid[1]	172	1.28 – 9.81
Sum of all acidic Δ-3-carene oxidation products		***4.05 – 13.00***
Oxidation products of sabinene		
Hydroxy sabinonic acid[2]	200	0.22 – 1.30
Sabinic acid[1]	186	0.35 – 8.03
Sum of all acidic sabinene oxidation products		***0.57 – 8.71***
Oxidation products of limonene		
Ketolimonic acid[2]	186	0.71 – 10.98
Norketolimononic acid[2]	172	BLQ – 35.46
Sum of all acidic limonene oxidation products		***0.97 – 38.24***
Sum of all acidic monoterpene oxidation products		***22.72 – 146.48***

[1]quantified with pinic acid
[2]quantified with pinonic acid
[3]quantified with carballylic acid
BLQ: Below limit of quantification

Twenty-three oxidation products of sesquiterpenes were identified in the collected aerosol from the Amazon rainforest. The total concentration of these sesquiterpene oxidation products ranged from 6 ng m^{-3} to 12 ng m^{-3}. The oxidation products were assigned to four terpene precursors: β-caryophyllene, aromadendrene, cedrene and isolongifolene. The concentrations of the oxidation products during the field campaign are shown in Figure 19.

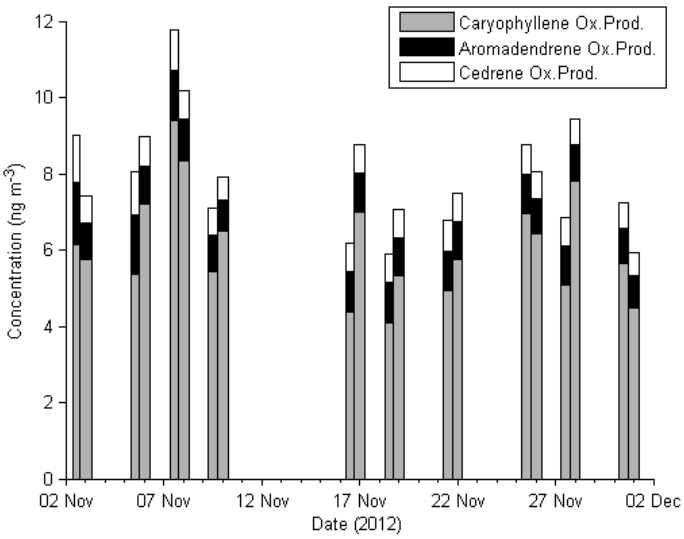


Figure 19: Concentration of sesquiterpene oxidation products summed according to their precursor terpene

The β-caryophyllene oxidation products were the most abundant sesquiterpene oxidation products in the sampled aerosols. On the filter collected on the 7th of November 2012 the highest concentration of sesquiterpene oxidation products was measured. This might be related to temperature influences, because on this day also the highest temperature during the filter sampling period of 308 K was measured.

β-CA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid) was the most abundant sesquiterpene oxidation product with concentrations of up to 7 ng m^{-3}, followed by nocaryophyllonic acid with a maximum concentration of 3 ng m^{-3} and caryophyllinic acid with concentrations of up to 1 ng m^{-3}. All other sesquiterpene oxidation products showed low concentrations in ambient air with median concentrations below 1 ng m^{-3} and in case of isolongifolene, all oxidation products were present in concentrations below the limit of quantification (<0.1 pg m^{-3}). The concentrations of all detected sesquiterpene oxidation products are listed in Table 10.

Table 10: Sesquiterpene oxidation products detected in the ambient aerosol samples from the Amazon rainforest, Brazil

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of β-caryophyllene		
β-CA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid)	198	0.69 – 6.55
β-CA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid)	200	0.12 – 0.51
Caryophyllinic acid	254	0.26 – 1.38
Caryophyllonic acid	252	BLQ
Hydroxy caryophyllonic acid[1]	268	BLQ – 0.39
Hydroxy nocaryophyllonic acid[3]	270	BLQ – 0.91
Nocaryophyllonic acid	254	0.42 – 2.56
Sum of all acidic β-caryophyllene oxidation products		***4.10 – 9.39***
Oxidation products of aromadendrene		
Aromadendrinic acid[2]	254	0.27 – 0.73
Aromadendronic acid[1]	252	BLQ
Hydroxy aromadendrinic acid[2]	270	0.22 – 0.56
Noraromadendrinic acid[2]	240	0.17 – 0.44
Noraromadendronic acid[1]	238	BLQ
Sum of all acidic aromadendrene oxidation products		***0.82 – 1.65***
Oxidation products of α-cedrene		
Cedrinic acid[2]	254	0.20 – 0.43
Cedronic acid[1]	252	BLQ
Hydroxy cedrinic acid[2]	270	0.19 – 0.40
Hydroxy cedronic acid[3]	268	BLQ
Hydroxy norcedronic acid[3]	254	BLQ
Norcedrinic acid[2]	240	0.19 – 0.39
Norcedronic acid[1]	238	BLQ
Sum of all acidic cedrene oxidation products		***0.59 – 1.22***
Oxidation products of isolongifolene		
Hydroxy isolongifolonic acid[1]	268	BLQ
Hydroxy norisolongifolonic acid[3]	254	BLQ
Isolongifolonic acid	252	BLQ
Norisolongifolonic acid[1]	238	BLQ
Sum of all acidic sesquiterpene oxidation products		***5.88 – 11.78***

[1]quantified with caryophyllonic acid
[2]quantified with caryophyllinic acid
[3]quantified with nocaryophyllonic acid
BLQ : Below limit of quantification

In general the sesquiterpene oxidation products are less present in ambient aerosol than monoterpene oxidation products. The amount of sesquiterpene oxidation products measured in the collected aerosols from the field campaign constitute on average 10 % and at its maximum 26 % of the mass of the monoterpene oxidation products. These values indicate that monoterpenes are emitted in a significant higher amount from the Amazon rainforest than sesquiterpenes. Nevertheless it has to be considered that the emission profiles of monoterpenes and sesquiterpenes from the Amazon rainforest and therefore also the composition of the aerosol formed over the Amazon rainforest might change regarding the amount and composition of terpenes during the wet, dry and transition season. Furthermore the possibility of high amounts of undetected sesquiterpene oxidation products present in ambient aerosol should not be neglected. Due to the lack of sesquiterpene emission profiles from the Amazon rainforest there are no data available about composition of the emitted sesquiterpenes. However, it cannot be excluded that probably other sesquiterpenes than the four measured in this study play a much more important role in the atmospheric chemistry of the Amazon rainforest.

4.5.2 Contribution of terpenes to organic particulate matter

Due to the lack of organic particulate matter or organic carbon measurements during the ATTO-IOP-2 campaign, values measured by Gilardoni *et al.* (2011) were used to estimate the contribution of the terpene oxidation products to the ambient organic particulate matter. The measurements of Gilardoni *et al.* (2011) were conducted in 2008 at a mostly pristine rainforest site located about 60 km NNW of Manaus, Brazil. The observed average PM 2.5 organic carbon concentrations by Gilardoni *et al.* (2011) were 2.3 µg m^{-3} during the dry and 1 µg m^{-3} during the wet season. Using the suggested factor of 1.7 by Gilardoni *et al.* (2011) the measured OC values were tranformed to organic particulate matter values of 3.91 µg m^{-3} during the dry and 1.7 µg m^{-3} during the wet season. Due to the fact that the ATTO-IOP2 campaign took place during the transition period from dry to wet season the two values obtained by Gilardoni *et al.* (2011) were averaged to obtain a mean organic matter value of 2.8 µg m^{-3}. With this values a contribution of all quantified monoterpene oxidation

products of 0.8-5.2 % (on average 3.4 %) to the total PM2.5 organic mass was estimated.

The total contribution of monoterpene SOA to the ambient organic matter was estimated using a tracer based method proposed by Kleindienst *et al.* (2007). The tracer mass fraction factor f_{SOA} of 0.168 for α-pinene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from pinene, sabinene, Δ-3-carene and limonene. The tracer mass fraction factor f_{SOA} is determined as the ratio of the total tracer compound concentration to the total aerosol mass formed from the precursor. From the nine α-pinene tracers used by Kleindienst *et al.* (2007) to experimentally determine the mass fraction factor f_{SOA} just pinic acid and pinonic acid were detected in this study. Since the other seven α-pinene tracer compounds were not detected in the collected aerosol, the additional tracers listed in Table 9 were used for the estimation of pinene SOA contribution. Taking into account that for each monoterpene precursor two to five oxidation products were identified in this study and used as tracer compounds whereas Kleindienst *et al.* (2007) used nine oxidation products to determine the mass fraction factor f_{SOA} for α-pinene it cannot be excluded that the estimated contribution of the monoterpenes to SOA in this study is partially underestimated due to missing tracer compounds. However, the estimated contribution of the monoterpene SOA of pinene, Δ-3-carene, sabinene and limonene to the total organic aerosol mass ranged from 5 to 31 % for this study.

Likewise, the contribution of sesquiterpene oxidation products to the ambient PM 2.5 organic mass was estimated. The estimated contribution of sesquiterpene oxidation products to organic particulate matter ranged from 0.2 to 0.4 % (on average 0.3 %).

The total contribution of sesquiterpenes to organic matter was also estimated using the tracer based method proposed by Kleindienst *et al.* (2007). The tracer mass fraction factor f_{SOA} of 0.0109 for β-caryophyllene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from β-caryophyllene, cedrene and aromadendrene. Taking into account that for each sesquiterpene precursor three to six oxidation products were quantified in this study and used as tracer compounds whereas Kleindienst *et al.* (2007) just used caryophyllinic acid to determine the mass fraction factor f_{SOA} for β-caryophyllene it cannot be excluded that the estimated contribution of the sesquiterpenes to SOA in this study might be

overestimated due to additionally used tracer compounds. The estimated contribution of the sesquiterpene SOA of β-caryophyllene, aromadendrene and cedrene to the total organic aerosol mass ranged from 19 to 39 % and hence is on the same order of magnitude as the contribution of the monoterpene precursors.

4.5.3 Influences of aerosol age

The field campaign can be split into two parts, from the 2nd to the 10th of November 2012 the monoterpene oxidation products in the collected ambient aerosol were dominated by intermediate volatile oranic compounds with vapor pressures above 10^{-3} Pa, whereas from the 15th of November to the 28th of November 2012 the amount of low volatile monoterpene oxidation products increaed significantly as shown in Figure 20.

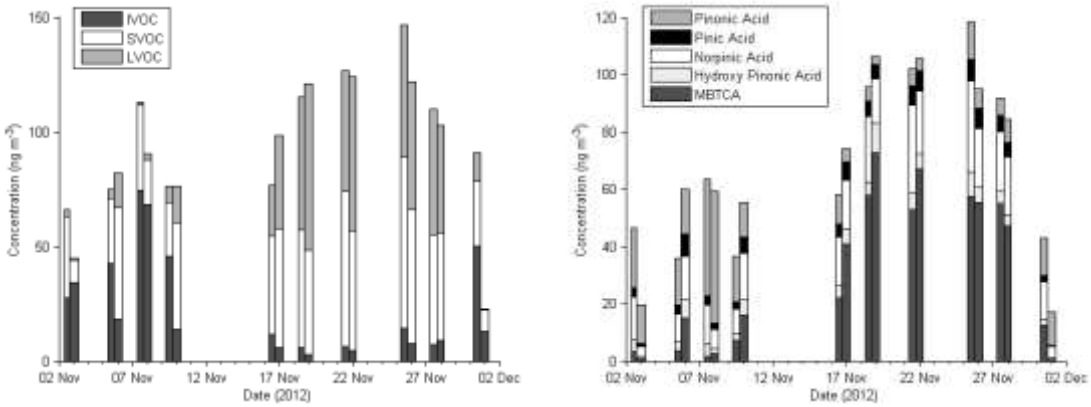


Figure 20: Concentration of monoterpene oxidation products summed according to their vapour pressure to IVOC, SVOC and LVOC (left); concentrations of pinene oxidation products during the field campaign (right)

The same behaviour is visible regarding the pinene oxidation products which were the dominating monoterpene species in the collected aerosol. During the first half of the field campaign the intermediate volatile compound pinonic acid was the most abundant pinene oxidation product whereas in the second half of the campaign the low volatile organic compound MBTCA showed the highest concentrations.

With regard to the sesquiterpene oxidation products, the same trend is visible. The first part of the field campaign was characterized by high concentrations of the intermediate volatile sesquiterpene oxidation products whereas during the second

part of the field campaign the amount of low volatile sesquiterpene oxidation products increased significantly as can be seen in Figure 21.

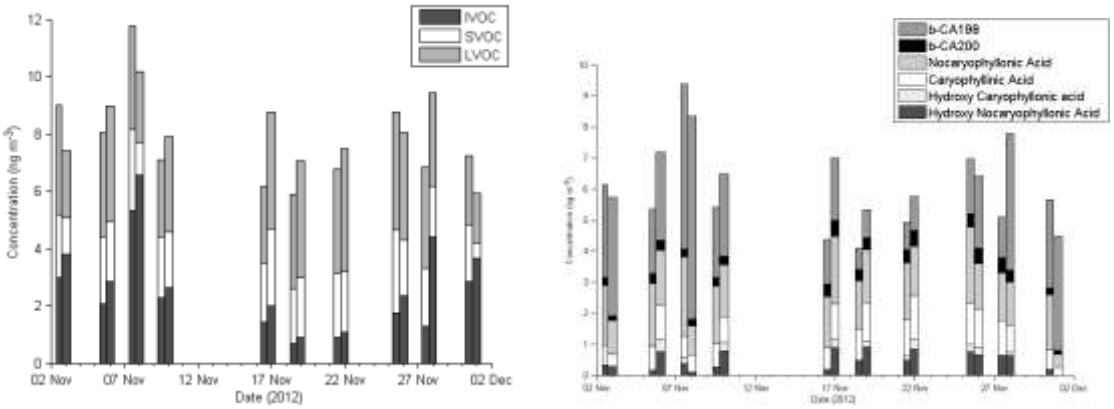


Figure 21: Concentration of sesquiterpene oxidation products summed according to their vapour pressure to IVOC, SVOC and LVOC (left); concentrations of β-caryophyllene oxidation products during the field campaign (right)

Also β-caryophyllene oxidation products, which were the dominating sesquiterpene species in the collected aerosol followed this trend. During the first half of the field campaign βCA198 was the most abundant β-caryophyllene oxidation product, whereas in the second half of the campaign the amount of βCA198 decreased significantly and the amount of caryophyllinic acid and hydroxy nocaryophyllonic acid increased slightly. Using the NOAA HYSPLIT model (http://www.arl.noaa.gov/ready.php) backward trajectories were generated (see Figure C1-C5 of the appendix) and the wind speed and the average time the air masses coming from the Atlantic spent over land, mainly rainforest, before reaching the ATTO site was estimated. During the first half of the campaign (until the 11th of November) the average wind speed was faster than during the second half of the campaign, resulting in shorter residence times of the air masses over land during the first half of the campaign (on average 5.5 days) and longer residence times during the second half of the field campaign (on average 8.5 days). The amount of several compounds in the aerosol phase increased significantly with the time a sampled air mass spent over land. Especially compounds with higher degree of oxidation and therefore with a lower vapor pressure accumulated in the particle phase. As can be seen in Figure 22 the dwelling time of the air masses over land influenced the ratio of intermediate, semi and low volatile terpene oxidation products.

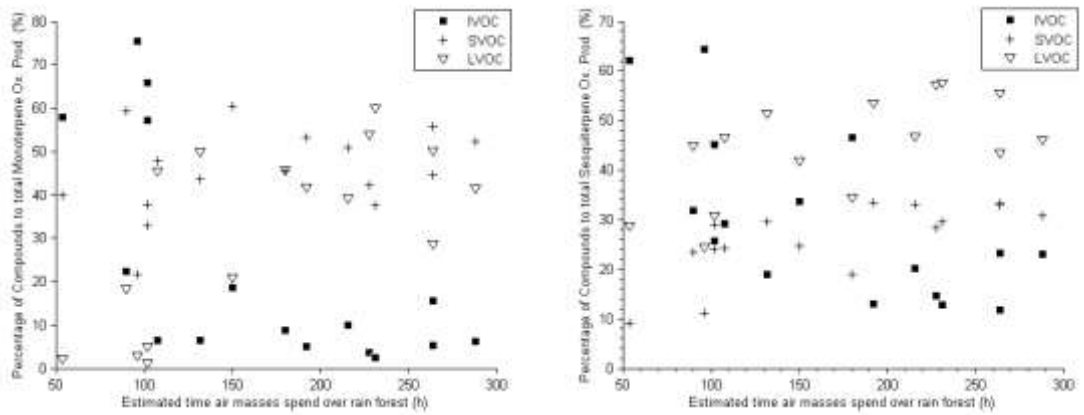


Figure 22: Concentration of monoterpene (left) and sesquiterpene (right) oxidation products classified according to their vapour pressure to IVOC, SVOC and LVOC depending on the dwelling time of the air masses over land.

A longer dwelling time of the air masses over the rainforest led to a decrease of IVOCs in the particulate phase. Due to oxidation of the particulate matter by atmospheric oxidants during the transport the IVOCs got oxidized and transformed into SVOCs and on a long term basis into LVOCs. The concentration of the SVOCs stayed more or less constant and seemed to be less affected by the dwelling times of the air masses over land. Longer dwelling times of the air masses over the rainforest led to a higher accumulation of the less volatile terpene oxidation products. Since they have a low volatility, transition from the gaseous into the particulate phase is favored and occurs to a larger extend than for intermediate or semi volatile organic compounds. In addition the transition from the particulate phase into the gas phase is low, which favors a longer stay of the low volatile terpene oxidation products in the particulate phase. These processes led to a significant accumulation of LVOCs and a decrease of IVOCs in the particulate phase at increasing dwelling times. This is also reflected by a slight increase of the oxygen to carbon ratio of the terpene oxidation products with increasing time the traveling air mass spent over land. The oxygen to carbon ratio of monoterpene and sesquiterpene oxidation products in the particulate phase for different dwelling times of the air masses over land is shown in Figure 23.

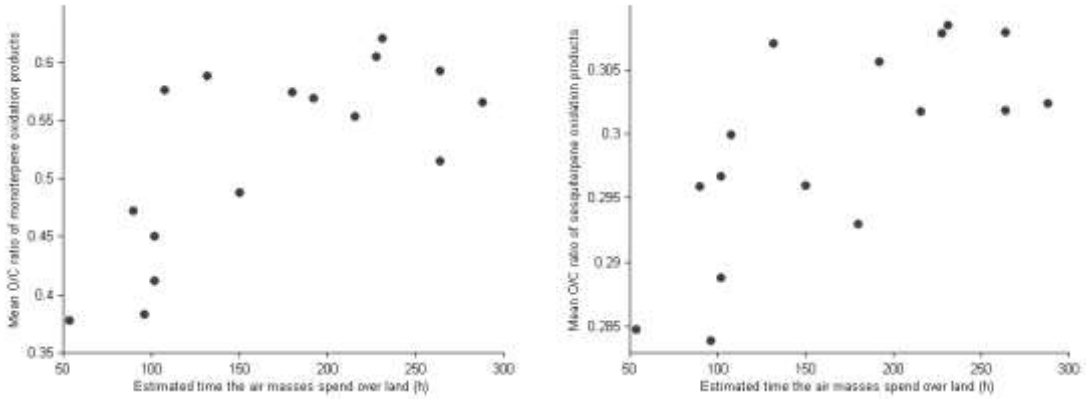


Figure 23: Oxygen to carbon ratio of monoterpene (left) and sesquiterpene (right) oxidation products correlated with the estimated time the collected aerosol spent over land.

The rainforest represents a permanent source of terpenes and terpene oxidation products. On their way over land the air masses continuously get into contact with freshly emitted terpenes or freshly formed terpene oxidation products in the gas phase above the canopy. These compounds can partition into the particulate phase transported by the air masses. In this way, the terpene oxidation products accumulate in the particulate phase of the air masses during their transport. Volatile oxidation products present in the aerosol phase get oxidized and form low volatility compounds during transport. As a result, especially the higher oxidized compounds accumulate in the particle phase. In addition, oxidation products with lower vapor pressures reside in the particle phase in higher fractions and therefore are less prone to degradation processes like photolysis or further oxidation.

4.6 Annual profile of biogenic tracer compounds in temperate mixed coniferous forest SOA

Although there have been several studies about the seasonal variation of isoprene and terpene emission (Monson *et al.*, 1994, Fuentes, Wang and Gu,1999; Hakola *et al.*, 2001; Birmili *et al.*, 2003; Hakola *et al.*, 2003; Kuhn *et al.*, 2004), data about the seasonal variation of SOA composition are rare. Annual BVOC tracer variations in SOA over the United States, Canada and Germany were measured by Kleindienst *et al.* (2007), Lewandowski *et al.* (2008), Fu *et al.* (2009), Zhang *et al.* (2009), Offenberg *et al.* (2011) and Wagener *et al.* (2012). With regard to the huge dimension of the estimated annual SOA production of 2.5 to 44.5 Tg arising from BVOC and BVOC oxidation (Tsigaridis and Kanakidou, 2003) further measurements of SOA composition and contribution of biogenic tracers to the SOA formation are needed. Moreover, measurements of the seasonal variation of SOA composition will improve annual SOA estimations and enable a more detailed determination of SOA contribution from different biogenic precursors.

4.6.1 Meteorological influences and vegetation

In Bavaria where the annual filter sampling took place about 36 % of the landmass is covered by forests. The Bavarian forest consists approximately to two third of coniferous trees and the remaining one third are deciduous trees. The dominant deciduous trees in the Bavarian forest are oak and beech trees and the dominating coniferous species are pines and spruces, with spruces being the most abundant tree species in Bavaria with approximately 44 % of the total tree population (NFI-2, 2002).
The monthly values of temperature, radiation, OH radicals and ozone concentration during the filter sampling period are listed in Table 11.

Table 11: Monthly values of temperature (T), global radiation (GR), OH radical concentration (OH) and ozone concentration during the filter sampling period

	$T_{average}$ (K)	T_{MIN} (K)	T_{MAX} (K)	$GR_{average}$ (Wm^{-2})	GR_{MAX} (Wm^{-2})	$OH_{average}$ (cm^{-3})	OH_{MAX} (cm^{-3})	$Ozone_{average}$ (ppb)	$Ozone_{MAX}$ (ppb)
Feb 2012	267	254	284	82	591	338542	5269363	32	69
Mar 2012	279	270	292	159	777	811033	5546103	38	62
Apr 2012	280	268	302	162	915	1070510	7445943	44	67
May 2012	285	273	299	244	995	1352784	8578624	52	72
June 2012	288	277	301	233	1014	1449205	7184963	47	75
July 2012	289	280	301	214	966	1446701	7759957	43	81
Aug 2012	290	280	303	231	923	1843866	8051987	48	74
Sep 2012	285	277	296	136	798	859449	7057839	37	96
Oct 2012	281	268	299	94	647	601789	4215548	26	58
Nov 2012	278	269	289	62	529	326692	2051404	28	67
Dec 2012	273	263	290	40	357	178631	1410191	32	48
Jan 2013	272	263	284	40	449	310692	3845746	23	48
Feb 2013	269	262	278	67	631	472720	3343711	33	57
Mar 2013	273	263	286	121	769	621284	4880168	40	57
Apr 2013	279	267	294	138	884	1007191	6563559	42	76

In June, July and August the average temperature reached a maximum, whereas in the period from December to March the lowest temperatures were measured. The global radiation peaked earlier: May, June, July and August were the radiation intensive months, whereas in November, December, January and February the radiation reached its minimum. Similar to radiation also the OH concentration changed during the year. The ozone concentration also had its maximum from May to August, but the minimum shifted towards the period of October to January.

4.6.2 Concentrations and precursors

The concentration of acidic terpene oxidation products identified in the collected aerosol ranged from BLQ to 24 ng m^{-3}. Thirteen terpene oxidation products were identified and quantified in the collected aerosol. The concentrations of the carboxylic terpene oxidation products are shown in Table 12.

Table 12: Terpene oxidation products detected in the ambient aerosol samples collected from February 2012 until April 2013 in Hohenpeissenberg, Germany

Acid	*M (g mol^{-1})*	*Concentration (ng m^{-3})*
Oxidation products of α- and β-pinene		
Hydroxy pinonic acid[2]	200	BLQ – 0.35
MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)[3]	204	BLQ – 13.83
Norpinic acid[1]	172	0.19 – 2.39
Pinic acid	186	0.21 – 2.69
Pinonic acid	184	0.16 – 6.19
Sum of all acidic pinene oxidation products		***1.24 – 18.58***
Oxidation products of Δ-3-carene		
Caric acid[1]	186	BLQ – 1.75
Caronic acid[2]	184	0.06 – 1.14
Norcaric acid[1]	172	BLQ – 0.37
Sum of all acidic Δ-3-carene oxidation products		***0.14 – 2.12***
Oxidation products of sabinene		
Hydroxy sabinonic acid[2]	200	BLQ – 0.44
Sabinic acid[1]	186	0.09 – 4.35
Sum of all acidic sabinene oxidation products		***0.10 – 4.79***
Oxidation products of limonene		
Ketolimonic acid[2]	186	BLQ – 0.49
Oxidation products of β-caryophyllene		
βCA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid)	198	BLQ – 0.39
βCA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutane carboxylic acid)	200	BLQ – 0.34
Sum of all acidic β-caryophyllene oxidation products		***BLQ – 0.55***

[1]quantified with pinic acid
[2]quantified with pinonic acid
[3]quantified with carballylic acid
BLQ: Below limit of quantification

The monoterpene oxidation products were most abundant in ambient aerosol. Oxidation products from four monoterpene precursors were identified in the collected aersosol, whereas with regard to the sesquiterpenes just oxidation products from β-caryophyllene were detected.

Hydroxy pinonic acid, pinic acid, pinonic acid, norpinonic acid and MBTCA (3-methyl-1,2,3-butanetricarboxylic acid) were identified as α- and β-pinene oxidation products.

The oxidation products of α- and β-pinene were the most abundant terpene oxidation products in the ambient aerosol with concentrations ranging from 1.24 ng m^{-3} to 18.58 ng m^{-3}. MBTCA and pinonic acid were the main pinene oxidation products with concentrations of up to 14 ng m^{-3} and 6 ng m^{-3}. Hydroxy sabinonic acid and sabinic acid were identified as sabinene oxidation products. The oxidation products of sabinene were the second most abundant terpene oxidation products. Caric acid, caronic acid and norcaric acid were identified as Δ-3-carene oxidation products. The lowest concentrations in ambient aerosol were measured for limonene oxidation products and β-caryophyllene oxidation products with concentrations below 0.5 ng m^{-3}. Ketolimononic acid was identified as limonene oxidation product and βCA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid) and βCA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid) were identified as β-caryophyllene oxidation products. Caryophyllinic acid which was often used as tracer for β-caryophyllene SOA in previous studies (Jaoui *et al.*, 2007; Kleindienst *et al.*, 2007; Hu *et al.*, 2008; Lewandowski *et al.*, 2008; Fu *et al.*, 2009, Ding, Wang and Zheng, 2011) was not detected in the ambient aerosol collected at Hohenpeissenberg.

During summer 2012 pinene was also the most abundant monoterpene measured in the ambient air at Hohenpeissenberg followed by sabinene and Δ-3-carene. Limonene was measured in much smaller concentrations. These observations are in agreement with the observed distribution of the monoterpene oxidation products in the particle phase. Also here, the pinene oxidation products were the most abundant monoterpene oxidation products followed by sabinene, Δ-3-carene and limonene.

4.6.3 Seasonal variations

Except from hydroxy pinonic acid, hydroxy sabinonic acid, norpinic acid and norcaric acid all detected terpene oxidation products showed a distinct annual pattern with increased concentrations during summer and decreased concentration in winter. However, the annual patterns differ strongly depending on the precursor terpene.

4.6.3.1 Elevated concentrations during spring, summer and autumn

The maximum of the total concentration of pinene oxidation products was located in late spring (May). The concentration stayed high during summer and a renewed significant increase of concentration was observed in autumn (September). The annual pattern of pinene oxidation products is shown in Figure 24.

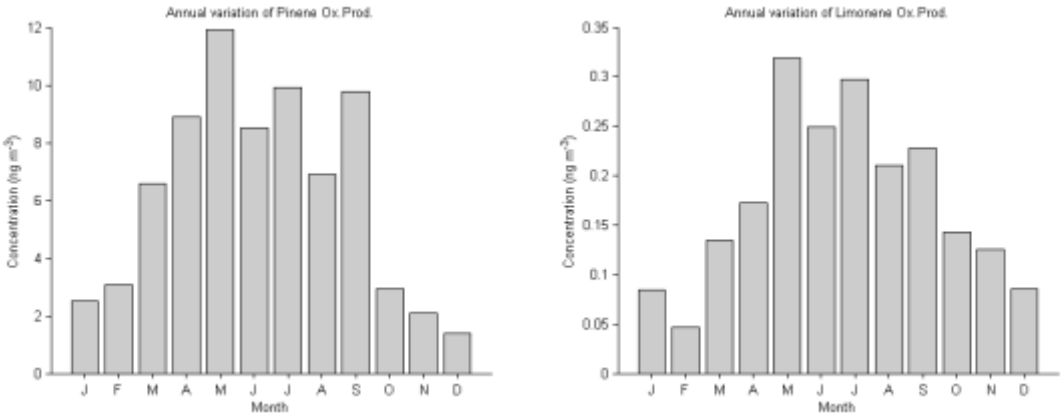


Figure 24: Annual concentration of pinene oxidation products (left) and limonene oxidation products (right)

The increase of pinene oxidation products in late spring was mainly due to an increase of pinic acid and pinonic acid, whereas the increase in autumn was mainly caused by increasing concentrations of MBTCA. Ketolimononic acid as only limonene oxidation product detected in the ambient aerosol had a similar annual pattern as the pinene oxidation products. The concentration increased significantly in May and stayed high during summer, whereas the renewed rise of ketolimononic acid in autumn was relatively weak. The annual course of ketolimononic acid is presented in Figure 24. The significant increase of pinene and limonene oxidation products in late spring is caused by increasing temperature and radiation leading to an elevated photosynthesis rate and higher emission of terpenes from coniferous trees. In addition the deciduous trees start their bud break in late spring, enabling also terpene emission from the new spread leaves. Contemporaneously also the coniferous trees sprout new shoots and the main blossom time of many trees, flowers, shrubs and grasses starts, providing another source of pinene and limonene. The concentration of pinene and limonene oxidation products stayed high during summer due to high temperatures and strong radiation leading to a more or less constant emission of pinene and limonene from

deciduous and coniferous trees. The increase of pinene and limonene oxidation products in autumn indicates that these two terpenes are also emitted by the freshly formed or ripe fruits of several coniferous and deciduous trees. Another potential source of pinene and limonene emission during autumn are the casted leafs from the deciduous trees which get metabolized by small animals and microorganisms on the forest floor leading to a destruction of the cell structure of the leaves exposing the terpene pools to ambient air. Moreover, the leaf casting itself or the connected changes in metabolism of plants and trees during autumn can also lead to an emission increase. Hakola *et al.* (2006) and Tarvainen *et al.* (2005) also measured an increase of terpene emission from Scots pine during autumn.

4.6.3.2 Elevated concentrations during spring and summer

β-Caryophyllene oxidation products showed a different annual pattern in ambient aerosol. They increased in late spring and stayed quite high during summer, but in autumn the β-caryopyhllene oxidation products were already strongly decreased. The increase in late spring was mainly caused by increased βCA200 and βCA198 concentrations, whereas the high concentrations in June were mainly triggered by high βCA198 concentrations. The annual pattern of β-caryophyllene oxidation products is shown in Figure 25.

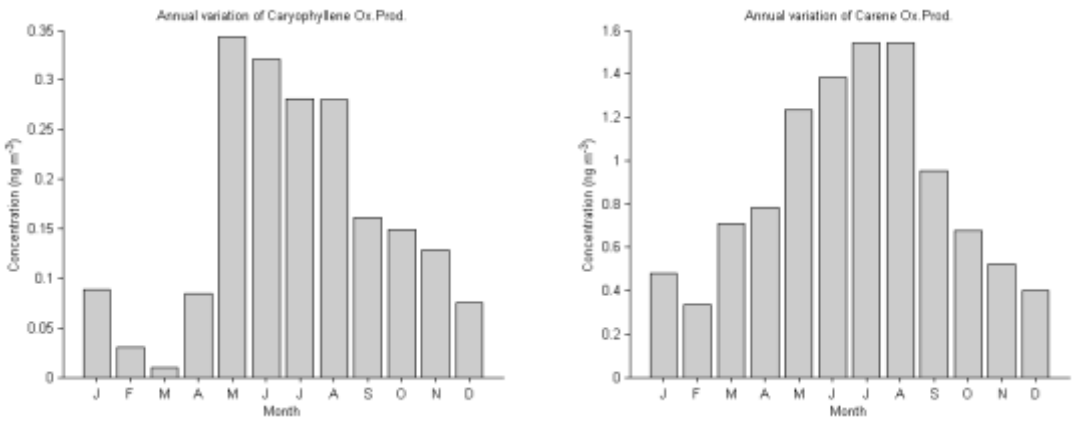


Figure 25: Annual concentration of β-caryophyllene oxidation products (left) and Δ-3-carene oxidation products (right)

A quite similar annual pattern was observed for Δ-3-carene oxidation products as shown in Figure 25. Here, the increase in late spring was triggered by caronic acid, whereas the extraordinary high concentrations in June, July and August were due to the increase of caric acid during summer.

Again, the significant increase of β-caryophyllene and carene oxidation products in late spring is caused by increasing temperature and radiation leading to a higher emission of terpenes from coniferous trees. Also the starting bud break of deciduous trees, the sprouting of new shoots from coniferous trees and the blossoming of many plant species form a new source for terpene emission from vegetation. The emission stayed high during summer and in case of Δ-3-carene also steadily increased during the summer months due to high temperatures and strong radiation leading to a more or less constant emission of β-caryophyllene and Δ-3-carene from deciduous and coniferous trees.

Δ-3-Carene oxidation products were the only identified terpene oxidation products with maximum concentrations during the summer months instead of late spring, indicating that the Δ-3-carene emission is strongly temperature dependant and therefore extraordinary high during high summer temperatures in July and August. This is also represented by a correlation coefficient of 0.95 for ambient temperature and the sum of Δ-3-carene oxidation products (see Figure D1 of the appendix).

4.6.3.3 Elevated concentrations during spring

Sabinene oxidation products showed a significant increase in late spring, during summer und autumn the concentrations decreased again. Since the concentration of hydroxy sabinonic acid showed no significant annual pattern the strong rise of sabinene oxidation products in late spring was mainly attributed to sabinic acid. The annual pattern of sabinene oxidation products is shown in Figure 26.

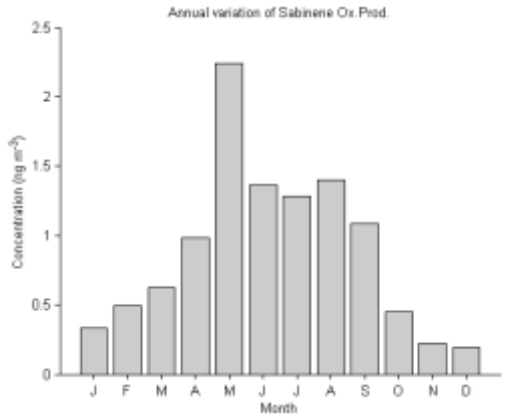


Figure 26: Annual concentration of sabinene oxidation products

The strong concentration increase in May is due to strong emissions of sabinene from the freshly formed young leaves of deciduous trees and new shoots from coniferous trees and their blooms. The fast decrease of sabinene oxidation products in summer indicates that sabinene is not emitted in high amounts from leafs every age but rather from young and freshly formed leaves leading to an extraordinary high amount of sabinene oxidation products during late spring and significant lower concentrations during summer time and autumn. A higher terpenoid emission from expanded foliage than from mature foliage was also observed by Isidorov, Zenkevich, and Ioffe (1985) and Gershenzon, McConkey, and Croteau (2000), although not explicit for sabinene. Another reason might be the radiation dependency of sabinene emission since the maximum of global radiation was also located in late spring. This dependency is represented by a correlation coefficient of 0.86 for global radiation and the concentraton of sabinene oxidation products (see Figure D2 of the appendix).

4.6.3.4 No distinct annual pattern

Four terpene oxidations products, norpinic acid, norcaric acid, hydroxy pinonic acid and hydroxy sabinonic acid showed no distinct annual pattern. Their concentrations did not increase significantly during summertime or decrease during wintertime. This indicates that small amounts of pinene, carene and sabinene are also emitted from pine trees in winter. In addition a longer residience time of terpenes and their oxidation products in ambient air is favored by low OH radical and ozone concentrations and also low precipitation during wintertime leading to a longer life of

the aerosol particles and the compounds therein. Another source of terpene oxidation products during wintertime might be the wood combustion in fireplaces and ovens performed on a large scale in rural areas of Germany. Wintertime terpene emissions were also reported in previous literature. Hakola *et al.* (2003) measured relatively high above canopy monoterpene concentrations during wintertime at the SMEAR II station in Hyytiälä, Finland. These unexpected high monoterpene values are explained by monoterpene emissions from pine species during wintertime and the longer lifetime of monoterpenes in this season due to lower levels of atmospheric oxidants.

4.6.4 Oxidation state of the aerosol components

The decrease of OH radicals and ozone in winter led to a decrease of the oxidation capacity of the lower atmosphere, influencing the oxidation state of the aerosol. During summertime when the OH radical concentration and also the ozone concentration were high, an averaged oxygen to carbon ratio of the total terpene oxidation products of 0.6 was measured. Whereas during early wintertime when the oxidation capacity of the lower atmosphere was at its lowest the oxygen to carbon ratio decreased to 0.4. This is also reflected in the distribution of the major terpene oxidation products in the collected aerosol. MBTCA and pinonic acid were the most abundant terpene oxidation products measured in the collected aerosols at Hohenpeissenberg. During summertime the amount of MBTCA was highly elevated, indicating that MBTCA as a later generation oxidation product is preferentially formed at high concentrations of atmospheric oxidants like ozone and OH radicals, whereas during wintertime the amount of pinonic acid, an earlier generation oxidation product compared to MBTCA, exceeded the amount of MBTCA due to a low concentration of atmospheric oxidants. The annual course of the two major terpene oxidation products is shown in Figure 27.

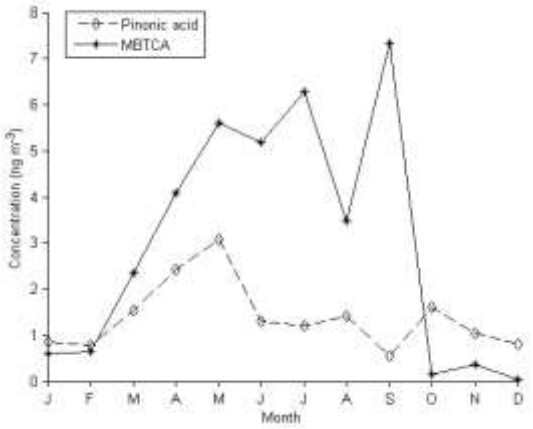


Figure 27: Annual course of MBTCA and pinonic acid

MBTCA accounted for approximately the half of all terpene oxidation products during summertime, whereas in winter the percentage of MBTCA to the total terpene oxidation products decreased to about 10 %. The concentration of pinonic acid showed an inverse behaviour: it rose from about 10 % of the total concentration of the terpene oxidation products in summer to about 30 % in the winter months.

4.6.5 Contribution of terpenes to organic particulate matter

The contribution of monoterpene and sesquiterpene oxidation products to the organic aerosol mass was estimated using a tracer based method proposed by Kleindienst *et al.* (2007). The identified acids hydroxy pinonic acid, pinic acid, pinonic acid, norpinic acid and MBTCA (3-methyl-1,2,3-butanetricarboxylic acid) were used as tracer compounds for α- and β-pinene derived secondary organic aerosol. Hydroxy sabinonic acid and sabinic acid were used as tracer compounds for sabinene derived SOA. Caric acid, caronic acid and norcaric acid were used as tracer compounds for Δ-3-carene derived SOA and ketolimononic acid was used as tracer for limonene SOA. The tracer mass fraction factor f_{SOA} of 0.168 for α-pinene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from pinene, sabinene, Δ-3-carene and limonene. The tracer mass fraction factor f_{SOA} is determined as the ratio of the total tracer compound concentration to the total aerosol mass formed from the precursor. From the nine α-pinene tracers used by Kleindienst *et al.* (2007) to experimentally determine the mass fraction factor f_{SOA} just pinic acid and pinonic acid were detected in this study. Since the other seven α-pinene tracer compounds were

not detected in the collected aerosol hydroxy pinonic acid, norpinic acid and MBTCA were used as additional tracers for pinene SOA. However, taking into account that for each monoterpene precursor one to five oxidation products were quantified in this study and used as tracer compounds, whereas Kleindienst *et al.* (2007) used nine oxidation products to determine the mass fraction factor f_{SOA} for α-pinene it cannot be excluded that the estimated contribution of the monoterpenes to organic aerosol in this study is partly underestimated due to missing tracer compounds.

The identified acids βCA198 (3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid) and βCA200 (2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid) were used as tracer compounds for β-caryophyllene derived SOA since caryophyllinic acid which is often used as β-caryophyllene tracer was not detected in the ambient air samples. The tracer mass fraction factor f_{SOA} of 0.0109 for β-caryophyllene determined by Kleindienst *et al.* (2007) was used to determine the total SOA mass derived from β-caryophyllene. Keeping in mind that Kleindienst *et al.* (2007) used caryophyllinic acid as tracer compound in the laboratory generated SOA to determine the carbon mass fraction factor f_{SOA} whereas in this study two other oxidation products of β-caryophyllene where used for the determination of the organic aerosol contribution of β-caryophyllene, deviations deriving from the use of different tracer compounds cannot be excluded. The estimated contribution of the terpene SOA to the total organic aerosol is presented in Figure 28.

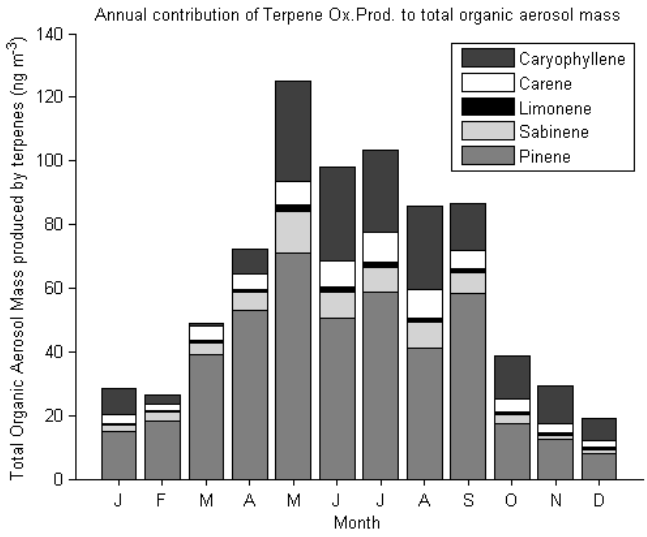


Figure 28: Contribution of terpenes to the total organic aerosol mass

The terpene SOA of pinene, Δ-3-carene, sabinene, limonene and β-caryophyllene contributed 19 to 125 ng m^{-3} to the organic particulate matter. The main contribution is provided by monoterpene SOA with monthly averages of 12-93 ng m^{-3}, whereas the sesquiterpene SOA contributed 1-31 ng m^{-3} to the total organic aerosol. Pinene SOA contributed 42-80 % to the terpene derived SOA with maxima in spring and autumn. Δ-3-carene SOA contributed 6-12 % with high values during summer. Sabinene SOA contributed 5-11 % to the terpene derived SOA with the highest contribution during late spring, whereas limonene SOA showed just small contributions of 1-3 %. β-Caryophyllene SOA was the second highest contributor to the total terpene SOA after pinene. It showed contributions from 2-40 %. Especially during summertime and in the early winter the contribution of sesquiterpene SOA was strongly increased.

During June, July and August 2012 organic particulate matter concentrations of 0.07-7.25 µg m^{-3} were measured at Hohenpeissenberg. In this time period monoterpene SOA contributed 2 to 5 % to the total organic aerosol whereas sesquiterpene SOA contributed 1 to 2 %. These values indicate that at least in the summer months mono- and sesquiterpene oxidation products are not the major contributors to organic carbon. Other compounds like isoprene oxidation products and short chain mono-, di- and tricarboxylic acids as well as anthropogenic emitted compounds and their oxidation products may play a more important role in SOA formation over Southern Germany than terpene oxidation products.

These results are in general agreement with estimations of previous literature, assuming that in densely populated and industrial areas like e.g. Germany the annual anthropogenic contribution to VOC emission can exceed the biogenic emission (Steinbrecher and Koppmann, 2007). The aerosol composition might reflect these issues and hence be less influenced by biogenic compounds like terpene oxidation products.

However, it cannot be excluded that some undetected monoterpene and especially sesquiterpene oxidation products also contribute significantly to the generated organic aerosol, but due to missing reference compounds and the limits of the used method (e.g. no detection of terpene oxidation products without any carboxylic group) were not identified in this study.

5 Conclusion and Outlook

This work investigated the role of high reactive volatile organic compounds emitted by terrestrial vegetation in aerosol formation. The contribution of monoterpene and sesquiterpene oxidation products to ambient organic aerosol formed over the boreal, temperate and tropical vegetation zone was determined.

At first, reference compounds of several monoterpene and sesquiterpene precursors were synthesized in the laboratory through preparative oxidation. Several of these synthesized compounds were used for the first time as pure substances for the unambiguous identification and quantification of biogenic SOA marker compounds. This procedure allows a reliable quantification and unmistakable assignment of the oxidation products to their precursor compounds. In addition analytical steps, such as sample preparation or chromatographic separation, were optimized.

Atmospheric simulation experiments were conducted in a reaction chamber to study the degradation pathway of β-caryophyllene. For the first time product yields of several acidic β-caryophyllene oxidation products were determined experimentally by quantification with authentic standard compounds. By application of the atmospheric chemistry box model CAABA/MECCA expected product yields were compared to experimental determined values. To do so, the reaction schemes within an existing chemical mechanism were extended by specific sesquiterpene reactions and products. The experiments and model runs showed that other acids than caryophyllinic acid which was often used as tracer in previous studies (Jaoui *et al.*, 2007; Kleindienst *et al.*, 2007; Fu *et al.*, 2009; Ding, Wang and Zheng, 2011) are the dominating carboxylic acid oxidation products in the particulate phase formed from the ozonolysis of β-caryophyllene. Furthermore, several discrepancies and gaps in the assumed degradation pathway of β-caryophyllene were revealed.

Aerosol samples representative for boreal forest environment were collected at the SMEAR II station in Hyytiälä, Finland during the HUMPPA-COPEC campaign summer 2010, and samples representative for the tropical rainforest environment were collected over the Amazon basin 150 km NE of Manaus, Brazil during the ATTO-IOP-2

campaign November 2012. Furthermore aerosol samples were taken over a period of 14 month from February 2012 until April 2013 at a rural site in Germany mainly covered by temperate mixed coniferous forest.

The concentration of the carboxylic terpene oxidation products in the collected ambient aerosol from the boreal and the tropical vegetation zone ranged between a few and several hundred nanogramms per cubicmeter. The concentrations of the monoterpene oxidation products in the particle phase collected over the temperate vegetation zone were decreased tenfold compared to the boreal and tropical aerosol samples, whereas the sesquiterpene oxidation products even showed a hundredfold decrease in concentration. However, the monoterpene oxidation products were the dominating terpene species in the collected aerosol from all three vegetation zones. They accounted on average for 98 % of the total mass of the detected terpene oxidation products in the temperate mixed coniferous forest aerosol samples, whereas their contribution in boreal aerosol samples accounted for 93 % and in aerosol samples collected over the Amazon rainforest for 91 %.

Although the sesquiterpene oxidation products show a minor contribution with regard to the total mass of the detected terpene oxidation products, the estimated contribution of the sesquiterpene SOA to the total organic aerosol mass increases significantly. Using the mass fraction factor f_{SOA} determined by Kleindienst *et al.* (2007) monoterpene SOA contributed for up to 16 % and sesquiterpene SOA for up to 17 % to ambient organic particulate matter in boreal forest environment. In tropical rainforest environment the contribution was even higher and accounted for up to 31 % and 38 % of the total organic aerosol mass. In the temperate vegetation zone the contribution to the total organic matter accounted for 5 % in case of monoterpene SOA and 2 % in case of sesquiterpene SOA, indicating that there is no strong biogenic influence on aerosol formation in southern Germany but rather mainly anthropogenic dominated particulate matter.

In all aerosol samples oxidation products from pinene, Δ-3-carene, sabinene, limonene and β-caryophyllene were identified. The aerosol samples collected over boreal forest and tropical rainforest environments also showed oxidation products from aromadendrene, cedrene and isolongifolene. In general the diversity of terpene oxidation products in the collected aerosols from the temperate zone was very low

and apart from β-caryophyllene oxidation products no other sesquiterpene oxidation products were identified. Pinene oxidation products were the most dominant monoterpene products and β-caryophllene oxidation products the most abundant sesquiterpene products in all three vegetation zones. Besides pinene oxidation products also Δ-3-carene oxidation products played a major role in the aerosol collected over boreal forest environment, whereas high concentrations of sabinene oxidation products were detected in the collected aerosol from the temperate zone and high limonene oxidation product concentrations were detected in the rainforest aerosol. Several of the detected terpene oxidation products were dentified and quantified in ambient aerosol for the first time.

Also the oxidation state of the terpene oxidation products varied in the different vegetation zones. In boreal forest aerosol the average oxygen to carbon ratio was 0.6 for monoterpene and 0.3 for sesquiterpene products. MBTCA, hydroxy pinonic acid and pinic acid were the most abundant monoterpene oxidation products and βCA198, βCA200 and hydroxy nocaryophyllonic acid were the most abundant sesquiterpene oxidation products. In tropical rainforest aerosol the oxygen to carbon ratio for monoterpene products was lower and amounted on average 0.5, the ratio for sesquiterpene products was also 0.3. MBTCA and pinonic acid were the most abundant monoterpene oxidation products and βCA198 and nocaryophyllonic acid the most abundant sesquiterpene oxidation products. The oxygen to carbon ratio in the aerosol samples collected at the temperate mixed coniferous forest showed an average value of 0.5 for monoterpene and 0.3 for sesquiterpene products, whereas this ratio as well as the oxidation state of the terpene oxidation products showed a distinct annual pattern. During summertime the ratio increased and MBTCA as a later generation oxidation product was the most abundant terpene oxidation product in the collected aerosol due to high concentrations of atmospheric oxidants. Whereas in winter the ratio was lower and the concentration of pinonic acid, an earlier generation oxidation product compared to MBTCA, exceeds the amount of MBTCA due to a low concentration of atmospheric oxidants and due to the lower temperature leading to an increased partition of low oxidized compounds into the particle phase and hence a reduced processing of these compounds in the gas phase.

The particulate phase over the boreal forest environment was influenced by forest fires. Significant increases in terpene oxidation product concentrations were observed in airmasses influenced by biomass burning. Furthermore the wind speed changed the particle composition over boreal as well as tropical forest environments. Longer residence times of the air masses over forested areas led to an increase of terpene oxidation products. In addition, aerosol aging processes occured during the transport of the aerosol due to atmospheric oxidants present in the ambient air, increasing the oxidation state of the compounds present in the particle phase.

In the aerosol samples collected at the temperate mixed coniferous forest a significant annual pattern with a strong increase during late spring was observed for most terpene oxidation products. Increasing temperatures and radiation during late spring as well as the starting bud break and blossoming lead to an elevated emission of terpenes from coniferous and deciduous trees.

The proofed seasonality of terpene emission reveals that more measurements of seasonal changes in aerosol composition are needed to investigate the exact role of biogenic and anthropogenic precursors in aerosol formation throughout the year, since vast changes in composition are likely. In addition, more measurements in various vegetation zones are essential to estimate the contribution of biogenic and anthropogenic emissions to aerosol formation on global scale as also here vast differences in biogenic contribution to aerosol formation were noted in the diverse ecosystems. Furthermore a simultaneous determination of hemi- and diterpene oxidation products as well as oxidation products of other biogenic emitted precursors seems useful besides the detection of mono- and sesquiterpene oxidation products in order to achieve a better and broader picture of biogenic secondary organic aerosol formation and its regional and global influences.

Acknowledgments

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Appendix

A Synthesis of reference compounds

The measured ^{1}H-NMR and ^{13}C-NMR data are presented in Figure A1-A10 with an assignment of the signals listed below the figures.

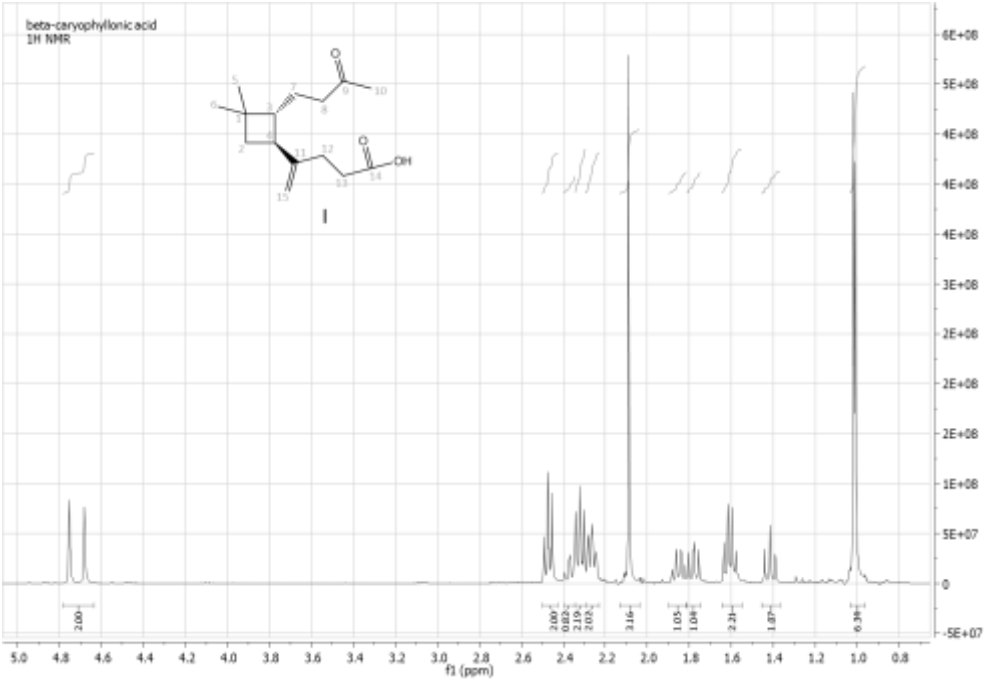

Figure A1: ^{1}H-NMR of caryophyllonic acid (I)

^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 4.77 (s, 1H, H_{15}), 4.70 (s, 1H, H_{15}), 2.52 - 2.45 (m, 2H, H_{13}), 2.42 – 2.25 (m, 5H, $H_{4,8,12}$), 2.13 (s, 3H, H_{10}), 1.91 – 1.83 (m, 1H, H_3), 1.83 – 1.77 (m, 1H, H_2), 1.67 – 1.58 (m, 2H, H_7), 1.44 (t, 1H, $^{3}J_{HH}$ = 10.2 Hz, H_2), 1.05 – 1.00 (m, 6H, $H_{5,6}$)

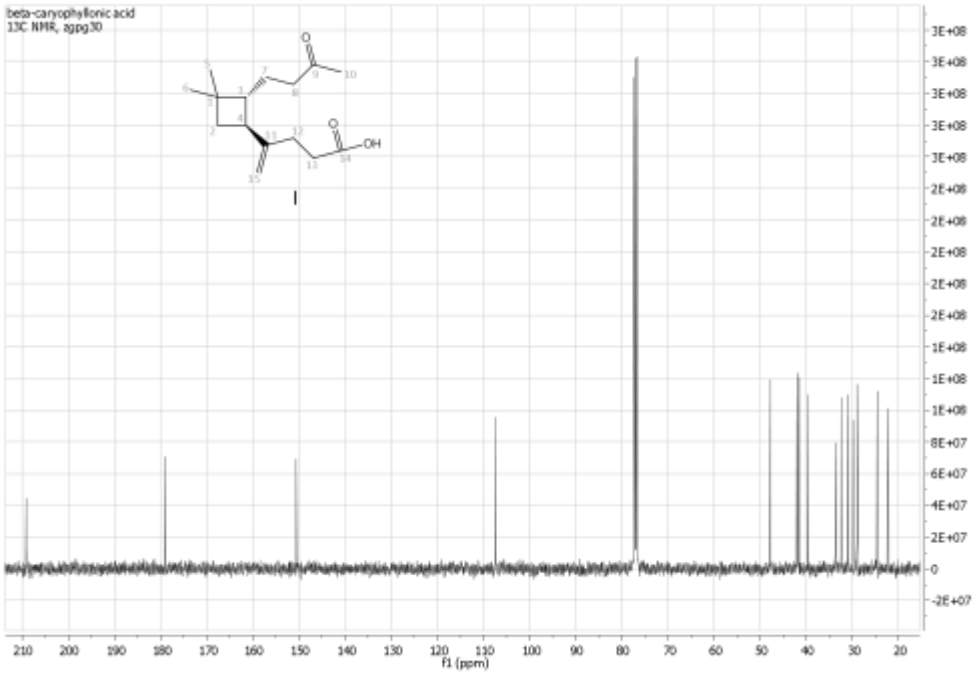

Figure A2: ^{13}C-NMR of caryophyllonic acid (I)

^{13}C NMR, HSQC (100 MHz, $CDCl_3$): δ = 209.1 (C_9), 179.1 (C_{14}), 150.6 (C_{11}), 107.4 (C_{15}), 47.8 (C_3), 41.9 (C_8), 41.6 (C_4), 39.7 (C_2), 33.6 (C_1), 32.4 (C_{13}), 31.0 ($C_{5,6}$), 29.9 (C_{10}), 28.9 (C_{12}), 24.6 (C_7), 22.3 ($C_{5,6}$)

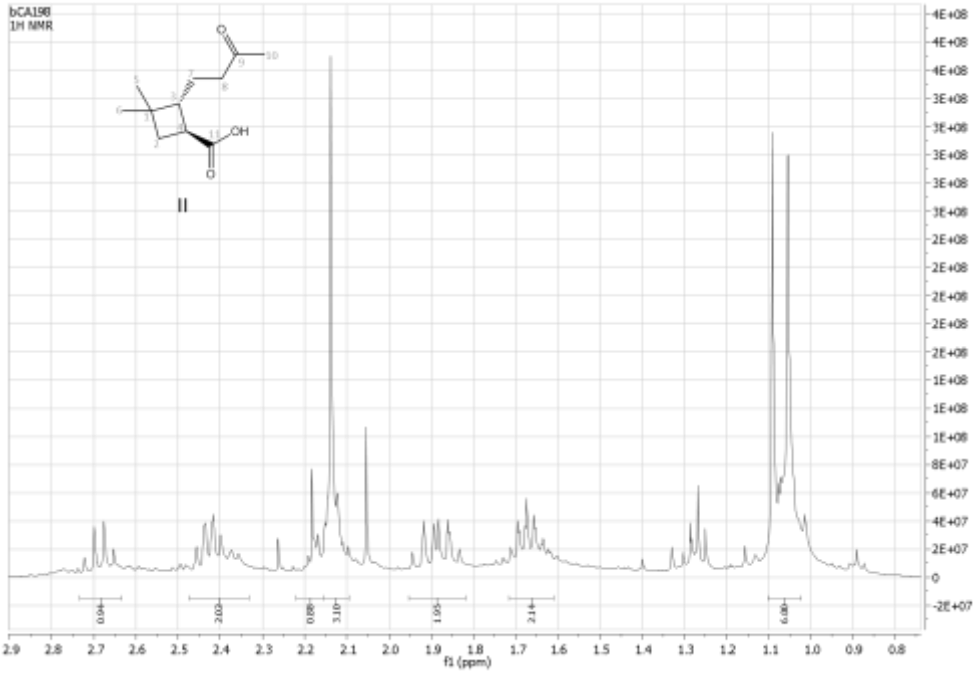

Figure A3: ^{1}H-NMR of βCA198 (II)

^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 2.71-2.62 (m, 1H, H_4), 2.46-2.32 (m, 2H, H_8), 2.19-2.14 (m, 1H, H_3), 2.12 (s, 3H, H_{10}), 1.94-1.80 (m, 2H, H_2), 1.70-1.59 (m, 2H, H_7), 1.12-0.99 (m, 6H, $H_{5,6}$)

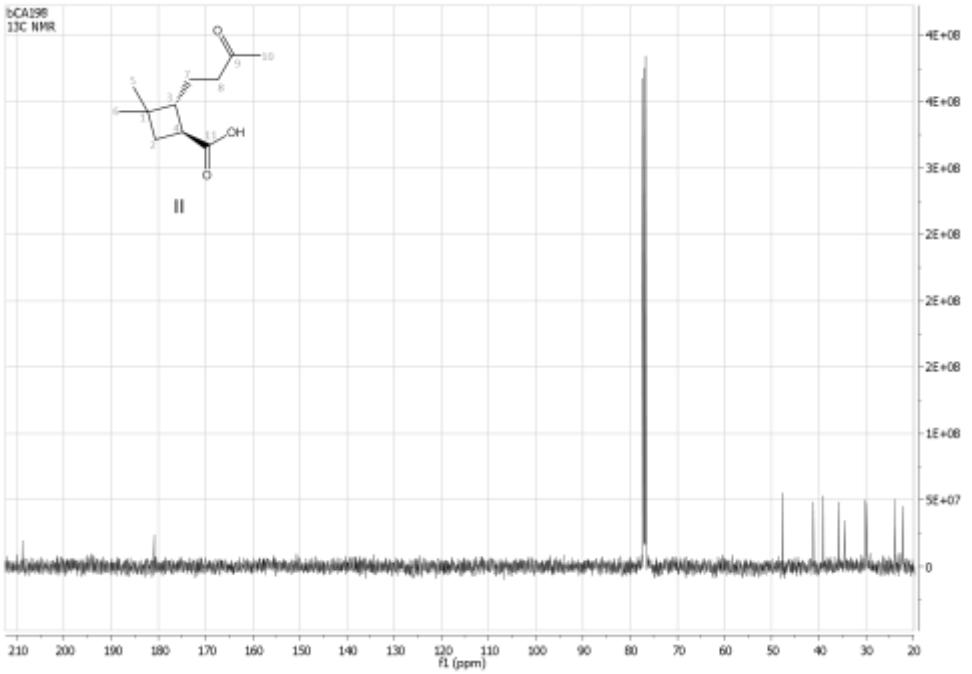

Figure A4: ^{13}C-NMR of βCA198 (II)

^{13}C NMR, HSQC (100 MHz, $CDCl_3$): δ = 208.8 (C_9), 180.9 (C_{11}), 47.7 (C_3), 41.2 (C_8), 39.2 (C_4), 35.9 (C_2), 34.5 (C_1), 30.1 ($C_{5,6}$), 29.9 (C_{10}), 23.9 (C_7), 22.3 ($C_{5,6}$)

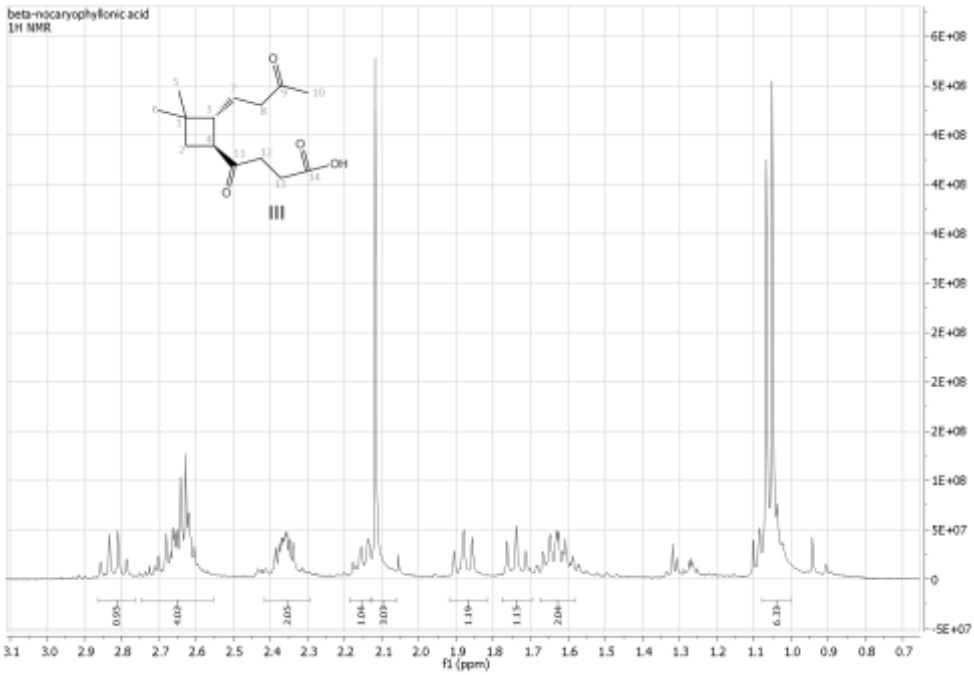

Figure A5: ^{1}H-NMR of nocaryophyllonic acid (III)

^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 2.81 (q, 1H, $^{3}J_{HH}$ = 9.3 Hz, H_4), 2.73-2.54 (m, 4H, $H_{12,13}$), 2.39-2.28 (m, 2H, H_8), 2.17-2.11 (m, 1H, H_3), 2.10 (s, 3H, H_{10}), 1.90-1.82 (m, 1H, H_2), 1.76-1.68 (m, 1H, H_2), 1.66-1.56 (m, 2H, H_7), 1.06-1.01 (m, 6H, $H_{5,6}$)

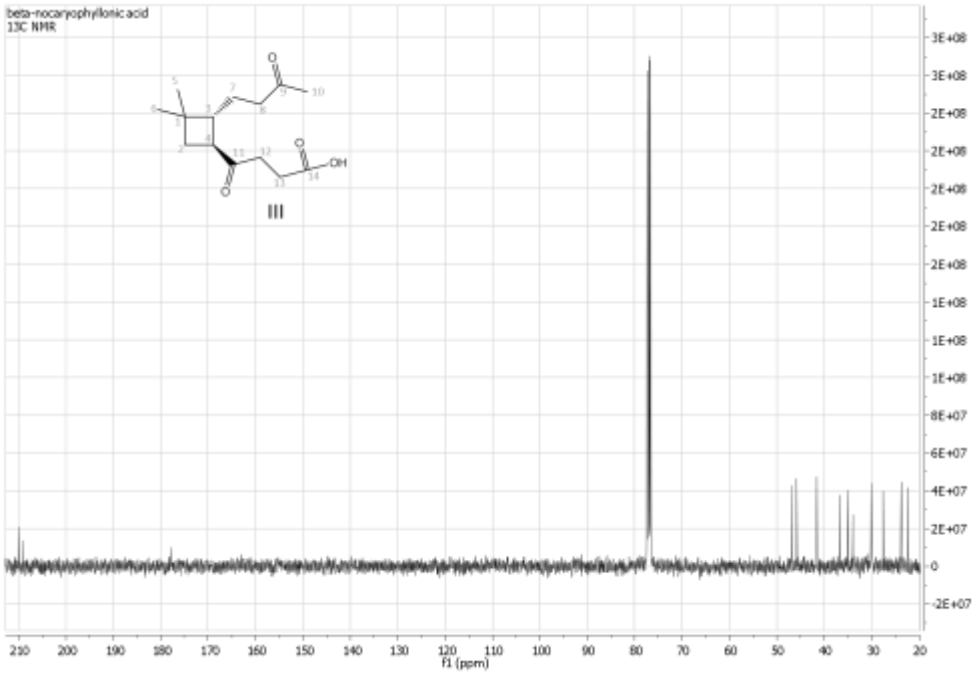

Figure A6: ^{13}C-NMR of nocaryophyllonic acid (III)

^{13}C NMR, HSQC (100 MHz, $CDCl_3$): δ = 210.0 (C_{11}), 208.9 (C_9), 177.8 (C_{14}), 46.7 (C_4), 45.8 (C_3), 41.6 (C_8), 36.7 (C_2), 34.9 (C_{13}), 33.9 (C_1), 30.1 (C_6), 29.9 (C_{10}), 27.6 (C_{12}), 23.7 (C_7), 22.4 (C_5)

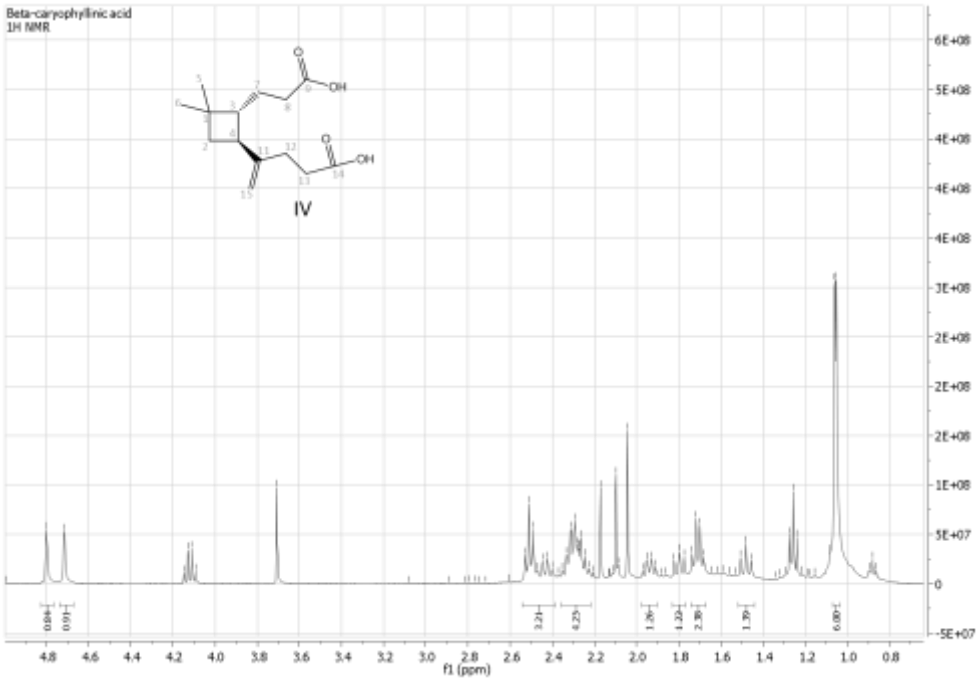

Figure A7: ^{1}H-NMR of caryophyllinic acid (IV)

^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 4.80 (s, 1H, H_{15}), 4.72 (s, 1H, H_{15}), 2.55-2.38 (m, 3H, $H_{13,4}$), 2.36-2.22 (m, 4H, $H_{8,12}$), 1.99-1.89 (m, 1H, H_3), 1.83-1.76 (m, 1H, H_2), 1.71 (q, 2H, $^{3}J_{HH}$ = 7.6 Hz, H_7), 1.52-1.43 (m, 1H, H_2), 1.07-1.03 (m, 6H, $H_{5,6}$)

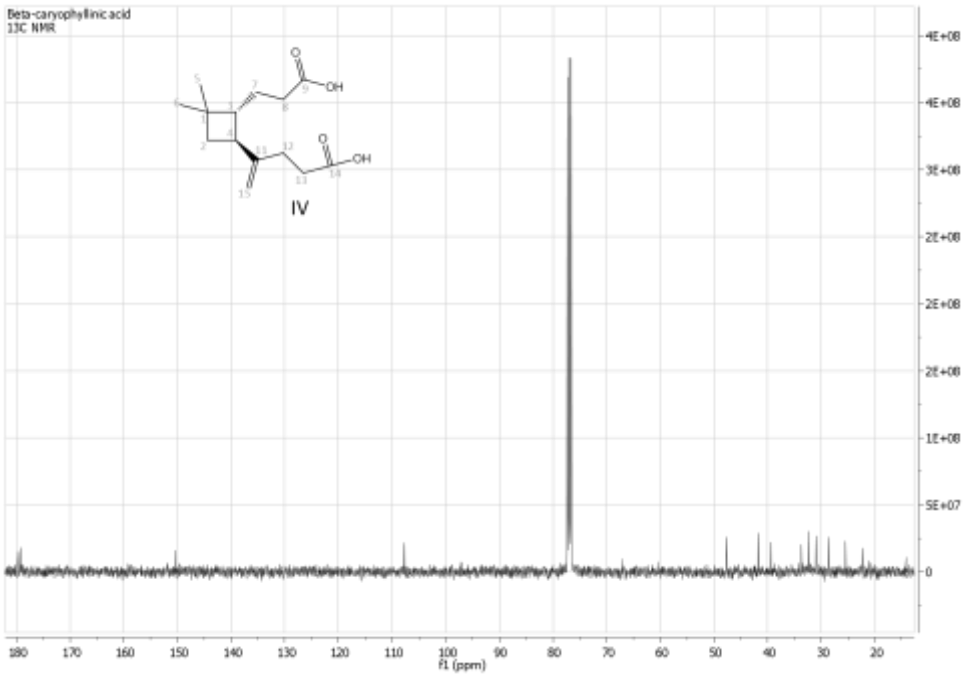

Figure A8: ^{13}C-NMR of caryophyllinic acid (IV)

^{13}C NMR, HSQC (100 MHz, $CDCl_3$): δ = 179.7 ($C_{14,9}$), 179.3 ($C_{14,9}$), 150.3 (C_{11}), 107.7 (C_{15}), 47.7 (C_3), 41.8 (C_4), 39.4 (C_2), 33.7 (C_1), 32.4 ($C_{13,12}$), 32.3 ($C_{13,12}$), 30.9 ($C_{5,6}$), 28.6 (C_8), 25.5 (C_7), 22.3 ($C_{5,6}$)

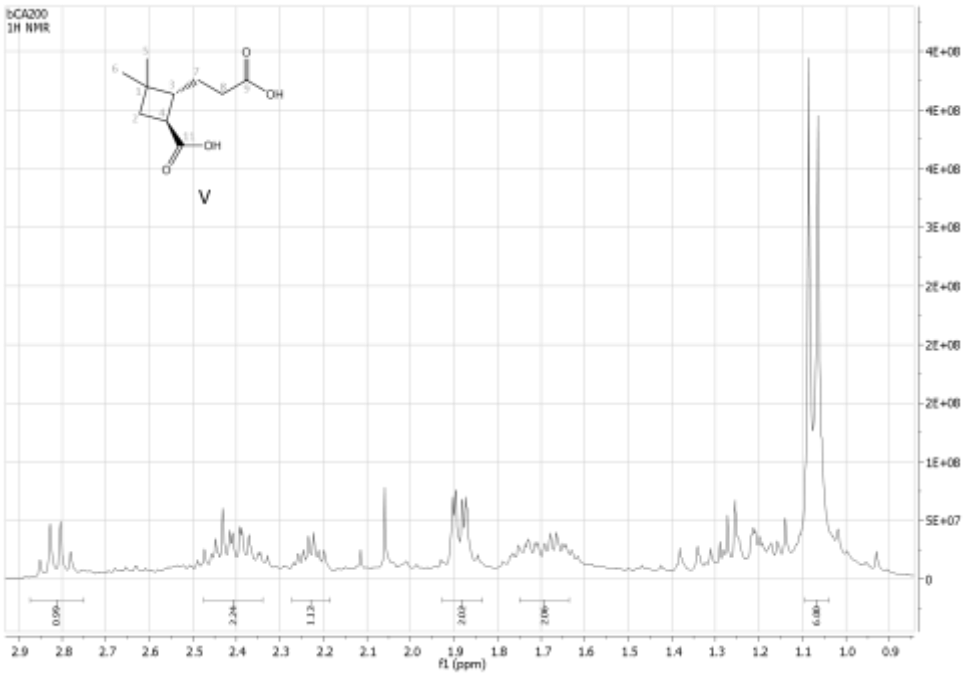

Figure A9: ^{1}H-NMR of βCA200 (V)

^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 2.80 (q, 1H, $^{3}J_{HH}$ = 9.4 Hz, H_4), 2.46-2.32 (m, 2H, H_8), 2.26-2.17 (m, 1H, H_3), 1.87 (dd, 2H, $^{3}J_{HH}$ = 2.7 Hz, $^{3}J_{HH}$ = 8.8 Hz, H_2), 1.76-1.59 (m, 2H, H_7), 1.08-1.01 (m, 6H, $H_{5,6}$)

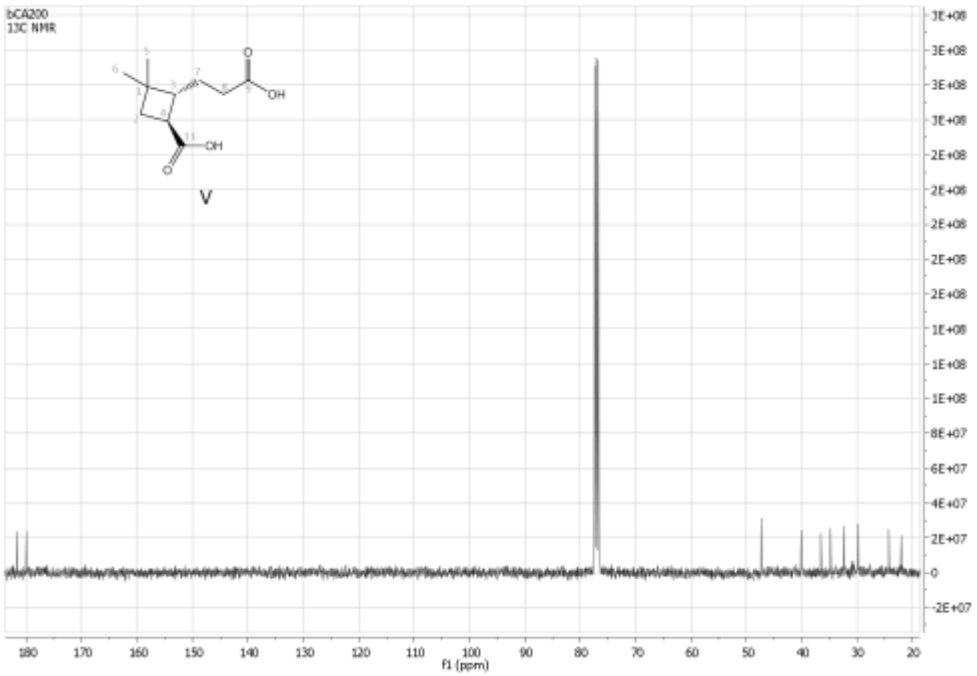

Figure A10: ^{13}C-NMR of βCA200 (V)

^{13}C NMR, HSQC (100 MHz, $CDCl_3$): δ = 181.7 ($C_{11,9}$), 180.1 ($C_{11,9}$), 47.3 (C_3), 40.0 (C_4), 36.5 (C_2), 34.8 (C_1), 32.4 (C_8), 29.8 ($C_{5,6}$), 24.2 (C_7), 22.0 ($C_{5,6}$)

The measured EI-spectra of the silylated compounds are presented in Figure A11-A15.

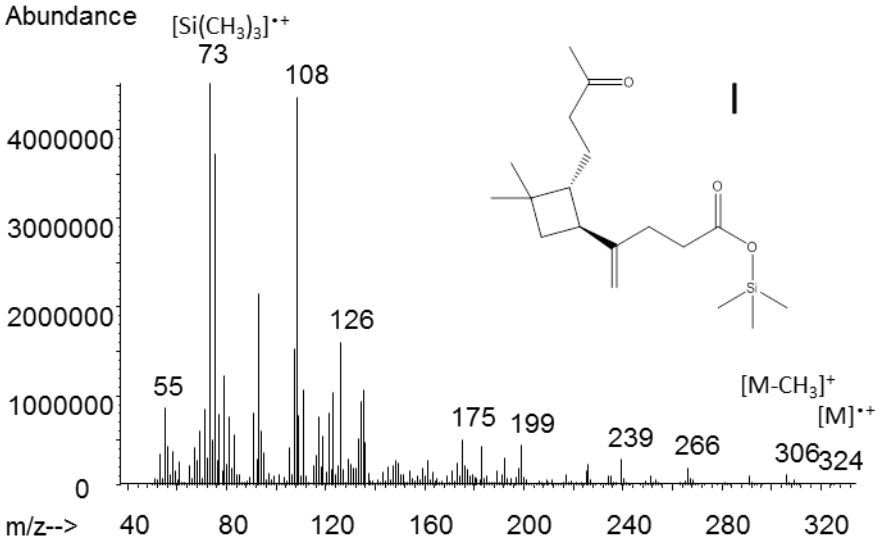

Figure A11: EI-spectrum of the silylated caryophyllonic acid (I)

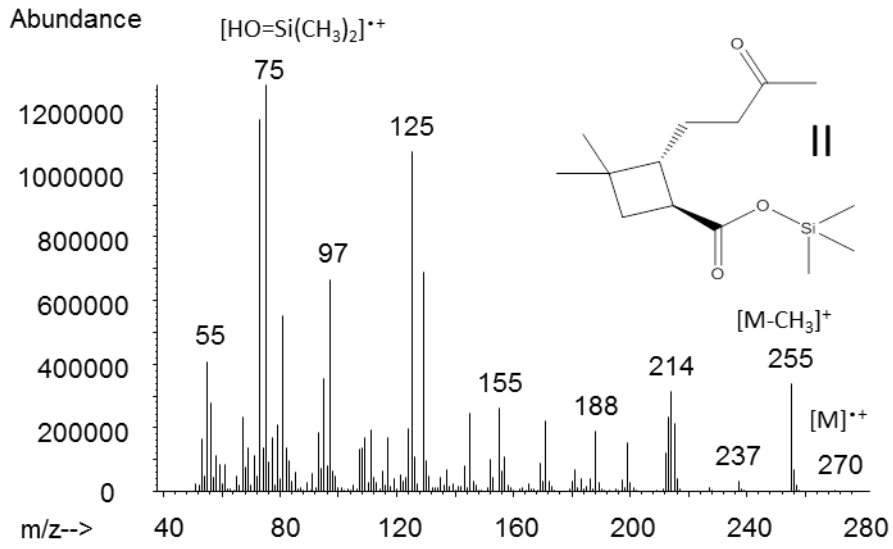

Figure A12: EI-spectrum of the silylated 3,3-dimethyl-2-(3-oxobutyl)cyclobutanecarboxylic acid (βCA198) (II)

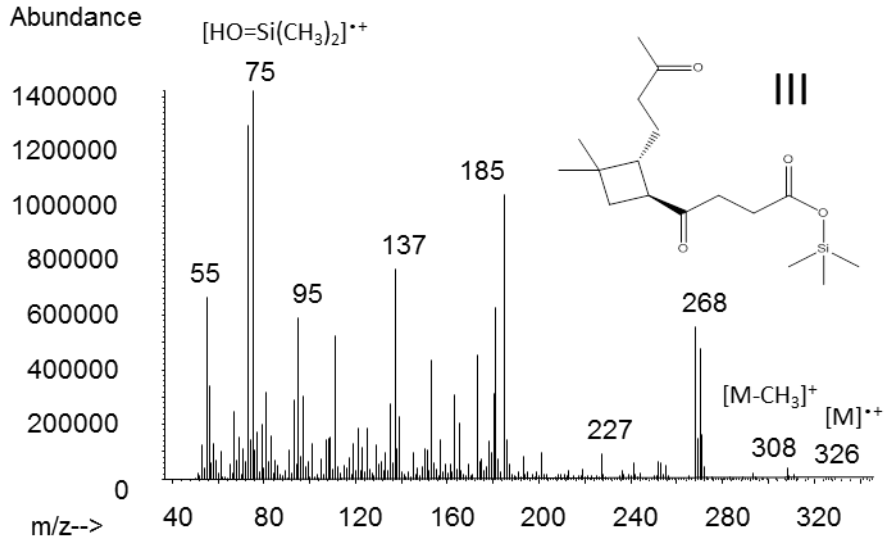

Figure A13: EI-spectrum of the silylated nocaryophyllonic acid (III)

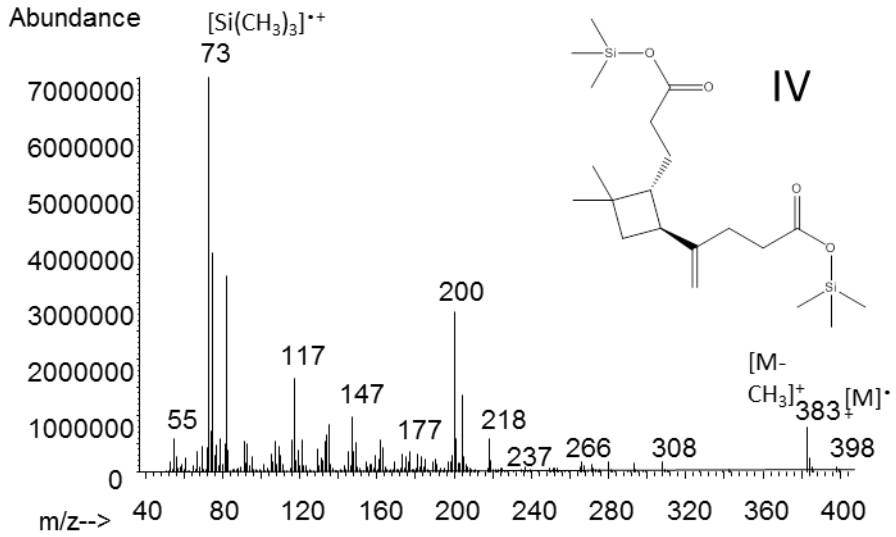

Figure A14: EI-spectrum of the silylated caryophyllinic acid (IV)

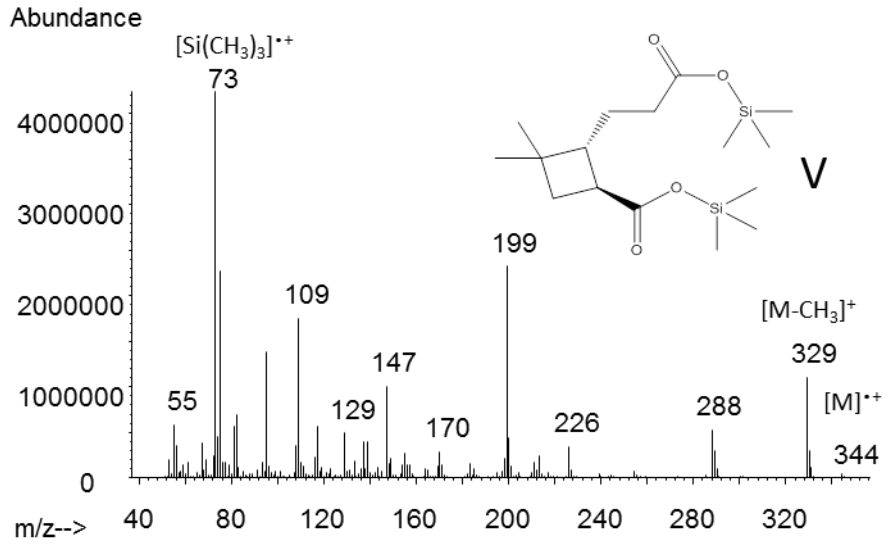

Figure A15: EI-spectrum of the silylated 2-(2-carboxyethyl)-3,3-dimethylcyclobutanecarboxylic acid (βCA200) (V)

B HUMPPA-COPEC campaign

The backward trajectories for the period of filter sampling during the HUMPPA-COPEC campaign 2010 generated with the NOAA Hysplit model (http://www.arl.noaa.gov/ready.php) are displayed in Figure B1.

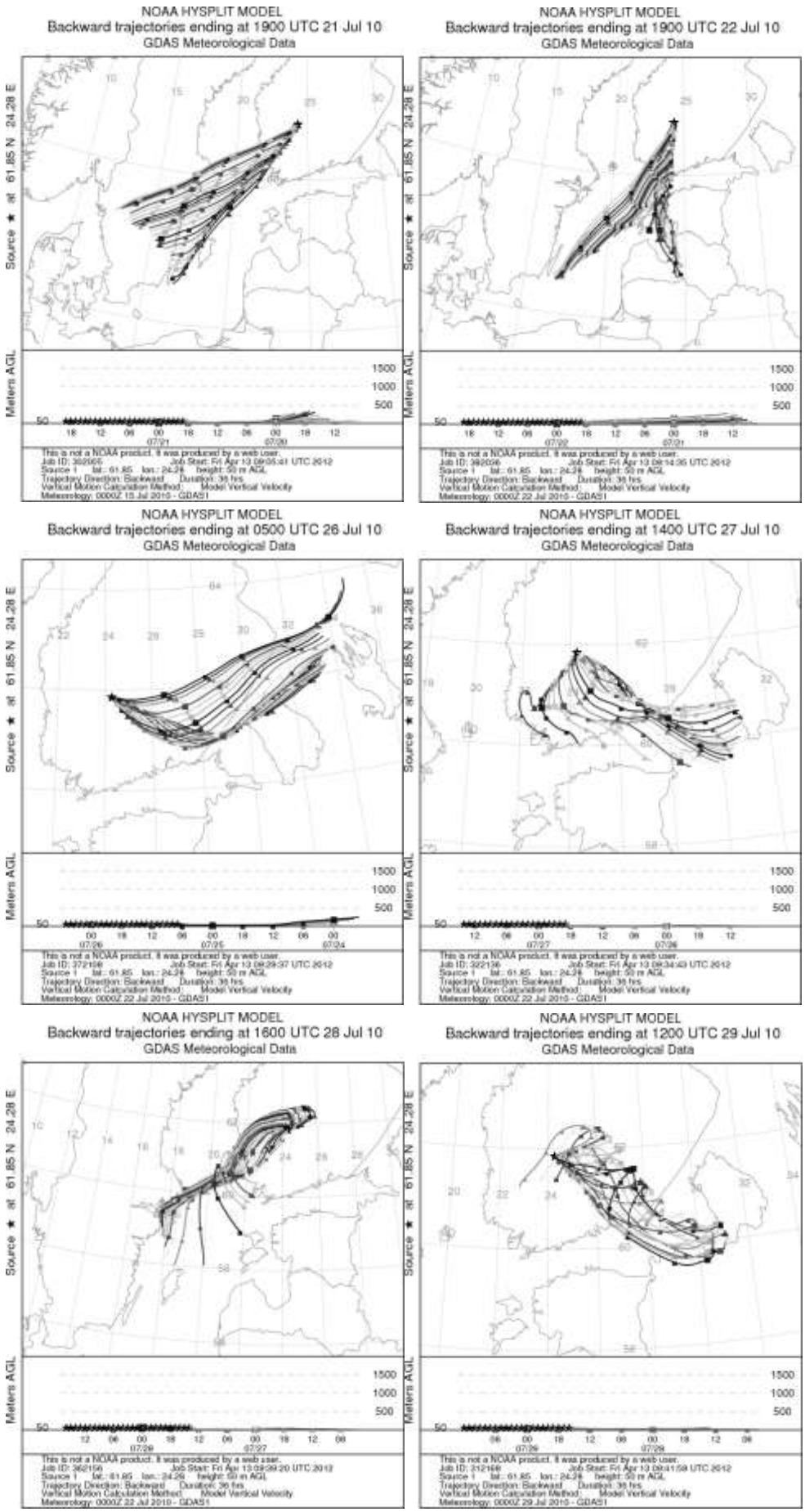

Figure B1: 36 hours backward trajectories during the filter sampling period at the HUMPPA-COPEC campaign 2010 generated with the NOAA Hysplit model

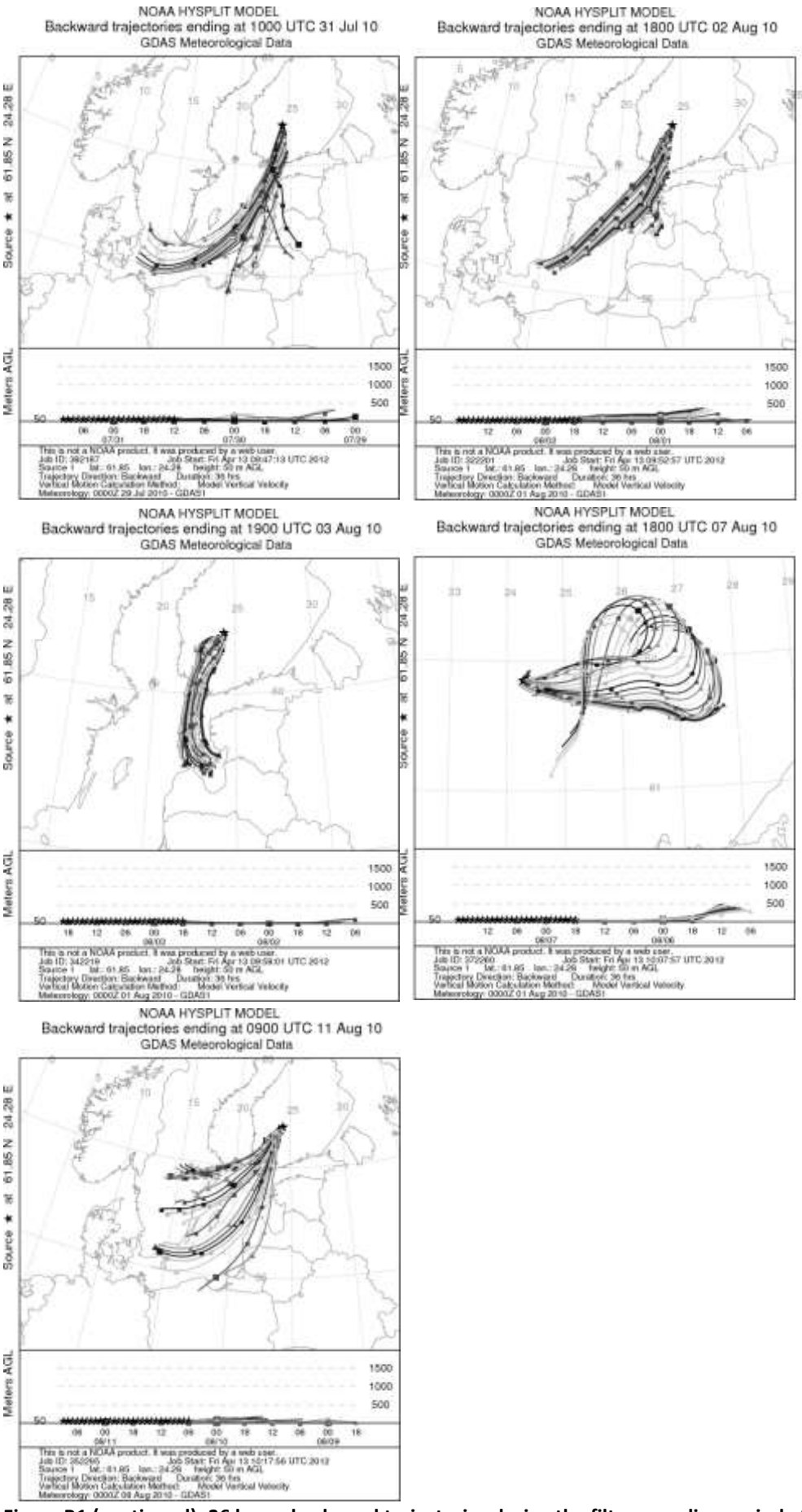

Figure B1 (continued): 36 hours backward trajectories during the filter sampling period at the HUMPPA-COPEC campaign 2010 generated with the NOAA Hysplit model

C ATTO-IOP-2 campaign

The backward trajectories for the period of filter sampling during the ATTO-IOP-2 campaign 2012 generated with the NOAA Hysplit model (http://www.arl.noaa.gov/ready.php) are displayed in Figure C1-C5.

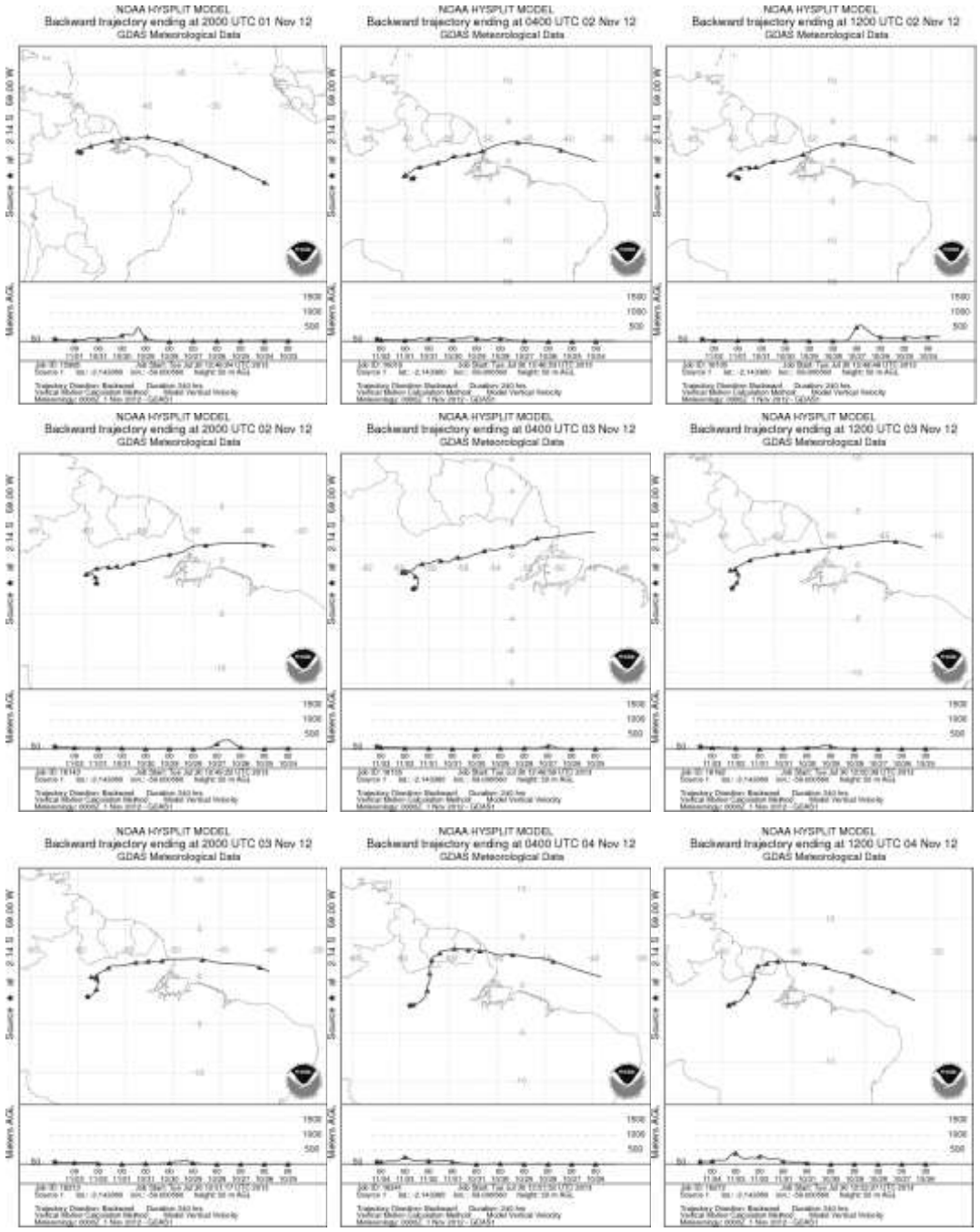

Figure C1: 240 h backward trajectories generated with NOAA Hysplit for the 1st until the 16th of November 2012.

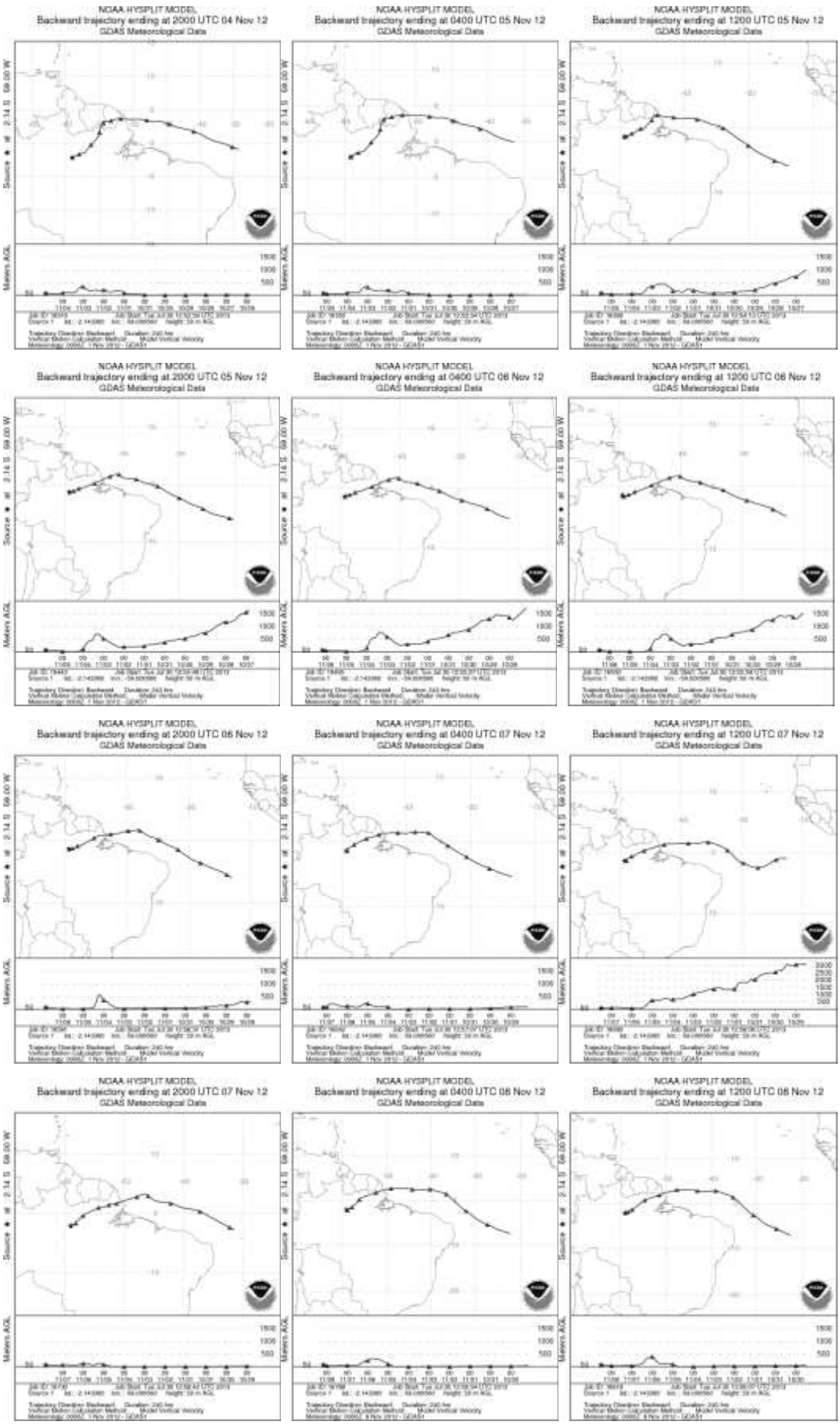

Figure C1 (continued): 240 h backward trajectories generated with NOAA Hysplit for the 1st until the 16th of November 2012.

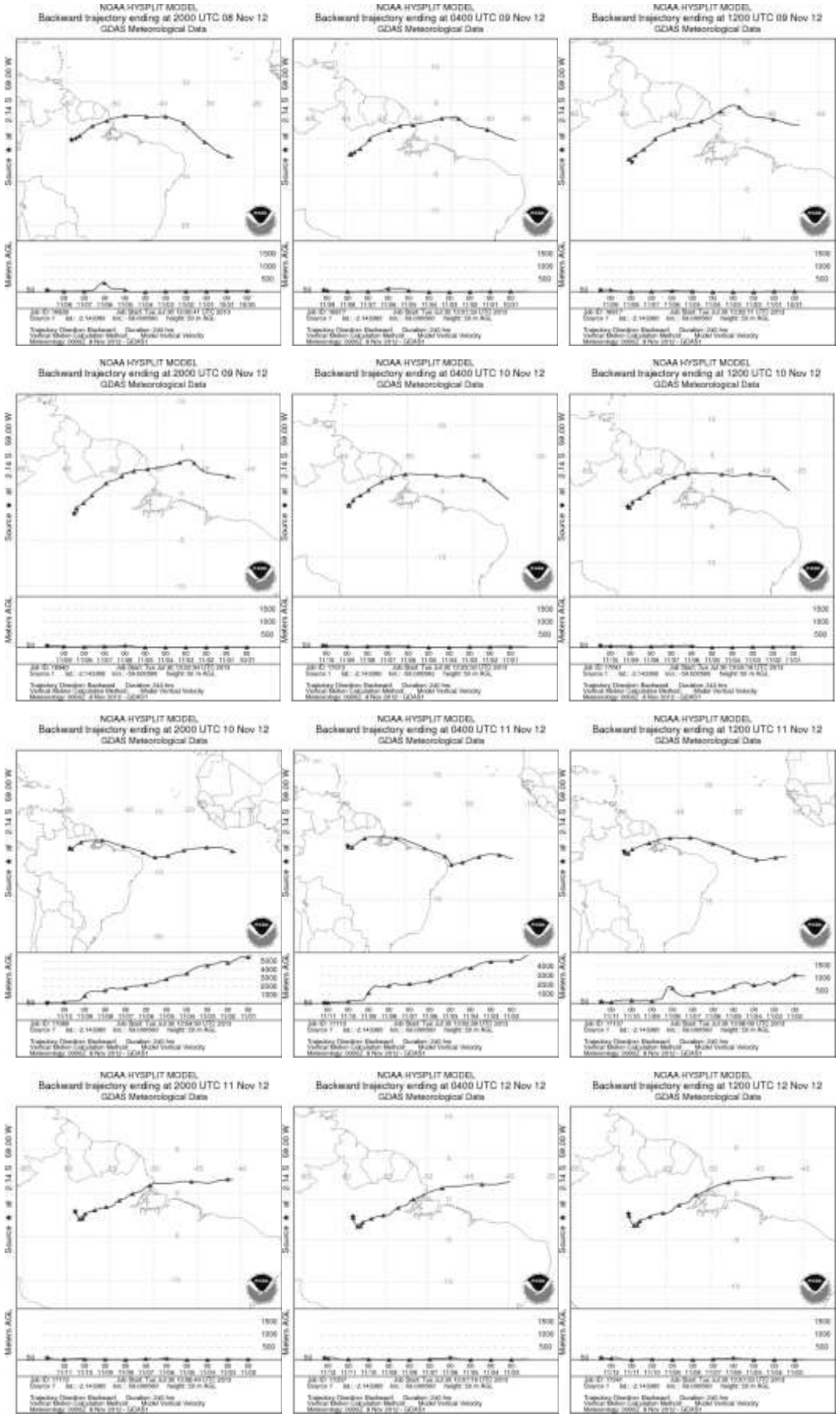

Figure C1 (continued): 240 h backward trajectories generated with NOAA Hysplit for the 1st until the 16th of November 2012.

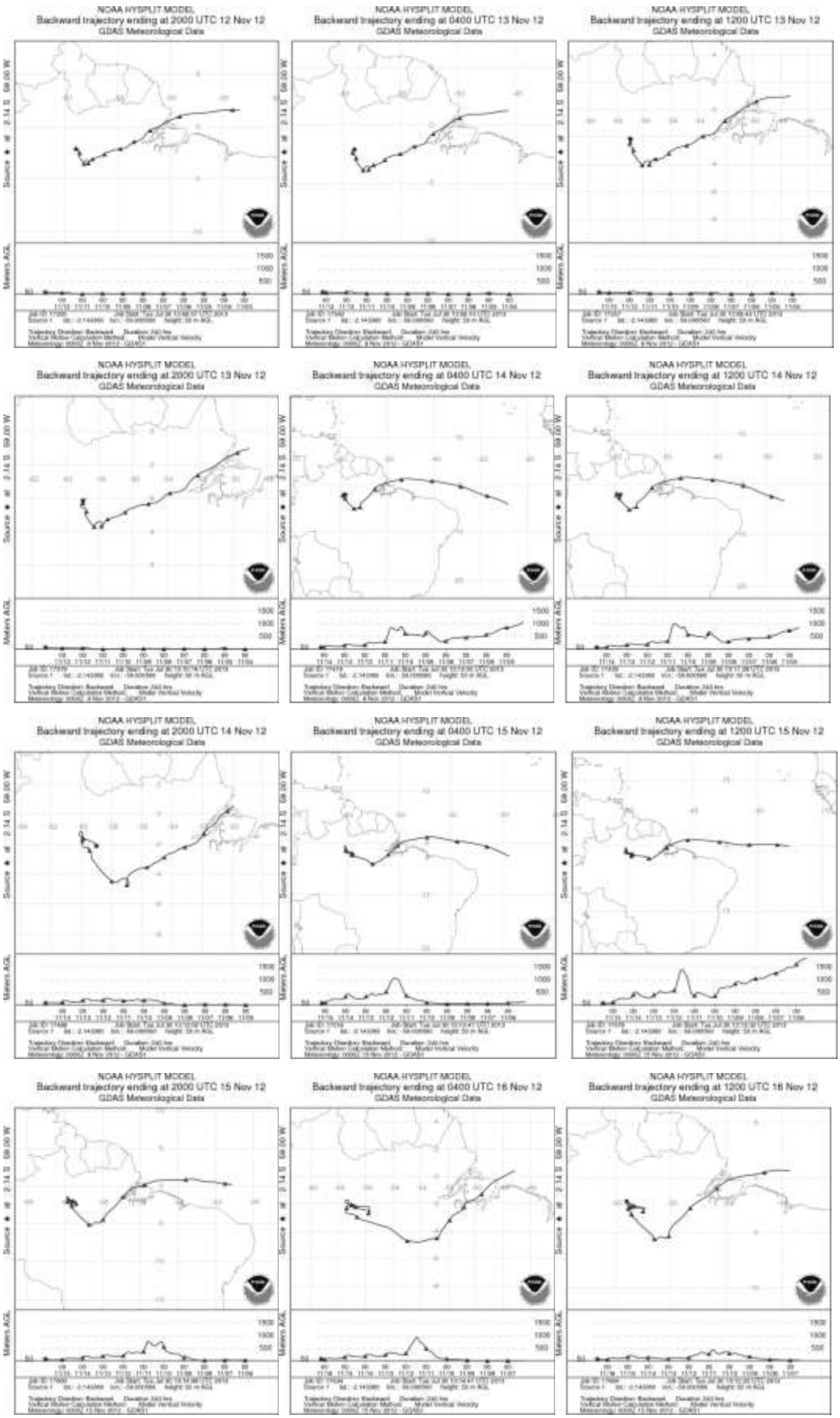

Figure C1 (continued): 240 h backward trajectories generated with NOAA Hysplit for the 1st until the 16th of November 2012.

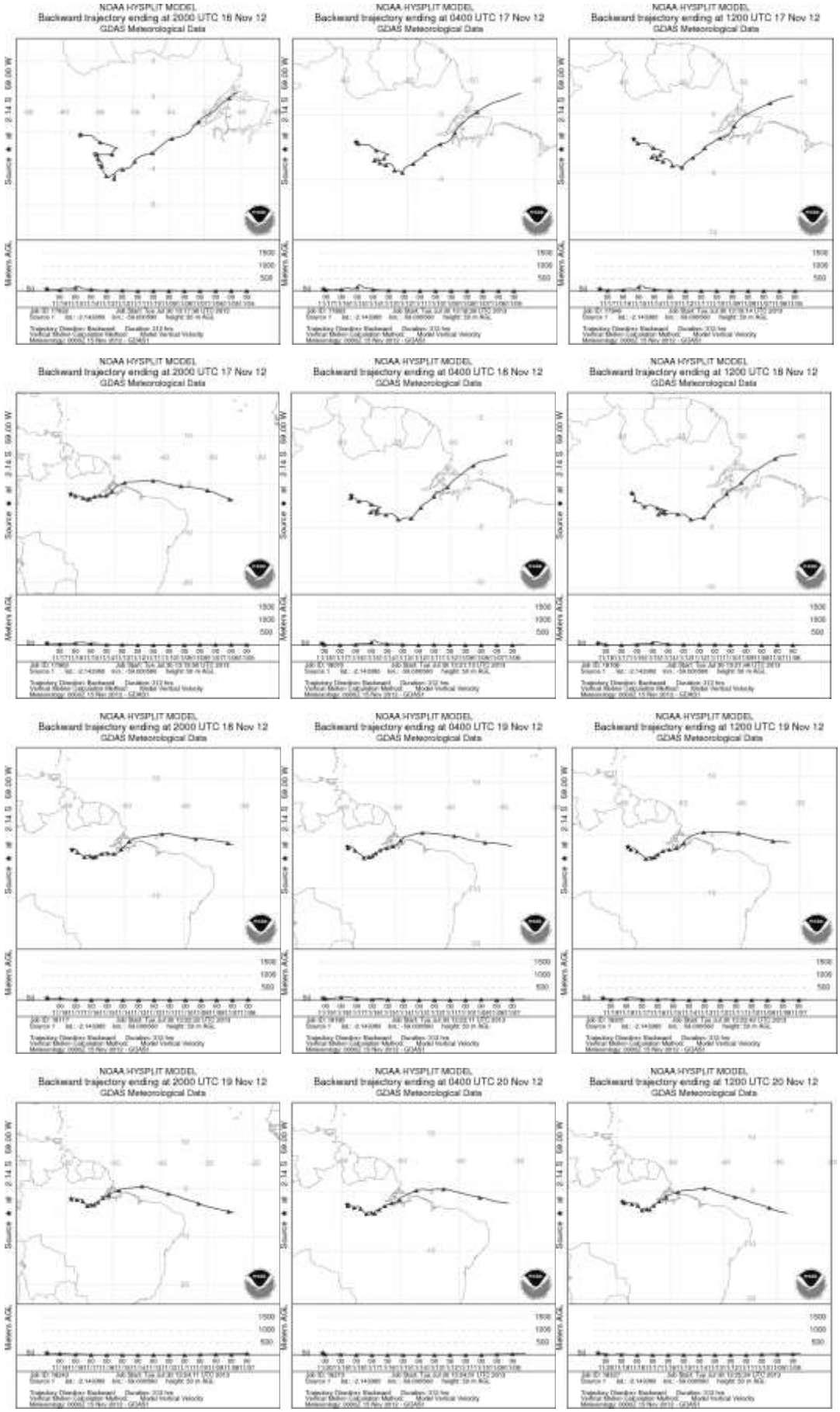

Figure C2: 312 h backward trajectories generated with NOAA Hysplit for the 16th until the 28th of November 2012

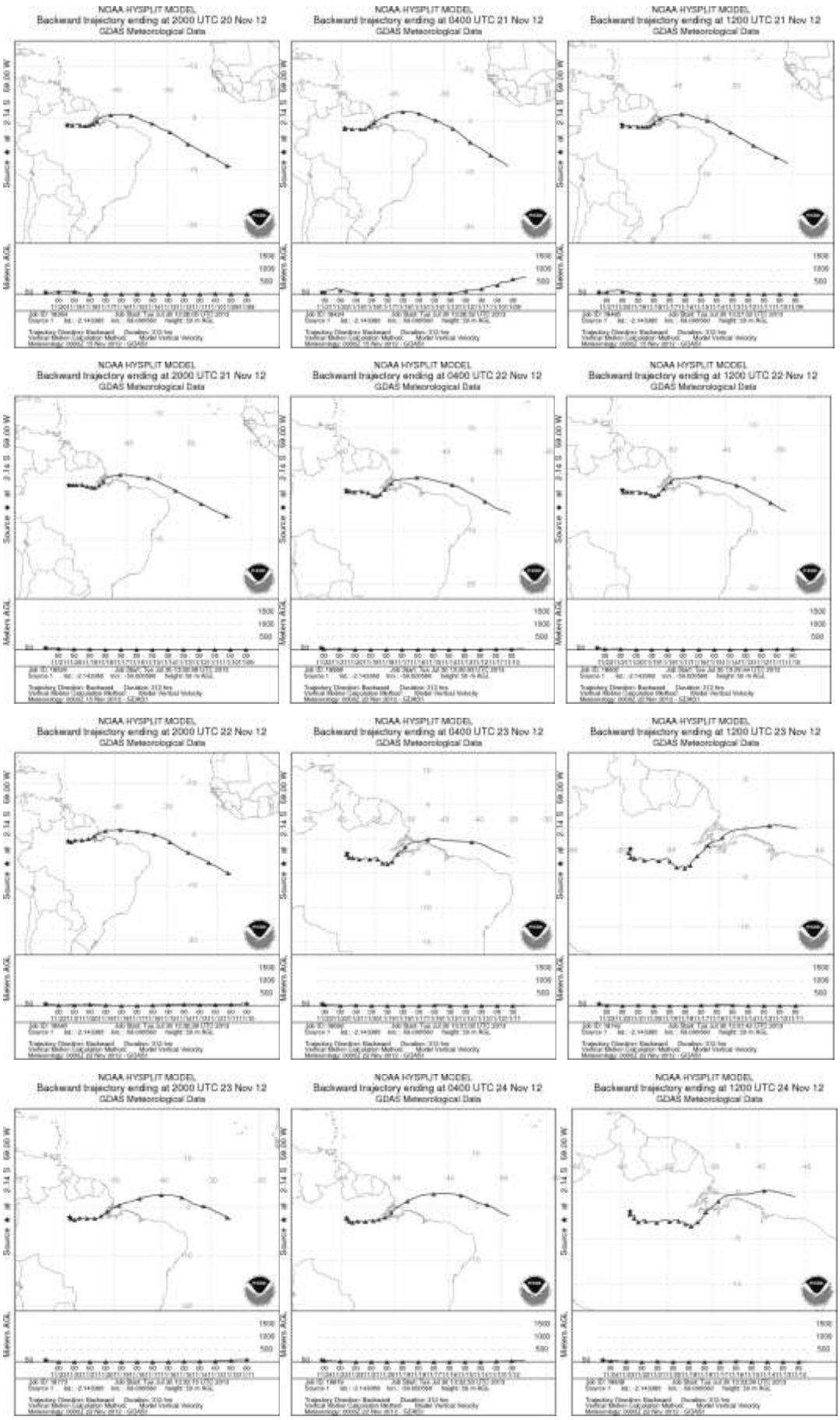

Figure C2 (continued): 312 h backward trajectories generated with NOAA Hysplit for the 16th until the 28th of November 2012

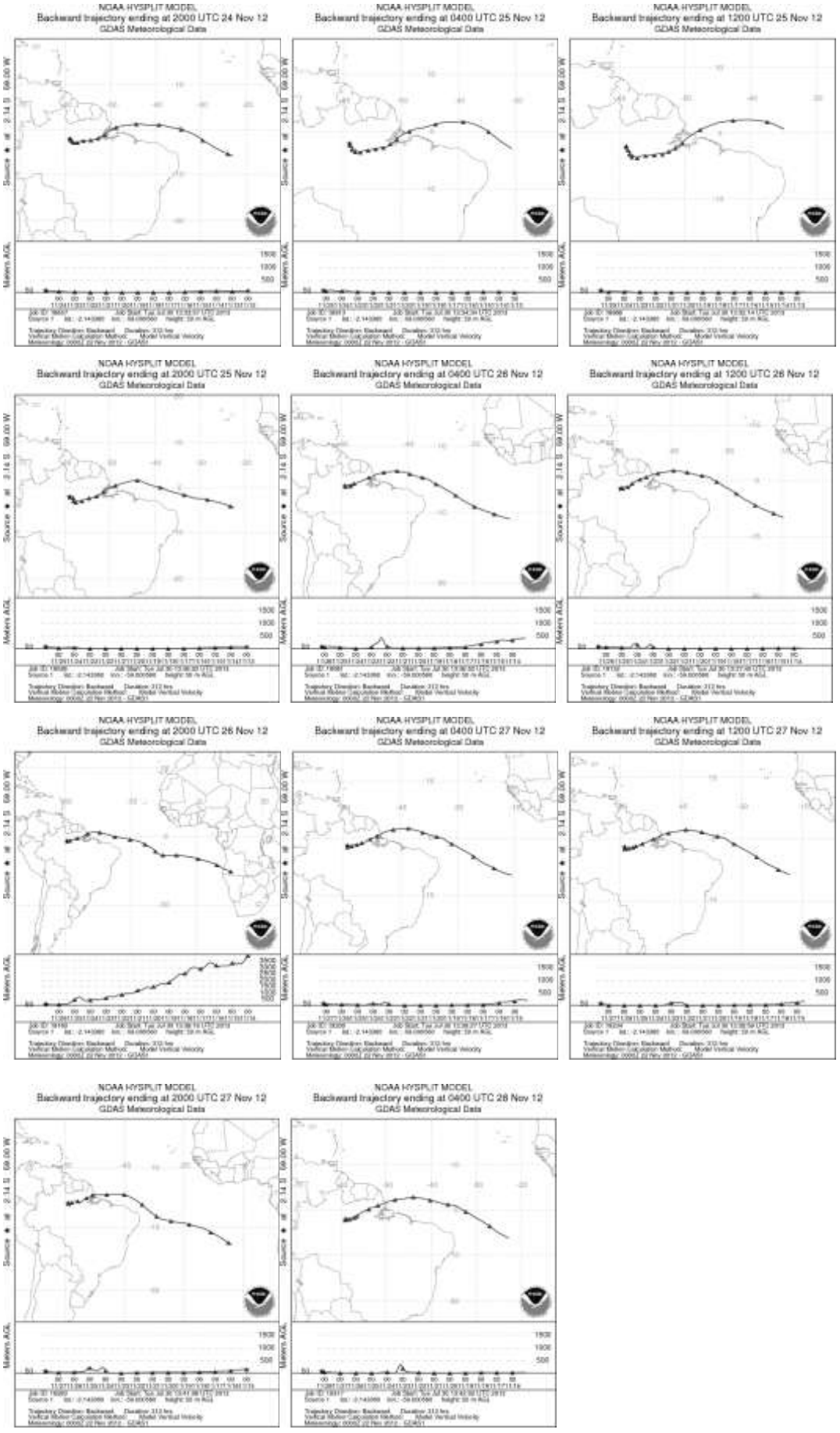

Figure C2 (continued): 312 h backward trajectories generated with NOAA Hysplit for the 16th until the 28th of November 2012

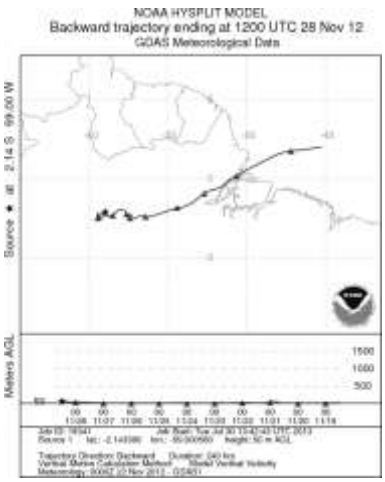

Figure C3: 240 h backward trajectory generated with NOAA Hysplit ending at 12 a.m. UTC on the 28th of November 2012

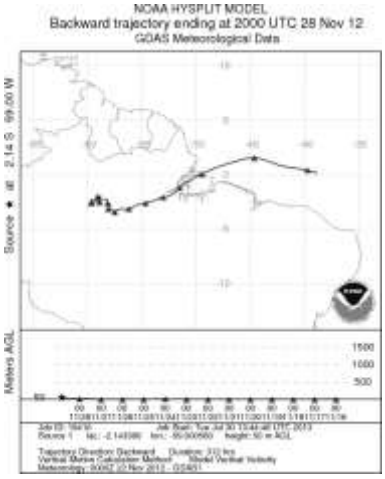

Figure C4: 312 h backward trajectory generated with NOAA Hysplit ending at 8 p.m. UTC on the 28th of November 2012

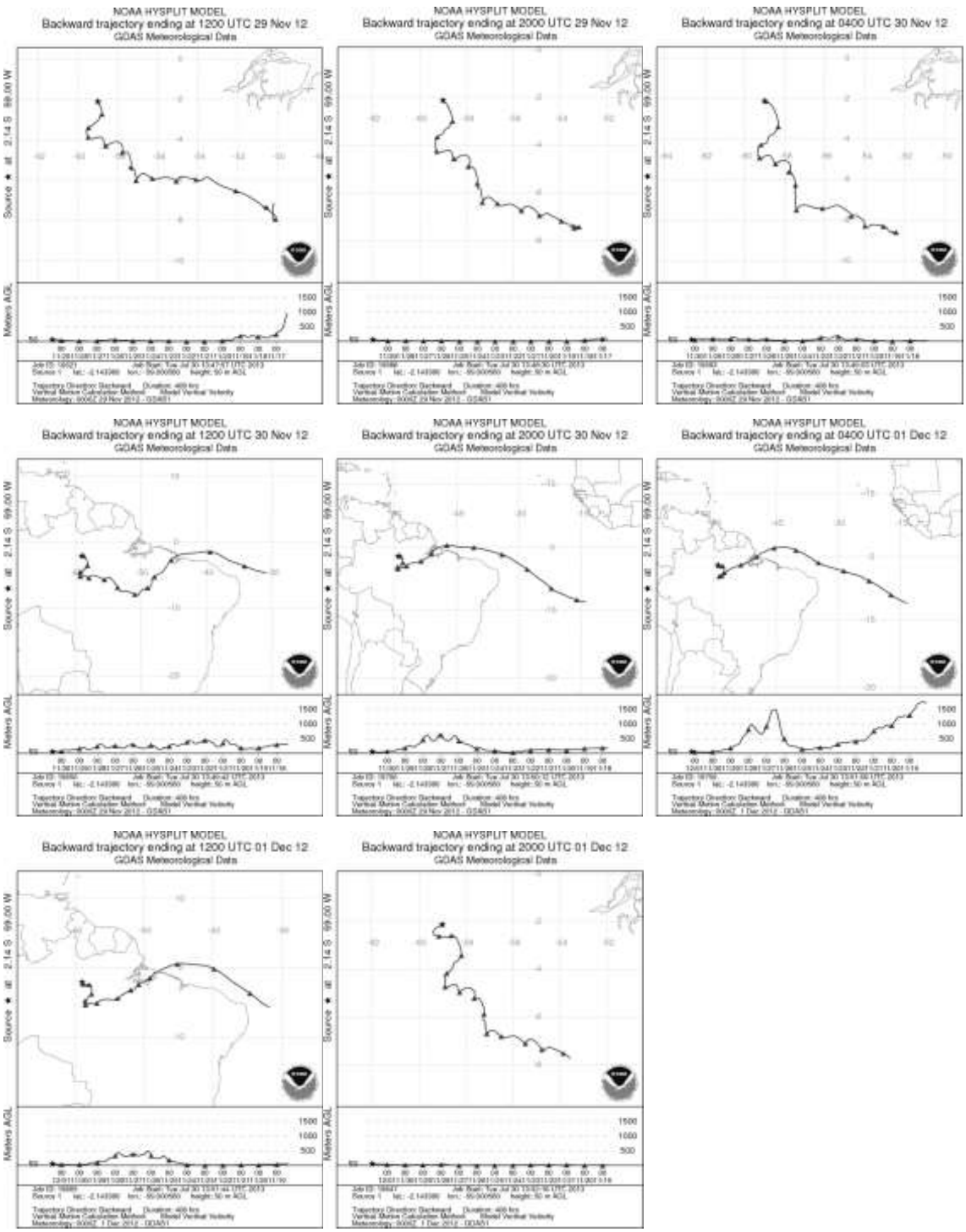

Figure C5: 408 h backward trajectories generated with NOAA Hysplit from the 29th of November until the 1st of December 2012

D Annual filter sampling at Hohenpeissenberg

The correlation of the concentration of Δ-3-carene oxidation products to ambient temperature is shown in Figure D1.

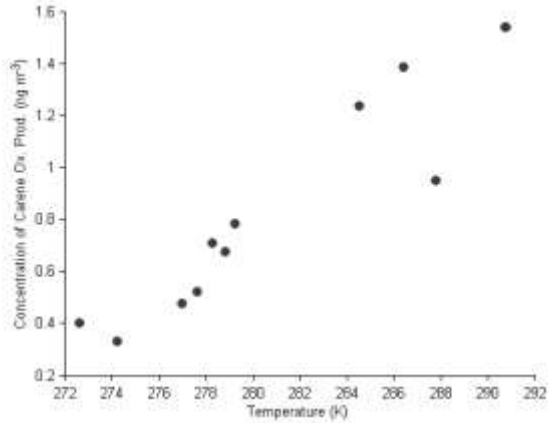

Figure D1: Correlation of temperature to total concentration of Δ-3-carene oxidation products

The ccorrelation of the concentration of sabinene oxidation products to radiation is shown in Figure D2.

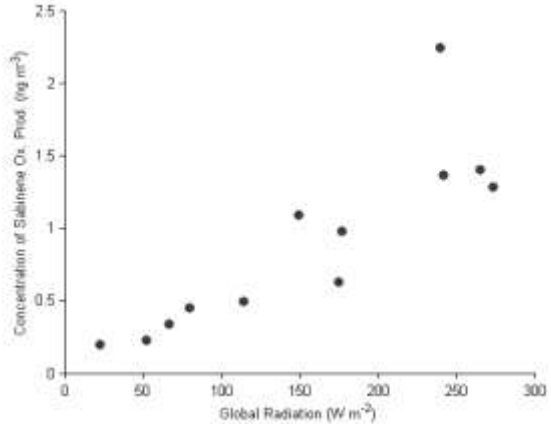

Figure D2: Correlation of radiation to total concentration of sabinene oxidation products