BIOSOL - Results

Formation mechanisms, marker compounds, and source apportionment for BIOgenic atmospheric aeroSOLs

DURATION OF THE PROJECT
15/12/2005 – 31/12/2010

BUDGET
1 045 872 €

KEYWORDS
Atmosphere, biogenic volatile organic compounds, secondary organic aerosols, indicator compounds, smog chambers, forested sites.

CONTEXT

Biogenic volatile organic compounds (BVOCs) play an important role in atmospheric chemistry and give rise to secondary aerosols, which have effects on climate and human health. Increased temperature and CO_2 concentrations will lead to increased plant photosynthesis and growth rates and higher emissions of BVOCs, which in turn result in a higher aerosol load from natural sources and partly offset the decreased cooling from anthropogenic aerosols. However, a considerable lack of knowledge exists concerning the formation of new particles from BVOCs and the organic chemical composition of natural aerosols.

OBJECTIVES

The objectives of the BIOSOL project included (1) study of the formation mechanisms of secondary organic aerosol (SOA) from isoprene and other BVOCs, assessing their role in particle formation and growth, examining the relative importance of homogeneous photo-oxidation and multi-phase processes, and modelling of the processes involved; (2) identification of particulate-phase oxidation products of isoprene and other BVOCs, which can be used as indicator compounds for source apportionment, and development/deployment of novel analytical techniques thereby; and (3) determination of the contribution from the BVOCs to the organic aerosol for various sites in Europe.

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CONCLUSIONS

For reaching objective (1), experiments and measurements were performed in the laboratory, at three forested European sites, and during an oceanic cruise in the Atlantic and at a remote island in the southern Indian Ocean. The BVOCs, their volatile organic oxidation products, and critical inorganic trace gases were determined, and aerosol samples were collected and subjected to comprehensive analyses; in addition, in-situ measurements of particle number concentrations and size distributions, of ion spectra, and of the particulate mass (PM) and particulate organic carbon (OC) were made, and radiation and standard meteorological measurements were performed.

In co-operation with Caltech, a study was performed to obtain insights into the formation mechanisms of SOA from isoprene, in particular the mechanisms that result in the formation of 2-methyltetrols, 2-methylglyceric acid (2-MG), and humic-like substances (HULIS). An extensive series of smog chamber experiments was performed under various conditions, in particular at low- and high-NO_x levels, and with and without seed aerosol. It was found that the chemical nature of the SOA was significantly different between the two NO_x regimes. At high-NO_x, the SOA components were acidic and formed upon the further oxidation of methacrolein; no other first-generation gas-phase products contributed to the high-NO_x SOA. In contrast, the low-NO_x SOA was neutral owing to the formation of polyols and organic peroxides. Oligomerisation was an important isoprene SOA formation pathway at both low- and high-NO_x. The nature of the oligomers was, however, distinctly different in each NO_x regime. The high-NO_x oligomers were characterised as oligo-esters involving 2-MG as the key monomeric unit, while the low-NO_x oligomers were hemiacetal derivatives of the 2-methyltetrols. Based on the results of this study mechanisms could be proposed for the formation of isoprene SOA under both high- and low-NO_x conditions.

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In co-operation with Caltech and US EPA smog chamber experiments were performed in order to study the mechanism and ubiquity of organosulphate formation in biogenic SOA. In addition, archived laboratory-generated isoprene SOA and ambient filter samples from the southeastern US were re-examined for organosulphates and nitrooxy organosulphates. Only SOA compounds that were also detected in ambient PM2.5 aerosol were selected for structural characterisation. By comparing the mass spectral data collected for both the laboratory-generated and ambient aerosol, previously uncharacterised ambient organic aerosol components were found to be organosulphates of isoprene, α-pinene, β-pinene, and limonene, thus demonstrating the ubiquity of organosulphate formation in ambient SOA. Several of the organosulphates characterised in this study provide ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. As to the contribution from organosulphates to the total organic mass fraction in ambient aerosols, the calculations for the PM10 samples from the 2003 K-puszta summer campaign indicated that this contribution can be as high as 30%.

A comprehensive field campaign was held at the forested site of K-puszta, Hungary, from 24 May to 29 June 2006. From the start of the campaign until 11 June, it was unusually cold with daily maximum temperatures between 12 and 23 °C, but from 12 June onward higher temperatures were noted with daily maxima from 24 to 36 °C. From the data for the volatile organic compounds (VOCs) and their oxidation products it was quite clear that much higher levels were observed during the warm period than during the cold one. This difference is to be expected, given that both formation and emission of the VOCs by plants increase with light and temperature. An increase with temperature was also observed for the 24-hr (or day-time or night-time) averaged concentrations of fine PM and fine OC (whereby fine = PM2.5) from the in-situ instruments and for the data of a number of components in the filter samples, such as the dicarboxylic acids (DCAs) and the mineral dust elements. The in-situ measurements of particle number concentrations and size distributions and of ion spectra indicated that there were particle production episodes around every second day, which is quite frequent. There seemed to be no relation between the particle production events and the in-situ VOC, fine PM or fine OC levels. Organic matter, estimated as 1.8 OC, was the major aerosol component in both PM2.5 and PM10 and in both the cold and warm periods and accounted for between 40 and 50% of the gravimetric PM. Sulphate was the second component in PM2.5, with percentage contributions of 22-24%.

From the results for OC, elemental carbon (EC), and the VOCs that were obtained in the course of 2007 at the forested site "De Inslag", Brasschaat, it appeared that the site is substantially impacted by anthropogenic activities. This is in contrast to the two other forested sites studied in this project. The fine size fraction samples of the Hi-Vol dichotomous sampler (HVDS) were analyzed for inorganic and organic ions by ion chromatography (IC) and for a variety of organic compounds by liquid chromatography/mass spectrometry (LC/MS). Known and new tracers for α-pinene SOA and a number of organosulphates, including nitrooxy organosulphates with a molecular weight (MW) of 295, were detected and quantified, in addition to the DCAs. Interestingly, rather low concentrations of the MW 295 SOA tracers were found during the first nights of the campaign (with maximum day-time temperatures > 22 °C). These results hint that the latter α-pinene SOA tracers are formed during nights following days where α-pinene was not fully consumed by photo-oxidation, leaving a portion of the emitted α-pinene available for processing by night-time NO_3 chemistry. The combined contribution of the measured organic compounds to the OC was, on average, 5.3% (with 4.1% from the IC compounds and 1.2% from the LC/MS compounds).

From 1 to 31 August 2007, a comprehensive field campaign was held at the SMEAR II forested site in Hyytiälä, Finland. Overall, the weather was nice during the campaign with little rain. The mean daily temperature rose from 13.4 °C on 1 August to around 20 °C in the period of 6-13 August and decreased to 6.1 °C on 31 August, with a secondary maximum of 17 °C on 22-24 August. From the time series of the in-situ data for the BVOCs, it appeared that the highest levels of the monoterpenes were noted in the nights of 7, 8, and 9 August, thus right after the start of the warm period. When looking at daily averages, there was clearly some relation between the concentrations of the BVOCs and temperature, with higher levels at higher temperatures. The time series for in-situ fine PM and fine OC was different from that for the BVOCs. The OC levels (and to a lesser extent also the PM levels) kept increasing from the beginning of the campaign until 13 August and decreased afterwards, with a second maximum on 22 to 24 August.

It seemed thus that there was little relation between the local concentrations of the BVOCs and fine OC at the SMEAR II site. It is thought that the levels of fine OC are more related to the total BVOC emissions upwind of the site during the last 5 days or so of air mass transport than to the local BVOC concentrations at SMEAR II itself. The mass size distributions for OC, as measured in cascade impactor samples collected at ambient relative humidity (RH), peaked in the accumulation size range, but there was also a clear coarse mode with peak at around 3-4 µm aerodynamic diameter. Like during the 2006 summer campaign at K-puszta, there was little EC in the aerosol at SMEAR II and most of the fine OC was water-soluble (i.e., 63%). The PM2.5 samples of the HVDS were analyzed for inorganic and organic ions by IC.

The organic compounds measured accounted, on average, for 2.0% of the OC and 3.1% of the water-soluble OC (WSOC). These percentages are about one third lower than those found at K-puszta. The results from the low-volume filter samples were used to examine to which extent aerosol chemical mass closure could be obtained. Eight aerosol types (components) were considered in the mass closure calculation. Organic matter was clearly the dominant component in both PM2.5 and PM10. It accounted for 73% and 64% of the average gravimetric PM in PM2.5 and PM10, respectively, and was in both cases followed by non-sea-salt sulphate, which represented 25% and 17% of the average gravimetric PM in PM2.5 and PM10, respectively.

The OC and EC data from the oceanic cruise in 2006 in the Northern Hemisphere (NH) indicated that there was a large impact from continental aerosol and from fossil-fuel combustion aerosol. This was in contrast with the OC and EC data from Amsterdam Island in the southern Indian Ocean. At the latter site, EC was below the detection limit and OC was substantially lower than during the NH cruise. A common feature of both marine study areas was that only around 30% of the fine OC was water-soluble. This percentage is similar to that found at urban sites, where most of the OC consists of primary organic aerosol from fossil fuel combustion. It seems that the fine OC for our two oceanic study areas was also mostly primary. It has been suggested that SOA from isoprene may be a large source of cloud condensation nuclei in some oceanic regions. There was clearly no evidence for SOA from isoprene in the samples from the NH cruise nor in those from Amsterdam Island. In both the coarse and fine size fractions of the HVDS samples from Amsterdam Island, sea salt was by far the major aerosol type; organic aerosol made up for less than 10% of the dry aerosol mass. Of the organic species measured, methanesulphonate, a gas-to-particle conversion product from dimethylsulphide, which is emitted by marine phytoplankton, was by far the major contributor to the fine WSOC, with an average contribution of about 17%. Various organosulphates were also present in the fine WSOC (with an average combined contribution of 0.8%); they were attributed to oxidation of primary algal biomass.

With regard to objective (2) of BIOSOL, studies were conducted to structurally characterise major particulate-phase oxidation products of α-pinene that occur at significant concentrations in ambient fine aerosol. Using mass spectrometric techniques and synthesis of reference compounds, the structures of two major α-pinene SOA marker compounds with MWs of 148 and 204 were established as 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), respectively. A formation mechanism for MBTCA was proposed, which involves OH-initiated oxidation in the presence of NO_x. Furthermore, major efforts were undertaken to elucidate the structure of a MW 172 compound and related compounds, which are formed upon photo-oxidation and ozonolysis of α-pinene (and other BVOCs) and are also present in ambient fine aerosol from sites with coniferous vegetation. The MW 172 compound was identified as the lactone-containing terpenylic acid. Terpenylic acid shows unique non-covalent dimer-forming properties upon electrospray ionisation in the negative ion mode [(–)ESI] and is thought to play a role in initial particle formation.

As to objective (3), we determined the contribution from the BVOCs to the organic aerosol for PM2.5 samples, which had been collected in summer 2003 in a mixed deciduous forest in Jülich, and for the PM2.5 size fraction of the HVDS samples from the 2003 summer campaign at K-puszta. We made thereby use of the laboratory-derived tracer mass fractions (f_{SOC}), which were obtained by Kleindienst et al. [2007] with gas chromatography/mass spectrometry (GC/MS). For the K-puszta samples, isoprene secondary organic carbon (SOC) and α-pinene SOC accounted, on average, for respectively 6.9% and at least 4.8% of the PM2.5 OC; for the Jülich samples, the average contributions from isoprene SOC and α-pinene were 2.5% and at least 2.4%, respectively. Although the data for α-pinene SOC should be regarded as minimum values because not all molecular tracers necessary to estimate α-pinene SOC were measured, these percentages are clearly much lower than expected. Although the uncertainty that is associated with our estimates is at least a factor of 2, one may wonder to what extent the values of Kleindienst et al. [2007] are applicable to ambient organic aerosol in various types of environments and different levels of NO_x, oxidants, RH, and other ambient parameters. More laboratory studies of the f_{SOC} values under various conditions (and also for additional BVOCs) are therefore recommended. It is also suggested that additional techniques, such as LC/MS, are used besides GC/MS in future studies on f_{SOC}.

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CONTRIBUTION OF THE PROJECT TO A SUSTAINABLE DEVELOPMENT POLICY.

Atmospheric aerosols have both direct and indirect effects on climate through their scattering and absorption of solar and terrestrial radiation and through their effects on the formation and lifetime of clouds. It is believed that the net effect of aerosols (and definitely that of biogenic aerosols) is cooling so that aerosols counteract to some extent the global warming which results from the greenhouse gases. However, aerosols also affect human health and welfare and as a consequence their concentrations should be reduced, at least on local and regional scales where the population is exposed to the aerosols. The fact that aerosols have both beneficial and harmful aspects gives rise to a dilemma. Some aerosol types, such as elemental carbon (black carbon, soot), lead to warming and are also harmful to humans, so that the concentrations of these aerosols should be reduced. On the other hand, most biogenic aerosols give rise to cooling and are thought to be not so harmful, so that their concentrations should not be reduced. The project contributed to the elucidation of the formation mechanisms of biogenic aerosols; several new marker compounds for such aerosols were discovered, these markers were used to estimate the contribution from the BVOCs to the organic aerosol and they can be used in future assessments of beneficial aerosols on local, regional, and global scales. Consequently, the work performed within this project contributes to the objectives of policy advisers and policy makers who deal with climate and human health.

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