

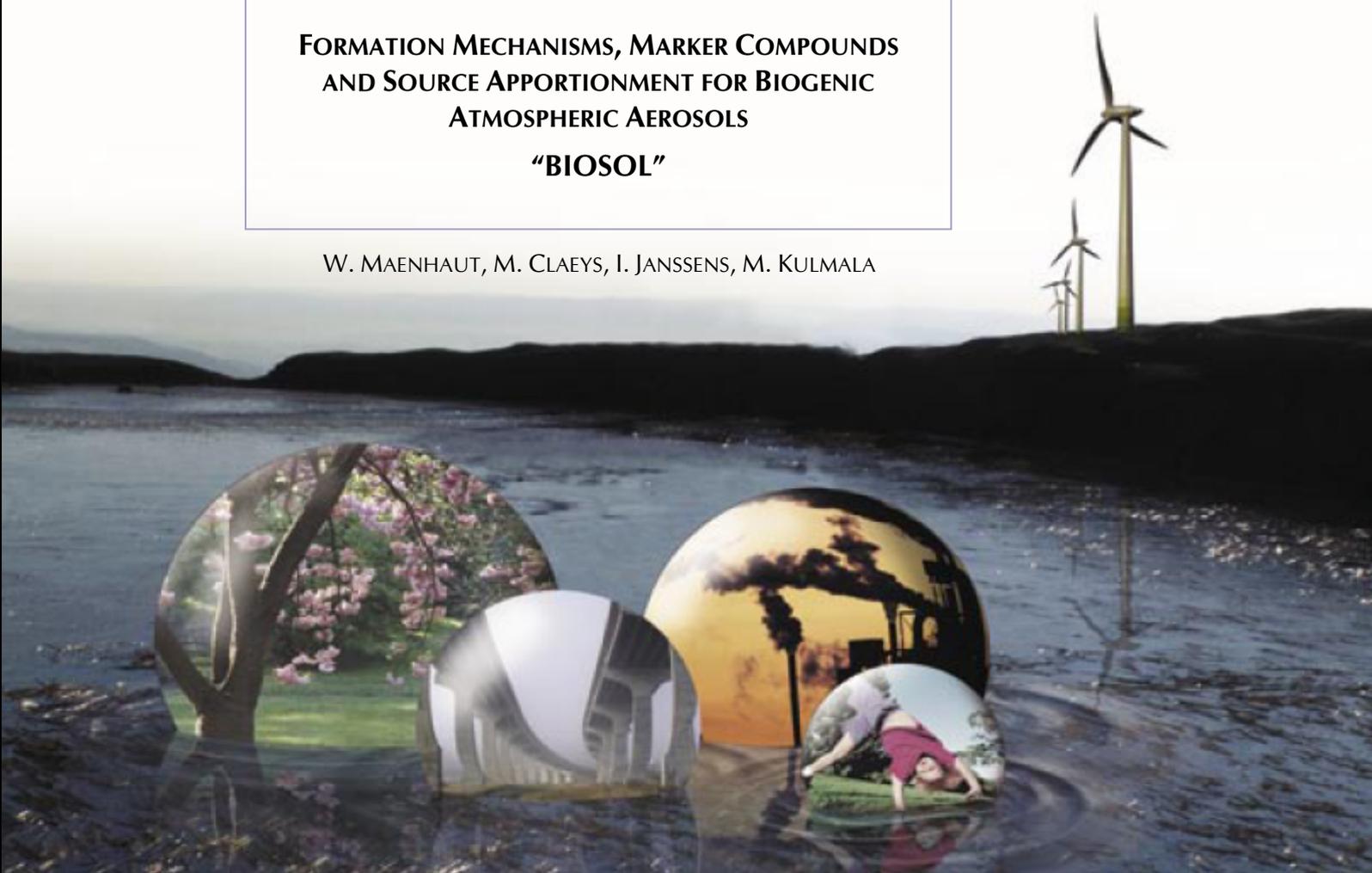
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SCIENCE FOR A SUSTAINABLE DEVELOPMENT



**FORMATION MECHANISMS, MARKER COMPOUNDS
AND SOURCE APPORTIONMENT FOR BIOGENIC
ATMOSPHERIC AEROSOLS
“BIOSOL”**

W. MAENHAUT, M. CLAEYS, I. JANSSENS, M. KULMALA



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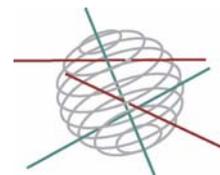
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Climate



FINAL REPORT
SUMMARY
**FORMATION MECHANISMS, MARKER COMPOUNDS
AND SOURCE APPORTIONMENT FOR BIOGENIC
ATMOSPHERIC AEROSOLS
“BIOSOL”**

SD/AT/02A

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Willy Maenhaut, Magda Claeys, Markku Kulmala, Ivan Janssens. ***Formation mechanisms, marker compounds and source apportionment for biogenic atmospheric aerosols "BIOSOL"***
Final Report Phase 1 Summary. Brussels : Belgian Science Policy 2009 – 8 p. (Research Programme Science for a Sustainable Development)

ABSTRACT

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 CO₂ 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.

The objectives of the BIOSOL project include (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.

For reaching objective (1), during Phase I of BIOSOL experiments and measurements were performed in the laboratory (i.e., in smog chambers and plant growth chambers), 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 smog-chamber SOA was significantly different between the two NO_x regimes. For the high-NO_x conditions, the SOA components were acidic and formed upon the further oxidation of methacrolein (MACR); no other first-generation gas-phase products

appeared to contribute to the high-NO_x SOA formation. In contrast, the low-NO_x SOA was neutral in nature owing to the formation of polyols and organic peroxides and MACR did not contribute to it. Acid-catalysis seemed to play a larger role under low-NO_x conditions. It was found that organic peroxides contributed significantly to the low-NO_x SOA mass [~61% for nucleation experiments (these are experiments without seed aerosol) and ~25% and 30% for dry seeded and acid seeded experiments, respectively]. Oligomerisation was an important isoprene SOA formation pathway under both low- and high-NO_x conditions. The nature of the oligomers was, however, distinctly different in each NO_x regime. The high-NO_x oligomers were characterised as oligo-esters, where their formation could be explained by particle-phase esterification reactions involving 2-MG as the key monomeric unit. These oligo-esters accounted for a substantial fraction (~22-34%) of the high-NO_x SOA mass. Tracer compounds for isoprene oxidation in the ambient atmosphere, which had been detected for samples from the Amazon Basin, were detected in the low-NO_x chamber experiments with isoprene. They included C₅-alkene triols and hemiacetal dimers, which were detected for the first time in a controlled laboratory experiment, suggesting that the oxidative conditions used in these experiments are relevant to remote regions of the world. It was elucidated that the hemiacetal dimers result from the reaction of 2-methyltetrols and C₅-alkene triols. The detection of C₅-alkene triols and unstable products, tentatively characterised as 2-methyltetrol performate derivatives, provides evidence for the rearrangement of hydroxyperoxy radicals or the decomposition/rearrangement of hydroperoxides, formed in the initial oxidation (by OH/O₂) of isoprene, into C₅-alkene triols and epoxydiols. Upon further acid-catalysed hydrolysis, the epoxydiol intermediates that result from this latter rearrangement/decomposition reaction likely form 2-methyltetrols in the particle phase. 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.

BIOSOL partner P2 collaborated in the interpretation of results on organosulphates which were obtained by Caltech and US EPA in smog chamber experiments with isoprene and α -pinene. In this study, experiments were done under different NO_x conditions in the absence and presence of sulphuric acid seed aerosol. Over the full range of NO_x conditions, resultant sulphate esters in isoprene and α -pinene SOA were identified and structurally elucidated. Sulphate esters were found to account for a larger fraction of the SOA mass with increased acidity of seed aerosol, providing an explanation for the “acid-effect” in SOA formation. Many of the isoprene and α -pinene sulphate esters identified in the chamber experiments were also found in aerosol collected from the southeastern US and K-puszta, Hungary, demonstrating the atmospheric relevance of these particle-phase reaction products. The isoprene and α -pinene photo-oxidation products of which organosulphate derivatives were identi-

fied include 2-methyltetrols, 2-methyltetrol *mono*-nitrate derivatives, 2-MG, and α -pinanediol hydroxynitrate.

In co-operation with the University of Kuopio, plant growth chamber experiments were carried out. SOA was produced from BVOCs emitted by Scots pine and Norway spruce after triggering the plants with methyl jasmonate. Some of the detected SOA compounds were identified as *cis*-pinic acid and *cis*-pinonic acid, which are known ozonolysis products of α -pinene. Also analogues of Δ^3 -carene, which was found to be a major monoterpene emitted from the Scots pine foliage, were observed. Furthermore, some compounds were tentatively assigned to 10-hydroxy-*cis*-pinonic acid and its Δ^3 -carene analogue.

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. The air mass origin was also quite different during the two periods. During the cold period (24 May – 11 June 2006), the air masses came from the northwest and often originated over the North Sea and/or the Atlantic Ocean. In contrast, during the warm period (12-29 June 2006), the air masses had essentially a continental character and they were more stagnant. From the data for the 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. The regression of the high-time resolution data for isoprene as a function of air temperature indicated that there was a factor of 4 increase in isoprene concentration per 10°C increase in temperature. This is much higher than the value typically observed for biological reactions (which is about 2). 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 = PM_{2.5}) from the in-situ instruments and for the data of a number of components in the filter samples. 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. During these episodes the total particle concentration in the 10 nm – 1 μ m size range rose from the background concentration of some thousand particles to tens of thousands particles per cm³. The lowest concentration detected was around 800 cm⁻³ and the highest one was over 40,000 cm⁻³. At first sight, there seemed to be no relation between the particle production events and the in-situ VOC, fine PM or fine OC levels. Elemental carbon (EC) represented only a minor fraction of the total carbon (TC, with TC = OC + EC), indicating that the K-puszta site was not much influenced by

automotive emissions or other fossil fuel combustion. Around 60% of the fine OC was water-soluble, suggesting that a large fraction of the OC consisted of oxygenated organics, including SOA. Organic matter (OM), estimated as 1.8 OC, was the major aerosol component in both PM_{2.5} 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 PM_{2.5}, with percentage contributions of 22-24%. Because of the high sulphate and OM concentrations in PM_{2.5}, significant concentrations of organo-sulphates are expected, which may be important contributors to HULIS. This will be examined by detailed organic analyses.

From the results for OC, 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. From the detailed organic analysis of the aerosol samples from Brasschaat and comparison with the aerosol composition of the other two sites, we hope to obtain insights to what extent the anthropogenic emissions affect the composition of the biogenic SOA.

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 then down to 6.1°C on 31 August, with a secondary maximum of 17°C on 22-24 August. The air masses came mostly from the West, except in the period from 9 to 14 August, when they first showed a recirculation pattern and on 13 and 14 August came from the South. In the period of 10-13 August there was extensive biomass burning in the southern part of European Russia, which considering the air mass transport could have affected our measurements at SMEAR II. 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 separate day-time and night-time

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 (AD). Two distinct submicrometer modes, with peaks at about 0.3 and 0.7 μm AD, termed “condensation” and “droplet” modes, were clearly present for the day-time samples, whereas in the night-time samples the two modes seemed to have consistently merged into one broad accumulation mode. The formation of the “droplet” mode is explained by activation of condensation mode particles to form fog or cloud drops followed by aqueous-phase chemistry in fogs or clouds and subsequent fog or cloud evaporation. As to the broad accumulation mode during the night, this is likely due to hygroscopic growth of the OC. The RH increased to 80–100% during the night, whereas it generally decreased to well below 60% during day-time. Like during the 2006 summer campaign at K-pusztá, there was little EC in the aerosol at SMEAR II and most of the fine OC was water-soluble (i.e., 63%).

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. At forested sites that are little affected by anthropogenic activities, such as K-pusztá and SMEAR II, and where a large fraction of the fine OC is presumably SOA, about twice as much of the OC is water-soluble. The percentage of 30% for our marine samples 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 nor from monoterpenes in the samples from the NH cruise. Whether SOA from these BVOCs is important at Amsterdam Island will be revealed by the planned detailed organic analyses of the samples from this site.

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 molecular weights (MWs) of 148 and 204 were firmly established as 3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), respectively. A formation mechanism for MBTCA was proposed, which involves participation of the OH radical, but it cannot be ruled out

that ozone is also involved. With the proposed pathway it is possible to explain smog chamber observations, which suggested that the MW 204 compound is formed at the expense of *cis*-pinic acid. The observations can be explained with *cis*-pinonic acid following two routes; namely, a short one leading to *cis*-pinic acid, and a longer one, leading to MBTCA. The formation of MBTCA likely takes place in the particle phase, but further work is required to confirm this hypothesis and obtain insights into the reaction mechanism.

As to objective (3), most of the work for it is planned for Phase II of the BIOSOL project. In Phase I, we determined the contribution from the BVOCs to the organic aerosol for PM_{2.5} samples, which had been collected in summer 2003 in a mixed deciduous forest in Jülich. The average contribution of isoprene SOA was estimated at 2.5% of the OC and that of α - β -pinene SOA at at least 2.4%, while the average contribution from wood smoke to the OC was estimated at 3.3% and that from fungal spores at 3.6%. The summed contribution of isoprene and α - β -pinene SOA, wood combustion, and fungal spores to the PM_{2.5} OC of the Jülich samples was thus at least 12%. It is clear that most of the OC remained unaccounted. Organosulphates, HULIS, and other primary biogenic aerosol besides fungal spores probably made up for a substantial fraction of the unexplained OC.

Keywords: atmosphere, biogenic volatile organic compounds, secondary organic aerosols, indicator compounds, smog chambers, forested sites.