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IMPACT OF BIOGENIC EMISSIONS ON ORGANIC AEROSOLS AND OXIDANTS IN THE TROPOSPHERE

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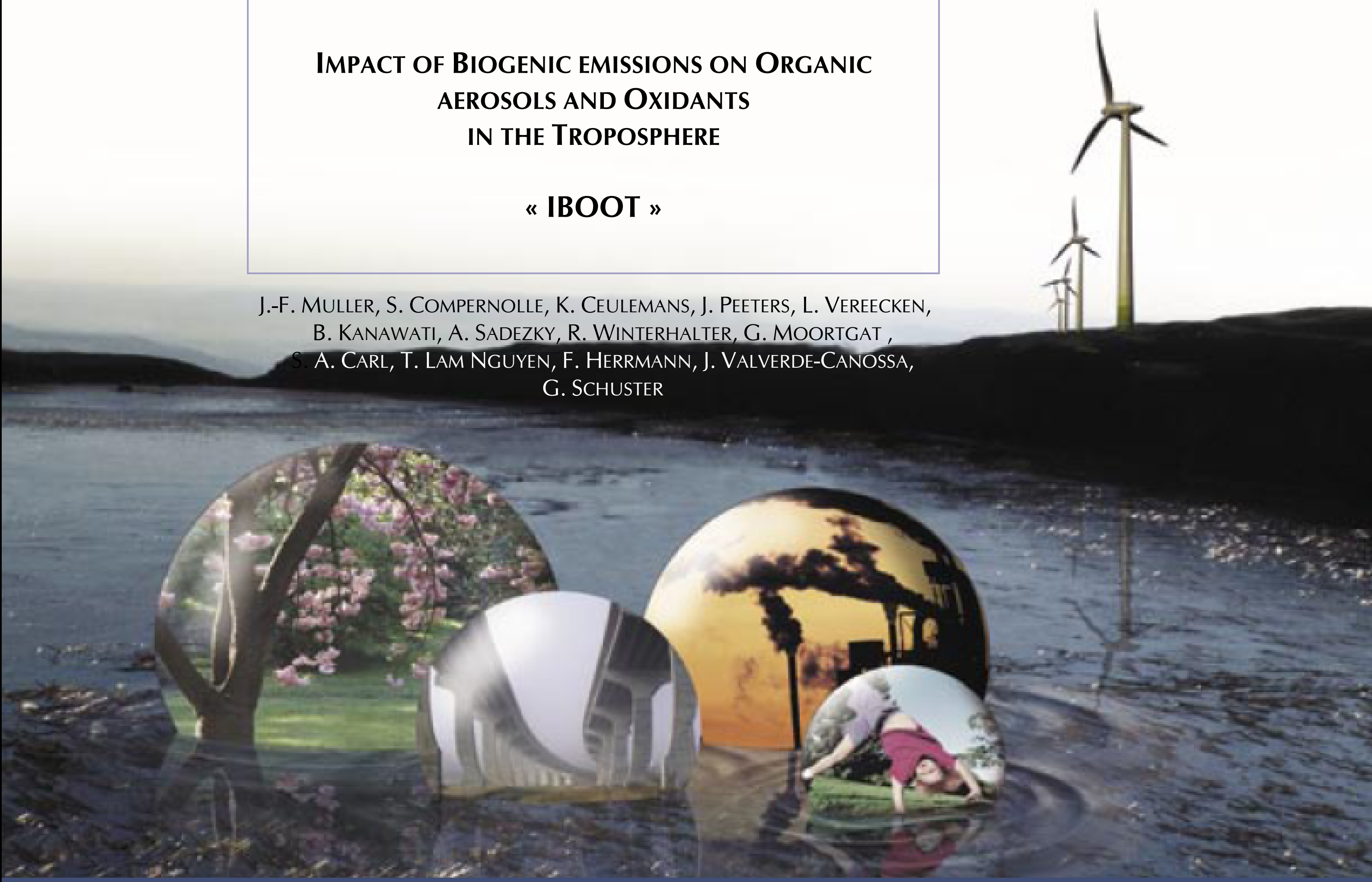

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SCIENCE FOR A SUSTAINABLE DEVELOPMENT (SSD)

Atmosphere

FINAL REPORT PHASE I
SUMMARY

IMPACT OF BIOGENIC EMISSIONS ON ORGANIC AEROSOLS AND OXIDANTS IN THE TROPOSPHERE

« IBOOT »

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April 2008

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Human activities and the biosphere release large amounts of reactive gases which have a profound impact on our environment. In contrast with other classes of pollutants, the non-methane volatile organic compounds (NMVOCs) are overwhelmingly biogenic (BVOCs). Secondary pollutants resulting from their oxidation in the air include ozone and aerosols, which are key actors in air quality and climate change issues. Their emissions also influence the oxidizing capacity of the atmosphere, mainly through their impact on the hydroxyl radical (OH). The general lines of their oxidation mechanisms are believed to be well-known, and many processes involved in the formation of Secondary Organic Aerosol (SOA) have been identified. SOA production is generally calculated based on the absorptive theory of *Pankow* (1994) and aerosol yields estimated from smog chamber experiments. However, the use of experimental product yields in atmospheric models is uncertain, due to large differences between the photochemical conditions in experimental setups and in the atmosphere. Near-explicit chemical mechanisms have been elaborated and validated for the degradation of pinenes by OH, up to the formation of primary products (*Peeters et al.,* 2001; *Capouet et al.*, 2004). These studies revealed important differences between the product yields in laboratory conditions and in the atmosphere, due in part to the existence of unexpected reaction sequences. Such detailed mechanisms are still lacking for other important reactions, like the ozonolysis of terpenes, and the degradation of primary products. In particular, the degradation mechanism of the very reactive sesquiterpenes is essentially unknown, in spite of its potentially great importance for new particle formation and SOA growth. Furthermore, heterogeneous and particle-phase reactions are still poorly characterized, although it is now well established that they generate low-volatility oligomers and increase the SOA yields in the oxidation of terpenes.

The IBOOT project adopts an integrated approach consisting of laboratory, theoretical and modeling investigations in order to address these issues and to better quantify the role of biogenic hydrocarbons, in particular with respect to the formation of ozone and aerosols and the oxidation capacity of the atmosphere. More specifically, the chemical degradation and aerosol formation potential of two important sesquiterpenes are investigated in the laboratory at the Max-Planck Institute in Mainz: β-caryophyllene (during Phase 1 of this project) and α-humulene (during Phase 2). The degradation mechanism of monoterpenes (α- and β-pinene) and sesquiterpenes (β-caryophyllene and α-humulene) are constructed by means of advanced theoretical methods in KULeuven, and validated by model simulations of laboratory experiments at IASB-BIRA in Brussels. The aerosols generated from these compounds are characterized by laboratory (Mainz) and modeling (Brussels) studies. The role of specific oxygenated organic compounds in the upper troposphere is also investigated at KULeuven. Finally, a global model will be used (during Phase 2) to test the BVOC oxidation mechanism and aerosol formation potential against field measurements, and to assess the overall importance of BVOC in the atmosphere. The results obtained during the first Phase of this project are summarized below.

Laboratory studies of mono- and sesquiterpene ozonolysis (MPI-Mainz)

Products studies using mass spectrometric methods of the reaction of ozone with the sesquiterpene β-caryophyllene were performed and a reaction mechanism was developed based on the observed products. Moreover, investigations on the applicability of potential analytical methods for the characterization of reactive oxidation products (H_2O_2 and organic peroxides) were conducted. Mechanistic studies included the determination of OH-radical yields from mono- and sesquiterpene ozonolysis and kinetic experiments with the aim to measure the rate constants for ozone with the various double bonds in poly-unsaturated sesquiterpenes. In another study, the aerosol yields from sesquiterpene-ozonolysis were determined under various experimental conditions and finally, in order to improve the understanding of aerosol nucleation processes, the formation of oligomers and polymers from simple alkenes and enol ethers was investigated using several mass spectrometers (LC-MS-MS-TOF, FTICR-MS-MS).

More than 20 components of the secondary organic aerosol (SOA) formed from the ozonolysis of β-caryophyllene were characterized by LC-MS-MS-TOF using two different ionization methods (ESI$^-$ and APCI$^+$). ESI$^-$ is known as a very sensitive technique for the measurement of carboxylic acids. Additionally, an ESI$^-$-method was developed to detect not only carboxylic acids anions, but also aldehydes as anions, thus extending the range of detectable products by ESI$^-$. Measurements with APCI$^+$ (high ionization efficiency of carbonyl groups) completed the investigations and allowed to compare the trace of each anion with its corresponding cation, to yield complementary information about the identity of the product. In depth analysis of CID (Collision Induced Dissociation) spectra of anion-cation pairs led in some cases to unequivocal structural determination. In other cases, where chromatographic co-elution was observed, structural determination of important isomeric oxidation products could be achieved. Besides the detected oxo- and dicarboxylic acids, multi-functional isomeric products bearing e.g. aldehydic, carbonyl and hydroxyl groups could be differentiated by examining their CID fragmentation pathways. Fragmentation mechanisms were proposed for the experimentally observed ions in all the CID experiments. Gas phase deprotonation potentials were calculated by DFT (Density Functional Theory) to estimate the most thermodynamically favourable deprotonation site for efficient negative ion formation in Electrospray (ESI).

The OH-radical yields from the ozonolysis of several mono- and sesquiterpenes were indirectly determined using an OH-radical scavenger (cyclohexane), whose reaction product with the OH-radical (cyclohexanone) was quantified by PTR-MS, and from its product yield the OH-radical yield could be calculated. For β-caryophyllene, the OH-radical yield from the second double bond was twice as large (21 %) as for the first more reactive double bond (8.5 %). For α-humulene, the first two double bonds gave the same OH-radical yield of 10 %, the OH yield from the third double bond was not determined (*Herrmann*, 2006).

The experimentally determined rate constant for the ozone attack of the second (less reactive) exocyclic double bond in β-caryophyllene was determined by simulation of the ozone consumption using Facsimile as $k_2 = 1.1 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. This value is two orders of magnitude lower than the rate constant for the ozone attack of the first reactive endocyclic double bond in β-caryophyllene, $k_1 = 1.16 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. The rate constant for the first, second and third ozone attack in α-humulene is 1.17×10^{-14}, 3.6×10^{-16} and 3.0×10^{-17} cm^3 molecule^{-1} s^{-1}, respectively.

The potential applicability of LC-MS-MS-TOF for the detection of standard peroxides was investigated, with negative results. H_2O_2 and simple α-hydroxy-hydroperoxides could be measured by HPLC. The yields of H_2O_2 were found to be 2 to 4 % for β-caryophyllene, and four times larger for □-humulene. In the aerosol phase also significant quantities of long-chain hydroperoxides (C_6 to C_{12}) were detected, with a relative yield of 12 % compared to H_2O_2.

Although the detected products in these laboratory experiments do not provide unambiguous information on the precise oxidation pathways occurring in the reactor, their nature represent useful constraints in the development of oxidation mechanisms using theoretical means, in particular with regard to the fate of the Criegee Intermediates. This development will be made possible by the ongoing advances in the realization of accurate Structure-Activity-Relationships for important classes of chemical reactions, as well as by the high-level theoretical calculations aiming at determining the fate of key specific intermediates produced in the degradation of the terpenes.

The aerosol yield from β-caryophyllene ranged from 6 to 24 % in the absence of CI-scavenger, while in the presence of CI-scavenger such as HCOOH, HCHO and H_2O the yield ranged from 9 to 41 %. The increasing aerosol yield by addition of water vapour and with higher concentrations of formic acid is unexpected, since previous studies of the ozonolysis with monoterpenes have indicated that the addition of HCOOH decreases the aerosol yields. It is suggested that formic acid adds to the CI to generate an intermediate product with sum formula of $C_{16}H_{26}O_5$**,** which then undergoes a rearrangement to yield the oxocarboxylic acid □-caryophyllonic acid, a non-volatile compound, and thus increases the aerosol yield. The SOA yield was also found to depend on aerosol mass (*Herrmann*, 2006).

Oligomer formation involving Criegee Intermediates, first observed in the ozonolysis of a variety of enol ethers (*Sadezky et al.*, 2006), was also shown to occur for small symmetric alkenes in an analogous way. The formed SOA was detected by a SMPS system and chemically characterized by a hybrid ESI-MS-MS-TOF technique in the mass range m/z 200–800. The chemical composition was confirmed by accurate mass measurements with an ESI Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer (in cooperation with the University of Giessen), which offers ultrahigh resolution and high sensitivity for the characterization of complex samples. All detected oligomers possess the basic structure of a linear oligoperoxide, $-[CH(R)-O-O]_n-$, with the repeated chain unit CH(R)OO having the same elementary compositions as the main Criegee Intermediates (CI) in these ozonolysis reactions. The elemental compositions of parent ions, fragment ions and fragmented neutrals determined by accurate mass measurements with the FTICR technique allows to assign a complete structure to the oligomer molecules. It is suggested that the formation of the oligoperoxidic chain units occurs through a new gas-phase reaction mechanism observed for the first time, which involves the addition of stabilized CI to organic peroxy radicals. This oligoperoxide formation involving CI-like chain units represents a new pathway for SOA and oligomer formation and shows its validity for a wide range of alkenes (*Sadezky et al.*, 2006).

Preliminary results for the sesquiterpene α-E,E-farnesene show that also the reactions of ozone with terpenes produce high-molecular weight compounds in the mass range 250 to 800 u. Future work will elucidate the possible formation of oligomers from other sesquiterpenes.

Development of predictive tools for mechanism development (KULeuven)

Progress has been made in the development of Structure-Activity Relationships (SARs) and predictive correlations for some key reaction classes in atmospheric chemistry. Such SARs are highly useful in the construction of atmospheric oxidation mechanisms of larger VOCs, including biogenics. The barrier height E_b for decomposition rate coefficient of alkoxy radicals depends primarily on the α- and β-substituents on either side of the breaking $^{\bullet}OC_{\alpha}–C_{\beta}$ bond. A easily applicable SAR was developed for the prediction of this barrier height, based on a large set of quantum chemical calculations including alkyl-, hydroxy-, oxo-, hydroperoxy-, alkylperoxy-, alkoxy-, nitrate- and nitrite functionalities, as well as unsaturated groups and some ring structures. Recently, a paper was published (*Peeters et al.*, 2007) on the site-specific addition of OH radicals on (poly)unsaturated hydrocarbons, based on the latest kinetic data recommendations available in the literature and direct experimental measurements. This SAR predicts the partial and total rate coefficients as a function of the substitution pattern directly surrounding the double bond or conjugated alkadiene.

A predictive correlation, linking the C–H bond strength to the rate of site-specific H-abstraction from hydrocarbons by OH radicals, is under active development. The data currently includes over 50 radical products and hundreds of conformers. Bond strengths are obtained at various levels of quantum chemical theory, while several models are explored to deduce the site-specific rate coefficients. The results are exported directly to a website, ensuring easy dissemination of the results.

Development of terpene oxidation mechanisms

The OH-initiated degradation of α-pinene was upgraded in a recent publication (*Vereecken et al.*, 2007), now including H-shift and ring closure reactions for certain peroxy-radical intermediates. This new chemistry explains the formation of some heavy poly-oxygenated reaction products observed experimentally. The predicted production of hydroperoxides and (hydroxy-)(di-)carbonyl compounds has a profound impact on the predicted SOA formation. The OH-initiated degradation mechanism of β-pinene is under active development, specifically focusing on the dependence of the product distribution on the concentration of NO and HO_2/RO_2. This chemistry is strongly influenced by non-traditional pathways, with (per)oxy radical ring closure reactions affecting most of the chemistry; the predicted product distributions are in good agreement with the scarce experimental data.

The research on the ozone-initiated oxidation of α- and β-pinene currently focuses on the formation of products with (multiple) carboxylic acid functionalities, using a combination of high-level quantum chemical calculations with MC-TST, while explicitly examining reaction through all four Criegee intermediates formed. The O_3-initiated oxidation of β-caryophyllene was investigated theoretically, the prediction being in good agreement with and complementing the extensive experimental investigation detailed in this report. A first-generation product distribution is presented, as well as T-dependent, site-specific and total thermal rate coefficients; this work will be submitted for publication during the first half of 2008. Preliminary work on the ozonolysis of α-humulene revealed that ozone addition on all three >C=C< sites proceeds without barrier, explaining the high total rate, but also implying a highly complex overall mechanism.

Modeling α-pinene degradation

The chemical box model describing the oxidation of α-pinene by OH developed in our previous work (*Capouet et al.*, 2004) has been extended to encompass the O_3- and NO_3-initiated oxidation, as well as the new pathways proposed by *Vereecken et al.* (2007). Given the lack of credible pathway leading to the formation of key polyfunctional acids known to be produced in the ozonolysis of α-pinene, an artificial pathway leading to these compounds has been implemented based on laboratory observations. Since a fully explicit terpene oxidation mechanism would be out of reach with the current computing capabilities, the degradation of the primary products is parameterized by the use of an extensive set of generic and semi-generic compounds. This development of our mechanism is based to a large extent on SARs developed within IBOOT by the KULeuven team. The generic compounds are grouped into volatility classes, and can therefore contribute to the growth of SOA.

The complete α-pinene degradation mechanism is published on a web page which allows users to explore it in a convenient way (http://www.aeronomie.be/tropo/boream/). The coupled gas phase/condensation model, BOREAM (Biogenic compounds Oxidation and RElated Aerosol formation Model) includes about 5000 reactions and 1200 species.

Organic aerosol modeling

Gas/particle partitioning follows the approach of *Pankow* (1994), with vapor pressures calculated following *Capouet and Müller* (2006). In order to account properly for the interactions between the different compounds entering the composition of SOA (including water), a parameterization built on UNIFAC (*Fredenslund et al.*, 1975) has been developed for calculating the activity coefficients. Since the interaction parameters for important functional groups (e.g. nitrates and hydroperoxides) are missing in the published versions of UNIFAC, we have estimated these parameters based on the SPARC calculator (*Hilal et al.*, 2004). The activity coefficient parameterization has been implemented in the organic aerosol model. The impact of non-ideality on SOA formation is found to be small in absence of water uptake, being typically of the order of 10% for individual species, although larger effects are found in the case of low-VOC experiments. When water is allowed to condense on SOA, non-ideality reduces the aerosol yields, especially at high relative humidity, due to repulsion between water and organics.

The α-pinene degradation mechanism and SOA formation model has been tested against a large number of laboratory experiments: about 30 photooxidation experiments and over 100 dark ozonolysis experiments from a total of 15 published studies. The model generally reproduces the measured SOA yields to within a factor of 2, a remarkable result considering the uncertainties on the vapour pressures and the preliminary nature of the ozonolysis mechanism. This relatively good agreement contrasts with the large underestimations of SOA found in several previous modelling studies, which found necessary to increase the partitioning coefficients by orders of magnitude in order to match the laboratory data. As expected, the formation channels leading to pinic acid and hydroxy pinonic acid have a strong influence on the yields, stressing the need for further efforts aiming at their elucidation.

Two types of oligomerization reactions have been tested with the model. The particle-phase association reactions of aldehydes and hydroperoxides are found to have only a moderate impact on the SOA yields, except in a few cases where the calculated yields were already high in absence of such reactions. The gas-phase oligomerization of stabilized Criegee Intermediates is found to be significant in the low-VOC ozonolysis experiments.

The temperature dependence of the SOA yields is not correctly reproduced by the model. The calculated SOA yields decrease rapidly when temperature increases, as a result of the temperature dependence of vapour pressures. The experiments indicate that SOA is formed in significant amounts even at high temperatures, suggesting the existence of unknown channels leading to extremely condensable compounds.

Impact of oxygenates on the upper troposphere

The reactions of oxygenates with OH are characterized by the formation of H-bonded pre-reactive complexes (PRC), affecting the energy of the abstraction transition states (TS), and resulting in complex temperature- and pressure dependences. Several papers are in preparation, detailing the different regimes of reaction, and illustrating some of the effects for complex reactants, including (deuterated) carboxylic acids.

The reactions of HO_2 radicals with some major carbonyl-bearing products of the isoprene and terpene degradation were investigated. The results indicate that these reactions, combined with subsequent reactions with NO/HO_2, can constitute effective sinks for some of these compounds near the tropopause. Additionally, we theoretically investigated the reactions with HO_2 of α-hydroxy-alkylperoxy adducts, formed in the HO_2 + carbonyl reactions as well as from α-hydroxy alkyl radicals. Recent experimental evidence indicates that these reactions have higher yields of alkoxy- and OH radicals than previously assumed. Papers are in preparation.