IBOOT - Results

Impact of Biogenic emissions on Organic aerosols and Oxidants in the Troposphere

DURATION OF THE PROJECT
15/12/2005 – 31/01/2010

BUDGET
685.568 €

KEYWORDS
Biogenic volatile organic compounds (BVOC); air quality; climate change; oxidizing capacity of the atmosphere; secondary organic aerosols (SOA); tropospheric ozone; hydroxyl radical; smog

CONTEXT

Terrestrial vegetation releases vast quantities of volatile organic compounds (VOCs) to the atmosphere, of the order of 1000 millions of tons each year. Although of natural origin, biogenic VOCs (BVOCs) are central to our understanding of the role played by human activities (e.g. land use changes and anthropogenic emissions) in climate change and air quality issues. Most importantly

- they influence the oxidizing capacity of the atmosphere and therefore the abundance of many key gases, especially the greenhouse gas methane, but also air quality compounds (e.g. carcinogenic benzene) and chemicals contributing to stratospheric ozone depletion (e.g. HCFCs)
- in polluted areas, they participate to summertime “ozone smog”episodes, i.e. to the build-up of noxious pollutants, primarily ozone, due the catalytic action of nitrogen oxides of anthropogenic origin
- they are a source of Secondary Organic Aerosol (SOA) which makes up a substantial fraction of fine aerosols (i.e. particulate matter or PM).

Aerosols play a central role in climate through direct radiative effects and through their influence on clouds. Along with ground-level ozone, fine aerosols are also a major component of smog over polluted regions. They have acute adverse effects on human health, in particular on the respiratory and cardiovascular systems; over Europe, PM pollution has been estimated to cause ~200,000 premature deaths per year.

Regulation measures in the United States and Europe are tightening as a growing body of scientific evidence suggests that there is no safe level of exposure to ozone or PM. Although anthropogenic emissions of ozone precursors have generally decreased in Europe since the 1990s, exposure to ground-level ozone has failed to decline substantially, and the number of premature deaths due to ground level ozone worldwide is expected to quadruple by 2030. This global pollution trend has also negative consequences for crop yields and for natural ecosystems and their ability to take up atmospheric carbon dioxide.

Although crucial to these issues, the effects of BVOCs remain poorly quantified, as illustrated by the failure of state-of-the-art models to reproduce field measurements of OH radicals over forests. A better understanding of the chemical and physical transformations affecting the BVOCs and their oxidation products is required in order to assess

- the role of the biosphere, and its evolution in response to climate and composition changes induced by anthropogenic emissions and land-use changes,
- the effect of regulatory measures aiming at the mitigation of air pollution and climate change, in particular at the European level (for air quality compounds) and in the framework of global climate negotiations

OBJECTIVES

The objectives of the IBOOT project were a better understanding and quantification of the role of BVOCs, in particular with respect to the formation of oxidants and aerosols, by means of laboratory, theoretical and modeling investigations of the chemical degradation and aerosol formation potential of important BVOCs.

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SCIENCE RESULTS

Laboratory studies (MPI-Mainz)

The reaction with ozone of two specific BVOCs (the sesquiterpenes b-caryophyllene and a-humulene) has been studied in the laboratory. This detailed investigation provided key insights on the degradation mechanism. In addition, the reaction rates and the yields of SOA, OH-radical and hydrogen peroxide were determined. Long-chain hydroperoxides were also detected.

In the case of b-caryophyllene, a dozen products could be identified in the particulate phase. The respective contributions of the hydroperoxide channel, the ester channel and collisional stabilisation of the Criegee Intermediates (CI) were estimated to 10%, 5-10% and > 80%. The stabilized CI can undergo ring closure to produce internal secondary ozonides (SOZ).
In the case of a-humulene, 37 compounds in the aerosol phase and 5 products in the gas phase were assigned.

The initial ozonolysis of a-humulene leads to 6 different CI's. Subsequent reaction with ozone leads to a wide range of products. The primary ozonide is found to decompose rapidly, and a large fraction of the excited CI is stabilized to form stable SOZ, while the hydroperoxide channel is a minor process.

Oligomers were observed in the SOA formed from ozonolysis of simple alkenes. They possess the basic structure of a linear oligoperoxide, $-[CH(R)-O-O]_n-$, with the repeated chain unit having the same elementary composition as the main CI in these ozonolysis reactions. This process represents a new pathway for SOA formation and is valid for a wide range of alkenes.

Theoretical development of BVOC oxidation mechanisms (KULeuven)

Tools (Structure-Activity Relationships) necessary for the construction of VOC oxidation mechanisms were developed or extended, in particular for OH-reactions and for reactions of alkoxy radicals. The OH-initiated degradation mechanism of α-pinene has been updated by inclusion of novel radical pathways. The OH-initiated degradation mechanism of β-pinene is being finalized. The ozonolysis of three important BVOCs was also investigated; the results, including the very fast primary ozonide formation and internal SOZ formation for β-caryophyllene, are confirmed by experimental data (see above).

The atmospheric oxidation of oxygenates (KULeuven)

Detailed theoretical analyses of reactions of oxygenated compounds with OH radicals were conducted and verified by experimental data. Reactions of HO_2 with oxygenated compounds and with $HOCH_2OO$ were investigated; in the latter case, the unexpected OH regeneration observed experimentally is confirmed by our calculations, but with co-products different from the proposed ones.

The oxidation of isoprene (KULeuven and BIRA-IASB)

Prompted by recent observations of unexpectedly high OH radical concentrations above forests (*Lelieveld et al*., 2008), we investigated the OH-initiated oxidation of isoprene using the highest levels of theory applicable, in order to rationalize the efficient HOx radical regeneration that clearly occurs, contrary to all current model predictions. In a first paper (*Peeters et al.,* 2009), we showed that much of the peroxy radicals react in new ways that directly and by subsequent processes give rise to ample HOx regeneration.

The new chemistry, with its impact on the global oxidizing capacity of the atmosphere, has been further addressed in a joint modeling effort of the KULeuven and BIRA teams.

Modeling α-pinene degradation and aerosol formation

The α-pinene oxidation and aerosol formation model BOREAM (Biogenic Oxidation and Related Aerosol formation Model) has been extended.

A parameterization has been developed to account for non-ideality of the aerosol. Non-ideality is found to have a moderate effect in dry conditions, and to reduce SOA yields in humid conditions, due to repulsion between water and organics. Our vapor pressure estimation method has been refined. The set of experimental data has been enlarged considerably, and the method now includes neighbor effects between functional groups, and treats the effect of multiple hydrogen bonding groups.

BOREAM has been tested against more than 130 smog chamber experiments. The model generally reproduces the measured SOA yields within a factor of 2-3, in contrast with large underestimations found in previous modeling studies. Specific particle-phase oligomerization reactions have been tested but found to have only a moderate impact on SOA yields.
Based on BOREAM, a parameterization for SOA formation from α-pinene has been developed and implemented in a global model. The parameterization accounts for water uptake and for the NOx-dependence of SOA. Highest yields are achieved in the OH-initiated oxidation at low NOx. The resulting model distribution of organic aerosol agrees fairly well with measurements in the Eastern US, providing support to the large SOA source inferred by the model (~100 Teragrams/year globally).

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CONTRIBUTION TO A SUSTAINABLE DEVELOPMENT POLICY

Environmental policy should be based on accurate information regarding the respective roles of natural and anthropogenic emissions on the abundance of air pollutants. IBOOT has contributed to answer the following questions:

Do BVOCs deplete the oxidizing capacity of the atmosphere?

BVOCs were previously believed to deplete hydroxyl radical (OH) concentrations and to reduce the oxidizing capacity of the atmosphere. However, recent observations have indicated that the oxidation of isoprene, the single-most important BVOC, regenerates OH radicals in remote areas, and that the overall effect of isoprene emissions on the oxidizing capacity of the atmosphere is weak. The theoretical work performed within IBOOT provides a first detailed explanation as to how this regeneration takes place. This finding is essential for policy-making, since it will strongly impact the model estimates of how anthropogenic activities (i.e. pollutants emissions and land-use changes) influence the abundance of key pollutants like ozone and the climate gas methane. A recent global modeling study has demonstrated the impact of the new chemistry on the expected future evolution of the oxidizing capacity of the atmosphere.

How much do BVOCs contribute to atmospheric aerosol concentrations?

Secondary organic aerosol (SOA) is a major component of fine aerosols over continents. Work within IBOOT provided new insights allowing improved estimations for the role of BVOCs as a source of secondary organic aerosols. Our model calculations show that biogenic SOA is by far the largest component of organic aerosol, although a large fraction of it is due to poorly characterized oligomerization processes in clouds and in aerosols. The presence of nitrogen oxides appears to partially inhibit the formation of SOA from α-pinene, in agreement with experimental data.

In conclusion, our work shows that BVOC emissions have only little impact on the oxidizing capacity, in particular at remote locations (e.g. rainforests). It appears therefore that, contrary to previous model estimations, deforestation is not expected to increase the self-cleansing property of the atmosphere and to mitigate pollutant build-up. However, BVOCs are a substantial source of organic aerosol having far-reaching effects on climate and air quality. The complex interaction of these emissions with anthropogenic emissions (e.g. NOx and sulfur compounds) warrants further investigation.

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