Biogenic VOC emissions and photochemistry in the boreal regions of Europe

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Biogenic VOC emissions and photochemistry in the boreal regions of Europe

Biphorep

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Edited by
Tuomas Laurila and Virpi Lindfors
Helsinki, March 1999

Research Directorate-General
Foreword

This report contains selected articles related to the Biphorep project (1996-98) supported by the EC environment research programme of DG XII.

The major goal of this project was to understand better the biogenic emissions of volatile organic compounds (VOCs) over north European forest regions and to develop photochemical schemes for the estimation of their oxidation in the atmosphere, in particular for terpenes.

The VOC emissions from boreal vegetation have been investigated at different levels, from leaf to regional, during intensive field campaigns in different boreal zones. The measurements coupled with photochemical modeling have permitted the importance of biogenic VOC species in photochemical processes and ozone formation to be assessed.

The report describes the results of all activities performed, indicating that there are now emission factors and tools to calculate regional emissions of key biogenic compounds, whose knowledge is essential to estimate the total ozone production in the European boreal region and then to develop appropriate policy measures for anthropogenic compounds.

On behalf of the European Commission, I would like to gratefully acknowledge the efforts of the five research groups involved and in particular of Tuomas Laurila and Virpi Lindfors for the coordination of the project and the editorial work on this report.

Giovanni Angeletti
European Commission, Research DG
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Summary

T. Laurila

Project Coordinator

Finnish Meteorological Institute, Air Quality Research
Sahaajankatu 20 E, FIN-00810 Helsinki, Finland

The goal of the BIPHOREP project was to gain a better understanding of biogenic VOC emissions over North European forest regions, and to develop photochemical schemes for the estimation of their oxidation in the atmosphere. Until this project, emission factor measurements of typical European boreal plants have been very limited. The boreal forests are dominated by coniferous trees, and the monoterpene emission rates exceed the isoprene emission rates. The photochemical degradation of terpenes is thus important for the atmospheric chemistry in this region. Species specific emission information is also crucial for the estimation of aerosol production from the biogenic VOCs, because aerosol yields are very much dependent on the reactivities of the monoterpenes and other VOCs.

BIPHOREP was built to address the following key questions:

- To make measurements of emission factors of biogenic VOCs from coniferous and deciduous trees, lichens, and ground flora.
- To test the dependence of these emission factors on environmental factors.
- To measure biogenic VOC emissions using micrometeorological methods.
- To make a boreal forest characterization and to develop a canopy model for the calculation of biogenic VOC emissions.
- To make measurements of concentrations of the most important biogenic VOCs in ambient air for understanding the seasonal cycle of concentrations and for using them as initial and validation data for the modeling exercise.
- To develop and test photochemical models to estimate biogenic emissions and the importance of biogenic emissions on the photochemical processes and ozone formation.
The main results of the BIPHOREP project are the new emission factor measurements. Emission rates of all dominant boreal tree species have been measured and emission information for ground flora and wetlands has been gathered. The project has addressed many previously poorly known aspects of the biogenic emissions. These include the seasonal cycles of the emissions, the emissions of oxygenated compounds, emissions from lichens and wetlands, and the characterization of emissions from pools and de novo synthesis. At the two intensive campaign sites, micrometeorological measurements were used to study the emission processes at the canopy scale, and for comparison with the emission calculations.

Project description

The boreal forest is one of the world’s major vegetation regions, forming a continuous belt around the whole Northern Hemisphere. Trees such as Norway spruce, Scots pine, downy birch, and silver birch characterize the boreal coniferous woodlands. The boreal forests are rich in mosses and lichens but poor in vascular plants.

During the BIPHOREP project, the VOC emissions from boreal vegetation were studied at three levels. At leaf level, the emissions from the most common trees and lichens were measured. At canopy level, micrometeorological measurements and canopy modelling were used. At regional level, a combination of emission and photochemical models together with measured ambient air concentrations were used to estimate biogenic emissions and their effect on atmospheric chemistry. The field work covered all regions of the North European boreal zone. In 1996, the intensive field campaign was at Pallas, North of the Arctic Circle. In 1997, the field campaign was carried out at Mekrijärvi in the Middle boreal zone. Extensive cuvette measurements at Björklinge (near Uppsala), and Asa and Ruotsinkylä in the South boreal zone complemented the field campaigns. Photochemical modelling and measurements of photochemically active trace species were conducted to assess the importance of biogenic VOC species in photochemical processes and ozone formation.

The European boreal forest area and the study sites are illustrated in Figure 1 which shows the percentage of coniferous forest in a landuse map. The ambient air samples at the Pallas site were taken on the top of a fjäll, roughly 250 m above the surroundings to get VOC concentrations representative for the boundary layer average. The micrometeorological campaign in July
Figure 1. More than half of the world’s 12 million km$^2$ of boreal forests is to be found in Scandinavia and the Russian Federation.

1996 was in a mixed birch, Norway spruce, and Scots pine forest. At Mekrijärvi, the micrometeorological campaign in 1997 was in a Scots pine forest, which is more typical for this region. The ambient air samples were collected on a hilltop in the same area. Concentration data from Utö, which is a background air quality monitoring station of the Finnish Meteorological Institute, was also used to characterise the air masses.

The work carried out in the project was organised into work packages, which are described in Table 1. The project methodologies include measurements of biogenic emissions from individual plants using cuvettes and/or Teflon bags. The emission factors were studied in relation to environmental parameters like light intensity and temperature and plant physiological parameters like net photosynthesis, leaf conductance, and transpiration. To get integrated emissions at the canopy scale, micrometeorological flux measurement of light hydrocarbons and terpenes were measured as part of the field campaign activities. Forest modelling and extensive use of forest inventories were an essential element in the up-scaling of the emission measurements over the boreal forest zone. Ambient air concentration measure-
### Table 1: Organisation and structure of the BIPHOREP project by work packages.

<table>
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<td>FMI)</td>
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</table>
ments of biogenic VOCs and oxygenated compounds at two representative sites during an extended summer period were used to study the seasonal composition and emission pattern of the VOCs, and as a reference for emission models. The effect of biogenic VOCs on the photochemical processes was studied by means of simple model scenarios.

Main results

Monoterpene emissions from trees

All dominant boreal tree species, Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), and birch (*Betula* sp.), had significant monoterpene emissions. The monoterpene emission profile was variable, but α-pinene and Δ3-carene were the most important compounds emitted by conifers. In the North boreal zone trees had lower normalized emission rates than in the South or Middle boreal zones. The total monoterpene emission rates of Juniper (*Juniperus communis*) and Scots pine were similar, and higher than that of Norway spruce. Using a new emission algorithm it was estimated that a substantial share of this emission originates from *de novo* synthesis in addition to emission from pools. Silver birch (*B. pendula*) and downy birch (*B. pubescens*) showed considerable changes in emissions during the growing season. After budbreak, the emission rates declined, increasing again after midsummer and exceeding the emission rates of the coniferous trees. The high emissions consisted mainly of sabinene and ocimenes (silver birch) and linalool and sesquiterpenes (downy birch). High variability was observed between the trees, possibly due to genetic variability. Grey alder (*Alnus incana*) had a low monoterpene emission rate and did not emit isoprene at all.

Isoprene emissions from trees

Aspen (*Populus tremula*) and willow (*Salix* sp.) were among the few high isoprene emitters in the boreal zone, but as a regional average their foliar biomass density was rather low. Their isoprene emissions began later than leaf development and photosynthetic activity would indicate. Norway spruce (*Picea abies*) and Siberian spruce (*Picea abies* ssp. *obovata*) were low isoprene emitters. However, their emissions were significant because their area integrated foliar biomass was very high. In addition to isoprene, other light alkene emissions were also observed but the emissions rates were low and they were dependent on the phenology.
Carbonyl emissions
The carbonyl emissions of coniferous trees were relatively high. Light carbonyl emissions consisted mainly of acetone. Their emission rates from Scots pine were higher than the monoterpane emission rates. The acetone emissions of Norway spruce were roughly as high as the monoterpane emissions.

Lichen, ground flora and wetland emissions
The first controlled measurements of exchange of aldehydes and organic acids between lichens and the atmosphere showed that the exchange is very much controlled by the environmental conditions, especially the thallus water content. The measurements showed emissions of acetaldehyde and also some other aldehydes and alcohols. Forest floors, covered with typical boreal forest species, emitted small amounts of terpenes and light hydrocarbons. High isoprene emissions were observed at two *Sphagnum* wetlands. The wetland emissions should be included in regional emission inventories because this is a common land cover type in the boreal zone.

Canopy scale emissions
At the canopy scale the monoterpane emissions were much higher than the isoprene emissions. The total emission rates of monoterpenes, measured by micrometeorological methods, were similar to those calculated using environmental, biomass and emission factor data. In early and late summer, the monoterpane species distribution at canopy scale was almost the same, with α-pinene accounting for 70% of the total flux over a Scots pine forest. The micrometeorological measurements revealed significant concentrations, and upward and downward concentration gradients, of many oxygenated species. As most of the cuvette measurements, also the micrometeorological results indicate that the temperature dependence of the emissions is significantly higher than the standard value 0.09 used in emission inventories. The monoterpane profiles in the ambient air concentration measurements and the micrometeorological canopy scale emission measurements were similar, while those obtained in the cuvette measurements showed a higher proportion of the more reactive compounds.

Ambient air VOC concentrations
Ambient air measurements of light hydrocarbons, terpenes and some oxygenated species showed that the total monoterpane concentrations surpass the isoprene concentrations in the
boreal region. The average seasonal cycle of isoprene was different from the monoterpenes. The isoprene concentration maximum occurred in July-August, which is later than the monoterpene maximum. Before June, the isoprene concentrations were very low, but in July and August they exceeded even the concentration of α-pinene, which is the dominant monoterpene. Other important terpenes were Δ3-carene, β-pinene and camphene. In July, the ambient sabinene concentration increased analogous to the birch cuvette emission measurements. In spite of the different monoterpene emission profiles of different tree species, ambient air data suggest that the monoterpene concentration distribution is rather similar over a Scots pine forest and over a mixed birch - Norway spruce forest.

Forest biomass
Coniferous trees dominate the foliar biomass of European boreal forests. The BIPHOREP campaigns were conducted in Finland, where Scots pine, Norway spruce and birch occupy 64.5, 25.7, and 7.3 % of the forest land, respectively. The foliar biomasses were calculated from the permanent sample plot network of the Finnish Forest Research Institute, and deduced from a LANDSAT 10x10 km² land cover analysis of the Finnish Environmental Information center. The average pine, spruce, and deciduous biomasses were 300, 900, and 400 g(dw) m⁻², respectively. After spatial aggregation, both Norway spruce and Scots pine had north-south gradients of needle biomass, with 43 % and 45 % reduction between the latitudes 60°N and 68°N, respectively.

Emission modeling
Coniferous forests account for 80-90 % of the forest VOC emissions in the boreal zone. There is considerable interannual variation of total biogenic emissions due to meteorological variability, with high emissions during the warm summer days. The mass based isoprene to total monoterpene emission ratio varies between 10 and 17 %, depending on the boreal zone and the year. The emissions decrease towards North, partly due to the decreasing biomass and partly due to the lower temperatures and the shorter growing season. The accumulated temperature above 5°C over the growing season describes well the interannual and spatial emission variations. On an average, the six-monthly isoprene emission per forest area unit in the North boreal zone is only 36% of the corresponding emission in the South boreal zone. Compared to monoterpenes, the other VOC (OVOC) emissions are of the same order of magnitude, when the default OVOC emission factor (e.g. CORINAIR Emission Inventory
Handbook) is used in emission modeling. The OVOC emission factors are still utterly unknown, however, and this is an area where further experimental information is urgently needed.

**Photochemical model development**

Photochemical schemes were developed for application in the boreal environment, including the degradation schemes of isoprene, α-pinene, and limonene. Three emission and initial concentration scenarios were created for typical clean, polluted, and isoprene-dominated boreal background atmosphere, to facilitate the evaluation of different chemical mechanisms for the degradation of biogenic VOCs. Box model intercomparisons of the RACM and FMI/PTM photochemical models gave consistent results on the degradation of biogenics and ozone formation. The model results also showed that in background conditions ozone is depleted in the boreal atmosphere, but if anthropogenic NOx emissions are set against the background of biogenic VOC emissions, substantial production of O$_3$ and other photo-oxidants may occur.

**Conclusion**

According to the BIPHOREP results, the regional annual isoprene emissions of European boreal forests are somewhat smaller and the total monoterpene emissions slightly smaller than previous estimates. The preliminary OVOC emission factor measurements indicate that the total OVOC emissions are of the same order of magnitude as the monoterpene emissions. Based on the micrometeorological and ambient air concentration measurements we estimate that the methodology used to calculate the foliar isoprene and total monoterpene emissions is well applicable to the boreal environment. The BIPHOREP results also show that the seasonal variation of the emission potentials, the effect of other than the tree foliar biomass (e.g. ground flora), and the emissions from land use classes other than forests (e.g. wetlands) whose emission potentials are not well known, are important factors which should be assessed in closer detail in the immediate future. The species distribution, emission factors, and emission algorithms of OVOCs should be studied extensively, as there is presently no quantitative information on those.

As a result of the BIPHOREP project, there are now species specific emission factors and tools to calculate the regional emissions of the key biogenic compounds, which are needed for the estimation of aerosol formation and tropospheric ozone production in the European boreal
areas. The BIPHOREP measurements have shown that in these regions, monoterpene and OVOC emissions surpass the isoprene emissions, indicating good potential for biogenic aerosol formation.

The biomass density of the boreal forest is typically very high, resulting in large amounts of biogenic VOCs being emitted in these regions during the warm summer months. The net ozone production rates are, however, low because the spatially averaged anthropogenic NOx emissions and the noontime solar radiation intensities, which are the main driving forces of the ozone production, are low. We estimate that the biogenic VOC emissions in Finland in June-August 1997 were 260 ktonnes. The estimated annual anthropogenic VOC emissions in Finland are 193 ktonnes. During the summer months, when the vegetation is exposed to elevated ozone concentrations, the biogenic VOC emissions are thus 5.5-fold compared to the anthropogenic emissions. To further highlight the importance of biogenic VOCs on ozone photochemistry we note that in May-September 1997, 80% of the biogenic isoprene in Central Finland was emitted during the days when the observed ozone concentrations exceeded 40 ppb which is the threshold for accumulating the AOT40 ozone exposure index. In northern Europe, the majority of the annual biogenic VOC emission load is emitted into continental air masses which have been exposed to considerable ozone precursor load and in which ozone production has already taken place.

Acknowledgement

The BIPHOREP project thanks the Finnish Forest Research Institute and especially Dr. Lasse Loven and Mr. Ahti Ovaskainen at the Pallasjärvi research station, and the Mekrijärvi Research Station of the University of Joensuu and M.Sc. Laura Jetsu for kind hospitality and for providing facilities during the BIPHOREP field campaigns.

This project (ENV4-CT95-0022) was part of the Environment and Climate Research Programme of the European Commission whose financial support is gratefully acknowledged.
This publication is the scientific final report of the Biphorep project (1996-98) supported by the EC environment research programme, devoted to the investigation of the biogenic emissions of volatile organic compounds (VOCs) over north European forest regions.

The project results take account of experiments during several field campaigns implemented at different locations by the five research groups involved.

The measurements performed in different boreal zones and the photochemical modelling have permitted the importance of biogenic VOC emissions in the total ozone production to be assessed in such a way as to contribute to the development of sound environmental policy measures for anthropogenic compounds.