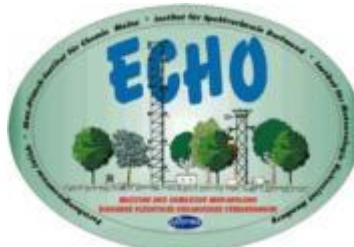


ECHO



Emission and CHemical Transformation of Biogenic Volatile Organic Compounds:

Investigations in and Above a Mixed Forest Stand



**A project of the german Atmospheric-Research-Program
2000**

AFO 2000

Partners

- Prof. Dr. R. Koppmann, Fachbereich Mathematik und Naturwissenschaften, Bergische Universität Wuppertal, Koordinator
- Prof. J. Kesselmeier, Max-Planck-Institut für Chemie, Mainz
- Dr. T. Hoffmann, Institut für Spektrochemie, Dortmund
- Prof. M. Schatzmann, Meteorologisches Institut Hamburg, Universität Hamburg

Aims of the project

Forests are complex sources of biogenic volatile organic compounds (VOC) in the planetary boundary layer. Previous studies estimate that global emissions of biogenic VOC are in the range of 490 Tg C/year to 1150 Tg C/year and thus a factor of 5 to 10 higher than anthropogenic emissions. Therefore, biogenic VOC contribute significantly to the formation of photo-oxidants in the troposphere. Due to fast vertical transport processes, they may even have an impact on the chemistry of the upper troposphere. Recent airborne measurements show surprisingly high mixing ratios of reactive compounds such as acetone, formaldehyde, methanol, hydrogen peroxide and organic hydroperoxides. These compounds are believed to originate from primary biogenic emissions or to be oxidation products of biogenic VOC.

All together, the impact of biogenic VOC on tropospheric photochemistry, air quality, and the formation of secondary products affecting our climate on a regional and global scale are far from being understood. A considerable lack of knowledge exists concerning a typical forest stand as a net source of reactive trace compounds, the amount of primary emitted VOC which are transported directly into the PBL, and the amount of VOC which are chemically processed within the canopy, the products of which are transported into the PBL. The gas phase chemistry above the canopy which is driven by high concentrations of reactive precursor compounds and high UV radiation is also not yet understood. The goal of the proposed project is to investigate these questions to improve our understanding of biosphere-atmosphere interactions and effects on the planetary boundary layer. This will be achieved by the investigation of the following themes:

1. Sources of reactive trace gases in a mixed forest stand: Emission rates of VOC from the trees will be investigated as well as the role of the soil as a source and sink of reactive trace compounds.
2. The forest stand as a chemical reactor: Chemical processes and formation of oxidation products of VOC (secondary VOC, photo-oxidants, organic aerosols) inside the forest stand will be studied.
3. The forest stand as a source of biogenic VOC and their oxidation products: The emission of trace compounds (primary emitted VOC, oxidation products, photo-oxidants, aerosols) from the canopy to the planetary boundary layer will be investigated. The net fluxes of these compounds will be quantified.
4. Atmospheric chemistry above the canopy: Chemical processes above the canopy, the influence of the emission of reactive compounds on these processes, and the formation of oxidation products will be investigated. Of primary interest is the influence of the vertical distribution of different trace gases on the chemical processing and the formation of photo-oxidants.

Contributions of the partners

- In the subproject proposed by the **Research Centre Jülich** the emissions of volatile organic compounds (VOC) from the different tree species at the field site (Stettener Forest, Jülich, Germany) will be measured. In parallel, experiments in plant chambers under defined conditions will be done in order to quantify the primary emissions of these compounds. In addition, their uptake by the plants will be investigated. The objective of these experiments is making emission algorithms available for later modelling. In two intensive field campaigns it will be investigated with which oxidizing agents (OH , HO_2 , NO_3 , O_3) VOC react predominantly in the canopy and to what extent photochemistry or night time chemistry (e.g. ozonolysis and reactions with NO_3) contribute to the oxidation of VOC. For this purpose it is planned for the first time to measure the concentration of radicals (OH , HO_2 , RO_2 , NO_3), a large set of trace gases (VOC, CO, O_3 , NOx, organic nitrates), and meteorological parameters at different heights in and above the forest stand. In order to quantify the photochemical activity in the forest stand, for the first time the solar actinic flux in the visible and ultraviolet will be measured spectrally resolved to derive photolysis frequencies of relevant radical precursors (O_3 , NO_2 , peroxides, oxygenated VOC). The chemical processing of the trace gas mixtures observed in the forest stand will be simulated in the atmosphere simulation chamber SAPHIR under controlled conditions. In the simulation experiments the same trace gases and parameters are measured as in the field experiments under application of the same equipment. This enables on the one hand the detailed study of the chemical processes under exclusion of transport processes and on the other hand sensitivity studies by direct modification of individual chemical parameters. The observations of the field experiments and of the simulation experiments will be compared further with chemical box model calculations. With the combination of field and simulation experiments it will be tried to quantify the chemical processing of the VOC, the photo-oxidant formation in the forest and the radical balance.
- The **Max Planck Institute for Chemistry** will investigate the release of VOC and NOx species as well as their fate within the atmosphere. Gaseous and reactive compounds, once emitted, are not easily quantified within the atmosphere as they underlie fast oxidative transformation processes. Quite often the products are unknown and/or end up within or on particles. Therefore, to quantify the total VOCs we will combine different investigation

and techniques with enclosure methods to perform analyses on the leaf and branch level as well as with mesoscalic integration by micrometeorological methods. Such a combination will give access to primary emissions and secondary fluxes. This work will be closely coupled to the investigations of processes of air chemistry (radical chemistry) and aerosols as planned within the Joint project. An interpretation of the influence of VOC onto the oxidation capacity of the atmosphere is impossible without knowing the NO_x-concentrations or the biogenic NO source strength of the soil, respectively. Complementing the studies of primary emissions and of VOC fluxes we will therefore perform intensive investigations of the biogenic NO-release from forest soils as well as of the vertical distribution of NO_x and its turbulent transport within and above the forest.

The combination of the different techniques and procedures for the determination of primary emissions, atmospheric concentrations and the fluxes will allow a better interpretation of biogenic emissions and their influence on the atmosphere. A high time resolution (1/s) of a new measuring technique for VOCs, the AP-CIMS technique, will provide accurate diurnal patterns and will give access to the short time variations of primary emissions. Furthermore, measuring organic acids will contribute to the understanding of the production processes and compositions of secondary organic aerosol. Quantification of biogenic NO-Emission, the understanding of the production controls (soil moisture and temperature, composition), the knowledge of the vertical NO_x-distribution and transport within and above the forest will build up a fundamental understanding of the oxidation processes, to which VOCs, radicals and NO_x are contributing in a very complex manner. Hence, measuring the primary emissions of trace gases and their fluxes will help to produce a budget in order to verify the physical and chemical transformation processes within and above the forest and the amount and quality of the trace compounds released into the background atmosphere in reality.

- The role of **ISAS Dortmund** within the overall project is focused on the investigation of the atmospheric degradation of the reactive natural VOCs in connection with their potential to form aerosols. Although the aerosol formation potential of biogenic VOCs as a consequence of the gas-to-particle conversion of their oxidation products is a well known phenomenon, detailed investigations in the field are lacking. The studies realised up to now concentrated essentially on the determination of the aerosol yields of biogenic and anthropogenic VOCs and the identification of gas and particle phase oxidation products in laboratory studies, indicating that the amount of organic aerosol formed strongly depends on the initial oxidation step (OH, NO₃ or O₃) as well as the temperature. Unfortunately, field studies considering these processes and therefore a validation of the lab results are rare, especially in anthropogenically influenced regions with a high variation of the actual NO_x and ozone concentrations which affect the routes to the formation of low volatile species. Therefore, the attempt to close the mass balance of tropospheric organic compounds still fails due to a missing understanding of the processes. In order to answer these questions, the following measurements are planned:
 1. Gradient measurements of biogenic VOCs and some of their oxidation products above a mixed forest in the vicinity of Jülich.
 2. Time resolved chemical characterisation of the organic particle phase, especially focusing on secondary organic aerosol components.
- The **Meteorological Institute Hamburg of the University of Hamburg** will deliver new information on vertical transport phenomena in the lower layers of the Troposphere. The

horizontal and vertical transport of tracers above a biogenic area source (finite forest area) will be modelled in a large boundary layer wind tunnel. Systematic investigations consisting of detailed high resolution flow and dispersion measurements will be carried out to extend the field data and to quantify reliability and representativeness of corresponding field measurements in space and time.

The project directly contributes to quality assurance of field data and their enhancement in terms of extending the database for situations that could not be measured in full scale.

Field and laboratory data together will lead to a high quality data set for model validation purposes. The sub-project is part of the project cluster ECHO which aims on a better understanding of the role of a forest stand as a complex source of volatile organic compounds on the climate system. The specific objectives of our sub-project are

1. support in effective planning of the field measurements done by the FZ Jülich group (repeating specific aspects of the field experiments in the new boundary layer wind tunnel, optimising and validating the location of sampling points for field measurements in terms of reliability of the results and their representativeness in space and time for different wind directions/wind speeds)
2. complementing field data with additional laboratory data for adjacent emission situations not captured during field data campaigns (extending the database by adding data for additional wind directions, different emission characteristics, measuring horizontal and vertical transport of momentum and species above the emitting area)
3. quantifying the variability of field data due to the variation of boundary conditions (quantifying the reliability of field data which is required for comparing the field data with results from numerical dispersion modelling)
4. compiling an extensive and completely documented set of reference data consisting of field data and high quality laboratory data. Publication of all results in an electronic database as well as in reviewed journals.

Proposed Measurements

Measurand	Measurement Instrumentation	Institution	Working Group
Emissions from plants	Enclosures, adsorption tubes GC-MS	ICG-II	Dr. Koppmann
Vertical distribution of VOC and oxidation products	on-line GC-MS	ICG-II	Dr. Koppmann
Soil emissions of VOC	Enclosures, adsorption tubes, GC-MS	ICG-II	Dr. Koppmann
Vertical distribution of HO _x -radicals	Laser-induced fluorescence	ICG-II	Dr. Hofzumahaus Dr. Holland
Measurement of photolysis frequencies	Spectral radiometer, filter radiometer	ICG-II	Dr. Hofzumahaus
Vertical distribution of peroxy radicals and NO ₃	Matrix-Isolation-Electron-Spin-Resonance	ICG-II	Dr. Mihelcic
Meteorological parameters	Meteorological tower, different masts in the forest stand	S	Dr. Knaps
Tracerexperiments	SF ₆ -Monitor and GC-ECD	S	Dipl.-Met. Möllmann-Coers
Emission and uptake of VOC by plants	Plant chambers, on-line GC-MS	ICG-III	Dr. Wildt
Simulation experiments	Atmospheric simulation chamber SAPHIR	ICG-II	Prof. Dr. Wahner
Plant emissions	Enclosures, adsorption tubes GC-MS	MPI	Prof. Kesselmeier
VOC fluxes	Eddy Covariance, CIMS	MPI	Prof. Kesselmeier
Physiological parameters of the plants	Measurements of CO ₂ , H ₂ O	MPI	Prof. Kesselmeier
VOC fluxes	Relaxed Eddy Accumulation	MPI	Prof. Kesselmeier
Vertical distribution of NO _x and Ozon	Chemiluminescence	MPI	Prof. Meixner
Soil emissions of NO	Automatic incubation system	MPI	Prof. Meixner
VOC and oxidation products in the gas phase	adsorptive preconcentration, thermo desorption/GC/MS	ISAS	Dr. Hoffmann
Particle bound VOC oxidation products	Filter/Impactor sampling followed by derivatisation/GC/MS resp. Micro-HPLC/MS	ISAS	Dr. Hoffmann
EC/OC-matter of the particle phase	Sampling with quartz filters	ISAS	Dr. Hoffmann

Measurand	Measurement Instrumentation	Institution	Working Group
Optimization of the field site in the wind tunnel	Wind tunnel	UHH	Prof. Schatzmann Dr. Leitl
Quantification of the variability of the field data	Wind tunnel	UHH	Prof. Schatzmann Dr. Leitl

Publications

FINAL REPORT

[Emission and chemical transformation of biogenic volatile organic compounds \(ECHO\) – Investigations in and above a mixed forest stand](#)

R. Koppmann, J. Kesselmeier, F. X. Meixner, M. Schatzmann, B. Leitl, T. Hoffmann, R. Dlugi, M. Zelger, J. Kleffmann, A. Neftel, J. Dommen, C. Thomas, T. Trautmann, B. Neininger, Emission and chemical transformation of biogenic volatile organic compounds (ECHO) - Investigations in and above a mixed forest stand, in: Results of the German Atmospheric Research Programme - AFO 2000, ed. by R. Winkler, pp. 29-39, Federal Ministry of Education and Research, Publications Division, Bonn, Berlin 2005.

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[Overview \(PDF-Format\)](#)

[FZJ \(PDF-Format\)](#)

"*Emission and Chemical Transformation of biogenic volatile Organic Compounds - Investigations in and above a Mixed Forest Stand (ECHO)"*

[MPI \(PDF-Format\)](#)

"*Simultaneous measurements of primary emission rates and fluxes of Volatile Organic Compounds (VOC) and nitrogen oxides (NOx) within and above canopy stands."*

[ISAS \(PDF-Format\)](#)

"*Field Studies for the Chemical Characterization of Tropospheric Organic Aerosol Particles"*

[UHH \(PDF-Format\)](#)

"*Wind tunnel study on the effects of horizontally inhomogeneous biogenic emission sources on the results of field measurements"*

ANNUAL REPORTS 2002

[FZJ \(PDF-Format\)](#)

"*Emission and Chemical Transformation of biogenic volatile Organic Compounds - Investigations in and above a Mixed Forest Stand (ECHO)"*

[**MPI**](#) (PDF-Format)

"Simultaneous measurements of primary emission rates and fluxes of Volatile Organic Compounds (VOC) and nitrogen oxides (NOx) within and above canopy stands."

[**ISAS**](#) (PDF-Format)

"Field Studies for the Chemical Characterization of Tropospheric Organic Aerosol Particles"

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13. R. Dlugi, M. Zelger, M. Berger
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30. M. Komenda and the ECHO Team
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September 2002, Heraklion, Griechenland
35. R. Koppmann and the ECHO-Team
Emission and Chemical Transformation of Biogenic Volatile Organic Compounds -
Investigations in and above a Mixed Forest Stand (ECHO): An Overview
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36. R. Koppmann and the ECHO-Team
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37. R. Koppmann, FZJ ECHO Team, J. Kesselmeier, F. X. Meixner, MPI ECHO Team, J. Warnke, T.
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51. A. Schaub, M. Komenda, and R. Koppmann
Description of the ECHO field site: Ecosystem compartments of a mixed deciduous forest and their implication for atmospheric chemistry

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56. I. Schlüter, R. Koppmann, K. H. Schlünzen
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12th International Symposium on Acoustic Remote Sensing, British Antarctic Survey,
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63. R. Winkler, H. Zock, R. Koppmann
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Chemical Characterisation of Organic Aerosol Particles by LC/MS, Atmospheric chemistry within the Earth System: from regional pollution to global change
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66. T. Hoffmann, J. Warnke, R. Bandur, S. Besche, B. Papke
Emission and CHemical Tranformation of Biogenic Volatile Organic Compounds: Field studies on the chemical characterisation of tropospheric organic aerosols
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67. J. Warnke, R. Bandur, T. Kühn, T. Hoffmann
Identifizierung und Quantifizierung von sauren Monoterpen-Oxidationsprodukten im atmosphärischen Aerosol mittels Kapillar-HPLC-ESI-MS/MS
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68. J. Warnke, R. Bandur, and T. Hoffmann
Characterisation of boreal forest aerosols by HPLC/MS
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Quantification of biogenic tracer compounds in organic aerosol particles by LC/MS in Central Europe
European Geoscience Union, 1st General Assembly, Nice, France, April 25-30, 2004

SELECTED PRESENTATIONS OF THE ECHO PROJECT

AFO 2000 Abschlusssymposium, Bad Tölz, 22.-24. März 2004 - Poster

Emission and CHemical Transformation of Biogenic Volatile Organic Compounds - Investigations in and above a Mixed Forest Stand (ECHO): An Overview

Ralf Koppmann and the ECHO-Team

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds - Investigations in and above a Mixed Forest Stand (ECHO)

Ralf Koppmann and the ECHO-Team

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds - Investigations in and above a Mixed Forest Stand (ECHO): Contribution of the Participating Research Groups

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Investigations of primary emissions and fluxes of volatile organic compounds (VOC) and nitrogen oxides (NOx) within and above vegetations stands

Jürgen Kesselmeier; Franz X. Meixner, and the ECHO Team

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Field studies on the chemical characterisation of tropospheric organic aerosols

Thorsten Hoffmann, Rolf Bandur, Susanne Besche, Anke Grundmann, Thorsten Kühn, Björn Papke, Jörg Warnke, Ralph Dlugi, Michael Zelger

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Wind Tunnel Experiments

Sandrine Aubrun; Bernd Leitl, Michael Schatzmann

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Quantitative Beschreibung der Nettoemissionen reaktiver Spurengase aus einem Mischwaldbestand in die Troposphäre

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Combined studies of primary emissions and fluxes of volatile organic compounds (VOC) and nitrogen oxides (NOx) within and above vegetation

Jürgen Kesselmeier; Franz X. Meixner, and the ECHO Team

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Field studies on the chemical characterisation of tropospheric organic aerosols

Thorsten Hoffmann; Jörg Warnke, Rolf Bandur

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds (ECHO): Wind Tunnel Experiments

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7th Scientific Conference of the International Global Atmospheric Chemistry Project (IGAC)

September 18.-25. 2002, Crete - Poster

Measurements of isoprene, methyl vinyl ketone, and methacrolein in and above a forest canopy during ECHO

M. Komenda, A. Schaub, and R. Koppmann

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Emission and CChemical Transformation of Biogenic Volatile Organic Compounds - ECHO

R. Koppmann, T. Hoffmann, J. Kesselmeier, and M. Schatzmann

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Gordon Research Conference on Biogenic Hydrocarbons & The Atmosphere 2002

1. - 6. September 2002, Oxford, Großbritannien - Poster

Measurements of isoprene, methyl vinyl ketone, and methacrolein in and above a forest canopy during ECHO

M. Komenda, A. Schaub, and R. Koppmann

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Description of the ECHO-Fiels site: Ecosystem compartments of a mixed deciduous forest and their implication for atmospheric chemistry ECHO

A. Schaub, M. Komenda, and R. Koppmann

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Biogenic VOC exchange in a mixed forest stand during the ECHO field campaign 2002

Tamara Dindorf et al.

[PDF-Format](#), 680 kB

The use of Proton Transfer Mass Spectrometry to measure ambient VOC concentrations

Albrecht Neftel et al.

[PDF-Format](#), 532 kB

EUROTRAC 2 Symposium 2002, 11.-15. März 2002, Garmisch-Partenkirchen - Poster

Physical Modelling of Biogenic Emissions from a Forest Area

S. Aubrun, B. Leitl, M. Schatzmann

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R. Koppmann, T. Hoffmann, J. Kesselmeier, and M. Schatzmann

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