

Determination of biogenic organic compounds in forest canopy particles



AFO 2000

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Motivation

In the global scale, biogenic emissions of volatile organic compounds (BVOC) exceed anthropogenic emissions in one order of magnitude. A lot of single species like ethene, isoprene and numerous monoterpenes, emitted mainly from terrestrial plants, were identified up to now. Furthermore, alcohols, carbonyl compounds as well as carboxylic acids were released. In contrast to mainly isoprene emitting broad-leaved trees coniferous trees are emitting predominantly different C_{10} -monoterpenes. These are extremely reactive against ozone, OH- and NO_3 -radicals, respectively.

In the course of numerous further reactions a great amount of polar oxidation products may be formed, which have a significantly reduced volatility against their precursors. Such low volatile substances are thought either to new build particles by homogeneous nucleation or to modify the surface of existing particles by condensation.

In the past, a lot of smog chamber experiments were performed from different aerosol researching groups for elucidation of such oxidation products. In contrast, their detection in field experiments was in the past rather rare.

Within the scope of the German Atmospheric Research Programme AFO2000 several field projects such as BEWA (Regional biogenic emissions from coniferous forests) are addressing a better understanding of particle formation and - modification following after biogenic emissions. The aim of this study as part of the more extensive BEWA project is the identification and quantification of the organic compounds of biogenic origin in airborne particles in two experiments in 2001 and 2002 with emphasis mainly of secondary formed organic carbon by means of sampling above and in forest canopy, respectively.

Sampling

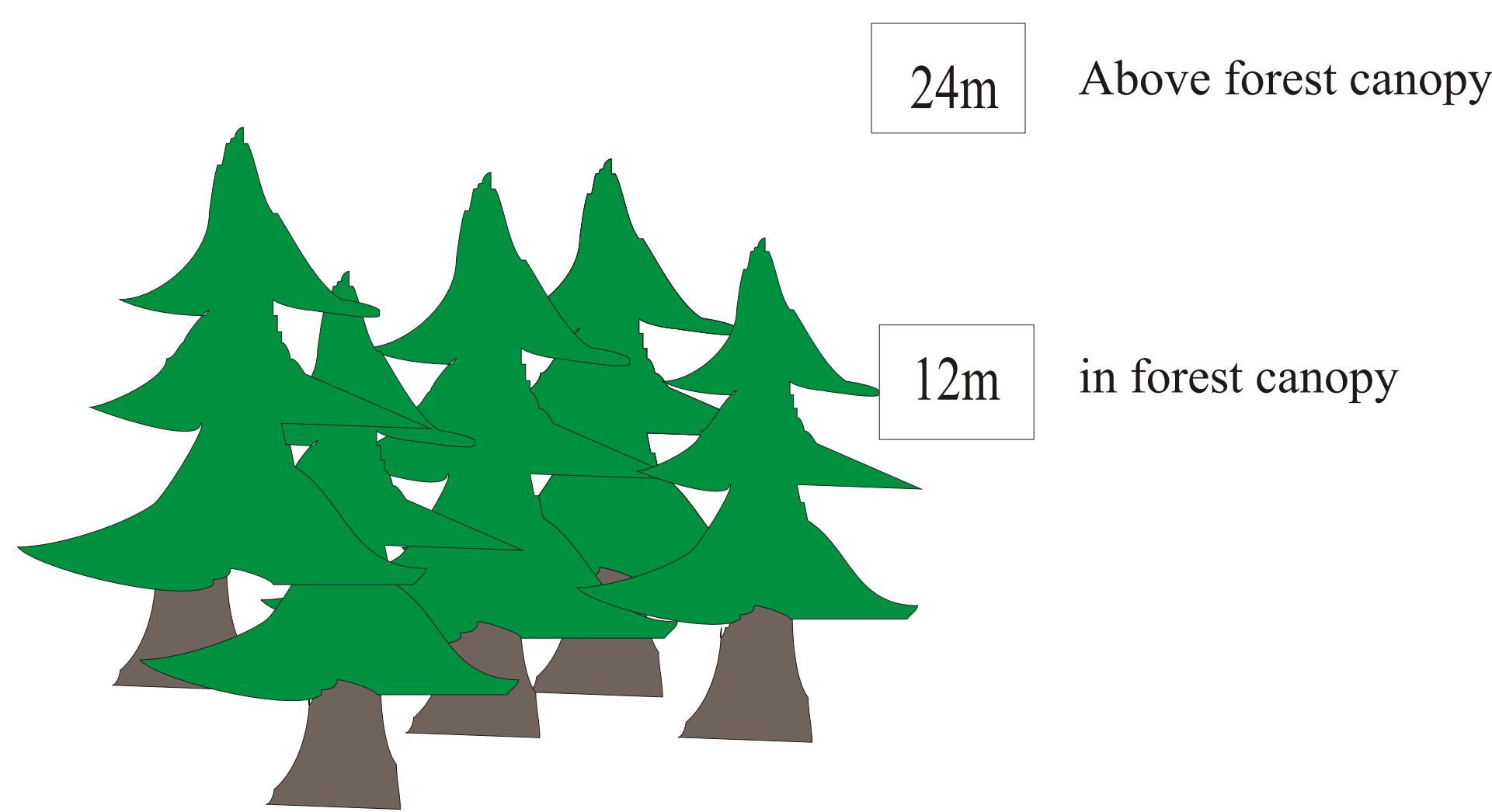


Figure 1: Sampling site Waldstein/Fichtelgebirge (Germany)

Sampling was performed in two heights:

particles (in 2001 and 2002):
- DIGITEL high volume sampling (500 l/min)

gas phase compounds (additional in 2002):



- two sampling devices with flow rates of 21 and 49 l/min, respectively

Instruments

* GC-MS: GC 6890 with 5973 MSD (Agilent, Waldbronn)
* capillary column: Hp5 MS 30m x 250 μ m x 0.25 μ m
* temperature programme:
start at 70°C for 1 minute, subsequently rising with 10°C/min to 150°C, then rising with 5°C/min to 290°C, hold for 5 min
* helium flow: 1.2 ml/min
* temperatures: injector - 270°C, Transferline - 240°C, Ionensource - 196°C, Quadrupol - 150°C
* electron energy: 70eV (after Gogou 1998)

Sample preparation

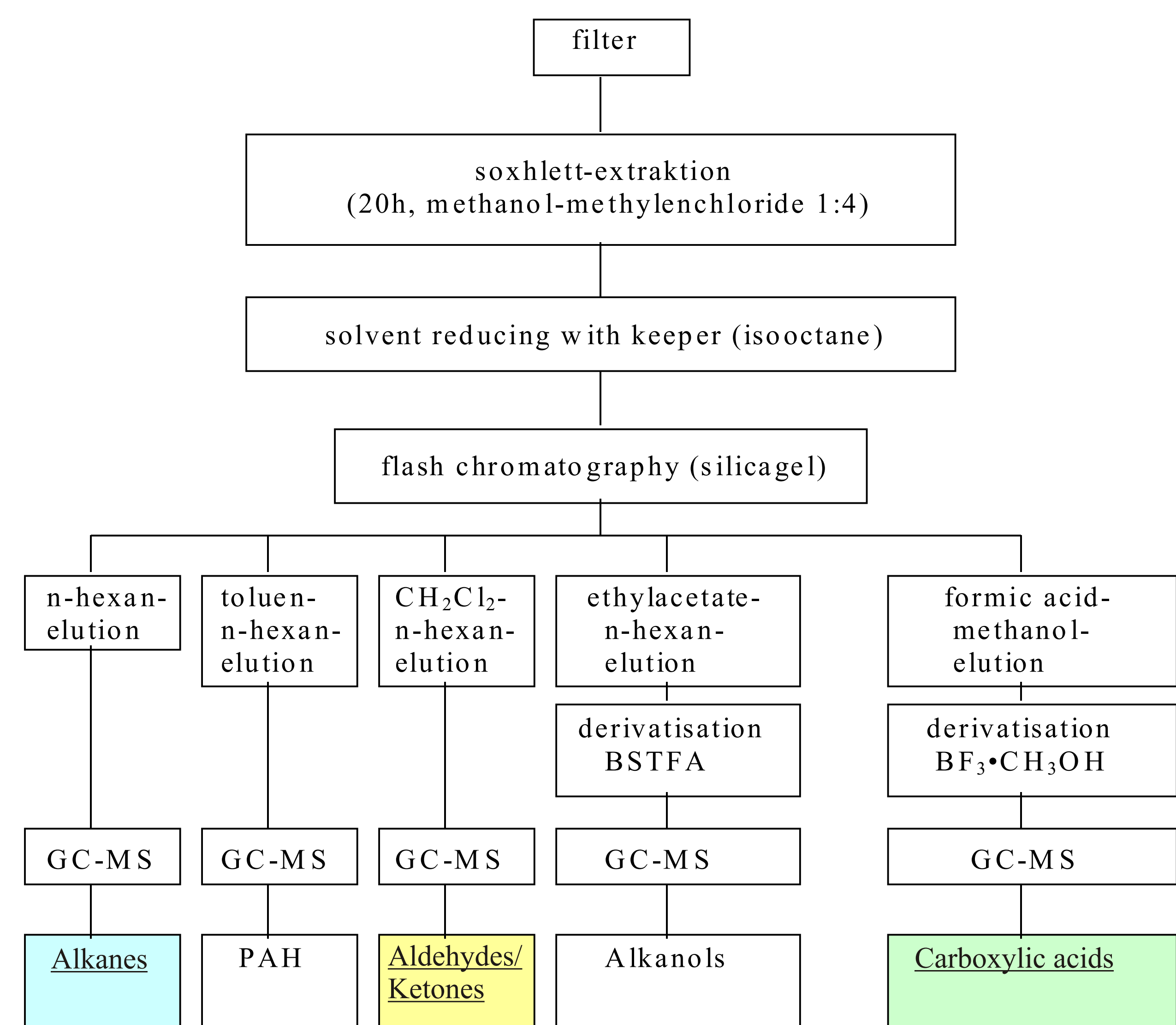


Figure 2: Sample preparation schema according Gogou 1998

Results

Alkanes

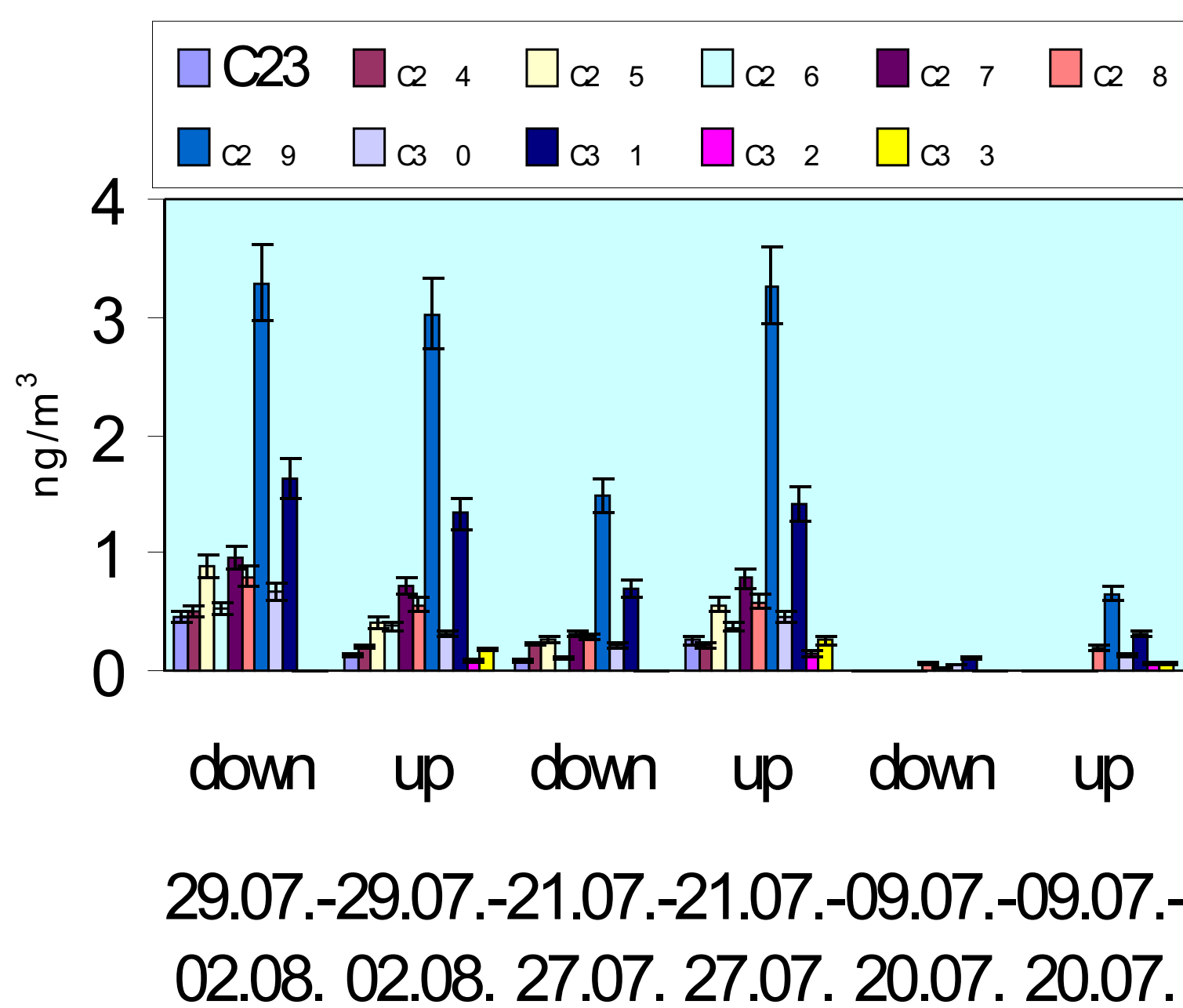


Figure 3: Alkane concentration subject to sampling periods and sampling height

Aldehydes and Ketones

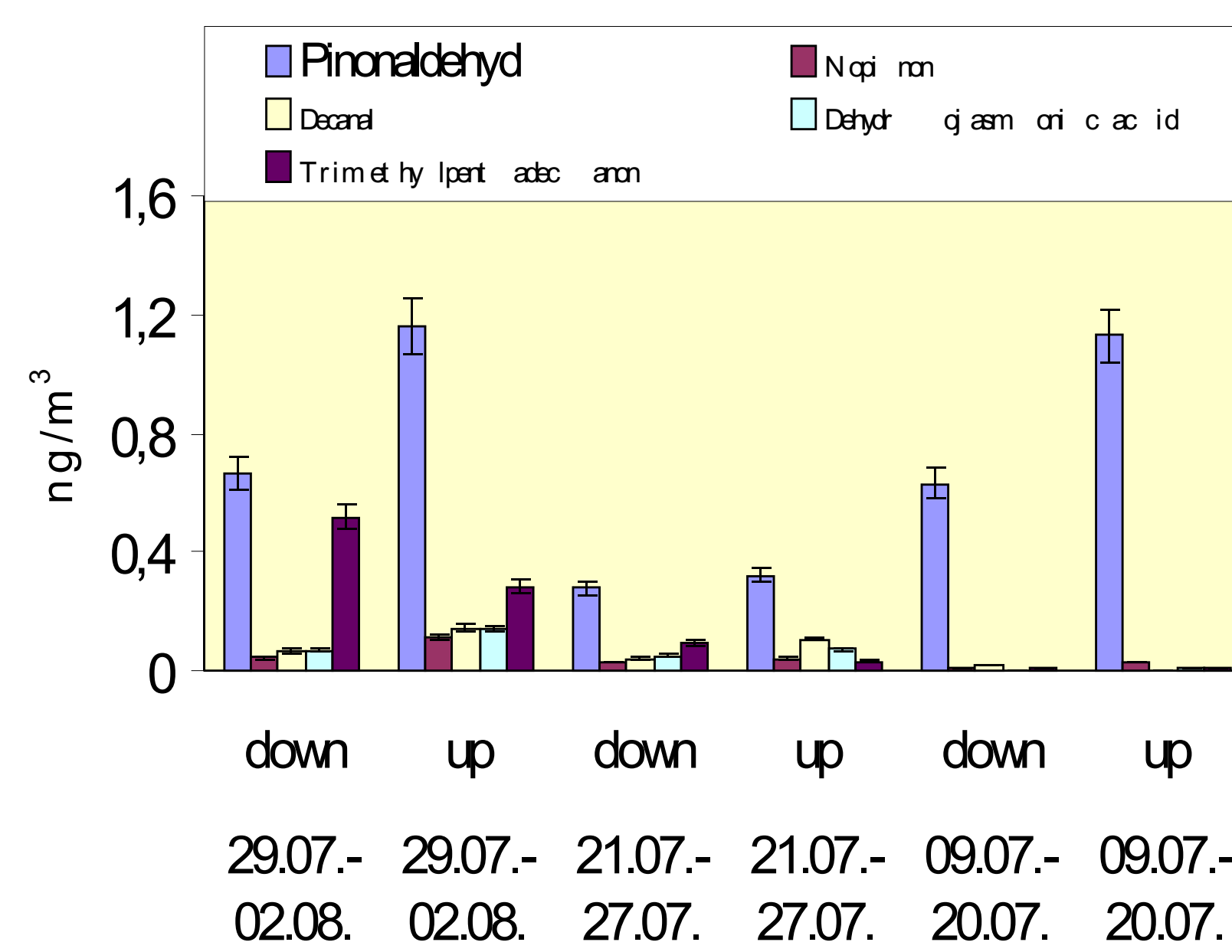


Figure 4: Content of different carbonyl compounds subject to sampling periods and sampling height

Carboxylic acids

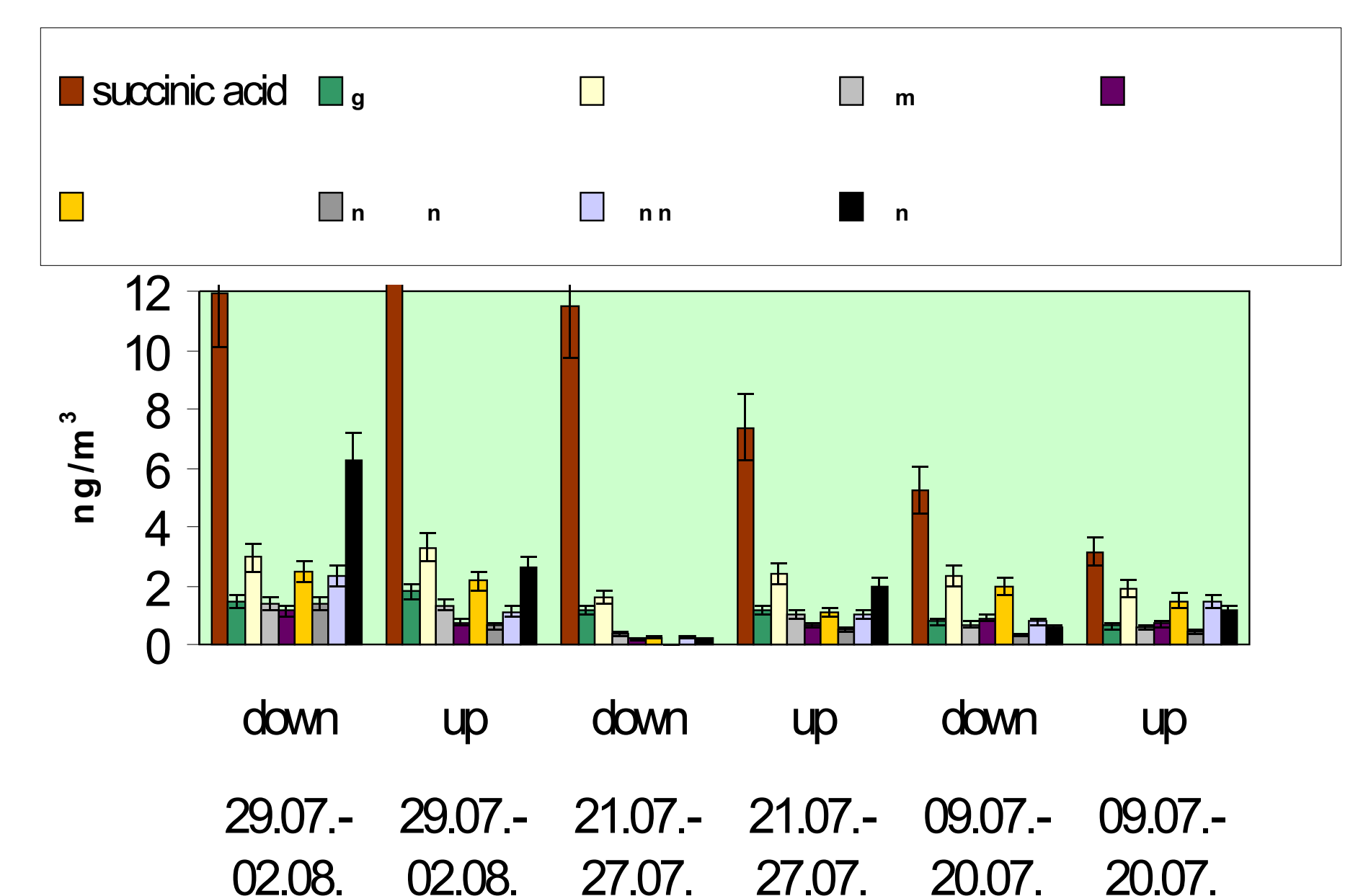


Figure 5: Carboxylic acid contents subject to different sampling periods and sampling heights

Discussion

In contrast to particle mass on filters, inorganic ion contents as well as organic carbon/ elemental carbon (OC/EC) contents show some organic single species differences between both sampling heights.

Alkanes:

Carbon numbers between C23 and C33 were quantified in amounts up to 3.5 μ g/m³

Coniferous typical higher alkanes C32 and C33 (Kavouras 1999) are quantified only in the above canopy samples with 0.05-0.23 ng/m³. An explanation may be the higher wind speed above the tree tops, which gives a stronger wax abrasion, possibly promoted also by higher temperatures above tree tops.

Concentration maximum in all samples was observed at C29, followed by C31. Also, the odd numbered predominance indicates the strong biogenic influence as well as the CPI_{odd} factors between 2.7 and 3.8.

The total concentration of alkanes correlates with the average temperature in the course of sampling.

Aldehydes and Ketones:

Pinonaldehyde, the first photooxidation product of α -Pinene as well as nopinon from β -pinene are increased above tree canopy, an indication for photooxidative processes. Furthermore, norpinonaldehyde was found in trace amounts.

Pinonaldehyde: 1.02 \pm 0.56 ng/m³ (24m) against 0.62 \pm 0.25 ng/m³ (12m)

nopinon: 0.07 \pm 0.05 ng/m³ (24m) against 0.03 \pm 0.02 ng/m³ (12m)

Above the tree tops the methyl dehydrojasmonate content is higher than in the canopy. This substance represents a plant hormone, released under injury. In contrast, 6,10,14-trimethyl-2-pentadecanon, an oxidation product of phytol from chlorophyll, is in the tree canopy more concentrated than above.

Carboxylic acids:

A lot of photooxidation products were detected and quantified in form of dicarboxylic acids in the range between C4 and C9 as well as the further photooxidation products from α -pinene like pinic, pinonic and norpinic acid.

Outlook

A second experiment this year serves for the verification of the results from the last year campaign. Furthermore, some expansions concerning sampling regime were made:

First, a strict differentiation between day- and night time samples was made. This differentiation is pointed on the one hand to the differing reactivity of oxidative agents and on the other hand to the stability of the oxidative agents as well as products.

Second, an attempt is started for simultaneous respectively combined sampling of particles and gas phase compounds in regard to gas-particle partitioning of oxidation products of biogenic emissions.

Acknowledgements

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References

A.I.G. Gogou, M. Apostolaki and E.G. Stephanou (1998). *J. Chromatogr. A*, 799, 215-231
I.G. Kavouras, N. Mihalopoulos and E.G. Stephanou (1999). *Environ. Sci. Technol.*, 33, 1028-1037