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*Supplement of*

## **Historic records of organic compounds from a high Alpine glacier: influences of biomass burning, anthropogenic emissions, and dust transport**

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## LC-MS method for the analysis of G and MG

The LC-MS method for the analysis of alpha-dicarbonyls (Müller-Tautges et al., 2014) was transferred to UHPLC. The UHPLC system was composed of degasser, binary gradient pump, temperate auto sampler, and temperate column compartment (Thermo Scientific): The eluent composition (A: ultrapure water with 2 % ACN and 0.04 % formic acid, B: ACN with 2 % ultrapure water) remained unchanged, except that water and ACN of higher purity (LC-MS grade) were used. The flow rate was raised from 200 to 500  $\mu\text{L}/\text{min}$ . The injection volume was reduced to 10  $\mu\text{L}$  per run. The optimized gradient was 50 % B at 0 min, 50 % B at 0.25 min, 75 % B at 1.05 min, 75 % B at 1.2 min, 99 % B at 1.25 min, 99 % B at 4.0 min, and 60 % B at 4.1 min. Including a re-equilibration time of 3 min, this led to a shortening of analysis time per run by a factor of eight as well as a reduced solvent consumption by a factor of three compared to the conventional HPLC method.

## Method for the analysis of mono- and dicarboxylic acids using SPE-UHPLC-MS

### Chemicals and materials

Adipic acid (>99.5 %), pimelic acid (98 %), sebacic acid (99 %), phthalic acid (>99.5 %), 4-methylphthalic acid (99 %), vanillic acid (>97 %), succinic acid-2,2,3,3-d<sub>4</sub> (98 atom % D), ammonium hydroxide (puriss. p.a.), acetyl chloride (>99.0 %), pentanol (99 %), and methanol (HPLC grade) were purchased from Sigma-Aldrich (Steinheim, Germany). Suberic acid (99 %), 4-hydroxybenzoic acid (99 %), and dodecanedioic acid (99 %) were obtained from Acros Organics (Geel, Belgium). *Cis*-Pinic acid ((1'R,3'R)-2-[3'-Carboxy-2'2'-dimethylcyclobutyl]acetic acid) was synthesized following a protocol by Moglioni et al. (2000). Acetonitrile (LC-MS grade) and water (LC-MS grade) were purchased from Fisher Scientific (Geel, Belgium). Formic acid (LC-MS grade) was purchased from LGC Standards (Wesel, Germany). Hydrochloric acid (30 %) was obtained from Merck (Darmstadt, Germany). Ethanol (HPLC gradient grade) and isopropanol (LC-MS grade) were purchased from Carl Roth (Karlsruhe, Germany). Ultrapure water (18.3 M $\Omega$  cm) was obtained using a Milli-Q water system from Millipore (Bedford, USA). SPE cartridges (SB, 3 mL, 500 mg bed weight) were purchased from Macherey-Nagel (Düren, Germany).

## SPE procedure

The SPE cartridges were equilibrated with 2x2.5 mL MeOH and 2x2.5 mL ultrapure water by means of reduced pressure in a vacuum manifold. Throughout the whole procedure, a flow rate of less than 1 mL/min was applied to ensure complete retention. To remove contaminations, the cartridges were eluted with three portions (each 1.5 mL) of 0.16 M hydrochloric acid (HCl) in ACN followed by 10 mL of ultrapure water. To change the counter ion of the strong anion exchange sorbent material from chloride to formate, 5x2.5 mL of 0.5 M formic acid were applied to the cartridges, followed by 2x2.5 mL of ultrapure water and 4.0 mL of ammonium hydroxide solution (pH 7-8). To about 80 mL of each melted ice sample, 0.1 mL of ammonium hydroxide solution were added for pH adjustment (pH 7-8). The samples were applied to the cartridges using reservoirs. After the retention step, a washing step was performed by applying 2.5 mL ammonium hydroxide solution to the cartridges, followed by 2.5 mL of ultrapure water and 1 mL of ACN. The cartridges were sucked dry for about 1 min before elution. Elution was performed manually with 1 mL of HCl in ACN using a flow rate of less than 1 mL/min and the eluate was reduced to a volume of about 200  $\mu$ L by means of a gentle nitrogen stream and heating to 35 °C. The elution step was repeated three times (4 mL HCl in ACN in total). After the last extraction step, 25  $\mu$ L of the internal standard solution (succinic acid-d4) were added to the residual eluate before evaporation to complete dryness.

## Derivatization

Pentanol with 10 % acetyl chloride was used as derivatization solution for the esterification of the analytes' carboxylic acid groups. The solution was stored at 4 °C and was stable over several months. For derivatization, 100  $\mu$ L of the derivatization solution were added to the extraction residue. The solution was heated to 70 °C for 30 min in a closed vial, cooled to room temperature and evaporated to dryness under a gentle stream of nitrogen at a temperature of 30 °C. Care was taken to remove the vial from the evaporation unit immediately upon complete solvent evaporation in order to prevent analyte loss. The residue was dissolved in 500  $\mu$ L of eluent solution (ACN/H<sub>2</sub>O 80/20 v/v) and provided for LC-MS analysis.

## Liquid chromatography – mass spectrometry

For the chromatographic separation, an *UltiMate 3000* UHPLC system (Dionex, Thermo scientific, Germany) was used. The UHPLC system was composed of degasser, binary gradient pump, temperate auto sampler, and temperate column compartment. The autosampler temperature was set to 20 °C and the analytical column (Hypersil Gold, C18, 50x2.0 mm, 1.9 µm particle size, Thermo Scientific) was tempered to 25 °C during analysis. Eluent A (ultrapure water with 2 % ACN and 0.04 % formic acid) and B (MeOH) were used in gradient mode with a flow rate of 500 µL/min. The optimized gradient was 60 % B at 0 min, 60 % B at 0.5 min, 70 % B at 1.0 min, 99 % B at 2.0 min, 99 % B at 5.0 min, and 60 % B at 5.1 min. The injection volume was 10 µL per run. High resolution mass spectra were obtained using a *Q-Exactive*<sup>TM</sup> hybrid quadrupole orbitrap mass spectrometer (Thermo Scientific, Germany) equipped with a HESI source. The optional heating of the solvent flow was not applied in this method, as the high fraction of organic solvent (60 %) at the beginning of the chromatographic run allowed stable spray conditions without additional heating. The HESI source was operated in positive ion mode with 40 psi sheat gas, 20 psi aux gas (both N<sub>2</sub>), 350 °C capillary temperature, and 3.5 kV spray voltage. The Full-MS mode was performed within a scan range of *m/z* 100-500, with a resolution setting of 70,000. The common contaminant ion *m/z* 391.28423 (diisooctyl phthalate, plasticizer) was used as a lock mass for internal mass calibration during mass analysis. Data analysis was performed using the software XCalibur® (Thermo Scientific) for both signal identification and integration.

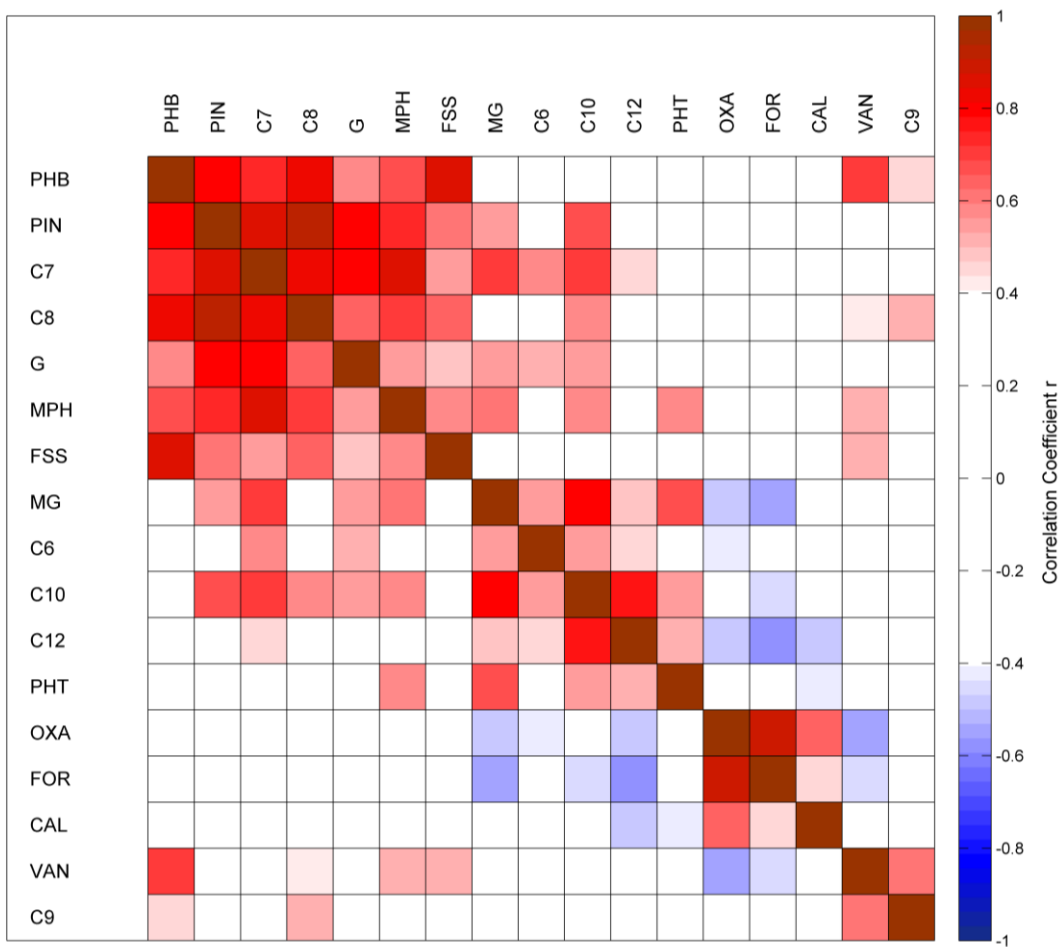


Fig. S1 Correlation matrix of compound concentrations detected in the ice core and burned area by fires in southern Switzerland (FSS). The color-coded scale gives the value of the correlation coefficient  $r$  for each pair of variables. (MATLAB function corrmmap.m by Barry M. Wise, Eigenvector Research, Inc., [www.eigenvector.com](http://www.eigenvector.com), accessed 2014-05-14).

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