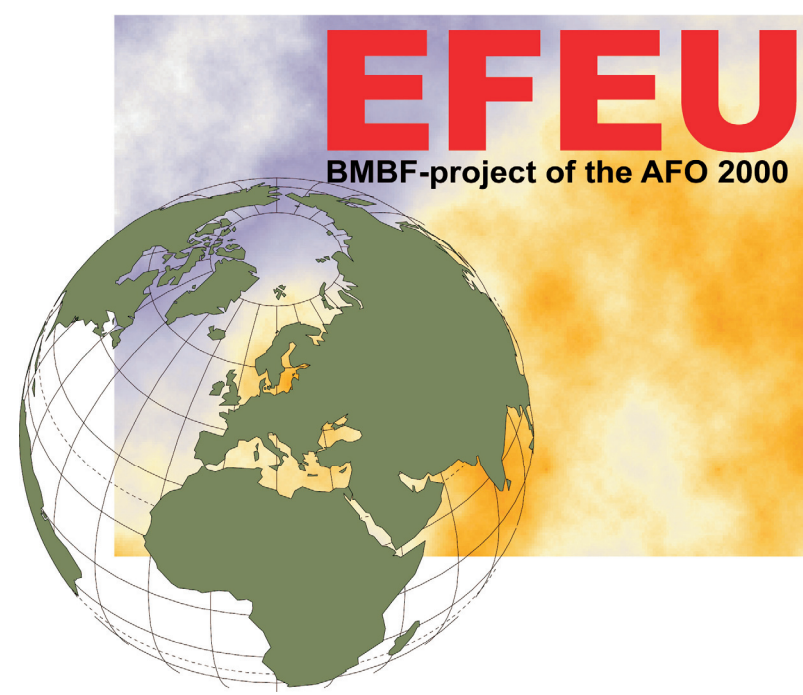


Size Resolved Chemical Characterisation of Biomass Burning Aerosols from Combustion of Northern-European Conifers, African Savannah, and Indonesian and German Peat



Yoshiteru Iinuma and Hartmut Herrmann

Leibniz-Institut für Troposphärenforschung
Permoserstr. 15, Leipzig, D-04318, Germany
<http://www.tropos.de/>



Introduction

Biomass burning contributes significantly to the global trace gas and aerosol burden. It is also an important source of elemental carbon as well as organic aerosols. Large scale wildfires occur naturally as well as the results of human activities in various parts of the world. Vegetation fire is among the most important biomass burning in terms of the climate effects and its particles primarily consist of decomposed lignin, cellulose, hemicellulose products as well as elemental carbon. Although considerable effort has been made by various studies to identify compounds in the biomass burning aerosol, only a limited number of data exist for the size segregated physical and chemical characterization of biomass burning particles under controlled condition. Thus, there is a need to characterize simultaneously biomass burning for physical and chemical properties in order to understand its effect on climate.

Experimental

A laboratory combustion facility designed to study gaseous species from biomass burning was used to produce aerosols under controlled conditions. The emission from the combustion facility was diluted in a container equipped with internal fans as a buffer in order to minimise sample overloading and temporal variability of samples. A field laboratory container was directly located underneath to sample particles in the first stage buffer container. The sample was diluted 20 times with a dilution tunnel in the field laboratory container using clean compressed air. The dilution tunnel was connected to particle sampling devices for chemical analysis together with various physical instruments for the measurements of size distribution, scattering, absorption and total particle concentration. In order to simulate wildfire conditions rather than fireplace or domestic heater burning conditions various parts of tree were burned in different mixture depending on the availability of burning materials. In order to have representative and comparable data for different kind of combusted biomass fuels, an average around 7% for the ratio of excess CO to CO₂ ($\Delta\text{CO}/\Delta\text{CO}_2$) was set as a target for the combustion condition which is generally found in typical biomass burning in nature. Table 1 shows general experimental information for the selected experiments. Samples from 5 stage Berner impactor were analysed using CPP-GC-MS for n-alkanes, n-alkenes, PAHs and oxy-PAHs, CE/ESI-MS for lignin decomposition products, nitrophenols, and resin acids, HPLC/ESI-MS for monosaccharide anhydrides, a thermographic method for EC and TOC analyser for WSOC (water soluble organic carbons).

Table 1. General experimental information

| Date | Exp. No. | Fuel | Average dCO/dCO ₂ (%) ^b |
|----------|----------|-----------------------------------|---|
| 19.09.03 | 18a | Spruce with green needles | 9 |
| 23.09.03 | 20a | Savannah grass | 6 |
| 24.09.03 | 22a | Pine with green needles | 7 |
| 24.09.03 | 23a | Musasa | 9 |
| 25.07.03 | 25a | Indonesian peat ^a | 47 |
| 26.07.03 | 26a | Northern German peat ^a | 39 |

a: samples were dried prior to the combustion session
b: courtesy of Dr. R. S. Parmar and Dr. G. Helas, Max Planck Institute for Chemistry, Mainz.

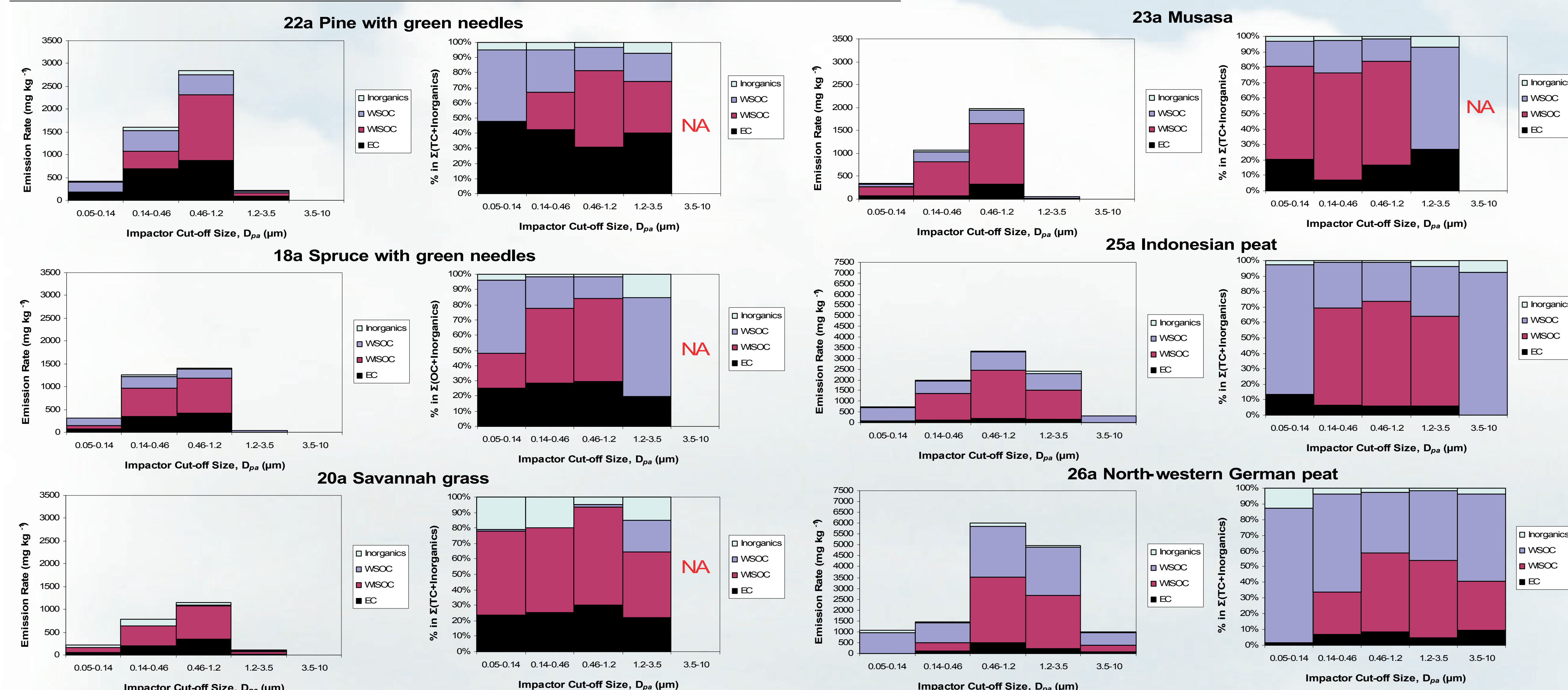


Figure 1. Mass size distribution and bulk chemical mass balance of selected biofuels shown in Table 1.

Table 2. Size resolved emission rates of detected organic compounds (categorised, milligram carbon emitted per kilogram biofuel combusted). Stage 5 data for wood combustion are not included as mass collected on stage 5 was negligible.

| Emission rates (mg kg ⁻¹) | 22a Pine with greens | | | | 20a Spruce with greens | | | | 18a Savannah grass | | | | 20a Mussasa | | | | 25a Indonesian peat | | | | 26a Northern German peat | | | | | |
|---------------------------------------|----------------------|-----------|----------|---------|------------------------|-----------|----------|---------|--------------------|-----------|----------|---------|-------------|-----------|----------|---------|---------------------|-----------|----------|---------|--------------------------|-----------|-----------|----------|---------|--------|
| | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 3.5-10 | 0.05-0.14 | 0.14-0.42 | 0.42-1.2 | 1.2-3.5 | 3.5-10 |
| Inorganics | 18.9 | 78.6 | 92.7 | 15.2 | 12.7 | 23.7 | 26.3 | 4.83 | 45.2 | 156 | 55.9 | 15.9 | 11.6 | 27.6 | 34 | 3.65 | 21 | 17.4 | 41.8 | 85.9 | 22.4 | 94 | 51.7 | 142 | 76.9 | 36.2 |
| n-Alkanes | 0.415 | 1.08 | 1.52 | 0.167 | 0.189 | 0.65 | 0.64 | 0.018 | 0.31 | 1.39 | 2.5 | 0.28 | 0.36 | 0.42 | 0.97 | 0.064 | 19.8 | 119 | 147 | 182 | N.D. | 13.2 | 37.9 | 288 | 566 | N.D. |
| n-Alkenes | 0.136 | 0.431 | 1.04 | 0.07 | 0.14 | 0.34 | 0.46 | 0.01 | 0.13 | 0.44 | 0.80 | 0.1 | 0.22 | 0.43 | 0.68 | 0.051 | 3.52 | 21.6 | 39.2 | 42.8 | N.D. | 1.14 | 4.77 | 51.7 | 122 | N.D. |
| PAHs | 1 | 3.17 | 10.1 | 0.28 | 0.59 | 1.25 | 1.43 | 0.096 | 0.57 | 1.35 | 3.58 | 0.06 | 2.27 | 1.21 | 4.01 | 0.24 | 1.21 | 3.6 | 9.15 | 6.44 | N.D. | 1.55 | 2.08 | 12.8 | 12 | N.D. |
| oxy-PAHs | 0.04 | 0.27 | 0.93 | 0.04 | 0.03 | 0.02 | 0.05 | N.D. | 0.01 | 0.05 | 0.26 | 0.01 | 0.07 | 0.13 | 0.59 | 0.04 | 0.21 | 0.36 | N.D. | 0.47 | N.D. | 0.08 | 0.08 | N.D. | 0.57 | N.D. |
| Lignin Decomposition Products | 11.7 | 35.1 | 53.6 | 5.87 | 15.6 | 55.9 | 54.1 | N.D. | 7.43 | 15.8 | 33.8 | 2.07 | 11.8 | 31.2 | 51 | 5.84 | 33.6 | 172 | 264 | 147 | 5.16 | 19.1 | 88.4 | 176 | 55.9 | 19.3 |
| Nitrophenols | 4.49 | 11.2 | 14.1 | 1.62 | 1.85 | 5.44 | 5.05 | N.D. | 0.50 | 1.25 | 1.85 | 0.07 | 1.55 | 3.42 | 5.8 | 0.29 | 0.55 | 2.47 | 1.45 | 0.09 | 0.05 | 0.17 | 0.55 | 0.58 | 0.12 | N.D. |
| Resin acid | 15.3 | 3.54 | 19.8 | 12.8 | 8.97 | 23 | 24.9 | 0.51 | N.D. | N.D. | 0.17 | 0.03 | N.D. | N.D. | 0.27 | N.D. | N.D. | 0.0008 | N.D. | N.D. | N.D. | N.D. | N.D. | 0.03 | N.D. | N.D. |
| Monosaccharide anhydrides | 47 | 333 | 716 | 27 | 150 | 557 | 558 | 5 | 65 | 180 | 287 | 22 | 63 | 188 | 282 | 9 | 283 | 562 | 1244 | 635 | 34 | 388 | 919 | 2104 | 2275 | 230 |

Reference

Dusek, U., G.P. Frank, G. Helas, Y. Iinuma, K. Zeromskiene, P. Gwaze, T. Hennig, A. Massling, O. Schmid, H. Herrmann, A. Wiedensohler, and M.O. Andreae (2005), "Missing" cloud condensation nuclei in peat smoke, *Geophys. Res. Lett.*, 32, L11802, doi:10.1029/2005GL022473.

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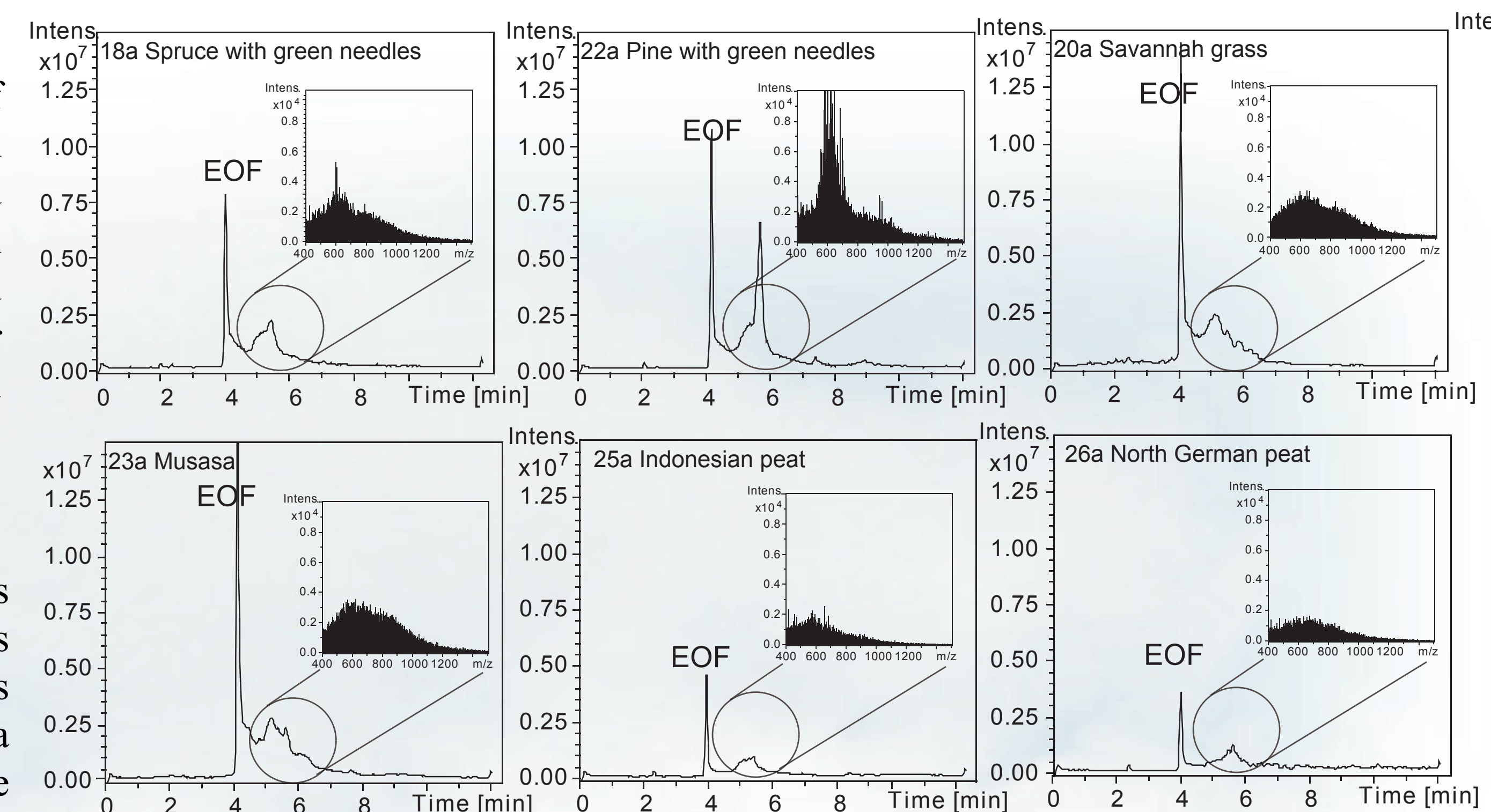
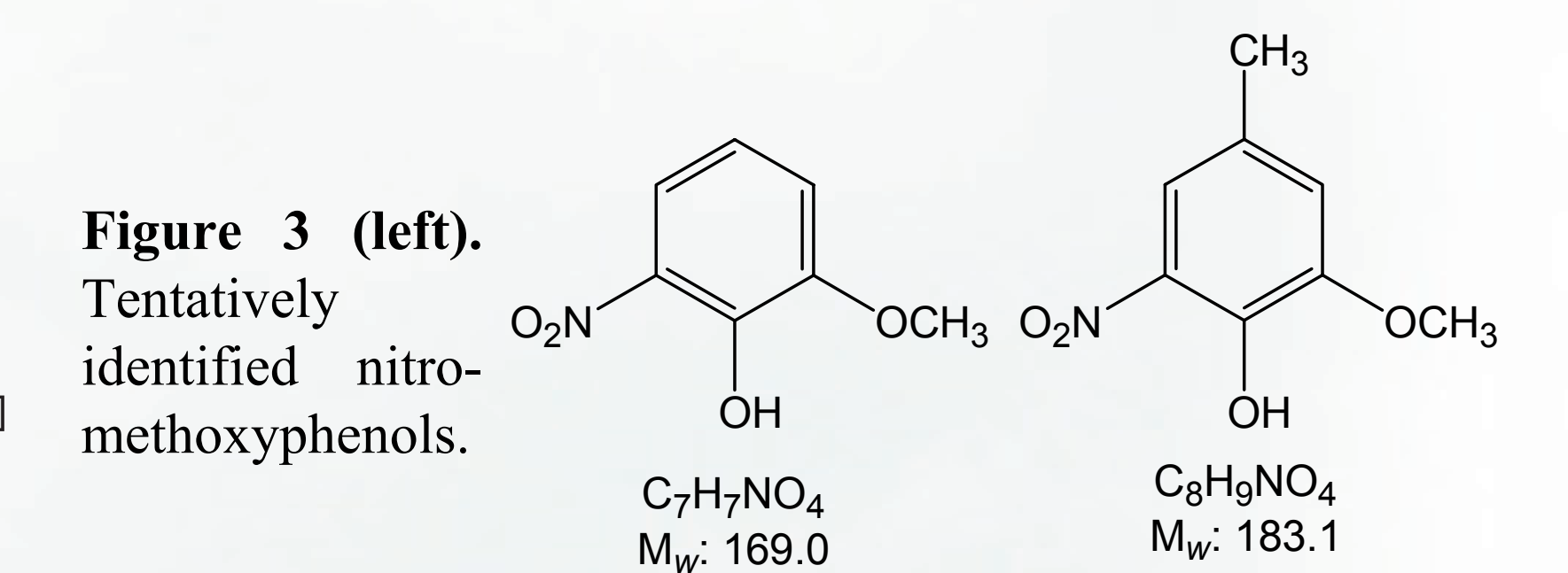


Figure 2. Example of extracted ion electropherogram of macromolecules (m/z 400-1500) using CE-MS.



Results and Discussions

Figure 1 shows the mass size distribution and bulk chemical balance of selected experiments. Table 2 summarizes the size resolved carbon emission rates from selected experiments. The determined bulk emission rates were 46-6637 mg kg⁻¹ (sum of five stages) for WSOC, 1324-6154 mg kg⁻¹ for water insoluble organic carbons (WISOC) 487-1840 mg kg⁻¹ for EC, 67.5-401 mg kg⁻¹ for inorganic ions, 0.4-905 mg kg⁻¹ for n-alkanes, 0.5-180 mg kg⁻¹ for n-alkenes, 1.4-28 mg kg⁻¹ for PAHs, 0.07-1.0 mg kg⁻¹ for oxy-PAHs, 66-622 mg kg⁻¹ for lignin decomposition products, 1.43-31.4 mg kg⁻¹ for nitrophenols, 0.0-113 mg kg⁻¹ for resin acids, and 554-5916 mg kg⁻¹ for cellulose and hemicellulose decomposition products. Among the ranges of biomass burning tracers detected, anhydromonosaccharides (levoglucosan and its isomers) were by far the largest contributor to total organic mass. The fractions of monosaccharide anhydrides in the emitted total carbon were higher in smaller particles ($D_{pa} < 0.46 \mu\text{m}$). Both aerosols from Indonesia and German peat combustion were enriched with only little amount of softwood lignin decomposition products. Resin acids were mostly found from conifer combustion. Both the combustion of Indonesian and German peat produced extremely high amount of alkanes and alkenes (C20-C34) with $\text{CPI}_{\text{odd/even}}$ 1.45 with C_{max} at C31 for Indonesian peat and $\text{CPI}_{\text{odd/even}}$ 1.81 with C_{max} at C33 for North-western German peat. This extremely high emission of long chain hydrocarbons may partly explain missing CCN (Cloud Condensation Nuclei) in peat smoke [Dusek *et al.*, 2005].

Figure 2 shows the examples of electropherograms from the analysis of macromolecules using CE/ESI-MS. Pine with green needles show distinctively high level of macromolecules which appeared to be classified as EC rather than OC. The hygroscopicity of the smoke particle was significantly enhanced with the presence of higher concentrations of inorganic ions. The emission rates of nitro-methoxyphenols were determined first time in the freshly emitted biomass burning aerosols. Detected nitro-methoxyphenols were tentatively identified as 2-nitroguaiacol and 2-nitro-4-methoxyguaiacol (Figure 3) based on the MS² experiments, CE/ESI-TOFMS analysis, and *o*, *p*, *m*-directing of a nitro group. The comprehensive chemical and physical characterization dataset obtained during the EFEU campaign can be potentially useful for the numerical models employed to investigate the impact of biomass burning on the micro to regional scale atmosphere.