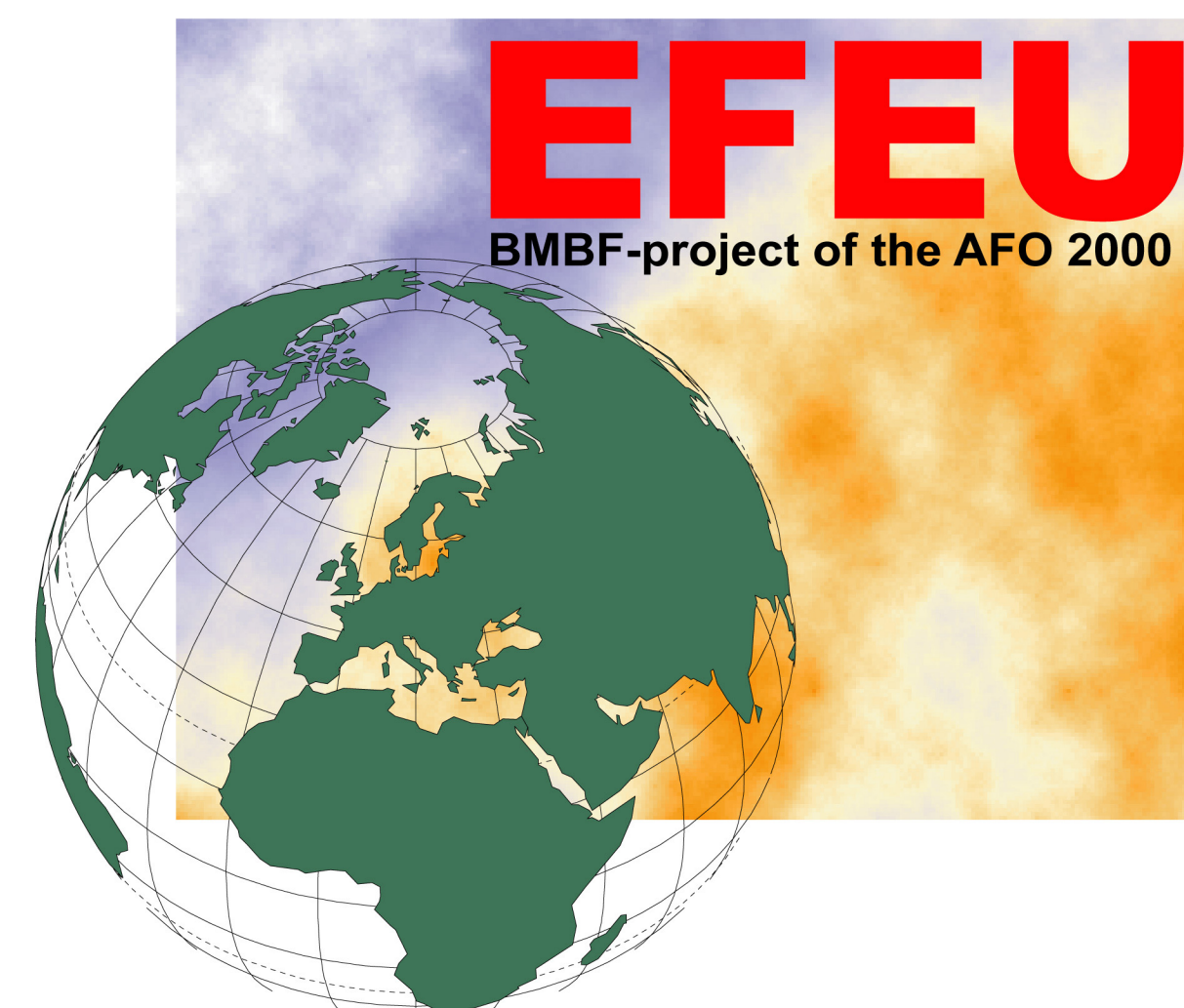


Source Characterisation of Biomass Burning Aerosol using CE-ESI-MS and HPLC-ESI-MS



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 minimize 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 transfer line from the buffer container to a dilution tunnel was approximately 1.5 m. 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 (dCO/dCO₂) 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. Pine wood, pine wood with green needles and Musasa were chosen to show the influence of vegetation types and their parts on the emitted particles. Indonesian peat and Northern German peat were also selected in order to illustrate the differences between fresh biofuels and "fossil" biofuels.

Samples from 5 stage Berner impactor were extracted in 250 µl of methanol for HPLC-MS analysis of anhydrosugars. A fraction of methanol extract (25 µl) was further diluted using 100 µl of Milli-Q water for CE-MS analysis of methoxyphenols. Extracts were further diluted using methanol (HPLC-MS analysis) or 20/80 CH₃OH/H₂O solution (CE-MS analysis) if necessary.

Table 1. General experimental information

Date	Exp. No.	Fuel	Average dCO/dCO ₂ (%) ^b
01.07.03	9a	Pine with green needles	6
03.07.03	12a	Pine	4
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.

Chemical Analysis

Samples from 5 stage Berner impactor were extracted in 0.5ml of methanol and ultrasonicated for 10 minutes. The extracts were filtered using membrane filters and vial and filters were further washed with 0.5 ml of methanol. The resulting extracts were dried under a gentle nitrogen stream and recovered in 250 ml of methanol for HPLC-MS analysis of anhydrosugars. A fraction of methanol extract (25 ml) was further diluted using 25 ml of Milli-Q water for CE-MS analysis of methoxyphenols. Extracts were further diluted using methanol (HPLC-MS analysis) or 20/80 CH₃OH/H₂O solution (CE-MS analysis) if necessary.

CE separations were carried out on Agilent CE instrument using 50 µm i.d. (365 µm o.d.) x 67 cm capillary and 20 mM ammonium acetate buffer at pH 9.1 (adjusted using NH₄OH) containing 10% methanol.

HPLC separations were carried out on Agilent 1100 series HPLC instrument using Phenomenex Luna amino column (250 mm length x 4.6 mm inner diameter, 5 µm particle size) with the eluent composition of 92.5% ACN/7.2% H₂O/0.3% acetic acid. The column temperature was kept at 7.5 °C.

A Bruker Esquire 3000 plus ion trap mass spectrometer was used as a detector for both separations. The detection was carried out using a negative mode of electrospray ionization. For the analysis of anhydrosugars, acetate adducts were used for the detection of anhydrosugars.

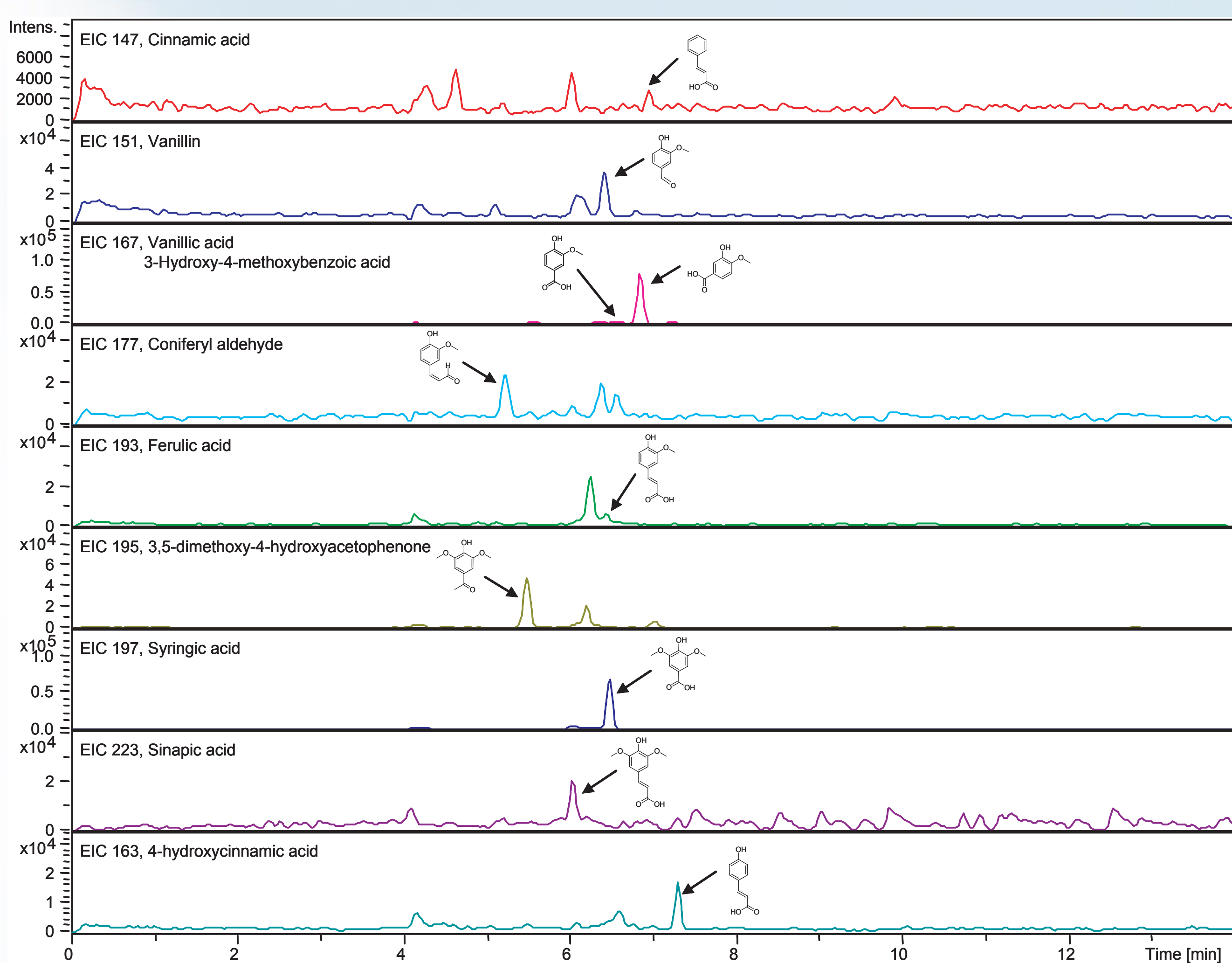


Figure 1. Example of extracted ion electropherograms of wood smoke tracers (methoxy phenols and aromatic acids) from the analysis of Indonesian peat aerosol (Exp 25a) using CE-MS.

Results and Discussions

Figures 1 and 2 show typical extracted ion chromatograms of wood smoke tracer analysis from CE-MS (methoxy phenols and aromatic acids) and HPLC-MS (anhydrosugars), respectively.

Table 2 summarises the emission ratio of selected softwood/hardwood tracers for various biofuels. Nearly no hardwood tracer was found from both pine wood combustions as the pine wood contains gymnosperm lignin enriched in coniferyl alcohol products which produces guaiacol (2-methoxyphenol) derivatives upon combustion. Contrary to softwood characteristics of pine wood combustion, peat smoke is enriched in all three groups of tracer compounds. This is not surprising as the peat is formed through a sequence of geo-bio-physical and chemical transformation of various plant remains. Therefore, tracers in peat smoke are expected to be maturity and origin (i.e. sampling location) specific. Musasa produced not only hardwood tracers but also some softwood tracer compounds as both softwood such as pine and hardwood produces guaiacol derivatives.

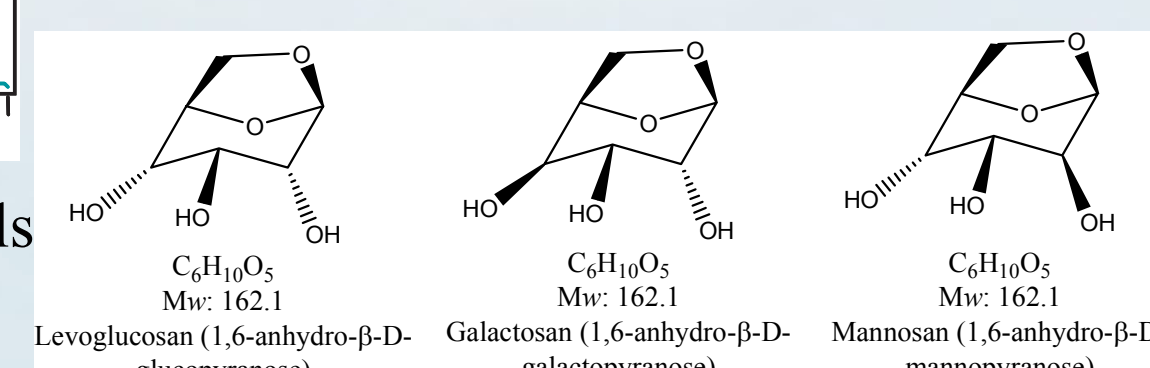


Figure 3. Structures of identified anhydrosugars

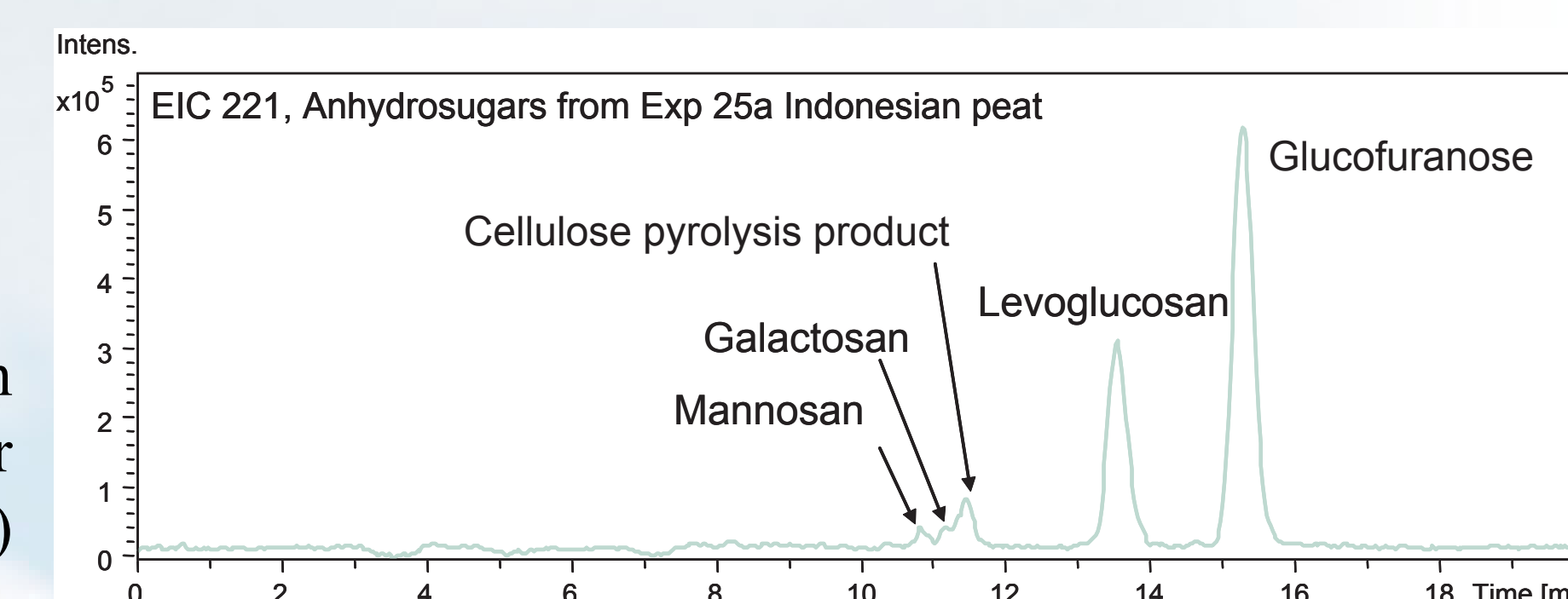


Figure 2. Example of extracted ion chromatogram of wood smoke tracers (anhydrosugars) from the analysis of Indonesian peat aerosol (Exp 25a) using HPLC-MS.

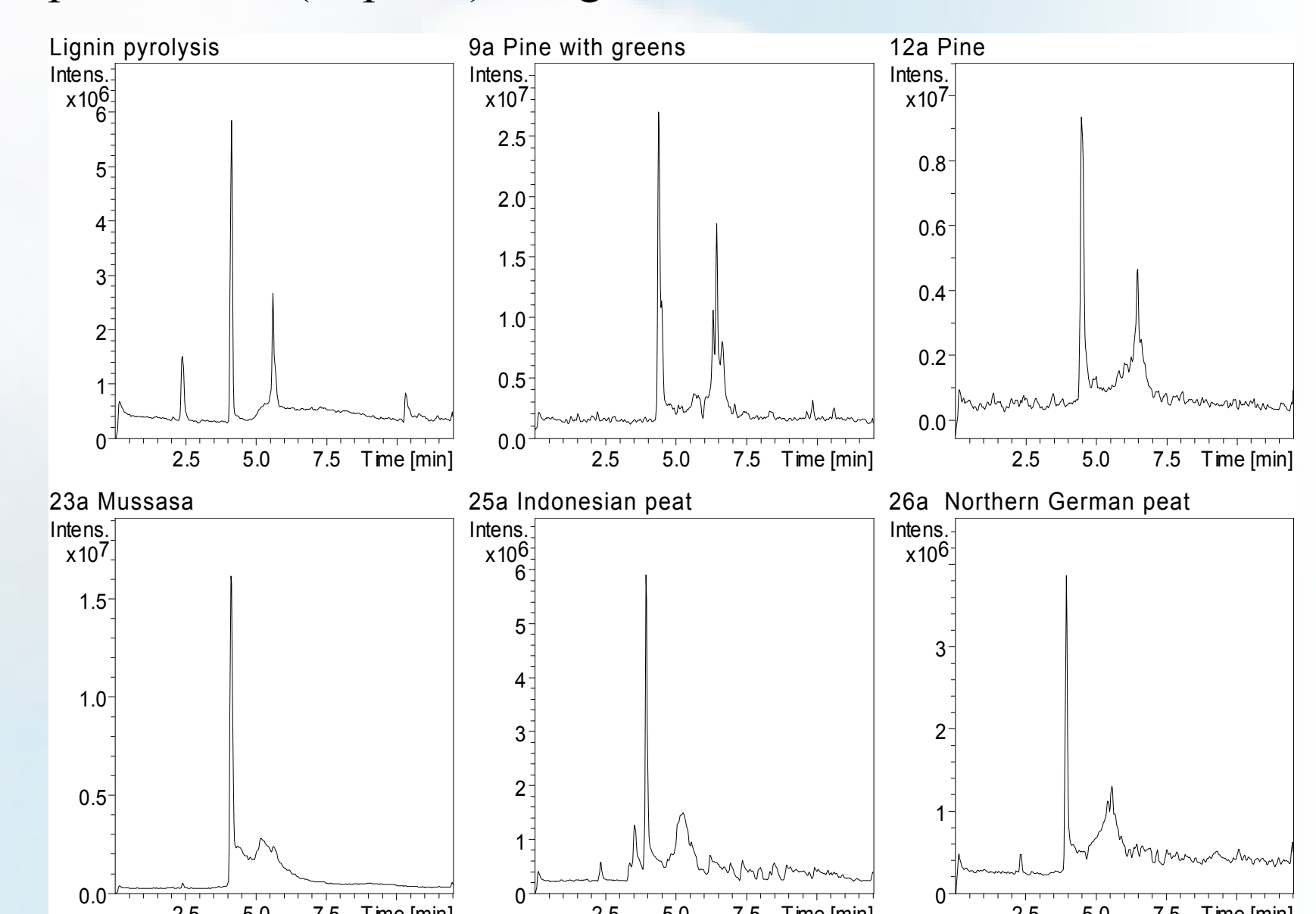


Figure 4. Example of extracted ion chromatogram of macromolecules (*m/z* 300-1500) using CE-MS.

Table 2. Emission ratio of wood smoke tracers (methoxy phenols, aromatic acids and anhydrosugars) for selected experiments. Stage 5 data for wood combustion are not included as mass collected on stage 5 was negligible.

Lignin Pyrolysis Products	Extracted Ion Chromatogram (m/z)	Wood type	Biofuels																						
			9a Pine with greens				12a Pine				23a Musasa				25a Indonesian Peat					26a Northern German Peat					
			1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	5	1	2	3	4	5	
Cinnamic acid	147	Soft and Hard	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.059	0.18	N.D.	N.D.	0.29	1.0	0.86	N.D.	N.D.	N.D.	N.D.	1.6	N.D.	N.D.
Vanillin	151	Soft	0.17	0.66	1.7	0.37	0.36	1.1	3.5	0.41	1.1	2.0	3.6	N.D.	3.6	6.5	13	12	N.D.	N.D.	2.6	16	5.5	N.D.	
Vanillic acid	167	Soft	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.57	1.2	1.4	N.D.	9.3	4.0	74	40	1.4	2.6	18	31	10	4.4	
3-Hydroxy-4-methoxybenzoic acid	167	Soft	0.23	1.1	2.9	0.29	1.4	3.5	8.1	1.3	N.D.	N.D.	1.1	0.11	0.35	2.1	6.5	2.7	N.D.	N.D.	N.D.	N.D.	1.7	1.1	0.22
Coniferyl aldehyde	177	Soft	0.4	1.8	4.6	0.52	1.8	5.6	10	1.7	0.81	2.7	4.0	0.13	1.1	1.8	6.4	3.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
Homovanillic acid	181	Soft	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
Ferulic acid	193	Soft	0.059	0.19	0.4	0.049	N.D.	0.77	0.99	N.D.	0.22	0.36	0.27	N.D.	N.D.	N.D.	N.D.	2.2	N.D.	N.D.	1.3	4.4	1.4	0.39	
3,5-dimethoxy-4-hydroxyacetophenone	195	Hard	N.D.	0.21	0.47	N.D.	N.D.	N.D.	0.3	N.D.	1.1	2.2	4.6	N.D.	3.8	15	47	30	0.64	0.84	3.7	13	6.1	1.8	
Syringic acid	197	Hard	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.61	1.6	0.14	7.1	20	42	37	1.3	1.3	5.0	19	8.6	2.0	
Sinapic acid	223	Hard	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.5	3.5	2.0	2.0	14	39	15	N.D.	N.D.	6.2	20	17	5.3	
4-hydroxycinnamic acid	163	Grass	0.13	0.47	1.5	0.19	N.D.	0.41	0.72	N.D.	N.D.	0.44	0.52	N.D.	N.D.	1.4	4.6	2.7	N.D.	0.59	1.2	3.1	1.4	0.5	
4-nitrocatechol	154		0.34	1.8	4.7	0.3	0.17	0.45	0.72	N.D.	0.26	0.56	0.72	0.071	0.28	0.64	0.87	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
C7H7NO4	168		1.3	6.4	18	1.2	0.69	4.4	7.9	N.D.	0.78	1.9	3.1	N.D.	0.43	1.2	0.67	0.34	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
C8H9NO4	182		0.44	2.0	6.0	0.32	0.34	2.1	3.9	N.D.	0.4	0.77	1.7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	
Cellulose and Hemicellulose Pyrolysis Products																									
Cellulose pyrolysis product 1 ¹			1.5	12	42	3.7	6.3	24	44	3.5	5.7	15	26	0.77	N.D.	N.D.	N.D.	N.D.	N.D.	10	19	31	33	11	
Mannosan			7.5	44	140	9.5	25	89	190	12	3.0	6.4	12	N.D.	28	44	97	49	N.D.	50	100	220	250	27	
Galactosan			5.2	33	90	5.6	20	69	140	11	2.7	7.1	9.6	0.21	8.1	15	47	19	N.D.	41	91	250	260	24	
Cellulose pyrolysis product 2 ¹			9.7	64	190	19	22	110	200	12	13	34	56	1.8	47	93	220	110	N.D.	47	94	280	270	28	
Levoglucosan			27	180	450	53	120	430	620	62	57	170	260	8.5	250	500	1100	570	34	300	720	1600	1800	180	
Cellulose pyrolysis products 3 ¹			23	160	440	43	81	330	570	55	42	110	170	4.2	440	920	2100	1200	54	500	1200	2700	3000	340	

1: tentatively identified from cellulose pyrolysis experiment and retention time of detected peak

Acknowledgements

This project is supported by BMBF within AFO2000 in the project EFEU under contract 07AFT47. We thank Mr. Steinmann and Mr. Kimman from the South Sumatra Forest Fire Management Project (SSFMP) and the Indonesian NGO Wahana Bumi Hijau for providing the Indonesian peat samples.