FIRES SMOKE
BIOMASS COMBUSTION
CONIFERS ANGIOSPERMS
PHENOLS LIGNIN
ANALYSIS GC - MS

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Methoxyphenols from burning of Scandinavian forest plant materials

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METHOXYPHENOLS FROM BURNING OF SCANDINAVIAN FOREST PLANT MATERIALS

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ABSTRACT

Semivolatile compounds in smoke from gram-scale incomplete burning of plant materials were assessed by gas chromatography and mass spectrometry. Gas syringe sampling was shown to be adequate by comparison with adsorbent sampling. Methoxyphenols as well as 1,6-anhydroglucose were released in amounts as large as 10 mg/kg of dry biomass at 90 % combustion efficiency.

Wood, twigs, bark and needles from the conifers Norway spruce and Scots pine emitted twelve reported 2-methoxyphenols in similar proportions. Grass, heather and birchwood released the same 2-methoxyphenols but also the corresponding 2,6-dimethoxyphenols which are characteristic of angiosperms. The methoxyphenols are formed from lignin and differ in structure by the group in *para* position relative to the phenolic OH group. Prominent phenols were those with *trans*-1-propenyl and ethenyl groups in that position. Vanillin, 4-hydroxy-3-methoxybenzaldehyde, was a prominent carbonyl compound from the conifer materials.

Keywords: Phenols, wood, lignin, combustion, fire, smoke

INTRODUCTION

Assessment of the chemical components in smoke from biomass burning is important for both accidental and planned fires and with respect to both environmental impact and health hazards.

The lignin of vascular plants decomposes to fuel-specific methoxyphenols from biomass burning. Qualitative gas chromatographic and mass spectrometric data for 36 methoxyphenols from wood burning were recently presented [1], with references to earlier qualitative studies. The semivolatile monocyclic methoxyphenols are emitted as gases, and quantitative proportions have been reported from controlled analytical pyrolysis of wood and pulp [2]. At ambient temperatures, the methoxyphenols tend to condense, and they are present in extracts of smoke aerosols together with non-volatile compounds [3]. Small amounts of the most volatile methoxyphenols remain gaseous in smoke from different forest biomass materials [4].

The purpose of this study was to determine the amount and proportions of methoxyphenols released from natural forest materials. Different biomass materials, characteristic for Scandinavian boreal forests, were compared. Fire behaviour in these forests has been described in some detail [5].

EXPERIMENTAL

The plant materials were collected in interior south Sweden. The following data apply to biomass materials and experimental methods.

Plant materials

Softwood (*Picea*) : Pieces of fresh stem sapwood, cut from Norway spruce (*Picea abies*)
Twigs (*Picea*) : Needle-free thin twigs with bark, taken three months after felling
Softwood (*Pinus*) : Pieces of fresh stem sapwood, cut from Scots pine (*Pinus sylvestris*)
Bark (*Pinus*) : Thin stem and litter sheets from Scots pine
Needles (*Pinus*) : Season's upper litter needles from a 20-30 year old planted pine forest
Fern : Stem and leaf pieces of dead winter-standing *Pteridium aquilinum*
Grass : Pieces of dead straws of the common forest grass *Deschampsia flexuosa*
Heather : Twigs of *Calluna vulgaris*, with manually defoliated living parts
Hardwood : Pieces of fresh stem sapwood, cut from white birch
Moss and lichen : The moss *Pleurosium schreberi* and the lichen *Cladonia rangiferina* were collected from pine forests

Fuels and burning

Fuel preparation : Wood cut into thin chips and match-size pieces, other fuels broken to pieces
Fuel drying : Openly indoors for several days, bark and heather also for one hour at 100 °C
Fuel dry weight : In the range 90-95 %, determined by heating at 105 °C to constant weight
Amount of fuel : In the range 1 g (fern, grass) to 10 g (softwood, hardwood)
Combustion pot : Ceramic, 1.5 l, with the pile of plant material on the bottom
Covering pot : Clay, 2 l, with bottom hole, placed upside-down for fire choking and sampling
Burning sequence : Flaming burning of half of the material, followed by choking and sampling

Determination of CO and CO_2

Smoke sampling : 30-40 ml, gas-tight syringe (50 ml, SGE)
Gas chromatograph : Perkin Elmer 3920 B, with gas sampling valves, 190 µl (CO) and 290 µl (CO_2)
Separation of CO : Molecular sieve 13 X, 1.7 m × 3.2 mm o.d. column, 80 °C, isothermal
Separation of CO_2 : HayeSep Q (60-80 mesh) porous polymer, 1.9 m × 3.2 mm o.d. column, 80 °C
Detector : Thermal conductivity, 200 °C, 150 mA, carrier gas helium, 25 ml min^{-1}
Calibrations : By injecting pure CO and CO_2 from gas tubes

Determination of methoxyphenols

Smoke sampling : 400-500 µl, gas-tight syringe (500 µl, SGE), pre-flushed with smoke 3-5 times
Gas chromatograph : Varian 3800 (MS-linked) with splitless injection (220°C)
Carrier gas : Helium, 1.1 ml min^{-1}
Column : 30 m × 0.25 mm i.d. FSOT (fused silica open tubular)
Stationary phase : Cyanopropylphenylsilicone, Rtx 1701, 0.25 µm stationary phase layer
Oven temperature : Increased 5 °C min^{-1} from 50 to 200 °C and then kept isothermal at 200 °C
Mass spectrometer : Varian Saturn 2000, ion trap (150 °C), EI (70 eV)
Mass spectra : Mass range *m/z* 35-400, 1 spectrum s^{-1} recorded and data-stored
Quantitative data : External calibration using guaiacol and vanillin

Adsorbent sampling

Cartridge : Injector glass liner with a narrow restriction at the lower end
Adsorbent : Tenax TA, 60-80 mesh, 0.1 g
Samples : Withdrawn using a 10 ml syringe connected with a teflon tube
Sampling volumes : 1 - 2 ml for pot burning and 5 - 10 ml for open burning
Biomass fuel : Needle-free thin spruce twigs with bark (*Picea abies*)
Open burning : On plate in fume-cupboard, flaming and glowing combustion
Desorption : Thermal, in the injector, temperature raised from 100 °C to 220 °C (60 °C min^{-1})

The methoxyphenols were identified using recently published chromatographic and mass spectrometric data [1]. Retention times are given in Table 1 for the specific polar gas chromatographic column used in this work. Automatic integration of peak areas, manually adjusted when required due to incorrect baseline drawing, was used for quantitative assessments. A few minor methoxyphenols overlapped with other compounds in the chromatograms. Selected ion monitoring for specific prominent ions was then used to determine peak areas. The mass spectra of the methoxyphenols are all characterised by an abundant molecular ion and a few prominent ions from specific fragmentations [1]. The difference in total ion response between the assessed methoxyphenols should be less than 20 %, because they all have similar proportions between C, H and O [6]. The response was therefore set equal for all compounds to facilitate comparisons. The response of vanillin was determined using a reference solution in acetonitrile. The magnitude of the response was confirmed for guaiacol using gas injection. A reference amount of guaiacol was then evaporated in a glass container (50 l) from which the gas sample was taken.

Carbon monoxide was not resolved from methane on the molecular sieve column used. Methane was optionally assessed specifically by changing from thermal conductivity to flame ionisation detection. The proportion of methane was shown to be less than 10 % for a wood smoke sample, as expected from other biomass studies [4]. No corrections for methane were therefore made for any of the carbon monoxide determinations.

RESULTS AND DISCUSSION

The data given in Table 1 summarise the results of the study and are arranged to permit comparisons between different smoke components as well as different biomass materials.

Methoxyphenol proportions

The conifer samples and the fern sample gave rise to 2-methoxyphenols only, whereas the angiosperm samples of grass, heather and hardwood gave rise to both 2-methoxyphenols and 2,6-dimethoxyphenols. The proportion of 2,6-dimethoxyphenols was very high (80 %) for birchwood and quite low (30 %) for the grass.

The formation and total proportion of 2,6-dimethoxyphenols reflect the long known characteristic lignin structures of angiosperm plants [7]. The lignins of conifers almost lack 2,6-dimethoxysubstituted units.

Table 1. Basic analytical data for smoke from biomass burning. Proportions (% weight) of prominent 2-methoxyphenols (Gu = guaiacyl, 4-hydroxy-3-methoxyphenyl compounds) and 2,6-dimethoxyphenols (Sy = syringyl, 4-hydroxy-3,5-dimethoxyphenyl compounds).

		Softwood *Picea*	Twigs *Picea*	Softwood *Pinus*	Bark *Pinus*	Needles *Pinus*	Fern *Pteridium*	Grass *Deschampsia*	Heather *Calluna*	Hardwood *Betula*
Combustion efficiency (%) molar ratio CO_2 / (CO_2+CO)		91	89	92	97	87	91	96	89	89
Carbon dioxide (g m^{-3})		13	19	36	23	16	44	45	59	31
Carbon monoxide (g m^{-3})		0.9	1.5	2.0	0.5	1.6	2.7	1.1	4.6	2.3
1,6-Anhydroglucose (mg m^{-3})		40	150	130	120	630	150	130	40	60
2-Methoxyphenols (mg m^{-3})		70	290	150	270	160	90	190	28	70
2,6-Dimethoxyphenols (mg m^{-3})		-	-	-	-	-	-	80	30	320
Gu/Sy Phenols	Retention (min)	Proportions (%)								
GuH	12.55 / 20.82	4	4	3	5	3	4	2 / 4	3 / 9	1 / 12
$\mathrm{GuCH_3}$	15.48 / 23.21	12	9	9	9	5	11	4 / 5	4 / 8	2 / 15
$\mathrm{GuCH_2CH_3}$	17.83 / 25.07	2	3	2	4	2	4	1 / 0.5	1 / 3	0.5 / 4
$\mathrm{GuCH{=}CH_2}$	19.38 / 26.47	9	13	11	19	12	20	24 / 5	8 / 6	3 / 11
$\mathrm{GuCH_2CH{=}CH_2}$	20.03 / 26.92	3	2	3	3	3	3	2 / 1	1 / 3	0.5 / 3
$\mathrm{GuCH{=}CHCH_3}$ (*Z*)	21.50 / 28.12	2	2	2	2	2	3	1 / 0.5	1 / 1	0.5 / 2
$\mathrm{GuCH{=}CHCH_3}$ (*E*)	22.85 / 29.48	19	20	29	22	19	22	19 / 6	15 / 11	5 / 17
GuCHO	23.32 / 30.10	18	20	12	13	16	13	9 / 3	5 / 4	3 / 6
$\mathrm{GuCH_2CHO}$	24.85 / 31.23	5	1	4	7	2	1	1 / 0.5	1 / 1	0.5 / 2
$\mathrm{GuCOCH_3}$	25.37 / 31.83	6	4	4	3	3	4	2 / 2	2 / 2	1 / 2
$\mathrm{GuCH_2COCH_3}$	26.63 / 33.12	6	6	5	4	8	4	2 / 0.5	2 / 2	1 / 3
$\mathrm{GuCH{=}CHCHO}$ (*E*)	32.83 / 45.07	5	5	8	3	9	6	3 / 1	1 / 0	1 / 1
Other methoxyphenols [a]		9	11	8	6	17	5	1 / 0	3 / 2	1 / 2

[a] Mainly $\mathrm{GuCH_2CH_2CH_3}$, $\mathrm{GuCOCH_2CH_3}$, $\mathrm{GuCH_2CH_2CHO}$, $\mathrm{GuCH_2CH_2CH_2OH}$ (prominent for twigs and needles), $\mathrm{GuCH{=}CHCH_2OH}$ (*E*) and $\mathrm{SyCH_2CH_2CH_3}$.

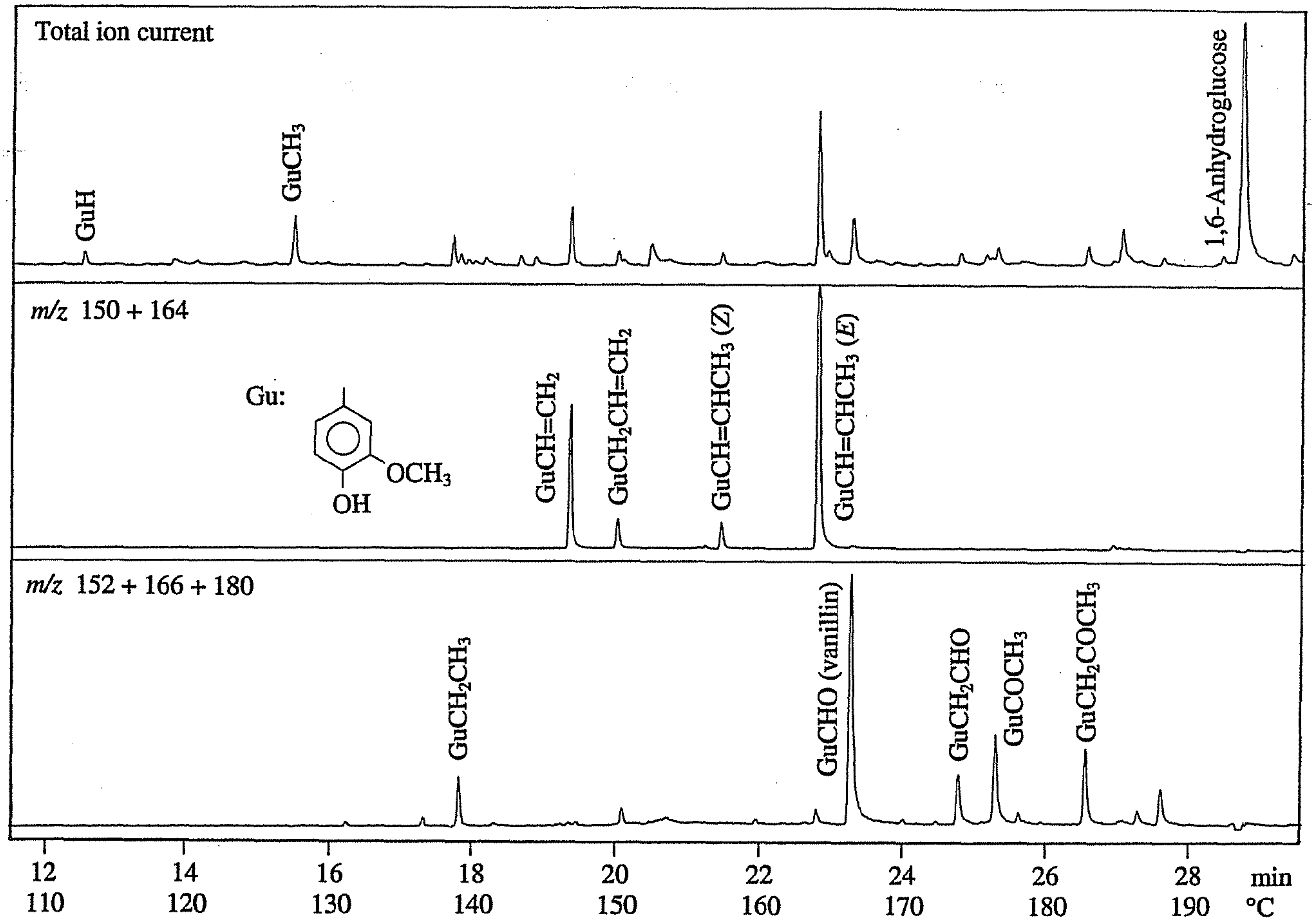

Fig 1. Chromatograms from GC-MS analyses of 4-hydroxy-3-methoxyphenyl (guaiacyl) compounds in smoke from pinewood burning (total ion current and ion currents corresponding to the molecular ions *m/z* 150 + 164 and 152 + 166 + 180).

The observed absence from *Pteridium* of 2,6-dimethoxyphenols emphasises the fundamental evolutionary difference between ferns and angiosperms. Lignin is characteristic of vascular plants, and no methoxyphenols were obtained from burning of two common Scandinavian moss and lichen species.

Percentage proportions of total methoxyphenols are given in Table 1 for twelve specific 2-methoxyphenols and the corresponding twelve 2,6-dimethoxyphenols. As explained in Table 1, these are referred to as guaiacyl (Gu) and syringyl (Sy) compounds with varying side chains. It is emphasised that the materials burn in different ways with respect to parameters such as temperature, flaming and glowing, which influence the proportions of phenols. Each material was allowed to burn uncontrolled which should reflect burning in forests better than pyrolysis and uniform burning conditions.

Guaiacol and its methyl and ethyl analogues (GuH, $GuCH_3$, $GuCH_2CH_3$) were significant products from all nine materials with $GuCH_3$ as the most prominent one. The corresponding Sy compounds were even more prominent relative to other Sy compounds.

The methoxyphenols with alkenyl side chains account for as much as 40 - 50 % of total methoxyphenols for all materials. The species with *trans*-1-propenyl side chains tended to be predominant, but the ethenyl phenols were also very prominent. The well-known eugenol, $GuCH_2CH{=}CH_2$, was formed in smaller amounts. In Figure 1, the four alkenyl phenols from sapwood of Scots pine are recorded by molecular ion monitoring below the total ion chromatogram.

The widely used food flavour additive vanillin, GuCHO, constitutes 10 - 20 % of the recorded 2-methoxyphenols and was the major carbonyl-containing phenol. Vanillin is probably partly formed by oxidation of unsaturated side chains, and its percent proportion tended to increase with increased air supply. Other prominent 2-methoxyphenols with carbonyl groups were $GuCH_2CHO$, $GuCOCH_3$ and $GuCH_2COCH_3$. In Figure 1, the presence and separation of these phenols in smoke from pine are illustrated by molecular ion monitoring. The prominent *trans*-coniferaldehyde, GuCH=CHCHO (*E*), was the latest eluting 2-methoxyphenol. The Sy compounds with low volatility tended to be recorded in lower proportions than the corresponding Gu compounds.

Sampling methods and combustion conditions

The recorded methoxyphenols differ considerably with respect to polarity and reactivity of the side chain. To confirm the results, an optional method for sampling was developed. Samples were then taken on Tenax adsorption cartridges and the methoxyphenols were analysed after thermal desorption. Comparative results are given in Table 2 for the two very different methods. The results demonstrate similar methoxyphenol proportions for the two methods, without significant losses of the most polar and reactive carbonyl compounds, alkenes and alcohols. Somewhat lower proportions for syringe sampling are indicated only for the most volatile and chemically stable phenols, guaiacol and methylguaiacol.

The comparisons in Table 2 also demonstrate significantly different methoxyphenol proportions for differing burning conditions. Choked flaming burning causes elevated proportions of the alkenyl phenols. For glowing and smouldering combustion, an increased proportion of coniferaldehyde was observed. Adsorbent cartridges permit larger sampling volumes than gas injection and can therefore be used for smoke from open burning. The results in Table 2 for open burning compare well with the results from pot burning. It is concluded that the results in Table 1 approximately reflect the methoxyphenol composition in smoke from open burning.

Comprehensive qualitative studies of compounds from wood pyrolysis [8, 9] include the reported methoxyphenols. Our qualitative results compare well with those reported from analytical pyrolysis of wood of the same spruce and birch species [2]. Apparently, oxidative pyrolysis conditions were applied in that study. Vanillin and other carbonyl compounds were even more prominent than in our results. In contrast, high proportions of alkenyl phenols but no carbonyl-containing phenols were reported from slow pyrolysis under nitrogen of wood from Salix, birch and spruce species [10]. A pyrolysis study of wheat straw lignin [11] reported low proportions of carbonyl compounds like vanillin. The major phenol was $GuCH=CH_2$, which was also the most prominent methoxyphenol from grass in our study.

Table 2. Composition (%) of methoxyphenols from spruce twigs. Comparison of differing burning conditions and sampling methods.

	Choked pot burning		Glowing pot burning		Open burning
	Syringe	Cartridge	Syringe	Cartridge	Cartridge
GuH	5	9	5	10	7
$GuCH_3$	6	11	6	9	10
$GuCH_2CH_3$	3	4	2	3	3
$GuCH=CH_2$	11	13	11	9	12
$GuCH_2CH=CH_2$	4	3	2	3	2
$GuCH=CHCH_3$ (*Z*)	3	2	2	2	2
$GuCH=CHCH_3$ (*E*)	17	15	12	10	12
GuCHO	11	11	13	13	13
$GuCOCH_3$	8	6	5	4	5
$GuCH_2COCH_3$	8	6	7	5	6
$GuCH_2CH_2CH_2OH$	9	8	12	11	9
$GuCH=CHCH_2OH$ (*E*)	5	5	6	5	4
GuCH=CHCHO (*E*)	7	4	13	12	9
Other methoxyphenols [a]	3	3	4	4	6

[a] Mainly $GuCH_2CH_2CH_3$, $GuCH_2CHO$, $GuCOCH_2CH_3$, $GuCH_2CH_2CHO$ and $GuCH=CHCH_2OH$ (*Z*)

Studies of methoxyphenols in smoke from biomass burning have been made mainly for particles and condensates. Smoke from residential wood stoves was reported to contain guaiacol and syringol as the most prominent methoxyphenols from softwood and hardwood [12]. Several alkenyl and carbonyl-containing methoxyphenols were observed in proportions similar to those given here, although the burning conditions were very different. Guaiacol and methylguaiacol were the most prominent among few methoxyphenols determined in condensates from burning of biomass related to ponderosa pine [4]. In contrast, carbonyl-containing methoxyphenols were observed to be the most prominent in fine particles from biomass burning [3, 13]. For toxicity testing, semi-volatile compounds from wood burning have been collected on Tenax cartridges with subsequent solvent extraction [14].

Smoke constituents

From Table 1 it is seen that the CO_2 concentration was typically 1 - 2 % for the nine burning experiments. The CO concentration was typically 0.1 - 0.2 % and the combustion efficiency consequently typically around 90 %.

The concentrations of methoxyphenols and other smoke components varied for the different plant materials, which were also burning in different ways. The highest 2-methoxyphenol concentrations were observed from pine bark and spruce twigs. The average amount of methoxyphenols relative to CO was as high as 10 % for the softwood samples and even higher for the birchwood sample. These amounts of methoxyphenols relative to CO are at least ten times higher than the amounts reported for each of the major volatile organic compounds methane, ethane, methanol, and acetic acid from smouldering combustion of forest biomass [4]. They are also ten times higher than the recorded methoxyphenol levels, evidently due to a low recovery of these semivolatile compounds.

Approximately 1 kg of CO_2 is formed from natural burning of 1 kg of forest biomass [4]. From the results in Table 1 it is concluded that the amount of released methoxyphenols was of the order 10 g/kg of burnt biomass. Previously, the complex mixture of volatile hydrocarbons has been studied for biomass burning under similar conditions [15]. The ratio of total non-methane volatile hydrocarbons varied from 10 g/kg for smouldering, to 0.1 g/kg for flaming combustion of wood. Similarly increased emissions with decreased combustion efficiency have been reported for other volatile compounds emitted from forest biomass burning [4]. It is concluded that methoxyphenol emissions markedly exceeding 10 g/kg are to be expected from the frequently occurring smouldering burning of lignin-containing forest biomass.

The predominant primary decomposition product from polysaccharides, 1,6-anhydroglucose, was formed in similar amounts as the total 2-methoxyphenols. In spite of its very polar nature with three alcoholic OH groups, satisfactory chromatographic performance was observed as illustrated in Figure 1 by the total ion chromatogram. Methoxyphenols and 1,6-anhydroglucose gave rise to all prominent recorded peaks from semivolatile compounds for most of the samples. This is illustrated in Figure 1 for the pinewood sample. Levoglucosan has been proposed as a tracer for smoke from biomass burning [16].

Condensation in the sampling syringe of 1,6-anhydroglucose and the methoxyphenols of low volatility was minimised by flushing the syringe with the hot smoke before sampling, and by injecting the sample within 30 s after sampling. Partial or complete losses of compounds of low volatility are likely to be a common source of errors in studies of methoxyphenols.

Many types of phenolic and other compounds of lower volatility than the methoxyphenols are released on burning, with immediate formation of smoke particles [3]. The semivolatile methoxyphenols are released as gases, but condense on the surface of particles as the temperature of the smoke decreases [12]. This means that the proportions of gaseous methoxyphenols in ambient air are biased towards the most volatile species.

CONCLUSIONS

The results demonstrate that methoxyphenols are formed in high concentrations and specific proportions from inefficient biomass burning. Syringe sampling immediately followed by GC-MS analysis permits adequate determination of the methoxyphenols in laboratory experiments. Adsorption on Tenax cartridges, followed by thermal desorption, is an optional method suitable also for field sampling.

The reported smoke components are indicative of emissions from accidental and planned forest fires and other inefficient biomass burning. A major environmental concern is the formation of ozone and other photo-oxidants from gaseous smoke constituents. The condensation of the methoxyphenols on particles decreases their contribution to ground-level ozone formation. Particles covered by adsorbed methoxyphenols and anhydrosugars should also have very different health effects compared with particles from traffic and other sources.

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