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BENZENE	BUTADIENE
GC ANALYSES	EXPOSURE

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Volatile hydrocarbons from the burning of grass and straw

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VOLATILE HYDROCARBONS FROM THE BURNING OF GRASS AND STRAW

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Abstract

The concentrations and proportions of 15 alkenes, 5 alkadienes and 14 other gaseous combustion-formed hydrocarbons were determined near to a controlled field burning of last year's grass. Small-scale model burning of grasses and of barley straw indicated similar hydrocarbon proportions for all these biomass fuels. Samples were taken on triple-layer adsorbent cartridges and were analyzed, after thermal desorption, by gas chromatography on an aluminium oxide column.

The observed proportions of ethene (20-50%) and ethyne (5-20%) increased for flaming fire and decreased for smouldering. Approximate proportions of prominent genotoxic hydrocarbons other than ethene were 10% benzene, 10% propene, and 3% 1,3-butadiene. Among the photochemically reactive C₄-C₈ alkenes, the unbranched 1-alkenes were the most prominent isomers. It is concluded that grass burning implies hazards with respect to human exposure as well as to photooxidant formation.

INTRODUCTION

Accidental grass fires and controlled burning of grass and straw occur widely and often near to smoke-exposed people. Emissions from grass and straw burning of total hydrocarbons, carbon monoxide, and carbon dioxide were early determined in California (Boubel et al., 1969). Gaseous emissions from grassland fires and forest fires have been studied and compared in several respects (Greenberg et al., 1984 ; Cofer et al., 1990). The importance of hydrocarbons from biomass burning for photooxidant formation has been demonstrated (Darley et al., 1966 ; Westberg et al., 1981). Proportions of prominent specific hydrocarbons have been reported for grassland fires in Africa and Brazil (Bonsang et al., 1991 ; Greenberg et al., 1984).

The purpose of this study was to determine in some detail the proportions of the numerous volatile hydrocarbons emitted from the burning of grass and straw. Comprehensive data of this type may be of great interest in studies of health hazards and photooxidant formation as well as in source reconciliation studies. The analytical approach was similar to that in previous studies of hydrocarbon proportions in vehicle-polluted urban air and in environmental tobacco smoke (Barrefors and Petersson, 1993).

EXPERIMENTAL

Field burning

A remote garden with meadow vegetation on poor ground in central southern Sweden was chosen for the purpose. A few square meters covered with last year's grass were burnt in the morning as the rising sun was removing the dew of the night. The grass was mainly fertile *Agrostis tenuis* which grows late in the season and retains its physical structure through the winter. Smaller proportions of the grasses *Poa pratensis* and *Festuca rubra* and of several meadow flowers were yearly growing in the place. A bottom layer of the green perennial mosses *Brachythecium albicans* and *Rhytidiadelphus squarrosus* was partially burnt by the fire. Green blades of the season's grasses were still scarce. The fire was supported somewhat by adding last year's grass, and proceeded as alternating flame and smouldering combustion with development of strongly smelling smoke.

Model burning

Small-scale burning, permitting immediate analysis of combustion gases in high concentrations, was performed in a 1 l ceramic pot. At the stage of combustion to be studied, a larger clay pot was placed upside down over the pot with the burning material, and samples were taken through a hole in the clay pot. Most samples were collected as soon as the flaming fire was extinguished, and therefore represent a mixture of flaming and smouldering combustion. The device also permitted samples representing merely smouldering to be taken.

Samples of last year's meadow grass *Agrostis tenuis* and forest grass *Deschampsia flexuosa* were collected from localities with easily identified fertile populations. The barley straw was obtained from a two-row variety cultivated in Sweden. The barley was harvested in the autumn, and the straw was stored indoors in bales through the winter. The samples burnt consisted mainly of stalks and contained only a small proportion of blades and ears. Sidestream cigarette smoke was also sampled from the ceramic pot after placing two lit Marlboro cigarettes on the bottom.

Adsorption sampling

Simultaneous sampling of all non-methane hydrocarbons was achieved by using triple-layer adsorption cartridges (Tenax TA, Carbotrap and Carbosive S-III) as previously described (Barrefors and Petersson, 1993).

For the field burning, triplicate samples were taken during ten minutes (08.28 - 08.38 a.m.). The three sampling cartridges were kept together, most of the time within the smoke plume which fluctuated in the weak irregular morning wind. To ascertain the proportions of the weakest retained hydrocarbons, notably ethyne, the main sample (~500 ml) was complemented with a small-volume (~25 ml) sample. The third sample (~100 ml) was taken on a cartridge with Tenax TA only, to confirm concentration levels and complete recovery of reactive hydrocarbons.

The cartridge sampling volumes for the pot burning studies were as small as 5-20 ml, preventing breakthrough losses of ethyne.

Analytical methods

The sampled volatile compounds were thermally desorbed (He, 235°C, 14 min) into a

cold (liquid nitrogen) trap made of a coil of an empty fused silica column (5 m x 0.32 mm i.d.). The gas chromatographic separations were performed on a Al₂O₃/ 5% KCl PLOT fused silica column (50 m x 0.32 mm i.d., Chrompack). Injection was made by rapidly heating the cold coil in an oil bath (150°C). The analytical temperature sequence was 30–110°C (10°C min⁻¹), 110°C (14 min isothermal), 110–200°C (4°C min⁻¹) and 200°C (isothermal). No corrections were made for minor differences in the response of the flame ionization detector for different hydrocarbons.

Complementary separations and identifications of hydrocarbons from model burning were made on a Varian Saturn II GC-MS system, using a methylsilicone column. Very different retention data on methylsilicone and aluminium oxide columns facilitate complete hydrocarbon determinations, as previously demonstrated for a wide range of alkenes (Ramnäs et al., 1994). Combustion-formed compounds, which were not resolved on the Al₂O₃ column using the normal temperature program, were separated and determined not only on the GC-MS system but also by modifying the temperature program.

RESULTS

The results given in Table 1 represent the essential outcome of the study. For the controlled field grass burning, plume concentrations are given. The hydrocarbon composition is compared with the results of model burning of the same meadow grass and of barley straw with different degrees of smouldering. Results for cigarette smoke are included to permit comparisons with a well-known plant-related source of air pollution.

Chromatographic separations

The gas chromatogram in Figure 1 illustrates the chromatographic separation and the proportions of combustion-formed hydrocarbons from grass. The aluminium oxide column favourably separates the whole range of volatile non-methane hydrocarbons desorbed from the triple-layer sampling cartridges. It is especially well suited to the separation of C₂-C₅ alkenes which are prominent key compounds from biomass combustion. The polar character of the column increases retention markedly in the order

Table 1. Volatile C₂-C₈ hydrocarbons from field burning of last year's grass, as compared with model burning of the same grass, of barley straw, and of commercial cigarettes^a

		Garden burning Meadow grass Downwind 1-3 m		Laboratory pot-burning experiments			
		$\mu\text{g m}^{-3}$	%	Grass (Fig.1) %	Straw Burning %	Straw Glowing %	Tobacco Cigarettes %
Alkenes							
C2	Ethene	1080	41.5	43.1	33.7	23.4	12.0
C3	Propene	220	8.5	8.8	9.4	11.2	6.7
C4	<i>trans</i> -2-Butene	7.1	0.27	0.34	0.66	1.03	1.13
	1-Butene	42	1.6	1.8	2.4	3.5	2.4
	Methylpropene	17	0.6	0.8	1.1	1.4	2.8
	<i>cis</i> -2-Butene	5.0	0.20	0.24	0.46	0.77	0.76
C5	3-Methyl-1-butene	5	0.2	0.2	0.3	0.3	0.6
	<i>trans</i> -2-Pentene	4.3	0.17	0.19	0.30	0.53	0.50
	2-Methyl-2-butene	1.9	0.07	0.08	0.26	0.35	3.5
	1-Pentene	10.3	0.40	0.47	0.68	0.57	0.98
	2-Methyl-1-butene	3.5	0.14	0.16	0.33	0.49	1.22
	<i>cis</i> -2-Pentene	3.0	0.12	0.14	0.18	0.35	0.26
C6	1-Hexene	16.3	0.63	0.70	0.97	0.59	1.14
C7	1-Heptene	6.6	0.25	0.27	0.45	0.28	0.55
C8	1-Octene	3.8	0.15	0.12	0.24	0.12	0.33
Alkadienes							
C3	Propadiene	15	0.6	0.5	0.4	0.6	0.1
C4	1,3-Butadiene	76	2.9	2.9	3.3	5.3	2.0
C5	Isoprene	6	0.2	0.1	0.4	0.4	25.2
	Cyclopentadiene	12	0.5	0.2	1.2	1.6	0.2
	<i>trans</i> -1,3-Pentadiene	6	0.2	0.2	0.5	0.9	0.7
Alkynes							
C2	Ethyne	445	17.1	15.1	11.9	6.7	0.5
C3	Propyne	43	1.7	2.0	1.7	2.2	0.4
C4	2-Butyne	1.9	0.07	0.09	0.13	0.30	0.05
	Butenyne	19.0	0.73	0.68	0.72	1.02	0.14
	1-Butyne	4.8	0.18	0.19	0.20	0.31	0.04
Alkanes							
C2	Ethane	115	4.4	5.2	9.5	11.9	3.2
C3	Propane	22	0.8	0.9	2.3	3.1	4.3
C4	Butane	6	0.2	0.6	0.7	1.1	2.0
C5	Pentane	1.5	0.06	0.1	0.2	0.2	0.6
Arenes							
C6	Benzene	248	9.5	8.7	7.4	9.1	3.8
C7	Methylbenzene	65	2.5	2.2	2.8	4.7	7.4
C8	Ethylbenzene	11.9	0.46	0.3	0.4	0.4	0.7
	Dimethylbenzenes	10	0.4	0.3	0.8	0.7	3.5
	Styrene	12	0.5	0.4	0.5	0.5	0.8

^a Total concentrations of C₂-C₈ hydrocarbons for the five reported burning experiments were 2.6, 50, 68, 29, and 42 mg m⁻³.

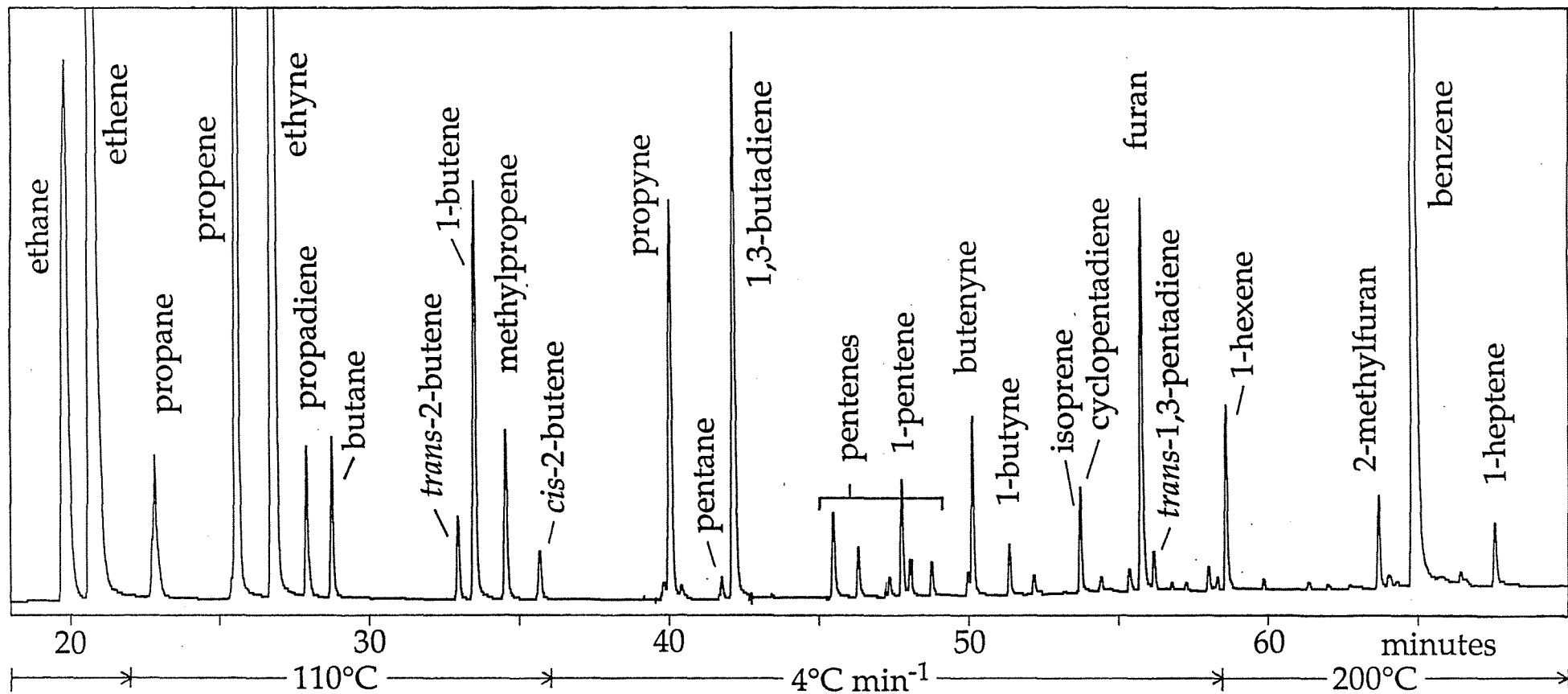


Fig. 1. Gas chromatographic separation of volatile hydrocarbons from grass burning (aluminium oxide column, pot-burning of last year's garden grass *Agrostis tenuis*, cf. Table 1)

alkanes < alkenes < alkadienes < alkynes for hydrocarbons with the same number of carbon atoms. Methylbenzene and the C₈ arenes elute later than benzene and are not included in the chromatogram. The only non-hydrocarbon compounds eluted from the column were the furans with their stable aromatic structure.

Hydrocarbon proportions

The hydrocarbons reported in Table 1 are arranged according to hydrocarbon class, number of carbon atoms, and retention order on the Al₂O₃ column. The hydrocarbon composition is quite uniform for the burning of grass and straw. The major hydrocarbon group is the alkenes, with ethene as the predominant single species and with decreasing proportions as the number of carbon atoms increases. The 1-alkenes are the major isomers for the C₄-C₈ alkenes. Similarly, the lowest analogues are the most prominent for the conjugated alkadienes (1,3-butadiene), the alkynes (ethyne), the alkanes (ethane), and the arenes (benzene). Cigarette smoke contains the same hydrocarbons but deviates by a large proportion of isoprene, increased proportions of branched alkenes, and low proportions of alkynes.

DISCUSSION

Combustion conditions

The remarkably similar hydrocarbon composition reported in Table 1 for the burning of grass in the field and in a pot indicates that emissions from open fires can be well simulated in easily performed model experiments. The results from field burning evidently correspond to a mixture of flaming and smouldering combustion. The two reported experiments for barley straw demonstrate that an increased degree of smouldering significantly influences the hydrocarbon composition. Barley straw burns with more glow and smouldering than fine-structured grasses like *Agrostis tenuis*. Cigarettes represent an extreme of smouldering. It is concluded that the proportions of ethene and especially ethyne increase markedly with an increasing proportion of flame combustion. Proportions exceeding 50% and 20%, respectively, were observed for pot-burning of last year's straw of the predominant forest grass *Deschampsia flexuosa*, which

was found to burn easily with little smoke development. As seen from Table 1, increased smouldering gives rise to increased proportions of complex alkenes. Basic aspects of flaming and smouldering have been discussed for large grassland and forest fires (Cofer et al., 1990).

Fuel structures

The chemical structure of grasses and other plants is characterized by high proportions of cellulose, various hemicelluloses and lignin. The proportions of hydrocarbon classes and several prominent specific hydrocarbons reported for Brazilian grassland fires (Greenberg et al., 1984) are quite similar to those in Table 1 for barley straw. Almost the same proportions have also been reported for major hydrocarbons from the burning of African savanna grasses (Bonsang et al., 1991). Complementary studies of different plant materials in the present study confirmed that great similarities are to be expected in the proportions of combustion-formed hydrocarbons from various biomass materials.

The observed amounts of furan and 2-methylfuran from the burning of barley straw were 6-8% and 2-3% as compared with the total non-methane hydrocarbons. The Brazilian study reports these furans in similar proportions as the only oxygen-containing organic compounds. The two furans are apparently formed from carbohydrates and may be used as specific tracers of volatile air pollutants from biomass fires.

Analysis by GC-MS of smoke samples from barley straw, taken with a gas syringe, demonstrated that the amount of semivolatile phenolic and other oxygenated compounds was considerably larger than that of true hydrocarbons. These types of compounds have been characterized in smoke from wood biomass (Hawthorne et al., 1992). Due to their polar nature and low volatility, they are rapidly transferred from the gaseous phase to the particulate phase.

The reported hydrocarbon proportions from biomass burning differ markedly from those of vehicle emissions, which are normally reflected in the proportions observed in urban air (Barrefors and Petersson, 1993). The C₅-C₆ alkanes in particular, but also butanes, methylbenzene and dimethylbenzenes, are minor combustion products but prominent components from unburnt petrol in vehicle emissions and urban air. The characteristic, high proportion of isoprene in cigarette smoke is thought to reflect a high content of terpenoid polymers in tobacco.

Human exposure and environmental aspects

The concentrations given in Table 1 for grass burning represent exposure levels for a person staying close to a fire. This situation often occurs in practice for people controlling deliberate grass burnings and for people trying to extinguish accidental fires. Ethene, propene, 1,3-butadiene, and benzene are recognized as representing major genotoxic health hazards among the volatile hydrocarbons (Törnqvist and Ehrenberg, 1990). Especially for ethene and 1,3-butadiene, the reported fire smoke concentrations are even higher than those recorded in extremely vehicle-polluted environments like road tunnels (Barrefors and Petersson, 1993). Obviously, long exposure times and unnecessary exposure to smoke from grass and straw burning should be avoided for health reasons.

Deliberate as well as accidental burning of last year's grass occurs mainly during the spring and early summer photooxidant season. Early quantitative determinations of emissions of total hydrocarbons by large-scale laboratory burning (Darley et al., 1966) included different American grasses (Boubel et al., 1969). The total volatile hydrocarbon emissions, normalized to carbon dioxide emissions, are of the same order of magnitude for grassland and forest fires (Greenberg et al., 1984 ; Cofer et al., 1990). Considerable ozone formation has been demonstrated for forest fires with proportions of prominent photochemically reactive alkenes similar to those from grass burning (Westberg et al., 1981). It is concluded that photooxidant formation provides a further argument for minimizing grass burning in the spring and summer seasons.

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