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ORGANIC COMPOUNDS IN THE PARTICULATE
MATTER FROM BURNING ORGANIC SOILS

Charles K. McMahon, +
Jerry D. White
USDA Forest Service, Southeastern
Forest Experiment Station, Dry
Branch, Georgia

Skevos N. Tsoukalas
Applied Biology, Inc., Decatur,
Georgia



This paper is directed to people interested in the environmental impact of natural emissions. Natural emissions are common and contribute significantly to tropospheric background levels.

Several million hectares of the United States are covered by organic soils. During droughts, these soils can ignite and support slow combustion which often persists for weeks causing serious air pollution problems in nearby populated areas. Small blocks of organic soil collected in south-central Florida were burned and monitored at the Southern Forest Fire Laboratory. The soils sustained combustion for up to 4 days, even through layers containing 135 percent moisture. Peak temperatures were in the 400-600°C range. Particulate matter emission factors ranged from 1 to 63 g kg⁻¹. The particulate matter was soot free and virtually all organic in nature (95 percent soluble in methylene chloride). The particulate matter was separated into neutral, strong acid, weak acid (phenolic) and basic fractions. The neutral fraction, which predominated (63 percent), was further separated by silicic acid column chromatography into four subfractions. The subfractions containing polynuclear aromatic hydrocarbons (PAH) were purified by gel permeation chromatography and analyzed by gas chromatography. Percent distributions of various PAH ring systems were determined. Organic soil particulate matter was found to contain high percentages of methyl and polymethyl PAH's in the three and four ring PAH systems. For 13 samples, the benzo(a)pyrene emission factor averaged 213 µg kg⁻¹ with a range between 9 and 785 µg kg⁻¹. Emission factors for carbon monoxide (269 ± 135 g kg⁻¹), nitrogen oxides (1.7 ± 1.8 g kg⁻¹), and total hydrocarbons (23 ± 15 g kg⁻¹) as methane are also reported.

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Introduction

Organic soils cover many millions of hectares in the United States,¹ including 2.8 million hectares in the Southern United States and about 1.0 million in south Florida². Organic soils form when plants such as pond weeds, grasses, shrubs, and trees die and are covered by water for extended periods. With oxygen excluded, decomposition is very slow. As residues accumulate, layers of organic material are formed. If these soils are sufficiently dry, they will support combustion when ignited by faster spreading surface fires. The danger of this happening is especially great on drained areas. Organic soils are generally consumed by smoldering fires that can last for months, burning down to the water table before going out. These slow burning fires produce visible smoke when burning near the surface but can become remarkably smoke free as they burn through deeper layers. Combustion is evident from a general haze over the area combined with a disagreeable and pungent odor from partially oxidized organic material. These soils can burn more rapidly and produce copious amounts of smoke around deep fissures in the soil or where the soil is overturned.

Benner³ examined emissions from gram-size samples of soil burned in an environmental chamber. However, he induced and sustained combustion with an external heat source (hot wire) rather than observing natural combustion. McFarlane⁴ and Skiotis, et al.⁵ report some organic constituents of "peat" smoke from studies designed to identify the flavor characteristics of scotch whiskey. To our knowledge, there have been no quantitative analyses of organic emissions from smoldering combustion of organic soil.

Core samples of organic soil were collected in south-central Florida and transferred to our combustion laboratory near Macon, Georgia. The samples were burned in a manner which simulated the slow smoldering that is common in the field. An earlier paper by McMahan, et al.⁶ reported on soil combustion characteristics and emissions of several EPA criteria pollutants. This paper is an extension of that work and focuses on the chemical characterization of the particulate matter emissions which are virtually soot-free, and consist almost entirely of complex organic compounds.

Materials and Methods

Sample Collection and Combustion

Six small (~ 6 kg) blocks of organic soil (three wet [$>50\%$] and three dry [$<10\%$]) were collected from south-central Florida and burned under controlled conditions in the laboratory. At periodic intervals, emissions were sampled by moving a modified high-volume sampler (with Type A glass fiber filter) over the soil container and platform balance. Temperatures at the surface of the filter ranged between 30°C and 40°C . Gaseous emissions were sampled by pumping a prefiltered sample through teflon tubing into a gas sampling bag. Six fires were conducted producing a total of forty-one filters from the various sampling intervals. Complete details on the soil characteristics, combustion procedures, and gas and particulate sampling methods have been reported earlier.⁶

Particulate Matter Analyses

Liquid-Liquid Extraction. Thirteen of the 41 Type A glass fiber filter samples were extracted with methylene chloride and the extract separated into strong acid, weak acid, basic, and neutral fractions using a liquid-liquid extraction procedure adapted from Cautreels and Van Cauwenberghe⁷ and Heuper, et al.⁸

In order to remove the basic compounds, the methylene chloride extract was reduced to 50 ml under a stream of nitrogen and partitioned three times with 20 ml of 1-N hydrochloric acid. The combined hydrochloric acid solutions were back partitioned with 20 ml of methylene chloride. After neutralization with 36 percent aqueous sodium hydroxide, the aqueous solution was repartitioned with methylene chloride to recover the basic compounds. In a similar manner, the methylene chloride solution was sequentially extracted with a 1-M sodium bicarbonate solution, and a 1-N sodium hydroxide solution, which removed, respectively, strong organic acids and phenols. Frequently, an insoluble precipitate was formed during the partitioning with 1-N sodium hydroxide. After a final partitioning with water, the remaining methylene chloride extract containing the neutral compounds was dried over anhydrous magnesium sulfate and filtered. A 5-ml aliquot was retained for HPLC after adjusting the volume to 50 ml under a stream of nitrogen.

Column Chromatography. The separation of neutral fraction by silicic acid column chromatography was accomplished using the procedure described by Snook, et al.⁹ and Severson, et al.¹⁰ The neutral fraction was transferred to a 500 ml spherical flask containing 20 grams of silicic acid and 50 ml of isooctane. The flask was placed on a rotary evaporator and traces of methylene chloride were removed at 50°C. The remaining isooctane solution containing the neutrals in a silicic acid slurry was added to the top of a 3 cm x 35 cm glass column filled with 100 grams of silicic acid (prepared as a slurry in petroleum ether [PE]). The column was operated at a pressure of 8 to 10 psi of nitrogen, and was eluted with four different solvent combinations of increasing polarity, yielding four neutral subfractions.

Subfraction 1 was eluted with 400 ml of PE and contained primarily saturated aliphatic hydrocarbons from C₁₄-C₃₆. Subfraction 2 was eluted with 1 liter of PE/Benzene(B), 75/25, and should contain primarily polynuclear aromatic hydrocarbons and polyunsaturated aliphatic hydrocarbons. Subfraction 3 was eluted with 1 liter of PE/B, 50/50, and is thought to contain indoles, carbazoles, and possibly some aliphatics. Subfraction 4 was eluted with 1 liter of ethyl ether(Ee)/B, 50/50, and may contain azaarenes, ketones, alcohols, and aromatic nitriles.

Each subfraction was concentrated to approximately 1 ml volume with a rotary evaporator in a waterbath at 40°C, with vacuum of a water aspirator. The solvent was removed with a stream of nitrogen and the weight of each subfraction from the silicic acid separation was obtained. Only the most volatile components of each subfraction was believed lost in this process since the glass fiber filter is not an efficient trap for volatile components. In cases where volatile components are trapped, a Kuderna-Danish evaporator is recommended.

Gel Permeation Chromatography. The polynuclear aromatic hydrocarbons (PAH's) were isolated from the neutral Subfraction 2 by a gel permeation

chromatography (GPC) procedure adapted from Snook, et al.⁹ and Severson, et al.¹⁰ The GPC system was made up of four 1.25 cm x 109 cm chromatronix liquid chromatography columns connected in series and packed with Biobeads SX-12 (Bio-Rad Laboratories) in benzene. The GPC column was 400 cm long and contained approximately 20 g of dry beads. Subfraction 2, from the silicic acid chromatographic separation, containing the PAH was introduced in the GPC column with a 2.0-ml injection loop. The eluting solvent, benzene, was pumped at a flow rate of 2 ml min⁻¹. The column effluent was monitored with a DuoMonitor UV detector at 254 nm and 280 nm. A fraction collector was used to collect the column eluate in 8 ml fractions. It was established elsewhere^{9,10} that polymethyl PAH's began eluting with the elution of a 2,3,6, trimethylnaphthalene standard and all were eluted by the end of the elution of the standard. The monomethyl and the parent PAH, on the other hand, elute after the 2,3,6, trimethylnaphthalene, beginning with the elution of fluoranthene. The polymethyl, monomethyl, and parent PAH's were collected by combining appropriate fractions. The fractions were further concentrated to approximately 0.2 ml by removal of the solvent under a stream of nitrogen and were then analyzed by gas chromatography.

Gas Chromatography. The GPC subfractions containing the purified PAH's and neutral Subfraction 1 containing the aliphatic hydrocarbons were further analyzed by gas chromatography and were quantitated using n-C₃₆ hydrocarbon as the neutral standard. A Varian 3700 gas chromatograph equipped with a 15 foot x 1/8 inch stainless steel column packed with 3 percent Dexsil 300 GC on 100/120 mesh chromosorb W-AW was used for the GC analysis. (Temperature program, 100 to 300°C at 4° min⁻¹ after an initial hold at 100°C for 10 minutes; 35 cc min⁻¹ He; injector temperature, 300°C; flame ionization detector, 325°C.)

High Pressure Liquid Chromatography. An aliquot of neutral compounds (5 ml) retained in a teflon-sealed graduated vial under refrigeration at 0°C was chromatographed on a model 601 Perkin-Elmer liquid chromatograph equipped with a model 204 Perkin-Elmer fluorescence detector and a model LC55 variable UV detector.

For Benzo(a)pyrene (BaP), reverse phase chromatography on a 10 micron octadecyl column (Perkin-Elmer HC-ODS-SIL-X, 25 x 0.26 cm) was used with a flow rate of 1 ml min⁻¹ of 75 percent methanol in water at 30°C column temperature. The detector's excitation wavelength was set at 381 nm and the emission wavelength at 403 nm. In a later study using a 5 micron reverse phase octadecyl column, it was determined that the 10 micron column did not resolve benzo(k)fluoranthene (BkF) from BaP. Thus, the results under these conditions must be considered combined BaP and BkF.

Results and Discussion

Combustion Characteristics

All samples burned slowly but completely over periods ranging between 30 and 70 hours. Weight-loss rates ranged from 0.2 g min⁻¹ to 6.3 g min⁻¹. The combustion zone moved downward from the point of ignition and then spread horizontally to the sides of the container. Often, the fuel near the surface did not burn completely until many hours of subsurface burning had taken place. In general, the wet samples burned more slowly than the dry samples. However, after some moisture was evaporated, a crust of dry, unburned surface fuels would collapse, bringing air and dry

fuel into the reaction zone. Combustion and smoke production rates would then increase. All samples burned to a grey ash through soil layers containing as much as 135 percent moisture (dry weight basis). There was never any evidence of gas phase flaming combustion. In fact, the ash mantle obscured the glowing combustion zone. After the surface fuels were consumed, the thermocouple readings and pungent odor were often the only physical evidence of combustion. The insulating properties of the ash mantle are believed to contribute to self-propagation of smoldering combustion in these soils.

Moist organic soil can sustain smoldering combustion when the heat generated exceeds that lost from the combustion zone. Initially, a high temperature ignition source (i.e., surface fires, propane torch, etc.) may be required for a long period to overcome heat losses from the top of the fuel, once an insulating layer of partially consumed fuel and ash builds up, however, sustained smoldering will occur. This same fundamental process has been suggested in modeling work on coal-bed burning and tobacco combustion, and can be expected to apply to the combustion of municipal waste dumps and other smoldering processes. Peak temperatures as measured in the center of the soil mass ranged from 416°C to 625°C and averaged 452°C in the wet soils and 558°C in the dry soils. This range is typical for smoldering combustion of polyurethane foams, cigarettes, and cellulosic fuels, but well below peak temperatures (900°C to 1400°C) reported for forest fires and piled woody fuels^{11,12}. Complete details of the combustion characteristics can be found in our earlier report.⁶

Gaseous Emissions

Gaseous emission factors were also reported earlier⁶, but are summarized here in order to provide a broader perspective for the particulate matter results which will follow. Emission factors are reported as grams of pollutant emitted per kilogram of organic soil burned (dry weight basis). Carbon monoxide emission factors were very high in all experiments, averaging 269 ± 135 g kg⁻¹. Total hydrocarbons, as measured by a flame ionization detector averaged 23 ± 15 g kg⁻¹ (as methane). Nitrogen oxides emission factors were low in all fires averaging 1.7 ± 1.8 g kg⁻¹ (as nitrogen dioxide). Sulfur oxides were not determined in this study. However, earlier work by Benner³, burning gram-size organic soil samples containing 0.25 percent sulfur produced 0.6 ± 0.5 g kg⁻¹ of sulfur dioxide. Benner also reported hydrogen sulfide emissions as 1.8 ± 1.3 g kg⁻¹.

Particulate Matter Emissions

The particulate matter emission factors ranged from below 1 g kg⁻¹ to above 60 g kg⁻¹. In general, the dry soils produced high emission factors for the first 24 hours of burning (30 ± 20 g kg⁻¹) and dramatically lower factors (1 ± 1 g kg⁻¹) for the latter stages when combustion rates dropped and the ash layer prevented air from entering the combustion zone. The reverse was true for the wet soils; 4.1 ± 3.8 g kg⁻¹ for the first 24 hours and 25 ± 20 g kg⁻¹ for the later periods. In the wet soils, the high emission rates occurred after fuels near the surface dried and collapsed into the burning zone in the center of the can. The particulate matter emitted in these fires appeared as bright yellow oil droplets on the surface of the glass fiber collection filter. No soot particles were evident. Although particle sizes were not measured, prior work with the pyrolysis of peat by Skiotis, et al.⁵ has shown the average aerodynamic

diameter to be less than 1 micron. This average is consistent with combustion theory and findings for other slow combustion processes such as cigarette smoke and smoldering wood.

Liquid-Liquid Extractions. Thirteen of the 41 filter samples were selected for additional study. Methylene chloride extracted a surprisingly high, 94 ± 5.6 percent of the material on these filters. This extract was further divided into broad organic classes as shown in Table I.

Table I. Composition of Methylene Chloride Extract of Organic Soil Particulate Matter.

<u>Fraction</u>	<u>Average Percent \pm S.D.</u>
Neutrals	63 ± 11
Strong Acids	1.9 ± 1.9
Weak Acids	4.1 ± 2.2
Basic Compounds	0.4 ± 0.4
Insoluble Precipitate	16.6 ± 9.0
Total Average Recovery	86 percent

Substantial amounts of a precipitate were formed during the extraction of methylene chloride solution with aqueous sodium hydroxide. Failure of this precipitate to be redissolved in methylene chloride suggests that it is a secondary product, possibly a product of alkaline condensation of carbonyl and phenolic compounds. This may account for the low percentage of weak acids (phenolics) found. We expected them to be present at much higher concentrations due to the high lignin content of organic soils. Total recovery averaged 86 percent of the methylene chloride extract. Losses of water soluble compounds may have occurred during the extractions of the methylene chloride solution with aqueous acid and alkali solutions.

Chromatography of the Neutral Fraction. Each of the neutral fractions was further separated into four subfractions by silicic acid column chromatography and each subfraction was expressed as a percentage of the neutral fraction. The results are tabulated in Table II.

Table II. Separation of Neutral Fractions by Silicic Acid Column Chromatography

<u>Subfraction (Possible Compounds)</u>	<u>Elution Solvent</u>	<u>Percent of Neutrals \pm SD</u>
1. (Aliphatic Hydrocarbons)	PE	43 ± 12
2. (Aromatic Hydrocarbons and Polyolefines)	PE/B, 75/25	18 ± 7
3. (Indoles and Carbazoles)	PE/B, 50/50	11 ± 4
4. (Alcohols, Ketones, Azaar- enes and Aromatic Nitriles)	EF/B, 50/50	27 ± 6

Clearly, Subfraction 1, containing the aliphatic hydrocarbons is the major neutral subfraction. Were all the aliphatic hydrocarbons separated from the particulate matter pyrolytic in origin? To answer this question, we extracted a quantity of organic soil with methylene chloride and subjected the extract to acid base extractions. The neutral fraction obtained weighed approximately 10 percent of the weight of the unburned organic soil. When the neutral fraction was separated by silicic acid column chromatography, it gave a 7.2 percent aliphatic hydrocarbon subfraction. It is therefore possible that some of the compounds in Subfraction 1 are of biological origin and distill off into the smoke during the burning of the soil. Figure 1 is an example of a gas chromatogram of Subfraction 1 containing C₁₄ to C₃₂ aliphatic hydrocarbons.

Four of the 13 Subfraction 2 samples containing aromatic hydrocarbons were selected for further analysis for polynuclear aromatic hydrocarbons (PAH). As described in the methods section, the Subfraction 2 was separated into parent and monomethyl PAH and polymethyl PAH by a gel permeation chromatography (GPC) procedure. Appropriate GPC fractions were then analyzed by gas chromatography. As shown in Figures 2 and 3, the chromatogram of each fraction was divided into six sections on the basis of the retention times of six key PAH's: naphthalene, fluorene, phenanthrene, pyrene, chrysene, and benzo(a)pyrene. The PAH's eluting within each section were grouped together and their total amount was calculated using the response factor for the PAH standard in the beginning of each group. All the PAH's, for example, eluting between naphthalene and fluorene were quantitated as a group using the response factor of naphthalene. The total PAH for each sample was obtained by addition of the amounts of all groups. For each sample, the percent distribution of the PAH falling within certain polynuclear ring systems was calculated and the results are shown in Table III. Emission factors for parent and monomethyl PAH and polymethyl PAH were calculated for each of the four samples and are shown in Table IV.

Table III. Percent Distribution of Particulate PAH's Among Various Aromatic Ring Systems

Sample (Fire#)	Napthalene	Fluorene	Phenanthrene	Pyrene	Chrysene	BaP and Higher
	to Fluorene	to Phenanthrene	to Pyrene	to Chrysene	to BaP	
-----Percent-----						
1(6G)	0.2	22.1	39.1	29.6	6.7	2.0
2(7B)	0.6	17.5	18.1	19.6	20.0	14.3
3(7C)	20.1	28.4	19.5	11.6	15.0	5.4
4(8B)	3.0	31.0	28.7	14.2	17.2	6.0

Table IV. Emission Factors of Particulate PAH's From Organic Soil Fires

Sample (Fire #)	Parent and Monomethyl PAH	Polymethyl PAH	Total Particulate PAH
----- $\mu\text{g g}^{-1}$ -----			
1(6G)	311	138	449
2(7B)	66	66	132
3(7C)	168	982	1150
4(8B)	16	165	181

The distribution of the PAH's is not too surprising when you realize that the glass fiber filter sample is not an efficient collector for the low molecular weight PAH's such as naphthalene. Furthermore, the relatively low temperatures, (400-600°C) are not conducive to pyrosynthesis of PAH's with more than four rings. Thus, PAH's with three and four ring systems predominate in the organic soil particulate matter. The "ultimate" PAH, i.e., soot, is also characteristically absent from organic soil combustion products. Organic soil PAH's are also characterized by a relatively high percentage of methyl and polymethyl PAH's. Methylated PAH's can be partly explained by the low combustion temperatures which fail to oxidize the highly methylated PAH precursors (lignin, etc.) in the fuel.

An aliquot of each of the 13 neutral samples was analyzed for benzo(a)pyrene (BaP) by high pressure liquid chromatography. In our earlier publication,⁶ BaP results were reported to average 319 $\mu\text{g kg}^{-1}$ with a range between 13 and 1178 $\mu\text{g kg}^{-1}$. Later, it was learned that the BaP peak also contained some benzo(k)fluoranthene (BkF). Using samples from another study involving North Carolina organic soils, and a 5 micron reverse phase octadecyl column, a BkF peak was resolved from the BaP peak in the approximate ratio of 2BaP:1BkF. Applying this correction factor to the 13 samples described above now gives a BaP emission factor which averages 213 $\mu\text{g kg}^{-1}$ with a range between 9 and 785 $\mu\text{g kg}^{-1}$. This range is quite typical for non-steady combustion of carbonaceous fuels and is within the range reported for burning pine needles¹³ and hardwood leaves¹⁴.

Summary and Conclusions

Small blocks of organic soil (three wet, three dry) collected from south-central Florida were burned under controlled conditions in the laboratory. Once combustion was self-propagating, all samples burned to grey ash, even through layers with moisture contents of 135 percent of dry weight. Peak temperatures ranged from 416°C to 625°C. Dry soils produced high particulate matter emission factors for the first 24 hours of burning ($30 \pm 20 \text{ g kg}^{-1}$) and low factors ($1 \pm 1 \text{ g kg}^{-1}$) for the later periods. The reverse was true for the wet soils: $4.1 \pm 3.8 \text{ g kg}^{-1}$ for the first 24 hours and $25 \pm 20 \text{ g kg}^{-1}$ for the later periods. Carbon monoxide levels were high for all fires, averaging 269 g kg^{-1} . Total hydrocarbons averaged 23 g kg^{-1} and nitrogen oxides, 1.7 g kg^{-1} .

The particulate matter produced by these fires was soot free and 95 percent soluble in methylene chloride. The methylene chloride extract was separated into neutral, strong acid, weak acid (phenolic) and basic

fractions. The neutral fraction containing complex aliphatic and aromatic hydrocarbons accounted for 62 percent of the extract. The neutral extract was further separated into four subfractions by silicic acid column chromatography. The subfraction containing polynuclear aromatic hydrocarbons (PAH) was purified by gel permeation chromatography and analyzed by gas chromatography. Percent distributions of various PAH ring systems were determined. Organic soil particulate matter was found to contain high percentages of methyl and polymethyl PAH's in the three and four ring PAH systems. For 13 samples, the benzo(a)pyrene emission factor averaged $213 \mu\text{g kg}^{-1}$ with a range between 9 and $785 \mu\text{g kg}^{-1}$.

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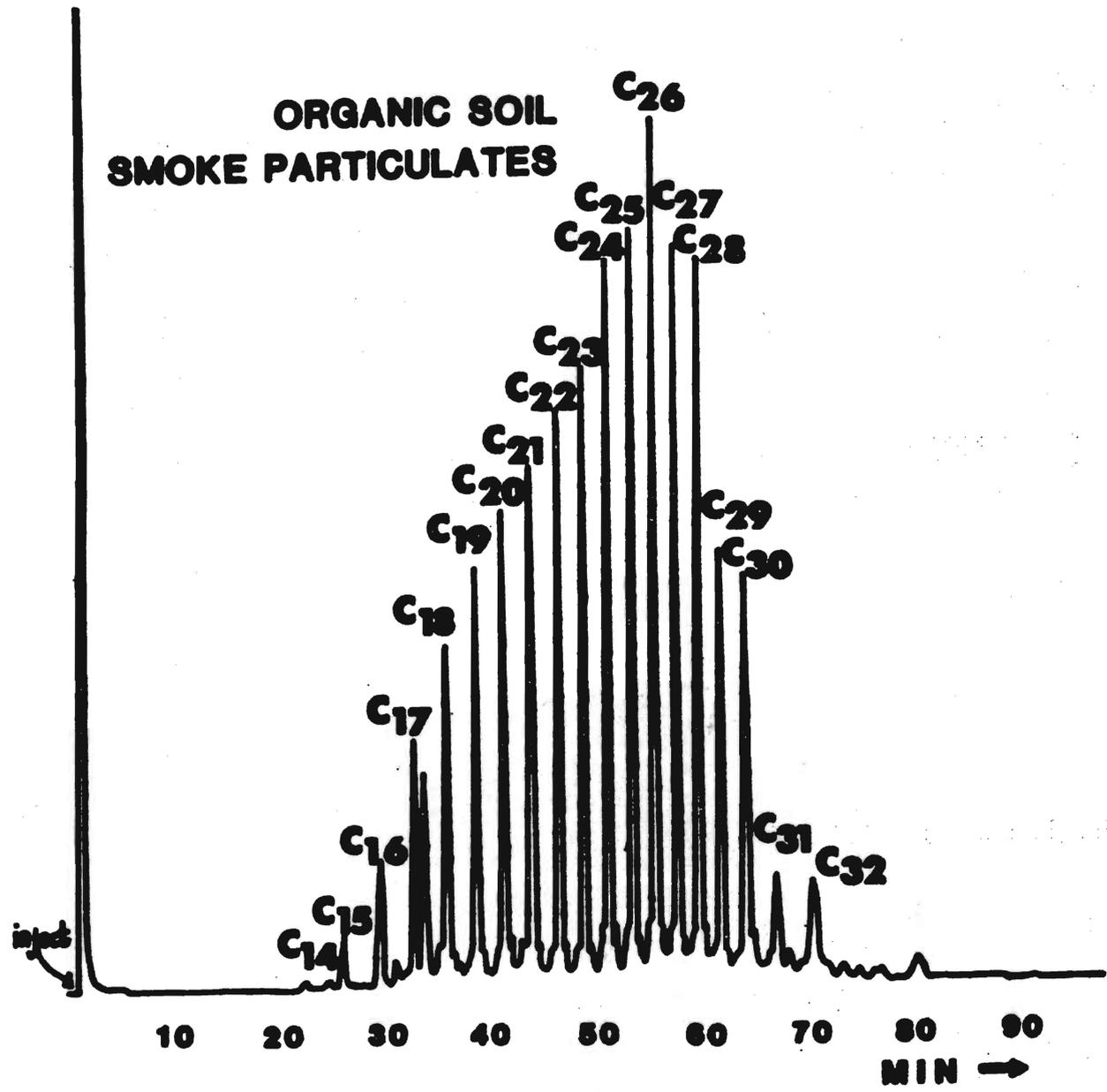


FIGURE 1 GAS CHROMATOGRAM OF ALIPHATIC HYDROCARBONS

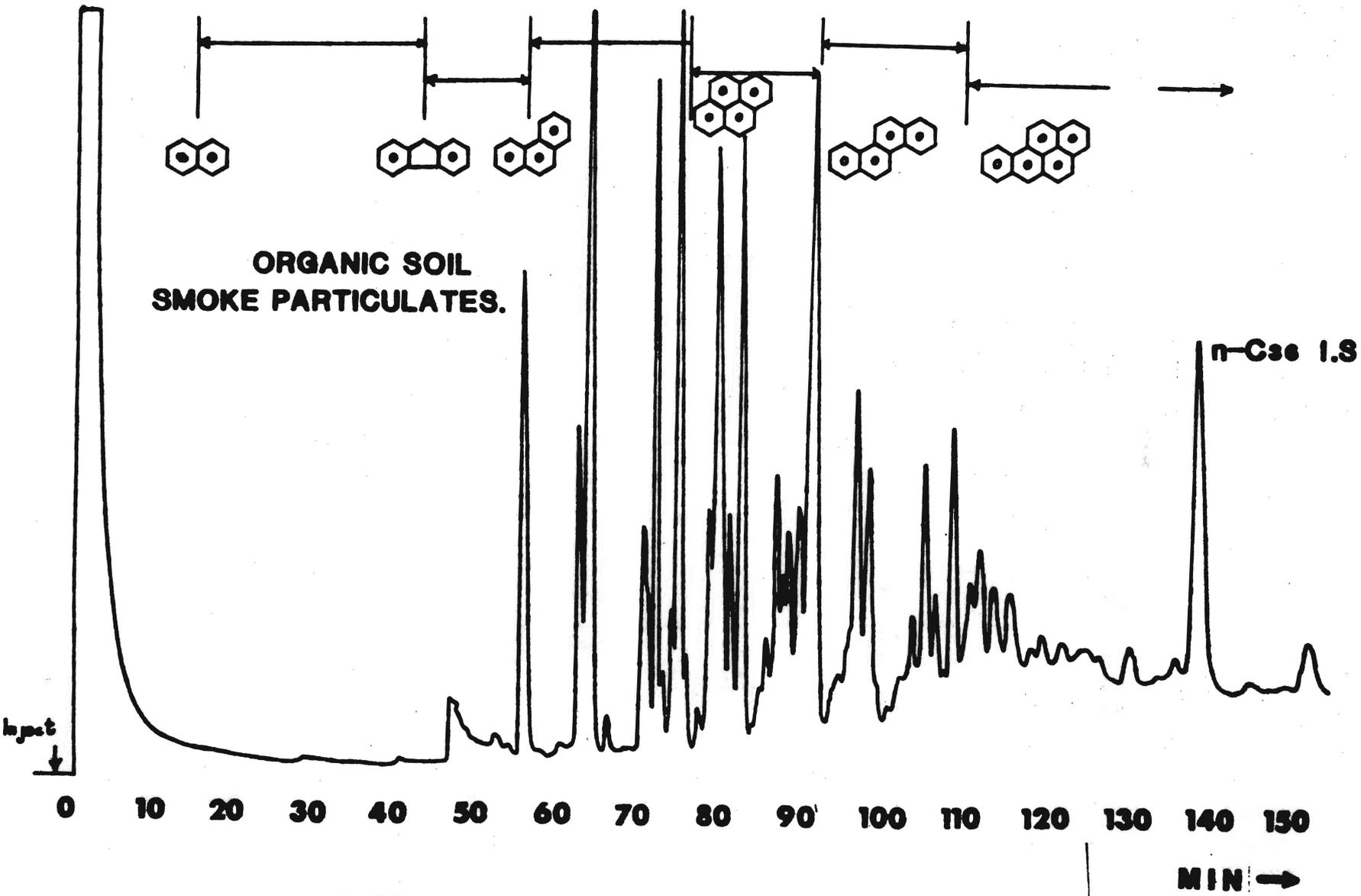
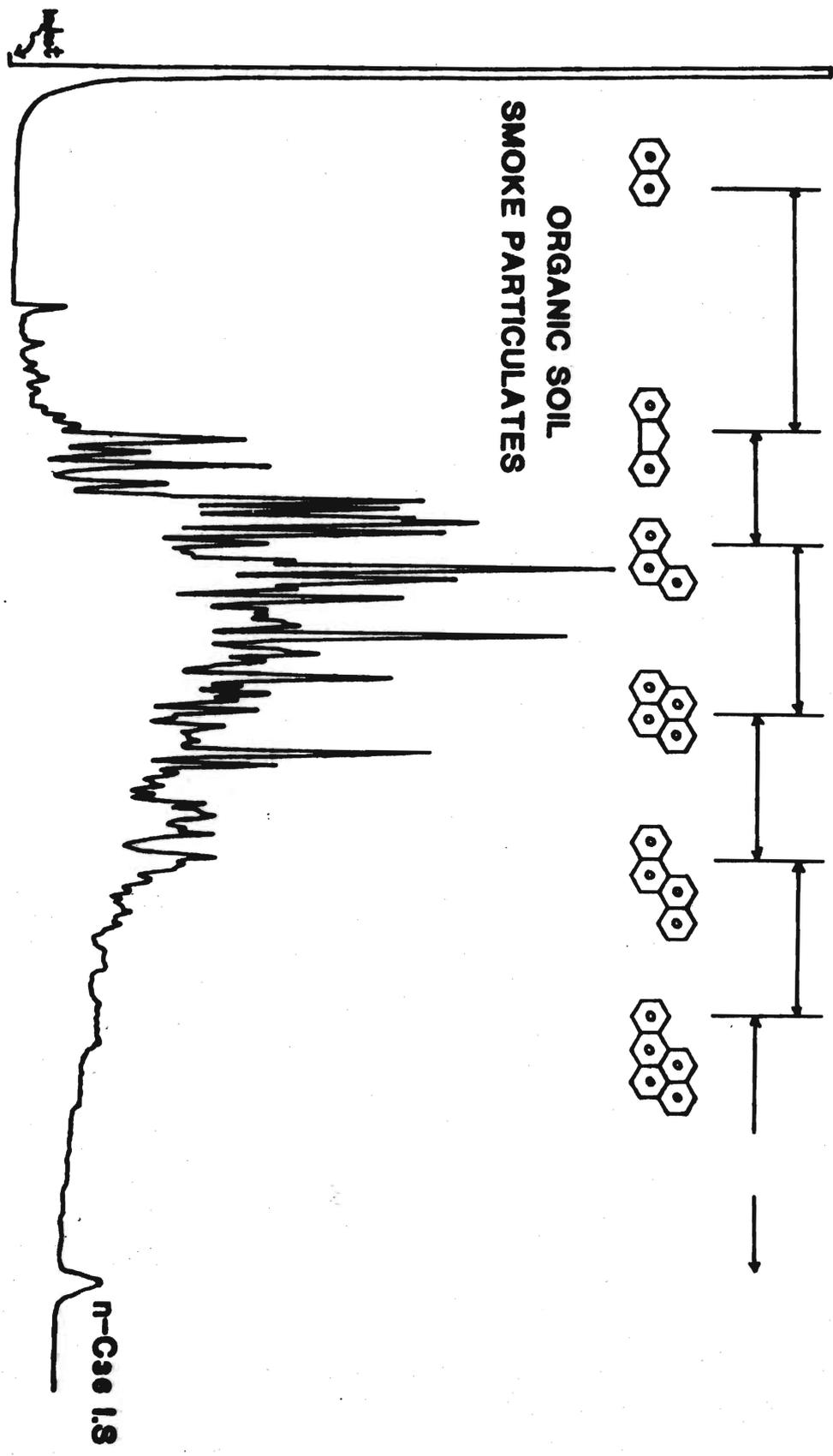


FIGURE 2 GAS CHROMATOGRAM OF MONOMETHYL AND PARENT P.A.H.



**FIGURE 3 GAS CHROMATOGRAM OF
POLYMETHYL P.A.H.**