NATURAL ORGANIC COMPOUNDS AS TRACERS FOR BIOMASS
COMBUSTION IN AEROSOLS

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ABSTRACT

Biomass combustion is an important primary source of carbonaceous particles in the global atmosphere. Although various molecular markers have already been proposed for this process, additional specific organic tracers need to be characterized.

The injection of natural product organic tracers to smoke occurs primarily by direct volatilization/steam stripping and by thermal alteration based on combustion temperature. The degree of alteration increases as the burn temperature rises and the moisture content of the fuel decreases. Although the molecular composition of organic matter in smoke particles is highly variable, the molecular structures of the tracers are generally source specific.

The homologous compound series and biomarkers present in smoke particles are derived directly from plant wax, gum and resin by volatilization and secondarily from pyrolysis of biopolymers (e.g., cellulose, lignin, cutin, suberin), wax, gum and resin. The complexity of the organic components of smoke aerosol is illustrated with examples from controlled burns of temperate and tropical biomass fuels. Burning of biomass from temperate regions (i.e., conifers) yields characteristic tracers from diterpenoids as well as phenolics and other oxygenated species, which are recognizable in urban airsheds. The major organic components of smoke particles from tropical biomass are straight-chain, aliphatic and oxygenated compounds and triterpenoids. Several compounds (e.g., amyrone, friedelin, aromatic A-noroleananes and other thermal derivatives from triterpenoids, lignin phenols) are potential key indicators for smoke components from combustion of such biomass. The precursor to product approach of organic geochemistry can be applied successfully to provide tracers for studying smoke plume chemistry and dispersion.

INTRODUCTION

Biogenic organic matter, consisting predominantly of lipids, soot and humic and fulvic acids, is now firmly established as a major carbonaceous fraction in atmospheric particles found in urban, rural and remote locales [i.e., Arpino *et al.*, 1972; Broddin *et al.*, 1980; Cox *et al.*, 1982; Duce *et al.*, 1983; Eichmann *et al.*, 1979, 1980; Gagosian *et al.*, 1981, 1982, 1987; Marty and Saliot, 1982; Matsumoto and Hanya, 1980; Mazurek and Simoneit, 1984; Mazurek *et al.*, 1989;

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Ohta and Handa, 1985; Rogge *et al.*, 1993a; Simoneit, 1977, 1979, 1980, 1984a,b, 1985, 1986, 1989; Simoneit and Mazurek, 1982, 1989; Simoneit *et al.*, 1977, 1980, 1983, 1988, 1990, 1991a,b,c]. However, in comparison to the relatively extensive studies that have been carried out on hydrocarbons of both biogenic and anthropogenic origins in these aerosols, only limited molecular information is available on polar compounds [e.g., Gagosian *et al.*, 1987; Hawthorne *et al.*, 1988, 1989, 1992; Mazurek *et al.*, 1989; Rogge *et al.*, 1993a,b; Schneider *et al.*, 1983; Simoneit, 1985, 1989; Simoneit and Mazurek, 1982; Simoneit *et al.*, 1983, 1988, 1993].

Biomass combustion is an important primary source of many trace substances that are reactants in atmospheric chemistry and of soot particulate matter which decreases visibility and absorbs incident radiation [e.g., Crutzen *et al.*, 1985; Levine, 1991; Lobert *et al.*, 1990; Seiler and Crutzen, 1980]. Thus, there is a need to demonstrate additional specific tracers for this input process and a limited number of molecular markers have been proposed.

This additional input of biogenic organic matter to the troposphere (urban, rural and remote) from biomass combustion occurs by natural, as well as man-made, fires. Thermally-altered (pyrolysis) and directly-emitted molecular markers may be used as indicators. This concept has been applied preliminarily to tracing biomass burning in Oregon [Standley and Simoneit, 1987, 1990, 1994], in China [Simoneit *et al.*, 1991b], and Amazonia, Brazil [Abas *et al.*, 1995]. For example, retene, a thermal alteration product from resin diterpenoids (e.g., abietic acid), has been found in aerosols in Elverum, Norway and in Oregon, and at trace levels in Los Angeles, California [Ramdahl, 1983; Mazurek *et al.*, 1989; Standley and Simoneit, 1987, 1990, 1994], and China [Simoneit *et al.*, 1991b]. Retene was not detectable in aerosols of the Harmattan or in urban samples of Nigeria, nor in rural aerosols of SE Australia, because conifer wood is not used for fuel in those areas [Simoneit *et al.*, 1988, 1991c]. Since there is no major non-combustion source for retene, it is useful as an indicator of wood burning, especially conifer, but is not always concentrated enough for detection. Thus, additional tracers of thermally-altered and directly-emitted natural products need to be characterized to assign input sources of organic matter from biomass combustion to aerosols.

EXPERIMENTAL METHODS

Samples

Large samples of smoke particulate matter were acquired by high volume filtration on prebaked quartz fiber filters and the complementary fine particle fractions ($d_p < 2 \mu\text{m}$) were collected after appropriate dilution on small prebaked quartz fiber filters (47 mm diam.) [e.g., Hildemann *et al.*, 1991a; Standley and Simoneit, 1987]. Data are discussed from various types of smoke samples consisting of (1) the fine fraction from pine and oak wood combustion in a fireplace [Hildemann *et al.*, 1991b; Rogge *et al.*, 1993a; unpublished data], (2) controlled burns of forest litter in Oregon [Standley and Simoneit, 1987, 1994], (3) alder wood combustion in a wood stove [Standley and Simoneit, 1990], (4) various grass and chaparral fires, and (5) a controlled fire of tropical forest litter in Amazonia, Brazil [Abas *et al.*, 1995].

Lipid Isolation and Separation

The filters with particulate matter were extracted with methylene chloride (CH_2Cl_2) or other polar solvent mixtures within the filter storage jars [Simoneit and Mazurek, 1982]. The solvent extracts were filtered for the removal of insoluble particles. Filtrates were first concentrated on a rotary evaporator and then using a stream of filtered nitrogen gas to a volume of approximately 5 mL. Volumes were then adjusted to 5.0 mL exactly by addition of CH_2Cl_2 .

Typically, an aliquot (2.5 mL) of the filtrate was transferred to a 5 mL heavy-walled, conical vial, and 30 μL perdeutero-*n*-tetracosane (90 $\mu\text{g/mL}$) was added as internal standard. The mixture was reduced in volume to 500 μL and 3.0 mL of BF_3 -methanol (Pierce) was added. The vial was capped and heated to approximately 60°C for 10 minutes to esterify carboxylic acids. After cooling the mixture was transferred to a separatory funnel with 30 mL of hexane and washed twice with saturated NaCl solution, discarding the aqueous layer. The organic layer was dried over Na_2SO_4 . The solvent was evaporated under nitrogen to almost dryness and reconstituted with a known volume of hexane (final volume 500 μL). The derivatized extract was subjected to thin layer

chromatography (TLC) using silica-gel plates (0.25 mm, Alltech) and eluted with a mixture of hexane and diethyl ether (9:1). The TLC plates had been cleaned prior to use by repetitive elutions with methanol and CH_2Cl_2 , and before sample application they were activated in an oven at 120°C for 45 minutes. An aliquot of the total extract was quantified by evaporation to dryness and weighing, and the fractions were quantified by gas chromatographic analyses.

The TLC fractions and the total and methylated extract fractions were subjected to gas chromatographic (GC) and gas chromatography-mass spectrometric (GC-MS) analyses. Alcohol fractions were converted to the trimethylsilyl ethers prior to GC and GC-MS analysis by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) for approximately 30 min at $\sim 70^\circ\text{C}$ under a nitrogen atmosphere.

Lipid Analyses

The GC analyses were carried out on a Hewlett-Packard Model 5840A gas chromatograph using a 25 m x 0.20 mm i.d. fused silica capillary column coated with DB-5 (J and W, Inc.). The GC-MS analyses were conducted on a Finnigan Model 4021 quadrupole mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph and equipped with a fused silica capillary column coated with DB-5 (30 m x 0.25 mm i.d.). The GC and GC-MS operating conditions were as follows: isothermal at 65°C for 2 min for GC only, temperature program $65\text{--}310^\circ\text{C}$ at 4°C per minute, hold isothermal at 310°C for 60 min and using helium as carrier gas. Mass spectrometric data were acquired and processed using a Finnigan-Incos Model 2300 data system. Molecular markers were identified by GC and GC-MS comparison with authentic standards and characterized mixtures. Unknown compounds were characterized by interpretation of their mass spectrometric fragmentation pattern.

RESULTS AND DISCUSSION

Combustion Process

Combustion by burning other than incineration at ultrahigh temperatures is not completely destructive to the organic matter in the fuels. Thus, the injection of organic tracer compounds into

smoke occurs primarily by direct volatilization/steam stripping and by thermal alteration based on combustion temperature. The degree of alteration of organic matter increases as the burn temperature rises and the moisture content of the fuel decreases. Although the molecular composition of organic matter in smoke particles is highly variable, the molecular tracers are generally still source specific [e.g., Hawthorne *et al.*, 1988, 1989, 1992; Standley and Simoneit, 1987, 1990, 1994, Abas *et al.*, 1995]. For example, retene, a thermal alteration product from resin diterpenoids (e.g., abietic acid) as described above, has been found in aerosols in Norway and Oregon, and at trace levels in some urban areas [Ramdahl, 1983; Mazurek *et al.*, 1991; Standley and Simoneit, 1987, 1994; Simoneit *et al.*, 1991a]. Retene was not detectable in aerosols of geographic regions where conifers do not grow to be used as fuel [Abas *et al.*, 1995; Simoneit *et al.*, 1988, 1991b]. Since there is no known non-combustion source for retene, it is useful as an indicator of conifer wood burning, but does not always have an ambient concentration adequate for detection. Definition of additional tracers of thermally-altered and directly-emitted natural products will aid the assessment of the impact of biomass combustion on aerosols.

Organic Tracers

Smoke particles contain homologous compound series and biomarkers which are derived directly from plant wax, gum and resin by volatilization and secondarily from pyrolysis of biopolymers (e.g., cellulose, lignin, cutin, suberin), wax, gum and resin. Biomarkers or molecular tracers are the indicator compounds best utilized for confirmation of genetic sources of carbonaceous fractions in smoke emissions. As applied here, biomarkers are utilized as indicators of origins from natural product compounds of vegetation and their altered derivatives (residues) by partial combustion. The complexity of the organic components of smoke aerosol particles will be illustrated with three examples.

Conifer Wood Smoke

The first example demonstrates that diterpenoids are excellent indicators for smoke from burning of gymnosperm wood [e.g., conifers, Ramdahl, 1983; Standley and Simoneit, 1987,

1994]. Resin acids such as abietic or pimaric acids are produced by conifers. These compounds and their derivatives at various stages of thermal alteration have been found in ambient aerosols [Simoneit and Mazurek, 1982; Simoneit, 1989] and in smoke from slash and wood burning [Standley and Simoneit, 1987, 1994; Simoneit *et al.*, 1993]. This can be illustrated with the mass fragmentograms for the extract fractions (acids as methylated derivatives) of fine aerosol particles from a fireplace where pine wood was burned [Fig. 1a, b; Rogge *et al.*, unpublished data; Simoneit *et al.*, 1993]. The major diterpenoid compounds in the smoke are pimaric (2, chemical structures are shown in Appendix 1), sandaracopimaric (3), isopimaric (4), dehydroabietic (5), and abietic (6) acids (Fig. 1a, b). Dehydroabietic acid can be regarded as an altered product from resin acids and the other diterpenoid acids are directly volatilized unaltered marker compounds. An aerosol sample taken during winter in Los Angeles is also shown for comparison (Fig. 1c, d). Dehydroabietic acid is the dominant diterpenoid marker and the other resin acids are present at reduced levels. $\Delta^{8,15}$ -Pimaradien-18-oic acid (1, Fig. 1) appears to be an alteration product due to double bond migration, and retene and other hydrocarbon diterpenoid derivatives occur at trace levels only. This demonstrates that diterpenoid acids are recognizable tracers in the urban atmosphere for wood smoke.

Mixed Temperate Forest Burn

The second example is smoke from a controlled slash burn of mixed temperate forest illustrating the ketones formed by combustion [Standley and Simoneit, 1987]. The ketone fraction consists primarily of *n*-alkan-2-ones, *n*-alkanals, and triterpenones (Fig. 2). The *n*-alkan-2-ones range from C₁₆ to C₃₃, with a C_{max} = 27 and strong odd-to-even carbon number preference. The *n*-alkanals range from C₁₉ to C₃₁, with a C_{max} = 23 and also a strong odd-to-even carbon number preference. Both *n*-alkanones and *n*-alkanals are partial oxidation products from alkanols, alkanes and other aliphatic moieties, analogous as is observed in laboratory hydrous pyrolysis experiments [Leif and Simoneit, 1995]. The triterpenones are mainly the amyrones, taraxerone, lupenone and a friedelin derivative (Fig. 2b). They are either natural products or low temperature oxidation

products from the respective triterpenol precursors, and are characteristic of their higher plant sources.

Amazon Biomass Smoke

The third example is a smoke sample from burning of composited vegetation in Amazonia [Abas *et al.*, 1995] and the various lipid fractions extracted from the particulate matter are shown in Fig. 3. The total extract is comprised mainly of *n*-alkanoic acids, *n*-alkanes, polynuclear aromatic hydrocarbons (PAH), and triterpenoids. The *n*-alkanes range from C₁₇ to C₃₇ with a C_{max} = 29/31 and high odd carbon number preference (Fig. 3b), which is similar as reported for aerosols from the Amazon region, indicating that alkanes from burning are indistinguishable from plant wax alkanes in the ambient aerosol [Simoneit *et al.*, 1990]. The same is the case for the *n*-alkanoic acids and *n*-alkanols (Fig. 3c, f).

More specific homologous aliphatic tracers for combustion are the *n*-alk-1-enes, *n*-alkan-2-ones and α,ω -alkanedioic acids (Fig. 3b, d, e). For example, the major series of *n*-alk-1-enes present ranges from C₁₇ to C₃₅, with C_{max} = 22 (minor at 29/31) and a slight even carbon number predominance (CPI = 0.8, Fig. 4b). Alkenes are not dominant components in aerosols or plant waxes. The origin of these compounds is inferred to be from the biomass fuel, and based on their carbon number distribution primarily from *n*-alkanols by dehydration (*n*-alkan-1-ols are easily dehydrated to *n*-alk-1-enes by high temperatures) and to a minor degree from the *n*-alkanes by oxidation during incomplete combustion (compare Fig. 4b with c and a, respectively). The even carbon number dominance and C_{max} = 22 are derived from the *n*-alkanol distribution, and the minor dominance of *n*-C₂₉ and *n*-C₃₁ reflects the dehydrogenation of the *n*-alkanes.

The aliphatic hydrocarbon fraction contains a group of derivatives from the amyrins (e.g., β -7) (peaks 1-6, Fig. 3b, structures also shown in Fig. 5) which are various triterpadienes (e.g., urs-2,12-diene), noroleanene, norursene, and diaromatic A-noroleananes and A-norursanes [Abas *et al.*, 1995]. These compounds are not known as natural products and are therefore indicators for combustion of biomass containing amyrin precursors. The α - and β -amyrins (7) are the predominant biomarkers in the total smoke lipids (Fig. 3f), and α - and β -amyrone (8) (mild

oxidation products of amyrins) and friedelin (9) are also significant (Fig. 3d, f). Phytosterols from plant waxes are trace components in this smoke sample and consist mainly of β -sitosterol (10) with lesser amounts of other C₂₉ and C₂₈ isomers. This is characteristic as observed for other smoke emissions from vegetation [e.g., Simoneit *et al.*, 1983, 1993].

The PAH are pyrogenic molecular markers in smoke, where the unsubstituted analogs are usually the characteristic compounds of higher temperature combustive processes. Major amounts of PAH are found in this sample (Figs. 3c and 6a, peaks 1-15) and consist primarily of phenanthrene (1), methylenepheneanthrene, methylphenanthrenes (2-5), fluoranthene (6), pyrene (7), and chrysene (9), and traces of benzo(a)fluoranthenes (10), benzo(e&a)pyrenes, anthanthrene, indenopyrene, benzo(ghi)perylene, and coronene. Oxy-PAH are also significant (Figs. 3e and 6b, peaks 16-23) and the predominant compounds are fluorenone (16), anthra-9,10-quinone (17), cyclopenta(def)phenanthren-4-one (18,11), benzo(a)fluoren-11-one (20,12), benzanthrone (13), and naphthanthrone (23,14), with minor amounts of methylanthra-9,10-quinones, benzo(c)fluoren-7-one and benz(a)anthra-7,12-quinone. The chemical structures of the PAH and oxy-PAH cannot be correlated to specific sources, they are resynthesis products from any high temperature combustive process using organic matter as fuel.

Phenolic products from the pyrolytic breakdown of lignin in vegetation have been proposed as tracers specific for plant classes (taxa) [e.g., Hawthorne *et al.*, 1988, 1989, 1992; Simoneit *et al.*, 1993]. The dominant markers for lignin in this smoke sample found in fraction 6 (Fig. 3f) are vanillin (15), vanillic acid (16), syringaldehyde (17), syringic acid (18), and guaiacylacetone (19), with traces of various other phenolic products. This group of tracers confirms the relative contribution to the smoke from each biomass taxon in the fuel [Abas *et al.*, 1995].

CONCLUSION

The major organic components of smoke particles from tropical biomass are straight-chain, aliphatic and oxygenated compounds and triterpenoids from vegetation waxes, resins/gums, and biopolymers. Several compounds (e.g., amyrins, friedelin, aromatic A-noroleananes, and other thermal derivatives from triterpenoids and from lignin – syringaldehyde, vanillin, syringic acid,

vanillic acid) are potential key indicators for smoke components from combustion of such biomass. Burning of biomass from temperate regions (i.e., conifers) yields characteristic tracers from diterpenoids as well as phenolics and other oxygenated species, which are recognizable in urban airsheds. Biomass combustion smoke from tropical areas (i.e., hardwoods) also yields characteristic tracers. The precursor to product approach of organic geochemistry can be applied successfully to delineate tracers (biomarkers) for the environmental process of biomass combustion.

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FIGURE LEGENDS

- Figure 1. Mass fragmentograms for the diterpenoid acids in pine wood smoke (a,b) and the fine particles of the West Los Angeles atmosphere in winter (c,d) (plots are molecular ions of methyl esters, m/z 314 and 316, numbers refer to compounds in text).
- Figure 2. Salient features of a GC-MS analysis of a ketone fraction from a smoke aerosol in Oregon: (a) m/z 58 fragmentogram, numerals refer to carbon chain length of *n*-alkan-2-ones (ip18 = 6,10,14-trimethylpentadecan-2-one); (b) total ion current trace (equivalent to GC trace of total fraction), peaks with dots are *n*-alkan-2-ones, peaks with dashes are *n*-alkanals, and the triterpenones are (1) taraxerone, (2) β -amyrone, (3) lupenone, and (4) a friedelenone.
- Figure 3. Representative gas chromatograms of the lipid fractions from an Amazon smoke sample: a) total, b) aliphatic hydrocarbons (F1, early eluting homolog of doublets is the *n*-alk-1-ene), c) PAH and esters (F2 + 3), d) ketones (F4), e) dicarboxylic acids and oxy-PAH (F5), and f) alcohols (F6) [n_i = carbon numbers of homologous series, additional numbers (i.e., b: 1-6, c: 1-10, e,f: 1-12) see text, U1 = unknown triterpenoid, F = friedelin and IS = internal standard, *n*-C₂₄D₅₀].
- Figure 4. Salient features of the GC-MS data for the aliphatic hydrocarbons (F1) from an Amazon smoke sample: (a) total ion current trace, (b) alkenes, key ion m/z 83, (c) alkanes, key ion m/z 99, (d) triterpenes, key ion m/z 218 (numbers 18-35 refer to carbon chain length of homologous series and 1-6 are biomarkers, discussed in the text).
- Figure 5. Thermal alteration products from amyrins in smoke.

Figure 6. Salient features of the GC-MS data for the PAH and oxy-PAH in the Amazon smoke sample: (a) PAH in fraction 2 + 3 – (1) phenanthrene, (2) 3-methylphenanthrene, (3) 2-methylphenanthrene, (4) 9-methylphenanthrene, (5) 1-methylphenanthrene, (6) fluoranthene, (7) pyrene, (8) , (9) chrysene (triphenylene), (10) benzo(a)fluoranthene, (11) benzo(e)pyrene, (12) benzo(a)pyrene, (13) anthanthrene, (14) indeno(1,2,3-cd)pyrene, (15) benzo(ghi)perylene; (b) oxy-PAH in fraction 4 – (16) 9*H*-fluoren-9-one, (17) anthra-9,10-quinone, (18) 4*H*-cyclopenta(def)phenanthren-4-one, (19) methylanthra-9,10-quinone, (20) 11*H*-benzo(a)fluoren-11-one, (21) 7*H*-benzo(c)fluoren-7-one, (22) benz(a)anthra-7,12-quinone, (23) naphthanthrone (6*H*-benzo(cd)pyren-6-one).

F.1

F.2

F.3

F.4

F. 5

F.6

Appendix I : Chemical Structures Cited

1. $\Delta^{8,15}$ -Pimaradien-18-oic acid

2. Pimaric acid

3. Sandaracopimaric acid

4. Isopimaric acid

5. Dehydroabietic acid

6. Abietic acid

7. β -Amyrin

8. α -Amyrone

9. Friedelin

10. β -Sitosterol

11. Cyclopenta(def)phenanthren-4-one

12. Benzo(a)fluoren-11-one

13. Benzanthrone

14. Naphthanthrone

15. Vanillin

16. Vanillic acid

17. Syringaldehyde

18. Syngic acid

19. Guaiacyl acetone