BNL-61634
ABSTR.

NATURAL PRODUCTS AND ALTERED DERIVATIVES AS TRACERS FOR BIOMASS COMBUSTION IN AEROSOLS

B. R. T. Simoneit[1], M. R. bin Abas[2], G. R. Cass[3],
W. F. Rogge[4], M. A. Mazurek, L. J. Standley[5], and L. M. Hildemann[6]
Environmental Chemistry Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

March 1995

For presentation before the
Division of Environmental Chemistry,
American Chemical Society,
Anaheim, CA
April 2-7, 1995

[1] Environmental Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331.
[2] Department of Chemistry, University of Malaya, Kuala Lumpur 59100, Malaysia.
[3] Environmental Engineering Science Department and Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA 91125.
[4] Department of Civil and Environmental Engineering, Florida International University, University Park, FL 33199.
[5] Stroud Water Research Center, Academy of Natural Sciences, Avondale, PA 19311.
[6] Department of Civil Engineering, Stanford University, Stanford, CA 94305.

This research was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-76CH00016.

"PREPRINT EXTENDED ABSTRACT"
Presented Before the Divison of Environmental Chemistry
American Chemical Society
Anaheim, CA April 2-7, 1995

NATURAL PRODUCTS AND ALTERED DERIVATIVES AS TRACERS FOR BIOMASS COMBUSTION IN AEROSOLS

Bernd R. T. Simoneit[1], M. Radzi bin Abas[2], G. R. Cass[3], W. F. Rogge[4], M. A. Mazurek[5], L. J. Standley[6], and L. M. Hildemann[7]

[1]Petroleum and Environmental Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, U.S.A.
[2]Department of Chemistry, University of Malaya, Kuala Lumpur 59100, Malaysia
[3]Environmental Engineering Science Department, California Institute of Technology, Pasadena, CA 91125, U.S.A.
[4]Department of Civil and Environmental Engineering, Florida International University, University Park, FL 33199, U.S.A.
[5]Environmental Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.
[6]Stroud Water Research Center, Academy of Natural Sciences, Avondale, PA 19311, U.S.A.
[7]Department of Civil Engineering, Stanford University, Stanford, CA 94305, U.S.A.

Introduction

Biomass combustion is an important primary source of particles in the global atmosphere. It contributes many trace organic substances which can be reactants in atmospheric chemistry and soot particles which decrease visibility and absorb incident radiation (e.g., Levine, 1991; Seiler and Crutzen, 1980). Thus, there is a need to characterize additional specific tracers for this input process, although various molecular markers have already been proposed (e.g., Hawthorne et al., 1992; Standley and Simoneit, 1987; Simoneit et al., 1993).

Process

Combustion is not completely destructive to organic matter in the fuels by burning other than incineration at ultrahigh temperatures. Thus, the injection of 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 tracers are generally still source specific (e.g., Standley and Simoneit, 1987). For example, retene, a thermal alteration product from resin diterpenoids (e.g., abietic acid), 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 rural or urban regions of Nigeria, SE Australia and Amazonia, Brazil, because no conifers grow there to be used for fuel (Abas et al., 1995; Simoneit et al., 1988, 1991b). Since there is no major non-combustion source for retene, it is useful as an indicator of wood burning, but only for conifer. However, retene is not always concentrated enough for detection. Thus, defining additional tracers of thermally-altered and directly-emitted natural products aids the assessment of organic matter input from biomass combustion to aerosols.

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., lignin, cutin, suberin), wax, gum and resin. The complexity of the organic components of smoke aerosol particles will be illustrated with two examples.

Conifer Wood Smoke

The first example demonstrates that diterpenoids are excellent indicators for smoke from burning of gymnosperm wood (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), 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, 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.

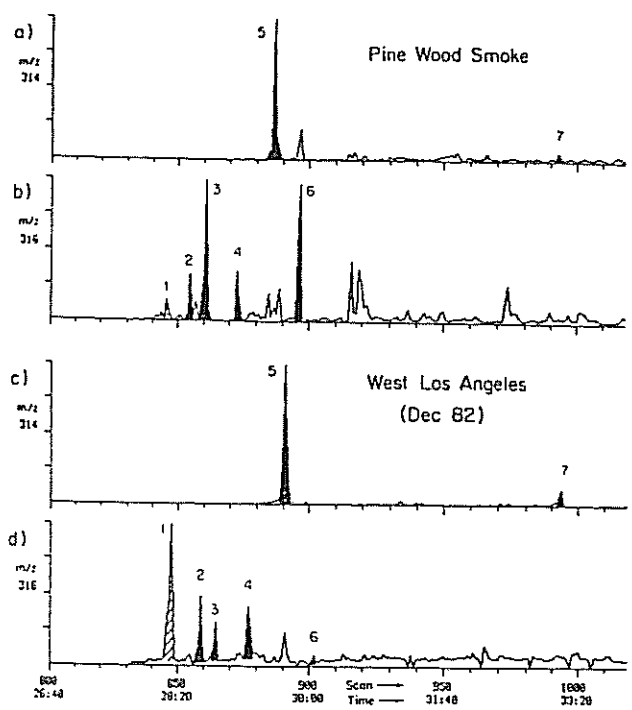

Figure 1. Mass fragmentograms for the diterpenoid acids in pine wood smoke (a,b) and the fine particles of the West Los Angeles atmosphere in winter (c,d) (plots are molecular ions of methyl esters, m/z 314 and 316, numbers refer to compounds in text).

Amazon Biomass Smoke

The second example is a smoke sample from composited vegetation in Amazonia (Abas et al., 1995) and the various bitumen fractions extracted from the particulate matter are shown in Fig. 2. The total extract is comprised mainly of *n*-alkanoic acids, *n*-alkanes, polynuclear aromatic hydrocarbons (PAH), and triterpenoids. The *n*-alkanes range from C_{17} to C_{37} with a C_{max} = 29/31 and high CPI (Fig. 2b), 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. 2c, f). More specific homologous aliphatic tracers for combustion may be the *n*-alk-1-enes, *n*-alkan-2-ones and α,ω-alkanedioic acids (Fig. 2b, d, e).

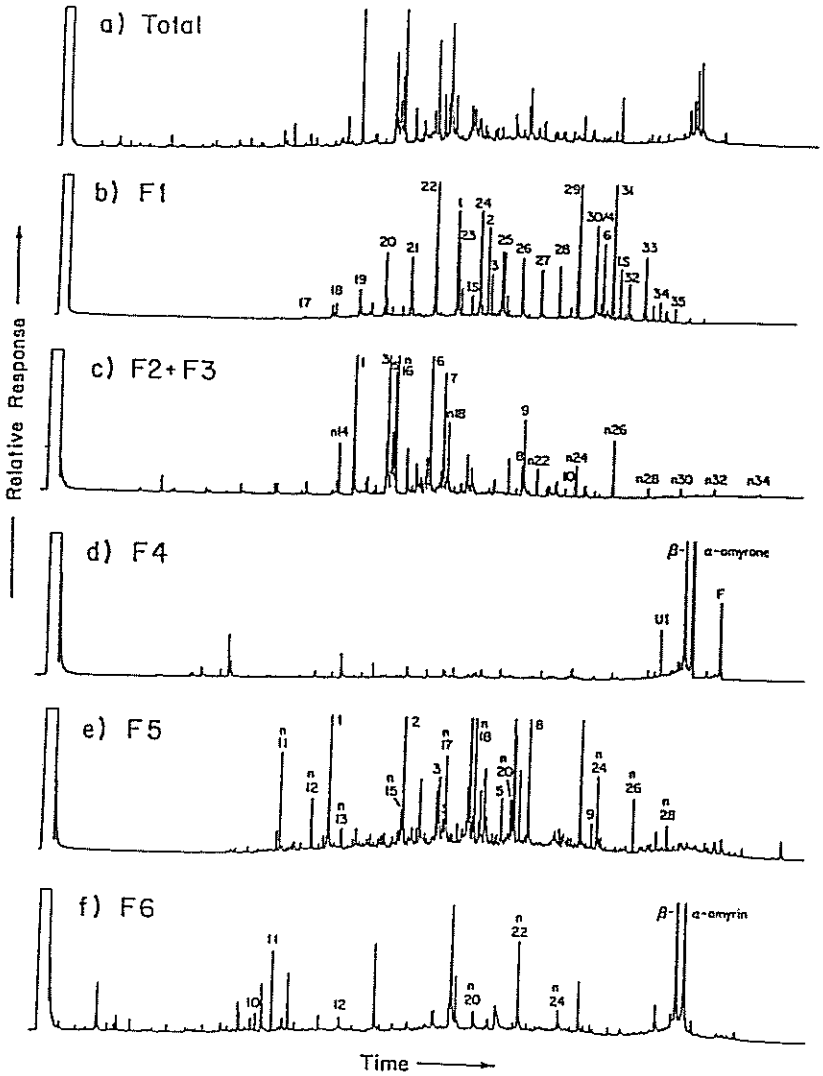

Figure 2. Representative gas chromatograms of the lipid fractions from an Amazon smoke sample: a) total, b) aliphatic hydrocarbons (F1, early eluting homolog of doublets is the *n*-alk-1-ene), c) PAH and esters (F2 + 3), d) ketones (F4), e) dicarboxylic acids and oxy-PAH (F5), and f) alcohols (F6) [ni = carbon numbers of homologous series, additional numbers (i.e., b: 1-6, c: 1-10, e,f: 1-12) see text, U1 = unknown, F = friedelin and IS = internal standard, n-$C_{24}D_{50}$].

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 alteration derivatives (residues) from partial combustion.

The aliphatic hydrocarbon fraction contains a group of derivatives from the amyrins (I) (peaks 1-6, Fig. 2b, Structures shown in Fig. 3) which are various triterpadienes (e.g. III), noroleanene, norursene (IV), and diaromatic A-noroleananes and A-norursanes (e.g. V) (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 are the predominant biomarkers in the total smoke lipids (Fig. 2f), and α- and β-amyrenones (II) (mild oxidation products of amyrins) and friedelin are also significant (Fig. 2d, f). Phytosterols from plant waxes are trace components in this smoke sample and consist mainly of β-sitosterol with lesser amounts of other C_{29} and C_{28} isomers. This is characteristic as observed for other smoke emissions from vegetation (e.g., Simoneit et al., 1993).

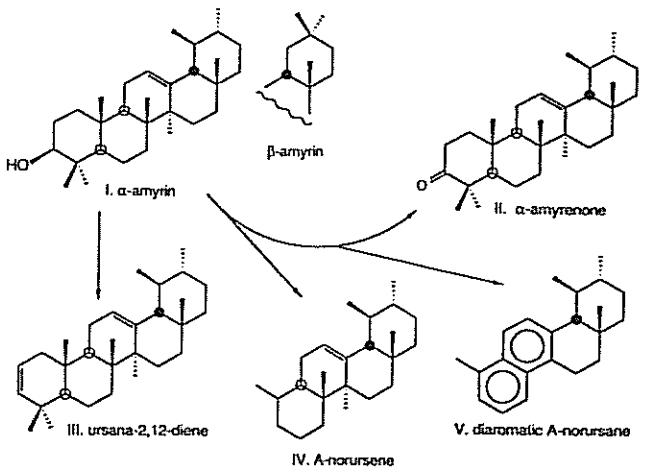

Figure 3. Thermal alteration products from amyrins in smoke.

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 (Fig. 2c, peaks 1-10) and consist primarily of phenanthrene (1), methylenephenanthrene, methylphenanthrenes (3,5), fluoranthene (6), pyrene (7), and chrysene (9), and traces of benzofluoranthenes (10), benzo(e+a)pyrenes, anthanthrene, indenopyrene, benzo(ghi)perylene, and coronene. Oxy-PAH are also significant (Fig. 2e, peaks 1-9) and the predominant compounds are fluorenone (1), anthra-9,10-quinone (2), cyclopenta(def)phenanthren-4-one (3), benzo(a)fluoren-11-one (5), benzanthrone (9), and naphthanthrone (8), with minor amounts of methylanthra-9,10-quinones, benzo(c)fluoren-7-one and benz(a)anthra-7,12-quinone.

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., 1992; Simoneit et al., 1993). The dominant markers for lignin in this smoke sample are vanillic acid, syringaldehyde, syringic acid, vanillin, and guaiacylacetone, with traces of various other phenolic products. This group of tracers confirms the relative contribution to the smoke from each biomass taxa 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., amyrones, friedelin, aromatic A-noroleananes and other thermal

derivatives from triterpenoids, 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. The precursor to product approach of organic geochemistry can be applied successfully to this environmental problem.

References

Abas, M.R., B.R.T. Simoneit, V. Elias, J.A. Cabral and J.N. Cardoso (1995). Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere*, in press.

Hawthorne, S.B., D.J. Miller, J.J. Langenfeld and M.S. Krieger (1992). PM-10 high-volume collection and quantitation of semi- and nonvolatile phenols, methoxylated phenols, alkanes and polycyclic aromatic hydrocarbons from winter urban air and their relationship to wood smoke emissions. *Environ. Sci. Techn.* **26**, 2251-2262.

Levine, J.S. (1991). Introduction: Global biomass burning: Atmospheric, climatic and biospheric implications. In: *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, J.S. Levine (ed.), MIT Press, Cambridge, MA, pp. xxv-xxx.

Mazurek, M.A., G.R. Cass and B.R.T. Simoneit (1991). Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States. *Environ. Sci. Techn.* **25**, 684-694.

Ramdahl, T. (1983). Retene - a molecular marker wood combustion in ambient air. *Nature* **306**, 580-582.

Seiler, W. and P.J. Crutzen (1980). Estimates of gross and net fluxes of carbon between the biosphere and the atmosphere from biomass burning. *Climatic Change* **2**, 207-247.

Simoneit, B.R.T. (1989). Organic matter of the Troposphere-V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmosph. Chem.* **8**, 251-275.

Simoneit, B.R.T. and M.A. Mazurek (1982). Organic matter of the troposphere II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmosph. Environ.* **16**, 2139-2159.

Simoneit, B.R.T., R.E. Cox and L.J. Standley (1988). Organic matter of the troposphere-IV: Lipids in Harmattan aerosols of Nigeria. *Atmosph. Environ.* **22**, 83-1004.

Simoneit, B.R.T., J.N. Cardoso and N. Robinson (1990). An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* **21**, 1285-1301.

Simoneit, B.R.T., G. Sheng, X. Chen, J. Fu, J. Zhang and Y. Xu (1991a). Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmosph. Environ.* **25A**, 2111-2129.

Simoneit, B.R.T., P.T. Crisp, M.A. Mazurek and L.J. Standley (1991b). Composition of extractable organic matter of aerosols from the Blue Mountains and southeast coast of Australia. *Environ. Internat.* **17**, 405-419.

Simoneit, B.R.T., W.F. Rogge, M.A. Mazurek, L.J. Standley, L.M. Hildemann and G.R. Cass (1993). Lignin pyrolysis products, lignans and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environ. Sci. Techn.* **27**, 2533-2541.

Standley, L.J. and B.R.T. Simoneit (1987). Composition of extractable plant wax, resin and thermally matured components in smoke particles from prescribed burns. *Environ. Sci. Techn.* **21**, 163-169.

Standley, L.J. and B.R.T. Simoneit (1994). Resin diterpenoids as tracers for biomass combustion aerosols. *J. Atmosph. Chem.* **18**, 1-15.