Distinguishing the Contributions of Residential Wood Combustion and Mobile Source Emissions Using Relative Concentrations of Dimethylphenanthrene Isomers[†]

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As part of the United States Environmental Protection Agency's Integrated Air Cancer Project, air particulate matter samples collected in Boise, ID, were analyzed by gas chromatography with mass spectrometric detection (GC–MS) and apportioned between their two main sources: residential wood combustion (RWC) and motor vehicle (MV) emissions. The technique used for distinguishing the source contributions involved comparison of the concentration of 1,7-dimethylphenanthrene (1,7-DMP), a polycyclic aromatic hydrocarbon (PAH) emitted primarily by burning soft woods (e.g., pines), with that of a PAH emitted in modest concentrations by both RWC and MV sources, 2,6-dimethylphenanthrene (2,6-DMP). These results were then compared with the mean 1,7-DMP/2,6-DMP ratio of 48 samples collected in a roadway tunnel, with any enrichment in the Boise sample ratios over the mean tunnel ratio attributable to the RWC source. These resulting RWC contributions were compared with fraction RWC results obtained by radiocarbon measurements ($^{14}C/$ ^{13}C) of the same extracts from Boise, with generally good correlations between the two techniques observed, suggesting that the methods are comparable when used to distinguish emissions of MVs from RWC of soft woods.

[†] The work described in this manuscript is dedicated to the memory of Professor Glen E. Gordon for his enthusiasm in the research and teaching of source apportionment of atmospheric aerosols.

Introduction

Source apportionment of the organic fraction of air particulate matter (PM) has been a continuing challenge for years. Problems in establishing unique organic "tracer" compounds for a given combustion source include variability in the composition of emissions from the same type of sources, degradation of the "tracer" as the PM ages, and the general lack of source composition data for all but a few classes of compounds. Polycyclic aromatic hydrocarbons (PAHs) are emitted by virtually all combustion sources and provide source information if the types of sources are known and if the relative abundances of specific PAHs are known for the sources contributing to the PM at a site. There have been a number of reports detailing the PAH composition of combustion sources and samples of environmental significance (1–12). An excellent review of work up to 1985 was presented by Daisey et al. (13) where ratios of some PAHs to benzo[e]pyrene differed from source to source. Schuetzle and Frazier (14) summarized PAH ratios from a number of urban and rural sites as well as from some important combustion sources. Some recent reports have attempted to apportion source contributions of the particulate matter collected at a site (15–25). Daisey (15) discussed the receptor/source apportionment modeling of four PAHs. This technique requires, however, a knowledge of the fractionation of the individual PAHs (chemical reactions and changes in particle size distributions) between the source and receptor as well as actual source emission data. Source emission data for PAHs are far from comprehensive, and less is known of long-range transport of specific PAHs. Li and Kamens (19) incorporated atmospheric reactivities into a chemical mass balance model using PAHs as the target species. They were able to apportion three sources provided the least significant source contributed greater than 10% of the total. Sheffield and co-workers (25) performed a rigorous study of organic, isotopic, and elemental species collected in the wintertime Albuquerque, NM, airshed. Although specific organic species considered indicative of wood burning (1,7-DMP, retene, and methyl dehydroabietate) correlated with compounds believed to be emitted by most combustion sources, factor analysis indicated that three factors (i.e., sources) were operative in Albuquerque. They proposed that one factor represented the bulk of the variance for wood-related species, the second composed most of the variance for PAHs with molecular weights greater than 228 amu, and a third resulted from partitioning of the more volatile species between the particle and vapor phases.

In 1985, the Environmental Protection Agency (EPA) began an ambitious project to identify the sources of airborne mutagens in a number of domestic airsheds (26). The initial work for the Integrated Air Cancer Project (IACP) was performed in Raleigh, NC, and in Albuquerque, NM. The Raleigh effort involved testing and refining the sampling and analytical schemes to be used for future studies, while the Albuquerque project represented a field test of the available methods in a region influenced mainly by two sources—motor vehicles (MVs) and residential wood combustion (RWC). The IACP was expanded to a more thorough treatment in Boise, ID, during the winter of 1986/1987. Boise is similar to Albuquerque in that RWC and MVs are

the important combustion sources in the region. This paper summarizes results of dimethylphenanthrene determinations from a limited number of samples (three samples) collected during the Albuquerque study and a more extensive set of data (36 samples) from the Boise project. In particular, it was observed that 1,7-dimethylphenanthrene was the most prominent dimethylphenanthrene in both sets of samples, while in a mobile source study (9) conducted in the Baltimore Harbor Tunnel, the 1,7-isomer was present at comparable levels to other dimethylphenanthrenes (DMPs). The enrichment of 1,7-DMP with respect to other DMPs in the Boise samples, attributed to input from soft wood burning, was used in calculating an enrichment factor representing the multiplier of the RWC contribution over that of MVs. The resulting apportionments using the enrichment of 1,7-DMP were compared with those obtained from $^{14}C/^{13}C$ measurements of the total extractable organic fraction (21).

Experimental Section

Sampling Sites. *Albuquerque Study.* Two of the samples from the Albuquerque project were collected at a residential site (Zuni Park, TSO#472A and TSO#472B) believed to be influenced primarily by RWC. Both of these samples are composites of two particulate matter air samples collected in parallel. Sample A was a nighttime collection (1900–0700 h, collected February 2–3, 1985), and sample B was a daytime collection (0700–1900 h, collected January 24, 1985). The third sample (TSO#472C) was a composite of eight samples collected during daytime periods (January 16–February 20, 1985) at a site in Albuquerque (San Mateo) believed to be influenced mainly by mobile sources.

Boise Study. The EPA selected two sites in Boise to provide PM samples representing each of the two main combustion sources in the area (MV and RWC). The fire station site was considered to be influenced predominantly by MVs whereas the Elm Grove Park location was believed to be a site influenced by RWC. A subset (36 samples) of the total number of filters was selected for this study using a factorial design (27). These samples, 18 from each site, were collected between November 8, 1986, and February 3, 1987.

Sampling. *Albuquerque and Boise.* For the organic and radiocarbon portions of the two field studies, air particulate matter samples were collected by the EPA on quartz filters using high-volume samplers (flow rates of approximately 1.1 m³/min) for 12-h periods (~800 m³ total sampling volume), beginning at 0700 and 1900. The samplers were equipped with impactors that enabled collection of particles with aerodynamic diameters of ≤2.5 μm.

In addition to ambient sampling, the EPA generated a number of source samples from wood stove test burns of different types of woods indigenous to the Boise region (6). Two extracts from test burns of a white pine (SPLL-1) and an eastern oak sample (SOLL-2, not indigenous to Boise) were generated as described previously (6). Briefly, the oak and pine woods were burned in a conventional stove, at a burn rate averaging 2.3 kg/h over an 8-h period, at an altitude of 90 m.

Sample Preparation. *Extraction.* The quartz filters were extracted for 24 h with dichloromethane, and the extracts were concentrated to 10 mL. The 10-mL extracts were shipped cold (<0 °C) to the National Institute of Standards and Technology for subsequent PAH and radiocarbon analyses.

The particle emissions from the wood test burns were collected on glass fiber filters, extracted with dichloromethane (as described above), and analyzed for the relative levels of dimethylphenanthrene isomers.

Sample Analysis. *Albuquerque Study.* For the Albuquerque samples, a liquid chromatographic procedure was employed to isolate a fraction enriched in PAHs (28) followed by measurement of the individual isomers by gas chromatography (GC) with flame ionization detection, using a 30 m × 0.25 mm, 5% phenylmethyl polysiloxane (0.25 μm film thickness) fused-silica capillary column. Confirmatory analyses of the PAH fractions were performed by GC with electron-impact ionization mass spectrometric detection (GC–MS) in the scan mode (100–300 amu, 2.9 scans/s), using either 30- or 60-m versions of the column described above.

Boise Study. The PAHs in the Boise extracts were detected by mass spectrometry (MS) in the selected-ion monitoring (SIM) mode using a Hewlett-Packard 5970 mass selective detector interfaced with an HP 5890 gas chromatograph. From 1 to 2 μL volumes of the extracts were injected (split ratio 30:1) into the GC–MS system after the samples were spiked with perdeuterated PAH standards, with phenanthrene-d_{10} used in quantifying the DMPs. No additional cleanup of the extracts was performed prior to GC–MS analysis. A 60 m × 0.25 mm, 5% phenylmethyl polysiloxane (0.25 μm film thickness) fused-silica capillary column was used for the analyses at a head pressure of 172 kPa (25 psig) He, a split flow of 30 mL/min (300 °C injector temperature), and a temperature program beginning at 150 °C for 2 min followed by a 4 °C/min ramp to 300 °C. The mass spectrometer monitored ions at m/z 188 (phenanthrene-d_{10}, internal standard) and m/z 206 (DMPs). Identification of the 1,7-DMP present in source and air particulate matter extracts was confirmed using an authentic standard of 1,7-DMP (Chiron Laboratories, Norway) combined with a solution containing phenanthrene and chrysene, generating retention indices for 1,7-DMP as described by Lee et al. (29). Good agreement was observed between retention indices determined in the standard for 1,7-DMP with those of peaks tentatively identified in source and sample extracts as 1,7-DMP. The other DMP isomers were tentatively identified by comparison with elution of DMP standards as noted by Garrigues et al. (31) performed on a similar GC stationary phase as that used for this work. Two of the dimethylphenanthrene peaks represent the coelutions of four (1,3-, 2,10-, 3,9-, and 3,10-substituted) and two (1,6- and 2,9-substituted) dimethylphenanthrenes, respectively. Detectable concentrations of 1,7-dimethylphenanthrene [1,7-DMP, 10 ± 1 ng/mL (95% confidence interval)] were observed in the three Boise field blanks provided by the EPA. Concentrations of 1,7-DMP in the sample extracts varied from 18 to 905 ng/mL, so in some cases the blank contamination of 1,7-DMP contributed significantly to the levels observed in the samples. The field blank concentrations of 1,7-DMP (10 ng/mL) were subtracted from the sample extract concentrations for the 36 extracts prior to converting to airborne concentration units (ng/m³).

Specifics of the radiocarbon analytical method have been discussed in detail previously (21). Briefly, separate extractable organic matter (EOM) samples were transferred to Vycor tubes, and the solvent was evaporated by passing dry N_2 over the sample until dry. Copper(II) oxide and silver were added to the sample residue, the tube was
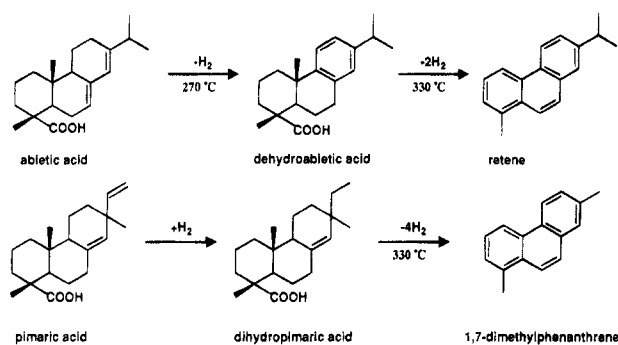
FIGURE 1. Mechanism of formation of retene and 1,7-dimethylphenanthrene from resin acids (32).

evacuated and sealed with a torch. The organic carbon in the sample was converted to CO_2 by heating to 900 °C for 5 h, and the CO_2 was quantified by manometry in a calibrated volume. The final step in the sample preparation involves the reduction of the sample CO_2 to graphite on iron wool in the presence of H_2 and Zn (30). The iron wool/graphite matrix was fused to a solid Fe-C bead, which was used as a target for accelerator mass spectrometric measurement of the C^{14}/C^{13} ratio.

Results and Discussion

The formation of some alkylated phenanthrenes has been investigated by Laflamme and Hites (32), who proposed a reaction sequence whereby abietic acid and pimaric acid were converted to retene (7-isopropyl-1-methylphenanthrene) and 1,7-DMP, respectively, under combustion conditions (see Figure 1). The two starting acids, abietic and pimaric, are both present in high concentrations in pine wood resin (33), and therefore the two disubstituted phenanthrene products would presumably be present in air particulate matter from a region influenced by wood burning where soft woods were used as fuels. Simoneit and Mazurek (34) proposed a similar reaction scheme to that of LaFlamme and Hites, beginning with various pimarane isomers and ending with 1,7-DMP. Ramdahl (35) reported the detection of retene in wood smoke and suggested it as a RWC marker for soft woods. In related work, Alexander et al. (36) found that 1-methylphenanthrene, 1,7-dimethylphenanthrene, and retene were enriched in sediments from the Jurassic period (1.6–1.8 million years ago) compared with those from the Permian age (2.5–2.8 million years ago). The authors state that kauri pine trees (Araucariaceae) became prevalent during the early to middle Jurassic period and that the enrichment of the alkylphenanthrenes mentioned above is believed to be due to similar reactions described by Laflamme and Hites (32) and Simoneit and Mazurek (34), except at lower temperatures and on a geological time scale.

The three samples from Albuquerque were selected for a preliminary study to investigate the potential of using selected PAHs as markers for the two combustion sources known to influence the airshed: RWC and MVs. Based on the sites and the collection period, these three samples were expected to represent high (TSO#472A), intermediate (TSO#472B), and low (TSO#472C) contribution from the RWC source. The reconstructed total ion chromatograms of these three samples are shown in Figure 2a–c, with selected ion traces for the dimethylphenanthrenes (206 amu) shown as insets. Although a 30-m GC column was used for the scan GC–MS analysis of extract TSO#472C
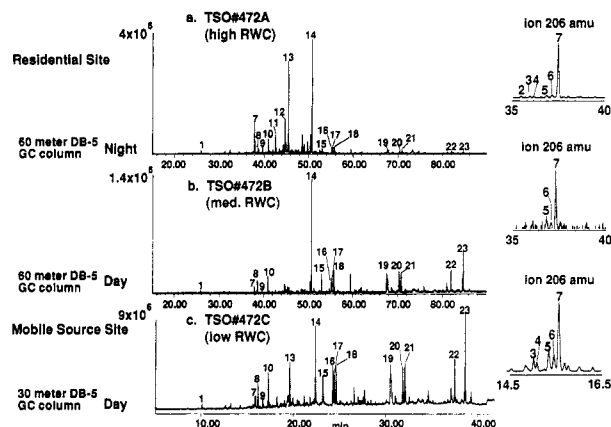
FIGURE 2. (a–c) Reconstructed total ion chromatograms of three Albuquerque IACP sample extracts. Peak identifications are as follows: (1) phenanthrene; (2) 2- and 9-ethylphenanthrenes and 3,6-dimethylphenanthrene; (3) 2,6-dimethylphenanthrene; (4) 2,7-dimethylphenanthrene; (5) 1,3-, 2,10-, 3,9-, and 3,10-dimethylphenanthrenes; (6) 1,6- and 2,9-dimethylphenanthrenes; (7) 1,7-dimethylphenanthrene; (8) fluoranthene; (9) acephenanthrylene; (10) pyrene; (11) C3-phenanthrene/anthracene; (12) methyl ester of abietic acid and isomer of methylfluoranthene/pyrene; (13) retene; (14) methyl ester of dehydroabietic acid; (15) benzo[ghi]fluoranthene; (16) cyclopenta[cd]pyrene; (17) benz[a]anthracene; (18) chrysene/triphenylene; (19) benzo[b]-, benzo[j]-, and benzo[k]fluoranthenes; (20) benzo[e]pyrene; (21) benzo[a]pyrene; (22) indeno[1,2,3-cd]pyrene; (23) benzo[ghi]perylene.

compared with a 60-m column used for the same analyses of extracts TSO#472A and TSO#472B, no significant differences were observed in the respective chromatographic resolutions. The major component in the PAH fraction of the samples was tentatively identified as the methyl ester of dehydroabietic acids (methyl dehydroabietate, peak 14). In addition to methyl dehydroabietate, retene (peak 13), methyl abietate (peak 12), and 1,7-dimethylphenanthrene (peak 7) were detected in relatively high concentrations in sample 472A, which was regarded as the sample with the greatest RWC contribution. Samples 472B and 472C had higher PAH concentrations (peaks 15–23) relative to methyl dehydroabietate than sample 472A, perhaps due to emissions from MVs. Results from analyses of samples collected in Albuquerque indicated that source information might be obtained from the relative concentrations of dimethylphenanthrene isomers.

A number of groups have reported results of the analyses of dimethylphenanthrenes in samples of environmental and geological significance (9, 31–37). Radke and co-workers (37) observed that the distribution patterns for phenanthrene and dimethylphenanthrenes for 24 German bituminous coals varied with their maturity, with the less strained DMPs enriched in the more mature coals. Garrigues et al. (31) used the relative concentrations of DMPs to indicate the maturity of coal and shale oil samples. The enrichment of 1,7-DMP in a bituminous coal sample was due to the resinous composition of the organic matter making up the coal. Garrigues and co-workers synthesized the 25 possible DMP isomers as well as the five possible ethylphenanthrenes and determined retention indices of all of these isomers on a CP-Sil 8CB capillary column, a similar phase to that used in this work (DB-5, 5% phenyl/95% methylpolysiloxane). Benner and co-workers (9) established the DMP patterns for mixed mobile source samples from emissions of both diesel and gasoline-fueled vehicles in a highway tunnel. The enrichment of the DMPs
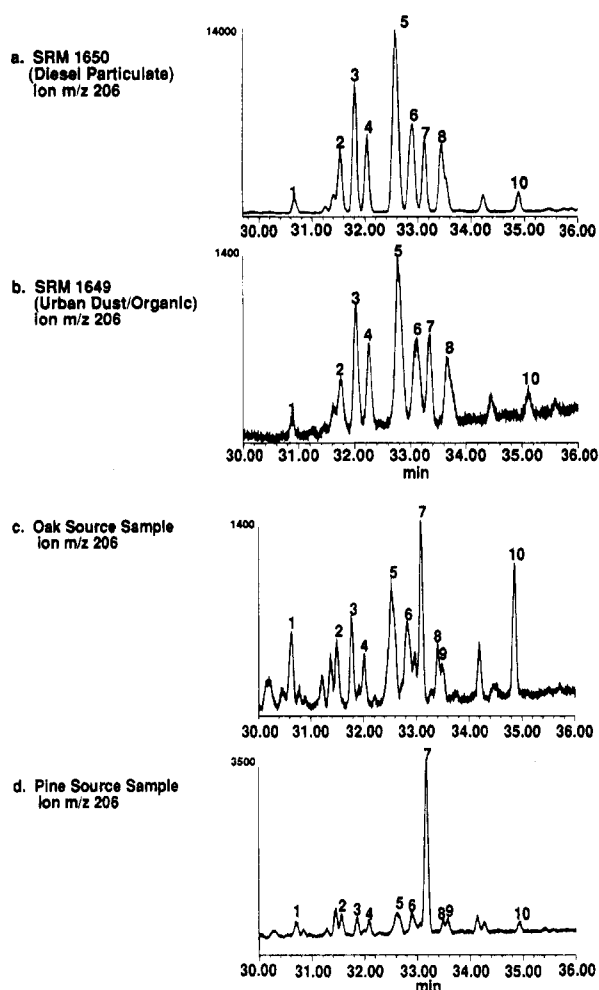
FIGURE 3. (a) Selected-ion chromatogram of dimethylphenanthrenes in extract of SRM 1650 (diesel particulate matter). (b) Selected-ion chromatogram of dimethylphenanthrenes in extract of SRM 1649 (urban dust/organics). (c) Selected-ion chromatogram of dimethylphenanthrenes in extract of eastern oak wood combustion emissions. (d) Selected-ion chromatogram of dimethylphenanthrenes in extract of white pine wood combustion emissions. See Table 1 for peak number identifications.

with respect to phenanthrene was attributed to unburned diesel fuel coating the particles, as was previously proposed by Andrews and co-workers (10).

From the review of recent data (9, 11), the DMP patterns for samples of environmental concern, e.g., air particulate matter, diesel particulate matter and marine sediment, were similar. Figure 3a,b displays the DMP profiles (selected ion chromatograms) for extracts of Standard Reference Materials (SRMs) 1650 (diesel particulate matter) and 1649 (urban dust/organics), respectively. Air particulate matter collected in a highway tunnel (9) yielded similar DMP profiles to the SRMs described above. Although the samples were collected in very different ways—SRM 1649 obtained over a period of 1 year in Washington, DC, SRM 1650 collected from a number of diesel engine test stands, and the tunnel samples obtained through conventional high-volume air sampling in the Baltimore Harbor Tunnel—the DMP patterns are quite similar. In all four sample types, peak 5, the coelution of four DMPs (1,3-, 2,10-, 3,9-, and 3,10-DMPs) is the largest peak in the group, with the peak identified as 1,7-DMP (peak 7) typically one-half the size of peak 5.

Results from the limited data set from the Albuquerque IACP, discussed above, encouraged investigation of a larger

TABLE 1
Concentrations of Alkylphenanthrenes in Pine and Oak Source Samples (ng of DMP/mg of residue)[a]

peak no.	DMP isomer[b]	pine source	oak source
1	3-ethylphenanthrene	4.0	2.5
2	2- and 9-ethylphenanthrene and 3,6-dimethylphenanthrene	8.1	2.5
3	2,6-dimethylphenanthrene	4.4	2.5
4	2,7-dimethylphenanthrene	2.8	1.0
5	1,3-, 2,10-, 3,9- and 3,10-dimethylphenanthrenes	6.74	4.6
6	1,6- and 2,9-dimethylphenanthrenes	8.8	4.4
7	1,7-dimethylphenanthrene	41	6.0
8	2,3-dimethylphenanthrene	2.4	1.6
9	1,9- and 4,9-dimethylphenanthrenes	3.2	1.1
10	1,8-dimethylphenanthrene	2.3	4.5

[a] Relative uncertainties estimated as ±10% of the listed ng of DMP/mg of residue concentrations, and they include the 95% confidence interval. The residue masses were determined gravimetrically by evaporating known volumes of the extracts. [b] Numbers identify peaks in Figures 3a−d and 5a,b. Identifications based on authentic standards and ref 31.

set of samples available from the Boise IACP project. As part of the Boise study, a number of wood stove test burns were performed using different types of wood indigenous to Boise and other western regions (6). The extracts from a white pine and an eastern oak burn were characterized for their DMP profiles. Figure 3c,d displays reconstructed selected-ion chromatograms for the DMPs in an eastern oak combustion extract and the white pine combustion extract from Boise, respectively. The profile for the white pine combustion extract (Figure 3d) shows a number of peaks dominated by one that was identified based on its retention index as 1,7-DMP. The DMP profile for the eastern oak sample extract (Figure 3c) is more complicated than the others already discussed (see above) and includes a number of peaks of similar amplitudes, with no one peak predominating. The concentrations of the DMP species present in the two source extracts are listed in Table 1. The relative levels of DMPs in the source samples are similar except for the 1,7-isomer, where the concentration in the pine source sample (41 ng/mg) is nearly 7 times that of the oak source sample (6.0 ng/mg). The wood source data along with that of the highway tunnel study (9) suggest that any significant enrichment of 1,7-DMP with respect to the other isomers would be due to the contribution of soft wood burning. Pines are the most commonly burned wood in the western mountain states (in Boise, 40% Douglas fir, 30% Ponderosa pine, and 30% Lodgepole pine, from U.S. Forest Service survey), so enrichment of the 1,7-DMP in the Boise samples is quite reasonable.

The concentrations of the DMP peaks for the 36 Boise samples are summarized in Table 2. The levels of 1,7-DMP ranged over 2 orders of magnitude from 0.10 to 11.7 ng/m^3. At this point, it was thought appropriate to quantify this observed enrichment of 1,7-DMP in the Boise samples for the purpose of apportioning the samples between their RWC and MVs sources. The concept of an enrichment factor in environmental studies was first described by Rahn (38) whereby the ratio of a specific element to that of aluminum in an air particulate matter sample was divided by the ratio of the same element to that of aluminum in soil. This elemental enrichment factor was useful in

TABLE 2

Concentrations of Dimethylphenanthrenes in Boise IACP Extracts (ng/m³)[a]

sample	date	start/site[b]	2,6-DMP	2,7-DMP	4-DMPs[c]	1,6 + 2,9-DMPs[d]	1,7-DMP	retene
31529	4JAN87	1900/FS	0.05	0.04	0.12	0.08	0.10	3.83
31449	14NOV86	0700/FS	0.61	0.38	1.14	0.74	1.18	11.7
31445	11NOV86	0700/FS	0.33	0.20	0.55	0.35	0.65	7.78
31738	6JAN87	0700/FS	0.34	0.20	0.62	0.42	0.76	7.54
31475	7DEC86	0700/FS	0.18	0.12	0.32	0.22	0.45	6.36
32255	3FEB87	1900/FS	0.42	0.27	0.75	0.53	1.10	17.2
31568	22NOV86	1900/FS	0.25	0.16	0.52	0.35	0.66	16.0
32207	21JAN87	0700/FS	0.47	0.29	0.83	0.58	1.34	15.5
31775	12JAN87	1900/FS	0.36	0.23	0.63	0.42	1.04	13.6
32201	20JAN87	0700/FS	0.41	0.26	0.69	0.49	1.18	9.87
31500	14DEC86	0700/FS	0.43	0.26	0.72	0.54	1.58	16.0
31461	28NOV86	1900/FS	0.30	0.19	0.58	0.44	1.12	16.2
30795	18NOV86	0700/EGP	0.09	0.05	0.15	0.15	0.28	4.03
30793	17NOV86	1900/EGP	0.15	0.00	0.31	0.31	0.72	9.23
31165	14NOV86	0700/EGP	0.23	0.16	0.41	0.34	1.13	11.0
31502	14DEC86	1900/FS	0.17	0.11	0.39	0.27	0.84	13.7
31767	13JAN87	0700/FS	0.32	0.21	0.62	0.52	1.61	9.85
31139	19DEC86	0700/EGP	0.11	0.07	0.21	0.15	0.57	12.0
31498	13DEC86	1900/FS	0.30	0.24	0.70	0.51	1.61	18.2
32291	18JAN87	0700/FS	0.39	0.26	0.71	0.55	2.09	26.3
30923	26JAN87	0700/EGP	0.33	0.21	0.61	0.55	2.00	19.9
30839	4DEC86	0700/EGP	0.75	0.43	1.30	1.23	4.72	62.2
30943	3FEB87	1900/EGP	0.45	0.29	1.12	0.96	2.83	36.3
31511	30DEC86	1900/FS	1.60	1.04	3.12	2.68	10.6	71.2
30326	8NOV86	0700/EGP	0.16	0.09	0.28	0.28	1.10	9.84
31091	27JAN87	1900/EGP	0.20	0.15	0.45	0.40	1.42	16.5
31126	12JAN87	0700/EGP	0.43	0.27	0.78	0.72	3.18	45.1
30876	15DEC86	1900/EGP	0.09	0.06	0.22	0.18	0.67	18.3
30829	29NOV86	1900/EGP	0.16	0.11	0.33	0.28	1.27	24.3
31116	14JAN87	1900/EGP	0.14	0.09	0.27	0.23	1.13	16.3
31103	18JAN87	0700/EGP	0.34	0.23	0.53	0.48	2.80	31.4
31773	15JAN87	1900/FS	0.25	0.22	0.68	0.48	2.23	26.7
31136	30DEC86	0700/EGP	0.54	0.39	1.20	1.06	4.89	46.5
30841	5DEC86	1900/EGP	0.64	0.44	1.39	1.40	7.76	84.3
31138	29DEC86	1900/EGP	0.94	0.63	2.00	1.98	11.7	103
30932	29JAN87	1900/EGP	0.09	0.07	0.25	0.21	1.17	24.7

[a] Uncertainties estimated at ±11% of the listed ng/m³ concentrations, and they include the 95% confidence interval. [b] Sample start time and site. FS is the fire station (mobile source) and EGP is the Elm Grove Park (residential wood combustion) site. [c] Coelution of 1,3-, 2,10-, 3,9-, and 3,10-dimethylphenanthrenes. [d] Coelution of 1,6- and 2,9-dimethylphenanthrenes.

documenting differences in the elemental compositions of different combustion sources and also in choosing tracer elements for the different sources. In an effort to quantify the observed enrichment of 1,7-DMP over the other DMP isomers in samples from Boise and Albuquerque, an organic enrichment factor was developed. The ratios of 1,7-DMP to 2,6-DMP in 48 samples collected in a roadway tunnel (9) were remarkably consistent [mean ratio = 0.74 ± 0.08 (standard deviation of the population)], so this mean ratio was used in generating a RWC enrichment factor for each of the 36 Boise IACP samples as shown below:

RWC enrichment factor (EF) =

$$\frac{[(1,7\text{-}DMP/2,6\text{-}DMP)_{Boise} - (1,7\text{-}DMP/2,6\text{-}DMP)_{Tunnel}]}{(1,7\text{-}DMP/2,6\text{-}DMP)_{Tunnel}}$$

(1)

where $(1,7\text{-}DMP/2,6\text{-}DMP)_{Boise}$ represents the ratios of the 1,7- to the 2,6-DMP in the individual Boise IACP samples ($n = 36$) and $(1,7\text{-}DMP/2,6\text{-}DMP)_{Tunnel}$ represents the mean ratio of the two DMPs from 48 samples collected in the Baltimore Harbor Tunnel in 1985 and 1986. Some assumptions were made in using this enrichment factor. We assumed that (a) the Boise airshed is influenced mainly by emissions from RWC and MVs, (b) the mobile source profiles for dimethylphenanthrenes in the tunnel are representative for MVs in Boise, (c) the enrichments of 1,7-DMP observed

in the Boise samples are due to pine burning as RWC, and (d) as observed in the pine source sample, the pine burning does not generate significant amounts of the other DMPs compared to the 1,7-isomer. Considering these assumptions, the RWC enrichment factor represents the multiplier of RWC importance over that of MVs for the specific Boise sample. For example, an enrichment factor of 10 represents a RWC contribution of 10 times the MV input to a specific sample. The actual fraction RWC can then be calculated from the following equation:

$$\text{fraction RWC} = EF/(EF + 1)$$

(2)

One important advantage of this enrichment factor is that it would be relatively insensitive to sampling temperatures since the two isomers used in the calculation have very similar vapor pressures (as evidenced by their similar GC retention times) and would be collected with similar efficiencies in the particle phase.

RWC and MV fractions for the individual Boise samples were calculated and are listed in Table 3 along with source apportionments from radiocarbon measurements of the same extracts (21). A graphical comparison of these data is displayed in Figure 4. Using the 1,7-DMP enrichment factor apportionment, the fraction RWC values ranged from a low of 0.61 to a high of 0.94, whereas the ¹⁴C method yielded generally lower RWC fractions from 0.51 to 0.89.

TABLE 3

Fraction Contribution of Residential Wood Combustion from 1,7-Dimethylphenanthrene Enrichment Factor and [14]C Measurements in Boise Air Particulate Extracts

sample	date	start/site[a]	EF[b]	1,7-DMP RWC fraction[c]	radiocarbon RWC fraction[d]
31529	4JAN87	1900/FS	1.55	0.61 ± 0.04	0.83 ± 0.04
31449	14NOV86	0700/FS	1.62	0.62 ± 0.09	0.58 ± 0.03
31445	11NOV86	0700/FS	1.64	0.62 ± 0.08	0.60 ± 0.03
31738	6JAN87	0700/FS	1.99	0.67 ± 0.07	0.52 ± 0.02
31475	7DEC86	0700/FS	2.41	0.71 ± 0.06	0.64 ± 0.03
32255	3FEB87	1900/FS	2.53	0.72 ± 0.07	0.74 ± 0.03
31568	22NOV86	1900/FS	2.57	0.72 ± 0.06	0.71 ± 0.03
32207	21JAN87	0700/FS	2.87	0.74 ± 0.06	0.59 ± 0.03
31775	13JAN87	0700/FS	2.90	0.74 ± 0.06	0.62 ± 0.03
32201	20JAN87	0700/FS	2.90	0.74 ± 0.06	0.51 ± 0.02
31500	14DEC86	0700/FS	4.00	0.80 ± 0.06	0.68 ± 0.03
31461	28NOV86	1900/FS	4.04	0.80 ± 0.05	0.83 ± 0.04
30795	18NOV86	0700/EGP	4.21	0.81 ± 0.04	0.72 ± 0.04
30793	17NOV86	1900/EGP	5.52	0.85 ± 0.03	0.83 ± 0.04
31165	14NOV86	0700/FS	5.55	0.85 ± 0.04	0.75 ± 0.03
31502	14DEC86	1900/FS	5.70	0.85 ± 0.03	0.81 ± 0.04
31767	15JAN87	1900/FS	5.90	0.86 ± 0.03	0.53 ± 0.02
31139	19DEC86	0700/EGP	6.16	0.86 ± 0.03	0.72 ± 0.03
31498	13DEC86	1900/FS	6.17	0.86 ± 0.03	0.73 ± 0.03
32291	18JAN87	0700/FS	6.20	0.86 ± 0.03	0.77 ± 0.04
30923	26JAN87	0700/EGP	7.20	0.88 ± 0.03	0.80 ± 0.04
30839	4DEC86	0700/EGP	7.57	0.88 ± 0.03	0.73 ± 0.03
30943	3FEB87	1900/EGP	7.58	0.88 ± 0.03	0.84 ± 0.04
31511	30DEC86	1900/FS	7.97	0.89 ± 0.03	0.78 ± 0.04
30326	8NOV86	0700/EGP	8.09	0.89 ± 0.03	0.79 ± 0.04
31091	27JAN87	1900/EGP	8.38	0.89 ± 0.03	0.87 ± 0.04
31126	12JAN87	0700/EGP	9.04	0.90 ± 0.02	0.80 ± 0.04
30876	15DEC86	1900/EGP	9.19	0.90 ± 0.02	0.85 ± 0.04
30829	29NOV86	1900/EGP	9.48	0.90 ± 0.02	0.82 ± 0.04
31116	14JAN87	1900/EGP	9.79	0.91 ± 0.02	0.89 ± 0.04
31103	18JAN87	0700/EGP	10.1	0.91 ± 0.02	0.84 ± 0.04
31773	12JAN87	1900/FS	11.0	0.92 ± 0.02	0.83 ± 0.04
31136	30DEC86	0700/EGP	11.3	0.92 ± 0.02	0.77 ± 0.04
30841	5DEC86	1900/EGP	15.4	0.94 ± 0.02	0.84 ± 0.04
31138	29DEC86	1900/EGP	15.9	0.94 ± 0.02	0.83 ± 0.04
30932	29JAN87	1900/EGP	16.4	0.94 ± 0.01	0.77 ± 0.04

[a] FS is the fire station (MV) site and EGP is the Elm Grove Park (RWC) site. [b] 1,7-Dimethylphenanthrene enrichment factor (see eq 1 in text). [c] Uncertainties estimated from the partial differentiation of the enrichment factor function, and they represent the 95% confidence interval for the individual fraction RWC results. [d] The age of the wood burned in Boise was estimated to have an average fraction of modern carbon (f_m) of 1.26 ± 0.06 that includes logs having ages from 10 to 90 years. This estimate is based on a tree-ring model, which assumes rings of equal masses (21). Linear regression data of 1,7-DMP RWC fraction versus radiocarbon RWC fraction: $r^2 = 0.40$ ($n = 36$), $r^2 = 0.69$ ($n = 33$) omitting three sample pairs with the worst agreements (samples 31529, 32201, and 31767).

FIGURE 4. Scatter plot of fraction residential wood combustion from radiocarbon (^{14}C/^{13}C) and 1,7-dimethylphenathrene enrichment factor methods. Data from Table 3.

FIGURE 5. (a) Selected-ion chromatogram of dimethylphenanthrenes in extract of Boise IACP sample 31449 (low RWC contribution, 62%). (b) Selected-ion chromatogram of dimethylphenanthrenes in extract of Boise IACP sample 30932 (high RWC contribution, 94%) See Table 1 for peak number identifications.

Comparing the plotted data with the line of slope = 1 suggests an offset in the data that may be explained by limitations in the four assumptions used in developing and interpreting the DMP enrichment factor method (see above). The DMP profiles of samples representing one of the lowest (#31449, RWC fraction = 0.62) and highest (#30932, RWC fraction = 0.94) RWC fraction as calculated by the DMP enrichment factor technique are shown in Figure 5a,b, respectively. The absolute concentrations of most of the DMPs were similar in these two samples except for the 2,6- isomer, which was seven times higher in sample 31449.

In general there is good agreement between the two apportionment techniques considering that the ^{14}C method is sensitive to the total extractable organic carbon from RWC and MVs (μg of carbon), while the 1,7-DMP apportionment is based on relative levels of species t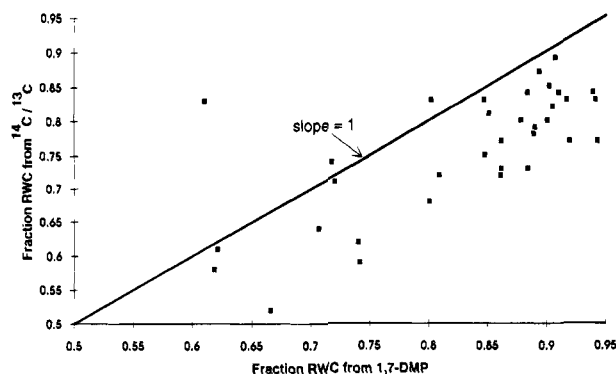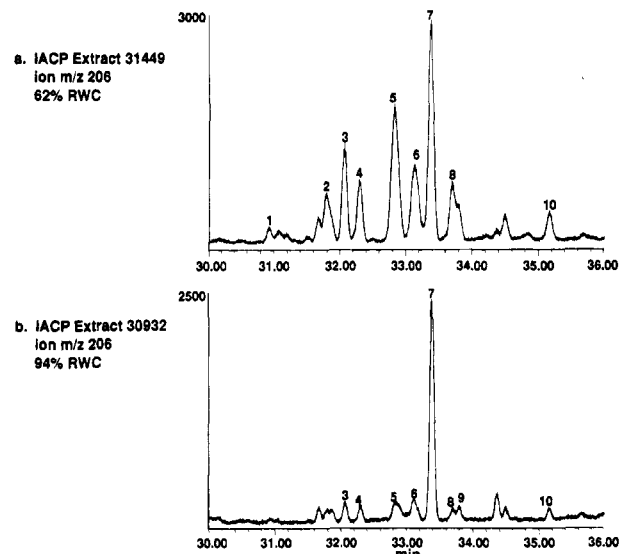hat compose a small fraction (<0.1%, pg to ng levels) of the total extractable organic matter. The ^{14}C apportionment method provided consistently lower RWC fraction results than those based on the DMP measurements. Linear correlation calculations of the two apportionment methods yielded r^2 values of 0.40 considering all 36 samples and 0.69 after dropping the three samples with the worst agreement between the two techniques (samples 31529, 32201, and 31767). Given the number of samples for the latter case ($n = 33$) and the correlation coefficient ($r^2 = 0.69$, $r = 0.83$), the probability that the measured (^{14}C/^{13}C ratios) and calculated (EF) RWC apportionments were randomly correlated is <0.1%.

Lewis and co-workers (22) found that airborne potassium concentrations corrected for soil contributions correlated with ^{14}C-derived RWC in Boise ($r^2 = 0.80$, $n = 34$). Similar results have been shown for Albuquerque, NM, and Raleigh, NC (23), and for Roanoke, VA (24), both of which have established the credibility of soil-corrected potassium as a RWC estimator. Figure 6 displays a plot of the airborne extractable organic matter (EOM) concentration attributable to RWC from the 1,7-DMP enrichment factor technique versus the airborne concentration of soil-corrected potassium. This graph appears similar to a plot of the RWC-contributed EOM concentrations from radiocarbon measurements versus the same soil-corrected potassium
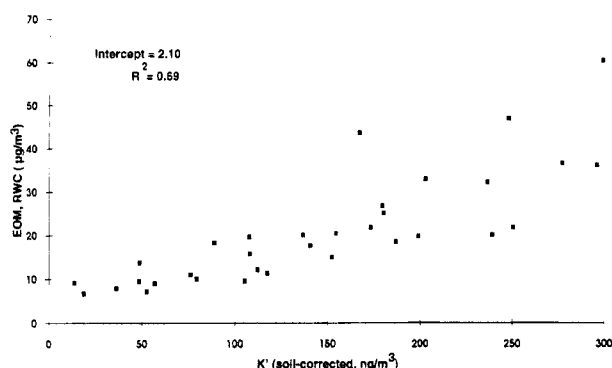
FIGURE 6. Scatter plot of concentration of extractable organic matter from residential wood combustion (1,7-dimethylphenathrene enrichment factor method) and soil-corrected potassium airborne concentrations.

TABLE 4

Comparison of Fraction of Residential Wood Combustion Determined by 1,7-DMP Enrichment and $^{14}C/^{13}C$ for Boise PAH Fractions

sample	start/site	1,7-DMP RWC fraction[a]	^{14}C RWC fraction[b]
32255	1900/FS	0.72	0.53 (0.74)
32291	0700/FS	0.86	0.67 (0.77)
30943	1900/EGP	0.88	0.65 (0.84)
31103	0700/EGP	0.91	0.78 (0.84)

[a] Based on DMP measurements of extracts without PAH fractionation. Uncertainties estimated at ±10% of the listed fractions RWC, and they represent the 95% confidence interval. [b] Based on $^{14}C/^{13}C$ measurements of extracts after PAH fractionation. Values in parentheses are from carbon isotope measurements performed on the extract without PAH fractionation. Uncertainties estimated at ±5% of the listed fractions RWC, and they represent the 95% confidence interval.

concentrations (22), suggesting that the 1,7-DMP enrichment factor and the ^{14}C apportionment methods yield similar source-distinguishing information.

There were poor correlations between the absolute concentrations of both 1,7-DMP and retene with respect to the ^{14}C-derived RWC fraction. This is probably due to temperature variations that would directly affect particle and vapor phase distributions of airborne species and emphasizes the need for normalized concentration data (i.e., the enrichment factor stated above) for comparison with data generated from the $^{14}C/^{13}C$ ratios. For this reason, retene, though perhaps a qualitative marker for soft wood burning, is not appropriate for source apportionment of PM since there are no known species suitable for normalizing the retene concentrations to correct for variable phase distributions. One would expect retene to be a quantitative soft wood tracer if both particle and vapor phase samples are collected.

Four of the 36 Boise extracts were processed through a liquid chromatographic procedure to isolate a fraction enriched in PAHs (28). The $^{14}C/^{13}C$ ratios were determined for these fractions, and the RWC fraction results are shown in Table 4. The ^{14}C apportionments for the total extractable organic matter from these samples agree with the 1,7-DMP apportionments better than the ^{14}C apportionments from the PAH chemical fraction. Perhaps this is because the species present in the PAH fraction as a whole do not differentiate the MV from the RWC sources, yet specific analytes that are present in the PAH fraction (e.g., 1,7-DMP) correlate with the RWC contribution to the total EOM.

The 1,7-DMP apportionments for two of the Albuquerque IACP samples yielded RWC fractions of 0.98 and 0.87 for samples TSO#472A and TSO#472C, respectively. The ^{14}C apportionment method produced RWC fractions of 1.00 and 0.53 for these samples (39).

Summary

Measurements of selected dimethylphenanthrene isomers in extracts of air particulate matter in Boise, ID, and in related combustion source samples suggest a consistent relationship between the relative concentrations of 1,7-dimethylphenanthrene present in the extracts and their apportionment between RWC and MV sources. Source apportionments for these samples generated using a DMP enrichment factor and $^{14}C/^{13}C$ measurements generally are in agreement, even though the DMP technique focused on species that are a small percentage (< 0.1%) of the total EOM, and the radiocarbon results relate to microgram quantities of carbon in the total (and/or fractionated) extracts. The apportionment method of samples influenced by RWC (soft wood) and MVs using the 1,7-DMP enrichment factor requires minimal processing of the extract compared with the ^{14}C technique and should be relatively insensitive to sample collection temperatures, since the species used in the enrichment factor have similar volatilities. In addition, the GC–MS technique used to determine the DMPs is both rapid and sensitive, employing instrumentation that is more available than that used in measuring carbon isotope ratios. This organic apportionment technique may thus be applicable to distinguishing inputs of RWC (soft woods) from that of MVs in regions influenced primarily by these two combustion sources. At the least, it may serve as a screening method for choosing subsets of samples for radiocarbon analyses.

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