**Atmospheric
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Source apportionment of elevated wintertime PAHs by compound-specific radiocarbon analysis

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Source apportionment of PAHs by CSRA

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Abstract

Natural abundance radiocarbon analysis facilitates distinct source apportionment between contemporary biomass/biofuel ([14]C "alive") versus fossil fuel ([14]C "dead") combustion. Here, the first compound-specific radiocarbon analysis (CSRA) of atmospheric polycyclic aromatic hydrocarbons (PAHs) was demonstrated for a set of samples collected in Lycksele, Sweden a small town with frequent episodes of severe atmospheric pollution in the winter. Renewed interest in residential wood combustion means than this type of seasonal pollution is of increasing concern in many areas. Five individual/paired PAH isolates from three pooled fortnight-long filter collections were analyzed by CSRA: phenanthrene, fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[cd]pyrene plus benzo[ghi]perylene; phenanthrene was the only compound also analyzed in the gas phase. The measured Δ^{14}C for PAHs spanned from −138.3‰ to 58.0‰. A simple isotopic mass balance model was applied to estimate the fraction biomass ($f_{biomass}$) contribution that was constrained to a range of 71% for indeno[cd]pyrene+benzo[ghi]perylene to 87% for the gas phase phenanthrene and particulate fluoranthene, respectively. Indeno[cd]pyrene plus benzo[ghi]perylene, known to be enhanced in gasoline-powered motor vehicle exhaust compared to diesel exhaust, had the lowest contribution of biomass combustion of the measured PAHs by 9%. The total organic carbon (TOC, defined as carbon remaining after removal of inorganic carbon) $f_{biomass}$ was estimated to be 77%, which falls within the range for PAHs. This CSRA data of atmospheric PAHs demonstrate the non-uniformity of biomass combustion contribution to different PAHs even in a location with limited local emission sources and illustrates that regulatory efforts would not evenly reduce all PAHs.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere and are primarily emitted by anthropogenic sources including fossil fuel and biomass combustion.

Some PAHs are very well known carcinogens and several studies indicate a negative impact of atmospheric PAHs on human and ecological health (Busby et al., 1997; Hedberg and Johansson, 2006; Choi et al., 2006; Sauvain et al., 2003; Schwarze et al., 2007). To abate the adverse health effects caused by these pollutants, source apportionment studies are needed to inform effective strategies and air quality regulations to control PAH emissions.

Apportioning PAHs to a specific combustion source can be difficult (Hays et al., 2003; Schauer et al., 2002, 2001; McDonald et al., 2003). Differences due to biomass or fossil fuel type and to combustion conditions determine PAH ratios (Benner et al., 1995; Yan et al., 2005; Yunker et al., 2002), and can confound efforts to apportion PAHs in an environmental sample; this also limits their utility as generic biomass or fossil fuel combustion tracers as very location- and source-specific profiles are needed for accurate apportionment (Mandalakis et al., 2004a; Lima et al., 2005). Factor-analysis-based source apportionment, such as principal component analysis and positive matrix factorization (PMF), has been used to attempt to define source contributions to PAHs with mixed success (Larsen and Baker, 2003). The advantage to methods like PMF is that it requires no source profile input, however the goal is often to define the factors as specific sources which does require knowledge of PAH distribution in local source emissions. PMF also requires a large dataset to be effective, which is not always feasible. There is interest both in ascertaining the sources of PAHs and in accurately using PAHs as source tracers in the atmosphere to quantify the contribution of emission sources to total atmospheric organic carbon (OC). Specific PAHs may be more valuable as molecular markers than others in source apportionment models for OC when used in conjunction with more unique tracers such as hopanes and levoglucosan (Chow et al., 2007; Jaeckels et al., 2007; Lough and Schauer, 2007). However, more investigation into the sources of individual atmospheric PAHs is warranted to inform current source apportionment techniques.

Natural abundance radiocarbon analysis enables determination of the contribution of fossil and non-fossil sources to carbonaceous compounds. Basically, the ^{14}C in at-

mospheric CO_2 dictates the ^{14}C in fresh carbon and this then decays with a half-life of 5730 years. Hence, radiocarbon is ideal to distinguish between fossil fuel (void of ^{14}C) and biomass/biofuel (contemporary ^{14}C) combustion sources. However, the large sample masses traditionally required for radiocarbon analysis has largely limited its

5 application in atmospheric particulate matter to characterizing total or bulk organic carbon (Hildemann et al., 1994; Jordan et al., 2006; Szidat et al., 2004a; Bench et al., 2007). For bulk carbon, contemporary sources can include both biogenic emission and biomass combustion sources, so these results can only be used to define contribution of fossil fuel combustion sources including motor vehicles and power generation.

10 Advances in molecular-level radiocarbon analysis (Eglinton et al., 1996) have allowed compound class-specific radiocarbon analysis (CCSRA) of atmospheric PAHs (Mandalakis et al., 2005; Zencak et al., 2007b; Kumata et al., 2006). These studies have revealed geographic differences in fossil vs modern biomass sources of PAH across Europe and in Japan. The study from Japan is compelling as it indicates the impor-

15 tance of isolating individual PAHs for compound-specific radiocarbon analysis (CSRA) by revealing differences in the contribution from biomass burning between pooled low versus high molecular weight PAHs (Kumata et al., 2006). These results combined with emission source profiles suggest that source contributions would not be uniform for all PAHs.

20 To further consider the source apportionment of individual atmospheric PAHs, a residential area in a northern Swedish town was chosen for a winter sampling campaign. Lycksele, Sweden has been the site of previous atmospheric studies due to the high levels of ambient particulate matter and PAHs (Johansson et al., 2004; Hedberg and Johansson, 2006) and the high percentage of households using biofuels for space

25 heating during wintertime (Hedberg and Johansson, 2006; Krecl et al., 2007); this is a typical situation for small towns in the northern boreal zone. The contribution of elemental carbon (EC) and OC to the total PM_{10} mass concentration was on average 11% and 35%, respectively, in winter 2006 (Krecl et al., 2008a). High correlations ($R>0.75$) were found among PM_1, PM_{10}, light absorbing carbon mass concentrations

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and particle number concentrations for Lycksele which were associated with known traffic emission and biomass burning particle size distributions (Krecl et al., 2008b). A large day-to-day and hour-to-hour variability in aerosol concentrations was also observed with evening aerosol concentrations significantly higher on weekends than on weekdays, presumably associated to residential wood combustion (RWC) emissions. Local traffic emissions were identified based upon their similar contribution every day and characteristic peak in the morning and in the evening (Krecl et al., 2008a). RWC and traffic emissions were thus identified as the two major local sources using several techniques, with long-range transport contributing to a lesser degree. In the current study, the relative impact of the RWC and traffic emissions is quantified by performing radiocarbon analysis of total carbon and CSRA of PAHs on atmospheric samples collected in Lycksele during the winter of 2006.

2 Experimental section

2.1 Sample collection and treatment

Sampling was carried out in a residential neighborhood (Forsdala) in the town of Lycksele (64.55° N, 18.72° E, 8600 inhabitants) over a 6-week period from 23 January to 8 March 2006. Details on the sampling site and meteorological conditions can be found elsewhere (Krecl et al., 2007; Krecl et al., 2008a). Two custom-built high-volume samplers were employed (Broman et al., 1991), each one consisting of an inverted filter holder which collected total suspended particle matter (TSP) on borosilicate glass fiber filters (GFF, 293 mm diameter, Millipore, USA). Downstream of the GFF filters were two sequentiall polyurethane foam (PUF) traps for collecting volatile compounds. Filter changes were made on a 2-week schedule while PUF were replaced on a 1-week schedule to limit potential breakthrough. During the initial two weeks (23 January–6 February), the sampling was conducted with both GFF and PUFs; sampler A had an average flow rate of $24 \, \text{m}^3 \, \text{h}^{-1}$ and sampler B had an average flow rate of $20 \, \text{m}^3 \, \text{h}^{-1}$.

For the final four weeks of the campaign (6 February–8 March), the sampling was performed only in the particle phase with an average flow rate of $\sim$35 m^3 h^{-1} for both samplers. In total, three sets of two-week filter samples and two sets of one-week PUF samples were collected. Additionally, one filter blank and two PUF blanks were transported to and from the measurement site together with the other filters and PUFs and were exposed outdoors in the sampling equipment for 30 s.

Prior to sampling, filters were baked at 450°C for 5 h and PUFs were pre-cleaned by washing in a washing machine at 90°C without detergent, dried at 35°C for 4 days and Soxhlet extracted first with toluene for two days and then with acetone for one day. PUFs were thereafter dried in a desiccator with vacuum suction for one day and finally wrapped in aluminum foil and sealed in airtight plastic bags until sampling. After sampling, filters were wrapped in aluminum foil, packed into airtight plastic bags and PUFs were wrapped in aluminum foil and sealed in airtight plastic bags. All samples were first stored for several days in a refrigerator (+4°C) and then in a freezer (−18°C) prior to analysis.

2.2 TOC Analysis

Total organic carbon (TOC) is here defined as the carbon remaining after inorganic carbon is removed by acid treatment (Zencak et al., 2007a). TOC analysis was conducted on 3 filter samples (Table 1). A 2.90 cm^2 portion of each filter sample was treated with 37% HCl fumes in a desiccator for 2 days to remove carbonates. The residual (TOC) was determined with a high-temperature catalytic elemental analyzer (Carlo Erba/Fisons, Italy) and blank corrected.

2.3 PAH Analysis

For each 2-week sample period, 75% of each filter from the two samplers were combined for extraction resulting in 3 filter samples. For the PUFs, a combined sample was extracted for each of the two 1-week PUF sample periods from the two samplers result-

ing in 2 PUF extracts. The filter and PUF samples were extracted with cyclohexane in a Soxhlet apparatus. After extraction, a 5% aliquot of the extract was spiked with deuterated PAHs (phenanthrene-d_{10}, fluoranthene-d_{10}, pyrene-d_{10}, and benzo[a]pyrene-d_{12}, benzo[g,h,i]-perylene-d_{12}). The remainder of the method is based on previously re-

5 ported work (Mandalakis et al., 2005; Zencak et al., 2007b). Briefly, the cyclohexane extracts were reduced to 2 ml by rotary evaporation. To purify the extracts, each was applied to a deactivated silica gel column (SiO_2 – 10% H_2O, 63–200 μm particle size, 10 cm×1 cm i.d.) and eluted with n-hexane. The samples were further treated with a dimethylformamide (DMF-5% water)-pentane partitioning cleanup procedure (Man-

10 dalakis et al., 2004b) to isolate PAHs from interfering aliphatic compounds. Extracts were then applied to a second deactivated silica gel column containing disodium sulfate (Na_2SO_4, anh.) to remove water. At this point, the extracts were spiked with a co-injection standard, chrysene-d_{12}, and analyzed by gas chromatography/mass spectrometry (Fisons 8060GC interfaced to a Fisons MD 800 mass spectrometer) with the

15 MS operated in selective ion monitoring mode (Mandalakis et al., 2004a).

2.4 Preparative capillary gas chromatography and accelerator mass spectroscopy

The details of the Gerstel preparative capillary gas chromatography (PCGC) method used for PAH isolation and harvesting have been reported previously (Mandalakis and Gustafsson, 2003; Mandalakis et al., 2004a) and are summarized here. Ninety-five

20 percent of each cyclohexane extract was first purified as described in the PAH analysis section except for the spiking with deuterated PAHs. Each purified extract was then repeatedly injected into the PCGC system (roughly 40 injections per extract) and the PAHs listed in Table 1 were trapped separately. PAHs harvested in the glass traps were then transferred using several rinses of hexane and passed through a small column

25 packed with SiO_2 (4 cm×0.5 cm i.d.) using hexane. A small aliquot from each trap was used to check purity and to quantify the harvested PAHs with GC-MS. Purities ranged from 92–100%, with an average of 97% and yields were low at 24–46% for all but benzo[ghi]perylene which had a yield of 15%. The low yield will not impact the radio-

carbon results, however, as Zencak et al showed that $\Delta^{14}C$ normalized, as these were, to a $\delta^{13}C$ of -25‰ corrects any putative isotopic fractionation during PCGC isolation (2007c). In order to achieve sufficient mass for the CSRA method, the PAHs from the 3 filter extracts were combined after harvesting. The harvested PAHs from the 2 PUF ex-
tracts were likewise combined (Table S1: http://www.atmos-chem-phys-discuss.net/8/ 20901/2008/acpd-8-20901-2008-supplement.pdf). This was the final step conducted at Stockholm University before the extracts were shipped out for further analysis.

Carbon isotope analysis was performed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility of the Woods Hole Oceanographic Institution (USA). Acid fumigated TOC and PCGC-isolated individual PAH samples were oxidized to CO_2, purified and quantified by manometry (Pearson et al., 1998). About 10% of CO_2 was kept for $\delta^{13}C$ analysis by isotope ratio mass spectrometry. The remaining 90% was reduced to graphite and subjected to accelerator mass spectrometry to de- termine the fraction of modern carbon, f_M, which is the $^{14}C/^{12}C$ ratio of the sample related to that of the reference year 1950. The reported $\Delta^{14}C$ error is the larger of the internal error (statistical error calculated using the number of counts measured from each AMS sample) and external error (error calculated from the reproducibility of indi- vidual analyses of a single sample) (Pearson et al., 1998). More details on radiocarbon conventions and metric, the routine AMS sample preparation and analysis procedures are available elsewhere (Zencak et al., 2007b; Klinedinst and Currie, 1999).

3 Results and discussion

3.1 Ambient concentrations

Previously reported work from the Lycksele winter 2006 campaign has demonstrated that a combination of winter-time residential wood burning and traffic emissions with stable atmospheric conditions can result in locally high PM events (Krecl et al., 2007; Krecl et al., 2008b). The measurements in the current study were collected during

an overlapping time period as these Krecl et al. studies, but on completely different time scales. The ambient concentrations reported here are based on integrating 1–2 week sample collection periods, thus any extreme short-duration events are effectively smoothed out over the collection interval.

Systematically high TOC and PAH concentrations were observed during the 2006 winter season in Lycksele, Sweden (Fig. 1). Gas phase samples were only collected in the first sampling period, but the cold winter temperatures ensured that the volatile component was important only for phenanthrene, the most volatile of the measured PAHs; other measured PAHs were predominantly present in the particulate phase. Despite the 14-day sampling integration, the three filter samples had different PAH concentrations and fingerprints. The lower molecular weight PAHs (fluoranthene and pyrene) have relatively higher concentrations in the first sampling period (23 January–6 February) while the higher molecular weight PAHs (chrysene to coronene) were higher in the second sampling period (6–22 February). The particulate TOC concentration for the three sampling periods parallels the trend seen for the higher molecular weight PAHs. To put these PAH concentrations in perspective, Table 2 compiles PAH concentrations from several previously reported studies of areas impacted by biomass burning (Sheesley et al., 2007; Schnelle-Kreis et al., 2007; Chowdhury et al., 2007; Schauer and Cass, 2000). The 2006 winter measurements (this study) are roughly in the same range as those reported for the same town in 2002. However, the low/high molecular weight PAH ratio was higher in 2002 than in 2006. Atmospheric levels in Lycksele are in the range of high PM event-level concentrations measured in the San Joaquin Valley, CA, USA (Schauer and Cass, 2000), but significantly lower than winter measurements in Indian cities (Chowdhury et al., 2007). Using chemical mass balance modeling with organic tracers, the contribution of biomass burning (wood fuel) was estimated to be 42% of the ambient $PM_{2.5}$ mass concentration in San Joaquin Valley (Schauer and Cass, 2000) and 12 to 20% in Indian cities during wintertime (Chowdhury et al., 2007).

3.2 Carbon isotope results

The high ambient PAH concentrations in Lycksele made it an ideal site for this CSRA-based source apportionment study. The five individual/paired PAHs of highest concentration were successfully isolated, harvested and quantified for radiocarbon content (Table 1). Results of ^{13}C isotope analysis are presented as δ^{13}C values relative to the Vienna Pee Dee Belemnite (VPDB) standard (Coplen, 1996). Radiocarbon data are reported as Δ^{14}C and fraction modern (f_M) relative to NBS Oxalic Acid I and have been corrected for carbon blank and isotopic fractionation both in the environment and during sample preparation using a δ^{13}C of −25‰ as described elsewhere (Klinedinst and Currie, 1999; Stuiver and Polach, 1977; Zencak et al., 2007c). Above-ground nuclear testing in the mid-twentieth century nearly doubled atmospheric Δ^{14}C values, but since that time this radiogenic "bomb spike" signal has been consistently decreasing (Levin et al., 2003), which means that biomass which grows over many years, such as trees, will have a higher Δ^{14}C than contemporary CO_2. Therefore, contemporary CO_2 and freshly produced biomass has a Δ^{14}C value of +70‰ (Levin and Kromer, 2004), while contemporary wood fuel sources have been reported to have a well-constrained Δ^{14}C between +225‰ and +218‰ (Currie et al., 1999; Klinedinst and Currie, 1999; Zencak et al., 2007a; Szidat et al., 2007; Szidat et al., 2004b) and fossil fuel sources have a Δ^{14}C of −1000‰.

For a case such as wintertime PAHs in Lycksele, biogenic emissions are not likely due to the very low air temperatures that reduce biological activity and volatile organic carbon emissions. Snow-covered ground during the entire sampling period prevented the occurrence of grass fires in the region and incineration of household vegetable waste is not a common practice in the area. The Δ^{14}C-PAH and- TOC signals are constrained to −138 to 59‰ and demonstrate that the modern carbon source is dominant for both TOC and individual PAHs. Wood fuel burning is assumed to be the dominant source of non-fossil PAHs in Lycksele. However, a fossil carbon and PAH source, most likely motor vehicle exhaust based on previous studies in the area (Krecl et al., 2008a;

Krecl et al., 2008b), is present in all samples. The Δ^{14}C for bulk TOC had a more limited range (−96 to −24‰) than the Δ^{14}C range for PAHs (−138 to 59‰), with fluoranthene the most enriched in ^{14}C and the paired indeno[cd]pyrene plus benzo[ghi]perylene the most depleted.

5   The δ^{13}C values in Lycksele are slightly more enriched in the TOC (−26.41‰ to −26.68‰) than in the PAHs (−27.82‰ to −28.88‰); the PAHs are in the same range reported for European background sites (Mandalakis et al., 2005). Additionally, the TOC and all the PAH δ^{13}C values are within the reported range for terrestrial C$_3$ plant combustion (Zencak et al., 2007a). It should be noted that although Δ^{14}C values re-
10 ported in the literature are commonly corrected for fractionation (Stuiver and Polach, 1977), the same is not true of δ^{13}C values. Therefore δ^{13}C results derived from samples prepared using PCGC may be biased if the entire peak was not collected (Zencak et al., 2007c).

3.3   Radiocarbon-based source apportionment

15 An isotopic mass balance equation was then applied to the TOC and PAH Δ^{14}C results to calculate fractional contribution of wood burning ($f_{biomass}$) and fossil fuel combustion ($f_{fossil}=1-f_{biomass}$) (Reddy et al., 2002; Currie et al., 1999; Mandalakis et al., 2004a; Reddy et al., 2003):

$$\Delta^{14}C_{sample} = \Delta^{14}C_{biomass}f_{biomass} + \Delta^{14}C_{fossil}(1 - f_{biomass}) \qquad (1)$$

20 In the above equation, $\Delta^{14}C_{sample}$ represents the radiocarbon results presented in Table 1 for TOC and PAHs and the $\Delta^{14}C_{biomass}$ is in the present study set to +218‰ (see above discussion). The resulting $f_{biomass}$ are presented in Fig. 2. The PAH $f_{biomass}$ results represent the full 6-week sampling period for all species except gas-phase phenanthrene (2-week sample), while the TOC average $f_{biomass}$±one standard devi-
25 ation is included in Fig. 2.

The $f_{biomass}$ ranges from 71–87% for all PAHs and the average for TOC is 77±3%. Hence, TOC is in the middle of the $f_{biomass}$ range for the measured PAHs. Several previous studies have reported the $f_{biomass}$ for pooled, compound-class specific radio-carbon analysis (CCSRA) of PAHs. Background site studies in Europe found a $f_{biomass}$

5   for particulate CCSRA-PAHs of 50%, 9% and 7% for Southern Sweden, Croatia and Greece, respectively (Mandalakis et al., 2005). The Croatian and Greek values repre-sent summer conditions whereas the Southern Sweden $f_{biomass}$ is a multi-year average; a winter event at the same Southern Sweden site had an $f_{biomass}$ for TOC of 75–85% (Zencak et al., 2007a), which illustrates the impact of seasonal sources such as RWC.

10   A more comprehensive study in the western Balkans measured $f_{biomass}$ in the range 35–65% for a selection of urban, industrial and rural sites (Zencak et al., 2007b). In a study in Tokyo, particulate CCSRA-PAHs in the PM_{10} fraction were split into low and high molecular weight fractions by season. The contribution of biomass burning to PM_{10} samples was 17–38% (summer) and 24–27% (winter) for low and high molecular

15   weight (MW) PAHs, respectively, with little seasonal differences. Road traffic emissions might be expected to dominate in and around a megacity like Tokyo, and therefore it is surprising to see the high fraction of PAH from biomass combustion in both summer and winter. The $f_{biomass}$ calculated for Lycksele is much higher than all three of these previously reported CCSRA-PAH studies. The $f_{biomass}$ of PAHs from this study plus the

20   $f_{biomass}$ of TOC from Southern Sweden (Zencak et al., 2007a) indicate the dominance of RWC during winter in the boreal zone.

To make a start at evaluating the isotopic (and source) heterogeneity between gas phase and particulate PAHs, this study afforded radiocarbon analysis on phenanthrene in both phases. The $f_{biomass}$ of gaseous and particulate phenanthrene were indistin-

25   guishable within three times the error in Lycksele. Although the gas and particulate phase phenanthrene samples for radiocarbon were not synchronous (23 January–6 February for gas phase, and 23 January–6 February and 22 February–8 March for particulate phase, see Table S1: http://www.atmos-chem-phys-discuss.net/8/20901/2008/acpd-8-20901-2008-supplement.pdf), the TOC radiocarbon results for the three,

two-week periods show stability in the source contributions despite differences in concentration (Table 1). Based on the imperfect comparison in this study, the partitioning of phenanthrene between the gaseous and particulate phase is apparently dominated by ambient conditions under these winter-time conditions and is less impacted by differences in the physical or chemical characteristics of RWC or motor vehicle exhaust.

3.4 Fraction biomass and molecular weight

We further sought to investigate isotopic heterogeneity as a function of PAH vapor pressure and/or size, however the number of samples inhibits statistical analysis. In Fig. 2, there is a small decrease in $f_{biomass}$ with increasing molecular weight for the five compounds/compound pairs analyzed here. The $f_{biomass}$ of phenanthrene, fluoranthene, pyrene and benzo[b+k]fluoranthene are relatively similar, and it is particularly the pair of MW 276 PAHs (indeno[cd]pyrene plus benzo[ghi]perylene) that have a much lower $f_{biomass}$. At 71%, the $f_{biomass}$ of indeno[cd]pyrene and benzo[ghi]perylene is 16% lower than gas phase phenanthrene and fluoranthene and 9% lower than benzo[b+k]fluoranthene. The results are broadly consistent with a PAH fingerprint skewed toward higher masses for high-temperature combustion processes such as fossil fuel combustion. In fact, both indeno[cd]pyrene and benzo[ghi]perylene have been used in organic molecular marker-chemical mass balance models (MM-CMB) to apportion the contribution of gasoline-powered motor vehicle exhaust to atmospheric particulate organic carbon (Sheesley et al., 2007; Chow et al., 2007). Figure S1 (http://www. atmos-chem-phys-discuss.net/8/20901/2008/acpd-8-20901-2008-supplement.pdf) illustrates that the PAH/OC ratio for benzo[ghi]perylene, in particular, is much higher for gasoline-powered motor vehicle exhaust (Lough et al., 2007) in comparison to the same ratio for wood smoke emission profiles (Lee et al., 2005; Schauer et al., 2001; Fine et al., 2002, 2004). Although there are few data points, the lower $f_{biomass}$ contribution for the MW 276 PAHs is substantiated in the emission profile literature. Furthermore, this indicates that gasoline-powered vehicles are the dominant fossil fuel source for the PAHs, as the reported diesel-powered motor vehicle exhaust profiles do not in-

clude high MW PAHs like indeno[cd]pyrene or benzo[ghi]perylene (Lough et al., 2007; Schauer et al., 1999).

3.5 Source contribution to ambient loadings

The mean contribution of wood combustion to ambient TOC was 2.4 μg m^{-3} whereas fossil fuel combustion, most likely traffic emissions, accounted for 0.7 μg m^{-3} in the period 23 January–8 March. The contribution of RWC to phenanthrene was 7.8 and 1.9 ng m^{-3}, while traffic emissions contributed 1.2 and 0.4 ng m^{-3} for gas and particle phase, respectively. For fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[cd]pyrene plus benzo[ghi]perylene the RWC contributions were 3.37, 2.94, 4.81 and 7.50 ng m^{-3}, respectively. The motor vehicle contributions were 0.5, 0.7, 1.2 and 3.1 ng m^{-3}, respectively. This illustrates one of the advantages of CSRA, which can be tailored to define source contributions of specific compounds like PAHs, which are of interest as carcinogenic compounds and as source tracers.

4 Conclusions

The results of the CSRA analysis in Lycksele conclusively demonstrate that high ambient concentrations of PAHs across the molecular weight spectrum, and TOC in general, are a result of RWC. Therefore, a significant reduction of carcinogenic atmospheric PAHs in Lycksele, and likely for many similar such towns in the boreal zone, would require targeting RWC emissions. With biomass burning contributions ranging from 87% for fluoranthene to 71% for ideno[cd]pyrene plus benzo[ghi]perylene, the CSRA shows that RWC contribution is dominant, but not uniform for all PAHs. Any decrease in RWC would have a larger impact on the lower molecular weight PAHs, as these have a higher $f_{biomass}$. CCSRA has been used in implicating RWC for total PAHs, however, the current work illustrates that it cannot be assumed that the contribution of RWC would be uniform; this should not be surprising as emission source testing has demonstrated

differences in PAH profiles.

For this system with 2 dominant local source factors (Krecl et al., 2008a), the CSRA could stand alone to separate the biomass burning and local traffic emissions. For Lycksele, the additional information gained from using CSRA instead of CCSRA enabled the attribution of gasoline-powered motor vehicle exhaust over diesel due to the enhanced contribution of fossil fuel for the MW 276 PAHs. In a more complicated system, CSRA would add a valuable additional tool when used in conjunction with other source apportionment and chemical characterization methods. In the case of urban centers with industrial sources, CSRA of PAHs would be particularly helpful as it has been shown that PAHs are not uniformly co-variant with motor vehicle or biomass burning tracers in these systems (Jaeckels et al., 2007).

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Table 1. Carbon isotope results for bulk TOC and individual PAHs in Lycksele during winter campaign 2006.

Dates	Compound[a]	Media	$\delta^{13}C$[b] (‰)	$\Delta^{14}C$ (‰)	f_M
2-week samples					
23 Jan–6 Feb	TOC[c]	GFF	−26.68	−23.7	0.983±0.010
6 Feb–20 Feb	TOC	GFF	−26.41	−75.1	0.931±0.008
22 Feb–8 Mar	TOC	GFF	−26.47	−95.7	0.910±0.008
Winter composites[d]					
23 Jan–6 Feb	Phen	PUF	−27.85	58.0	1.065±0.017
23 Jan–8 Mar	Phen	GFF	−28.19	14.7	1.022±0.020
23 Jan–8 Mar	Fluor	GFF	−28.48	58.8	1.066±0.014
23 Jan–8 Mar	Pyr	GFF	−27.94	−26.8	0.980±0.012
23 Jan–8 Mar	B[b+k]F	GFF	−27.82	−23.5	0.983±0.014
23 Jan–8 Mar	I[cd]P+B[ghi]P	GFF	−28.55	−138.3	0.868±0.019
23 Jan–8 Mar	Sum of PAHs	PUF, GFF	−28.88	−46.2	0.960±0.010

[a] Phenanthrene (Phen), fluoranthene (Fluor), pyrene (Pyr), benzo[b]fluoranthene plus benzo[k]fluoranthene (B[b+k]F), indeno[cd]pyrene (I[cd]P), benzo[ghi]perylene (B[ghi]P). [b] $\delta^{13}C$ and $\Delta^{14}C$ are reported in ‰ relative to VPDB and NBS oxalic acid I, respectively. [c] Total organic carbon (elemental carbon + organic carbon) is defined as carbon remaining after inorganic carbon has been removed by acid treatment. [d] Samples from both samplers were combined to achieve sufficient mass for CSRA analysis (see Table S1: http://www.atmos-chem-phys-discuss.net/8/20901/2008/acpd-8-20901-2008-supplement.pdf).

Table 2. Concentrations of representative PAH (ng m^{-3}) from studies in areas impacted by biomass burning.

Location	North Carolina, USA[b]	San Joaquin Valley, CA USA[c]	Lycksele, Sweden		Delhi, Kolkata and Mumbai, India[f]	Augsburg, Germany[g]
PAH[a]/Season	2003-4 winter range	1995-6 winter 2 event range	2002[d] winter range	2006[e] winter	2001-2 winter range	2003-4 winter
Phen	NA[h]	NA	22.0–40.0	11.3	NA	NA
Fluor	NA	0.4–2.5	7.5–17.0	5.2	NA	NA
Pyr	NA	0.5–3.3	7.4–18.0	4.6	NA	NA
B[b]F	0.3–0.8	2.5–10.7	2.3–6.2	2.7	6.7–53.6	NA
B[k]F	ND[i]–0.4	2.1–8.7	0.8–2.0	3.2	5.6–40.9	NA
sum B[b+k]F						4.0
I[cd]P	0.2–0.5	2.6–6.8	1.6–3.8	4.2	3.6–18.5	0.6
B[ghi]P	0.4–0.7	3.5–9.8	2.0–3.7	6.3	NA	0.8

[a] Phenanthrene (Phen), fluoranthene (Fluor), pyrene (Pyr), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), indeno[cd]pyrene (I[cd]P), benzo[ghi]perylene (B[ghi]P). [b] (Sheesley et al., 2007), 4 semi-urban sites, particle phase, PM$_{2.5}$ fraction. [c] (Schauer and Cass, 2000) 2 sites, 2 winter events, particle phase, PM$_{2.5}$ fraction. [d] (Johansson et al., 2004), Norrmalm and Forsdala residential neighborhoods, gas + particle phases, PM$_{10}$ fraction. [e] gas + particle phases, TSP. [f] (Chowdhury et al., 2007), particle phase, PM$_{2.5}$ fraction. [g] (Schnelle-Kreis et al., 2007), particle phase, PM$_{2.5}$ fraction. [h] NA: not available. [i] ND: not detectable.
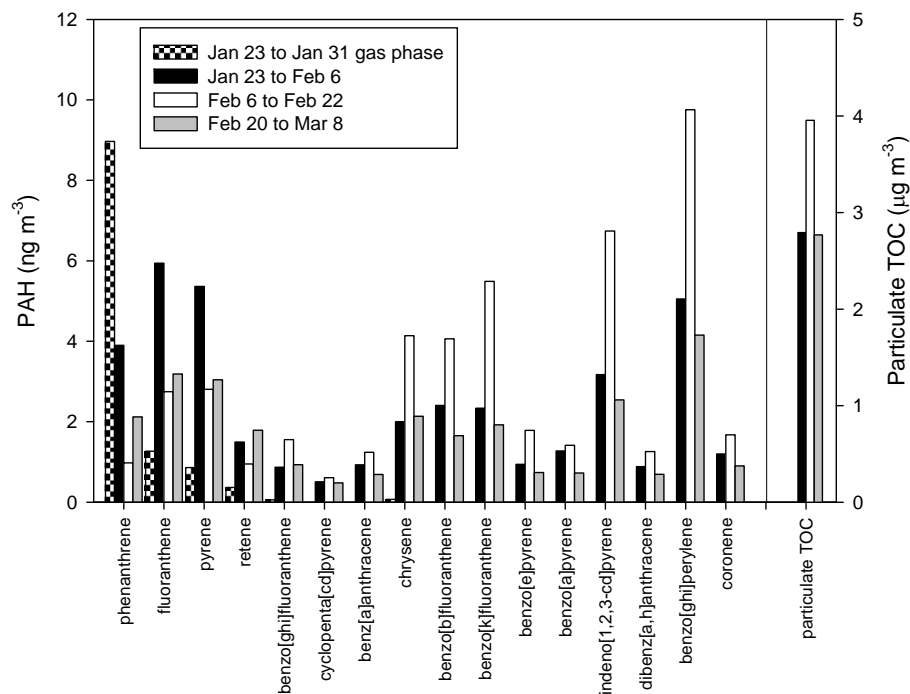
Fig. 1. Left side: Ambient concentrations of individual PAHs in Lycksele, Sweden for gas phase and particulate phases for each sample set. Right side: Particulate TOC concentration for each sample set.
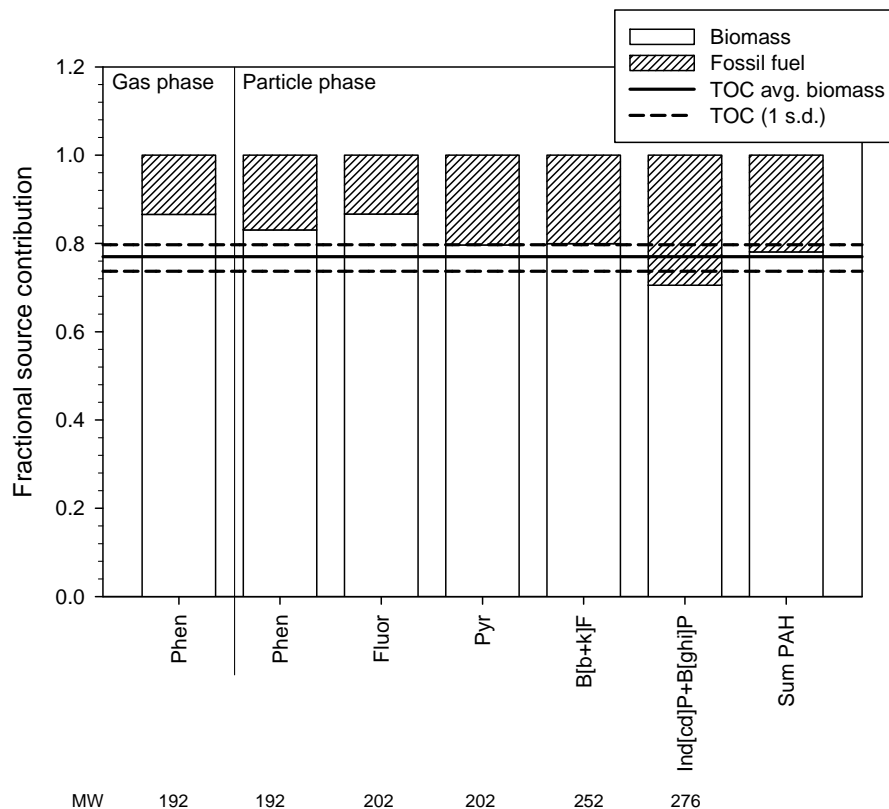
Fig. 2. Fractional contributions of biomass and fossil fuel combustion sources for individual PAHs and sum of PAHs in Lycksele. Mean ±1 STD contribution of biomass burning to TOC for the three, two-week samples is displayed as horizontal lines. The molecular weight (MW) for each individual/paired PAH is listed at the bottom for comparison.