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Source apportionment of PAHs in Central European soils with compound-specific triple isotopes ($\delta^{13}C$, $\Delta^{14}C$ & $\delta^{2}H$)

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ABSTRACT

This paper reports the first study applying a triple-isotope approach for source apportionment of polycyclic aromatic hydrocarbons (PAHs). The $^{13}C/^{12}C$, $^{14}C/^{12}C$ and $^{2}H/^{1}H$ isotope ratios of PAHs were determined in forest soils from mountainous areas of the Czech Republic, European Union. Statistical modeling applying a Bayesian Markov Chain Monte Carlo (MCMC) framework to the environmental triple isotope PAH data and an end-member PAH isotope database allowed comprehensive accounting of uncertainties and quantitative constraints on the PAH sources between biomass combustion, liquid fossil fuel combustion, and coal combustion at low and high temperatures. The results suggest that PAHs in this central European region had a clear predominance of coal combustion sources (75 ± 6%; uncertainties represent 1 SD), mainly coal pyrolysis at low temperature (~650 ºC) (61 ± 8%). Combustion of liquid fossil fuels and biomass represented 16 ± 3% and 9 ± 3% of the total PAH burden (ΣPAH_{14}), respectively. Although some soils were located close to potential PAH point sources, the source distribution was within a narrow range throughout the region. These observation-based top-down constraints on sources of environmental PAHs provides a reference for both improved bottom-up emission inventories and guidance for efforts to mitigate PAH emissions.

Keywords: Bayesian statistics, polycyclic aromatic hydrocarbons, coal combustion, radiocarbon, stable carbon isotope, stable hydrogen isotope

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous, predominantly anthropogenic, organic molecules of environmental concern due to the mutagenic and carcinogenic properties of some congeners (e. g., benzo[a]pyrene)[1]. Therefore, owing to their toxicity, they can pose a threat to humans and the environment. Although PAHs are present in uncombusted petroleum (i.e., petrogenic PAHs), the most important sources of PAHs in the environment are from the incomplete combustion of biomass (e.g., wood) and fossil fuels (e.g., petroleum and coal) (i.e., pyrogenic PAHs)[2,3]. In addition to their own negative effects, PAHs have also been extensively used as molecular tracers of combustion-related airborne particles[3,4], which cause numerous human health problems (e.g., lung cancer, respiratory and heart diseases)[5,6]. Among atmospheric contaminants, PAHs account for most (35-82%) of the total mutagenic activity of airborne particles[7] and hence, a reduction of PAH emissions is essential to improve air quality.

Potential sources of airborne PAHs are vehicle exhaust, power generation, residential heating/cooking, abrasion of tires and asphalt surfaces, waste incineration, and industrial processes. A better understanding of PAH sources is essential to mitigate air pollution, but unfortunately the relative contributions of different sources to PAHs are still poorly understood. A variety of techniques to apportion sources of PAHs exist in the literature, based on either molecular or isotopic compositions[3]. For instance, numerous studies have used diagnostic ratios of PAH concentrations, usually isomeric ratios, to infer PAH sources[3,8,9]. However, the molecular composition of PAHs is affected by differential atmospheric removal and transformation processes[9-11]. Furthermore, these isomeric ratios are not source specific and show considerable intrasource variability[9]. The intrinsic carbon isotope composition of an individual PAH molecule is a more conservative source tracer[12-15]. Although $\delta^{13}C$ analysis on individual PAHs is a well-established technique[12,16,17], combining both compound-specific stable isotope and (natural abundance) radiocarbon analyses (CSIA and CSRA, respectively) offers a potentially far more powerful tool for quantitatively determining the sources of contaminants in the environment. In the literature, combined compound-specific $\delta^{13}C$ and $\Delta^{14}C$ measurements have been applied to apportion PAH sources in sediments[13,14], soils[18] and air[15,19-22]. Introducing more isotope systems would naturally offer further improvements in PAH source constraining capacity. As with any mass-balance approach the number of sources that can be differentiated by N markers is N+1. Thus, the advantage of triple-isotope analysis is that we can resolve four sources, rather than two (one marker) or three (two markers). Sun and collaborators[23] reported the potential use of the stable hydrogen isotope in combination with carbon isotopes for source apportionment of PAHs, but very few $\delta^{2}H$-PAH measurements in both emissions and ambient samples have been published to date. The only $\delta^{2}H$ determinations performed in ambient emissions was limited to naphthalene, the simplest PAH, from emissions of a combustion process in an alumina refinery[24]. Combining both stable carbon and radiocarbon isotopes, with the hydrogen isotope analyses represents a promising approach for elucidating sources of PAHs.

The aim of the present study is to demonstrate the triple-isotope approach ($\delta^{13}C$, $\Delta^{14}C$, $\delta^{2}H$) for the source apportionment of different PAHs by application to forest soils from the Czech Republic. The Czech Republic is considered one of the most industrially-developed countries among the new member states of the European Union and is used here as a representative for Central Europe. The reason for studying the soil compartment is that PAHs in soil reflect a longer-term input of pollutants compared to airborne concentrations. To the best of our knowledge, by analyzing simultaneously three isotopes (stable carbon and hydrogen, and radiocarbon), this study represents the first compound-specific application for source apportionment using a triple-isotope approach.

EXPERIMENTAL SECTION

Study Area. Ten forest soil samples from mountainous sites within Czech Republic were collected during September 2009 (Figure 1, Table 1). These mountain soils, which have been repeatedly studied since 1995[25], mainly reflect atmospheric transport and deposition. Three samples (#1, #2 and #3) were collected in the north-western part of the country. This border region shared by Germany, Poland and Czech Republic and known as the "black triangle", is characterized by extremely high levels of pollutant emissions[26]. Sample #1 was taken from the Krušné Mts., relatively close to the town Litvínov, site of the largest oil refinery in the Czech Republic. Three more samples (#4, #5 and #6) were collected in the Moravian Region (NE Czech Republic). Two of them (#5 and #6) in the Beskydy Mts., located at the border with Slovakia and adjacent to the industrial centers of Valasske Mezirici and Ostrava, which contain a coal tar refinery (DEZA Corporation), a black carbon production plant (CABOT CS) and seven hard coal mines (OKD Corp.). Sample #7 was collected near the observatory of Košetice, a regional background station for international and national air monitoring programmes. Samples #8, #9 and #10 were forest soils from the Bohemian Region (SW Czech Republic), the Czech Bavarian forest. Spruce trees were the main vegetation type found in all sampling sites. Details on soil sampling are described in the supplementary material.

Quantification of PAHs. Analyses of PAHs were performed at the Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic. Briefly, an aliquot of ca. 10 g dry soil was extracted using automated warm Soxhlet extraction with dichloromethane (DCM). The extract was cleaned-up using activated silica flash column chromatography and analytes eluted with DCM. The eluate was concentrated using a stream of nitrogen in a concentrator unit, and transferred into a mini vial. Before injection, an internal standard of terphenyl was added. Samples were analyzed by a 6890N GC (Agilent, USA) capillary gas chromatography coupled to a mass spectrometer 5973N MS (Agilent, USA) using electronic ionization (70 eV). PAHs were analyzed by selective ion recording (SIR). Further details on sample extraction, clean-up, instrumental analysis and quality control procedures are included in the supplementary material.

Extraction of PAHs for Isotope Analysis. Sample extraction for the isotope analysis was performed at RECETOX, Brno, Czech Republic. Based on the concentrations found in the individual soil samples in the previous step, the soil sample size needed to provide a sufficient quantity of selected PAHs was determined. It varied between 500 and 1500 g of soil among the top soil samples. Soxhlet-extracted samples with DCM were pre-cleaned using large volume silica gel columns and concentrated. As the mountain forest soils contain large amounts of organic material, additional clean-up was needed. Gel-permeation chromatography was applied to remove high molecular weight compounds from the samples. Samples were concentrated to a final volume of 1 ml for further isotope analyses. Further information on these clean-up procedures is provided in the supplementary material. It has been showed and reported that these purification procedures do not affect the original molecular isotopic signatures. Results from studies on isotope fractionation during purification procedures are included in the supplementary material.

Isolation of PAHs for Radiocarbon Analysis. Isolation of PAHs from soil extracts was carried out at Stockholm University as previously described[14,27,28]. Extracts were repeatedly injected onto a preparative capillary gas chromatography (pcGC) system programmed to trap selected PAHs[14,29,30]. The pcGC system consisted of a gas chromatograph coupled to a flame ionization detector 6890N GC (Agilent, Palo Alto, USA) and an autoinjector (7683A, Agilent) integrated with a Gerstel cooled injection system (CIS), a zero-dead volume effluent splitter and a Gerstel preparative trapping device. Since the abundance of the target PAH compounds present in these soil samples was quite low relative to the requirements for ^{14}C measurements (~20-100 μg), individual PAHs were pooled and trapped as follows: 1.

Phenanthrene (PHEN) + anthracene (ANTH); 2: fluoranthene (FLU) + pyrene (PYR); 3: benz[a]anthracene (BaA) + triphenylene (TP) + chrysene (CHRY); 4: benzo[b]fluoranthene (BbF) + benzo[j]fluoranthene (BjF) + benzo[k]fluoranthene (BkF); 5: benzo[e]pyrene (BeP) + benzo[a]pyrene (BaP); 6: indeno[1,2,3-cd]pyrene (IcdP) + benzo[ghi]perylene (BghiP). Additional details about chromatographic conditions and trapping procedures are included in the Supporting Information.

Analysis of Stable Carbon and Hydrogen Isotopes. $\delta^{13}C$ and $\delta^{2}H$ analyses of soil extracts were performed at The University of Bristol, UK. The $\delta^{13}C$ and $\delta^{2}H$ isotope ratio determinations were performed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS). $\delta^{13}C$ analyses were performed using a ThermoQuest Finnigan DeltaPlusXL IRMS coupled to an Agilent 6890 GC *via* a ThermoQuest Finnigan GC Combustion III interface. $\delta^{2}H$ determinations were performed using a Thermo DeltaVPlus IRMS coupled to a Trace GC *via* a GC Isolink and ConfloIV interface. For both $\delta^{13}C$ and $\delta^{2}H$ analyses, chromatographic peaks were integrated in groups using the same 'chromatographic windows' described above corresponding to those compounds which were isolated by pcGC, so as to accurately represent the content of the samples analyzed by accelerator mass spectrometry (AMS). The reported isotopic results, expressed in the per mil deviation (‰) of the isotope ratio from the standards Peedee belemnite (PDB) and Vienna Standard Mean Ocean Water (VSMOW) for C and H, respectively, represent the arithmetic means of triplicate analyses. Further information on the instrumental analysis and quality procedures is provided in the supplementary material.

Analysis of Radiocarbon. The extracts for ^{14}C analysis were shipped to the US National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility (Woods Hole, MA, USA). The pcGC isolates were first purified, then combusted at 850 ºC for its conversion to carbon dioxide and finally reduced to graphite. Targets of graphite were analyzed for ^{14}C by AMS according to standard procedures[30-32]. All ^{14}C determinations are expressed as the per mil (‰) deviation from NBS oxalic acid I. Further details about the ^{14}C analysis are included in the Supplementary Information.

Bayesian Markov Chain Monte Carlo method for source apportionment. The three-dimensional isotope signatures of the different PAHs were used in an isotopic mass balance source apportionment model to differentiate four main sources: biomass, liquid fossil (e.g., petroleum and oil), low temperature (~650 ºC) coal combustion and high temperature (~900 ºC) coal combustion, largely following our earlier dual-isotope (three source) approaches[15,33,34]. The current study's four sources were selected based on two criteria: 1) they encompass the majority of PAHs emitted in this region[35], 2) they are differentiable by means of $\delta^{13}C$, $\Delta^{14}C$ and $\delta^{2}H$ isotopic signatures. In particular, we note that PAHs emitted from high temperature coal combustion are more depleted in ^{13}C while more enriched in ^{2}H, compared to coal combustion at lower temperatures[17].

The source-specific isotope values (end members) were collected from the literature, and are summarized in Table S1. These end members are associated with significant variability and uncertainties, especially in the $\delta^{2}H$ dimension. Such variability has recently been shown to affect not only the precision of the source apportionment calculations, but also the estimated central values (e.g., mean and median) of the source fractions[33]. To account for this variability a Bayesian Markov Chain Monte Carlo (MCMC) approach was implemented[36], in which the end member distributions are modelled as normal distributions with mean and standard deviation defined by the literature values. The source-specific isotope values used in the present study are listed in Table 2 and its calculation is detailed in the Supporting Information. The MCMC approach effectively samples the 4-dimensional fractional source space while satisfying the mass-balance criterion and accounting for the end member variability. The result of the Bayesian approach is a probability density function (pdf) of the relative source contribution for each source (Figure 3A). From this pdf the statistical parameters of interest (e.g., mean, median, standard deviation or confidence intervals) may be computed. The MCMC computations were run using an in-house written MATLAB version 2014a (The MathWorks, Natick, MA, USA) script, with 200,000 iterations, a burn-in (initial search phase) of 10,000 and a data thinning of 10. The details of the Bayesian calculation is published elsewhere[34] and the MATLAB script is presented in the present paper's Supporting Information.

RESULTS AND DISCUSSION

PAH Concentrations and Composition. The PAHs input to mountain soils is mainly through dry or wet deposition of aerosol particles or residues of vegetative litter, and by processes of air-soil partitioning[37,38]. Forest soils are usually rich in organic matter, which favors the accumulation of PAHs. The content of PAHs (sum of 14 PAHs) in the central European forest soils ranged from 0.53 to 9.1 $\mu g \cdot g^{-1}$ (4.3 ± 2.8 $\mu g \cdot g^{-1}$, $\mu \pm \sigma$)(Table 1). These concentrations were in agreement with previously reported concentrations at the same sampling sites[25,39] (1.7-8.2 $\mu g \cdot g^{-1}$). As was expected from their proximity to emission sources, the highest PAH loadings were observed at both northwestern (7.4 and 5.5 $\mu g \cdot g^{-1}$ for #1 and #2 respectively) and eastern border regions (9.1 and 5.9 $\mu g \cdot g^{-1}$ for #5 and #6, respectively). The lowest concentrations were found at Mt. Sumava, close to the border region shared with Germany-Czech Republic-Austria (#9, 0.53 $\mu g \cdot g^{-1}$) and at the regional site of Kosetice (#7, 0.87 $\mu g \cdot g^{-1}$). All samples, except for #9, had a PAH content slightly higher than reported for other remote/forest sites in Europe, such as in the Pyrenees[40] (0.77 $\mu g \cdot g^{-1}$), Alps[41] (1.3 ± 0.6 $\mu g \cdot g^{-1}$) and Tatras[41] (1.6 ± 0.4 $\mu g \cdot g^{-1}$). However, these border mountain soils may be also affected by long range transport contamination coming from Poland, Germany, Slovakia or Austria besides Czech Republic[42].

Relative PAH concentrations (Diagnostic Ratios, DR) are typically used for conventional semiquantitative source apportionment through the comparison of the ambient ratios with specific PAH source signatures. However, PAHs are affected by different atmospheric processes and therefore the relative proportions of the PAH species are not conserved between the emission source and the receptor site[10]. It is known that ANTH, BaA and BaP are photochemically less stable in the atmosphere than PHEN, CHRY and BeP[43,44]. In the present study, DRs were used to assess the extent of photochemical degradation of the studied samples. Microbial degradation of PAHs that may change their isomer composition in background surface soils is deemed unlikely to have a substantial effect on the source apportionment results, considering the limited degradation observed in soils with high content of organic matter affected by diffuse PAH pollution[45]. The BaA/(BaA+CHRY) and BaP/(BeP+BaP) ratios ranged from 0.09 to 0.26 and from 0.13 to 0.44, respectively, and correlate positively (R^2 = 0.90) (Table S2). Samples #1, #6 and #7 showed the largest observed DRs (BaA/(BaP+BeP)>0.40 and BaA/(BaA+CHRY)>0.26, Table S2), indicating that PAHs had been transported the shortest distance from the source. In contrast sample #10 presented the lowest ratios, thus the largest distance to the source.

Carbon Isotope Composition of PAHs in Soils. Compound-specific stable carbon isotope is used to apportion sources. Polycyclic aromatic hydrocarbon (PAH) extracts from all samples were analyzed for their stable carbon isotope composition ($\delta^{13}C$). The $\delta^{13}C$ values ranged between -25.3‰ and -23.0‰ (-24.0 ± 0.1‰, $\mu\pm\sigma$) (Table 1 and Table S3). No substantial variation was observed among sampling sites, which suggests a relatively homogenous source. However, there was a consistent $\delta^{13}C$ variability between the different PAH compounds, with the PAH group BaA + TP + CHRY (m/z 228) having the highest $\delta^{13}C$ values (-23.4 ± 0.3‰) and the PAH group IcdP+BghiP (m/z 276) having the lowest $\delta^{13}C$

values (-24.6 ± 0.3‰) (Figure 2A). This suggests that generation processes differed for the different PAH molecules. During polyaromatization reactions, ^{13}C is preferentially lost during C=C bond formation leading to a relative depletion in $\delta^{13}C$ values[46]. However, no positive correlation was observed between molecular weight and $\delta^{13}C$ values. Overall the $\delta^{13}C$ values of the PAHs in the present study were comparable to those observed in aerosols from Chinese cities[47] (-26.3 to -24.4‰ in Chongqing and Hangzhou and -25.5 to -23.5‰ in Beijing) and soils from a domestic coal-burning village near Glasgow, UK[48] (-25‰). $\delta^{13}C$ were, however, generally more enriched in ^{13}C relative to ambient samples from other European countries such as Sweden[15] (-28.9‰), Croatia[20] (-29.2‰) or Greece[20] (-29.0‰) and from archipelago sediments in Stockholm, Sweden[14] (-27.0 to -24.8‰).

The radiocarbon content was determined for only those samples with sufficient analyte concentrations (n = 7 sites). The determined $\Delta^{14}C$ values ranged between -960‰ and -768‰ (-892 ± 37‰) (Table 1 and Table S4). The radiocarbon composition exhibited very low variability between different sampling sites and PAH compounds (Figure 2B), suggesting a relatively homogenous source, which is consistent with the ^{13}C data. These highly depleted ^{14}C signatures confirm that PAHs in these Czech forest soils are of a mainly fossil fuel origin. Although the soil sample from Kosetice (#7) had slightly more modern carbon (less negative signal) (-819‰, Table 1), those samples with the highest concentrations of PAHs had $\Delta^{14}C$ values reflecting the largest fossil fuel contribution (#1, #2, #5 and #6 with $\Delta^{14}C$ ~ -942 and -897‰, Table 1). Whereas the Czech border sites are mostly affected by long-range transport of pollutants from industrial regions, more local impact is expected in Kosetice (#7). This regional site belongs to an agricultural region with several small villages within 5-10 km in all directions where wood is usually burned for domestic heating. PAHs in Czech Republic had generally very high fossil contributions compared to PAHs from many other worldwide sites, e.g., rural and background sites in Sweden[15,20] (-138 to +58‰ and -388 to -381‰, respectively), western Balkans[22] (-568 to -288‰) and even a residential area in Tokyo[19] (-514 to -787‰).However, the Δ^{14}C-PAH values were similar to airborne PAHs from Croatia[20] (-888‰), Greece[20] (-914‰), Alabama, US[21] (-980‰) and sediments from Stockholm, Sweden[14] (-891 to -709‰).

Hydrogen Isotope Composition of PAHs in Soils. This is the first study complementing the earlier reported dual compound-specific carbon isotope system of PAHs[14,15,22] with hydrogen stable isotopic analyses. The PAH extracts exhibited δ^2H values between -263‰ and -53‰ (-129 ± 44‰) (Table 1 and Table S5). In contrast to both carbon isotope systems (δ^{13}C and Δ^{14}C), the deuterium system showed a higher variability among sampling sites. The western border soil (#1) had a relatively much more ^{2}H-depleted value (-226‰) compared to #5 (δ^2H ~ 135‰) or the remaining studied soils (#2, #6, #7, #8 and #10, δ^2H ~ -109‰). Other studies have suggested that deuterium enrichment takes place simultaneously with ^{13}C depletion during PAH generation[23]. However, in the present study no correlation was found between PAH δ^{13}C and δ^2H values. Furthermore, no significant variability was observed between the δ^2H values and the different PAHs (Figure 2A). Therefore, these data suggest that the relatively more ^{2}H-depleted signature at site #1 reveals a PAH source different from the other soils. To date, there have been no other studies on δ^2H values of PAHs in modern soils.

Monte Carlo Simulations for Source Apportionment. The compound-specific triple-isotope approach allowed elucidation of up to four different sources. In the present study three isotope signatures were analyzed, δ^{13}C, Δ^{14}C and δ^2H, for PAHs in forest soils from the Czech Republic. The stable carbon isotope (δ^{13}C) is a priori informative for source apportionment but it also has been shown that atmospheric photochemical processes can lead to ^{13}C shifts[49,50]. However, O'Malley and collaborators evaluated the effects of evaporation, photodecomposition and microbial degradation on the δ^{13}C values of individual PAHs and no significant alterations were observed[12]. Furthermore, in the present study, no correlation was found between the diagnostic ratios for photochemical degradation (BaA to BaA + CHRY and BaP to BaP + BeP) and their respective $\delta^{13}C$ values (Figure S1). Based on this analysis, carbon isotopic fractionation of PAHs during atmospheric transport was therefore likely insignificant and $\delta^{13}C$ values were used to apportion PAH sources.

The natural abundance of radiocarbon ($\Delta^{14}C$) was utilized to differentiate between fossil fuel (-1000‰) *versus* combustion of contemporary sources (+137.5 ± 21.9‰) for PAHs. Stable carbon isotope ratio determinations of individual PAHs showed different $\delta^{13}C$ values for the combustion of C_3 terrestrial vegetation[51-53] (e.g., wood, ~ -28.7‰) and liquid fossil fuels[23,52,54] (e.g., gasoline, ~ -24.1‰, diesel, ~ -26.5‰). Regarding the individual PAHs derived from coal combustion sources, $\delta^{13}C$ values have been shown to vary over a wide range by ca. 8‰[17,23,52,55-57] (-31 to -23‰) and overlapping with C_3 wood and liquid fossil fuel sources. The $\delta^{13}C$ values of coal-derived PAHs are normally dictated by both the isotopic signature of the parent fuels and the temperature of combustion. In general, PAHs derived from carbonization processes at low temperatures (~650 ºC) have isotopic values similar to those of the parent coals[17,52,58-60] (-25.4 to -21‰), because they are mainly primary devolatilisation products from mild combustion processes[17]. Instead, $\delta^{13}C$ values of PAHs became lighter when the temperature of carbonization is higher (~900 ºC) because they are then products of condensation reactions, which result in a kinetic isotope effect with ^{12}C-^{12}C bonds forming more easily than ^{13}C-^{12}C bonds[17,23,52,55] (-29.4 to -24.2‰).

In contrast to their $\delta^{13}C$ values, the $\delta^{2}H$ values of PAHs generated by coal, biomass and liquid fuel pyrolysis differ substantially (e.g., liquid fossil fuels[23,53], -76 to -47‰; C_3 wood[53] ~ -94‰; high coal pyrolysis[23], -81 to -65‰; bulk coals[58,60], -170 to -87‰; and bulk peat[61-63], -240 to -79‰). However, only few source-specific $\delta^{2}H$ values have been reported in the scientific literature to date. Therefore, in the future there is the need to better characterize the hydrogen isotopic signature of primary sources. Although $\delta^{2}H$ literature values are currently limited, the simultaneous use of $\delta^{13}C$, $\Delta^{14}C$ and $\delta^{2}H$ provide a greater differentiation and allowed quantitatively to apportion the relative contribution of four different combustion source classes to the PAH. Source-specific $\delta^{13}C$ and $\delta^{2}H$ values reported in literature are summarized in the Supporting Information (Table S1).

The choice of sources to perform the Bayesian-based method (see Experimental Section) was based on existing bottom-up emission inventories and past PAH fingerprinting studies indicating the major sources of PAHs in the Czech Republic[35,64-66]. By combining the isotopic signatures of sample data and primary PAH sources in two-dimensional plots (Figures 2A+B), the following four sources were chosen: combustion of liquid fuels, C_3 wood combustion, as well as coal combustion at low (~650 ºC) and high (~900 ºC) temperatures. The isotopic signatures used for the primary PAHs sources are detailed in Table 2.

Natural peat fires in the border mountainous Czech areas were a priori a potential source of PAHs in Czech Republic. However, the present PAH-isotope data did not support this hypothesis (Figure 2A+B). Furthermore, the soil from the northwestern part of the country (#1) had a hydrogen stable-isotope composition which was more depleted in ^{2}H than the other samples and moreover, did not match any of the primary sources explored for $\delta^{2}H$ values of PAHs in the literature to date (Figure 2A+B). Shifts in the $\delta^{2}H$ values of organic molecules have been observed as a result of many degradation processes with potentially quite large enrichment factors[67]. However, such deuterium fractionation is generally accompanied with a shift also in the $\delta^{13}C$ values, which was not observed in the case of sample #1. It is worth noting here that the lack of reported source-specific data for the hydrogen isotope composition makes it difficult to draw other interpretations of sample #1. As a result, sample #1 was not considered for the Bayesian-based data analysis due to the inability to associate its $\delta^{2}H$ values to either a primary source or a degradation process. Nevertheless, the results of the radiocarbon analyses of site #1 enabled the calculation of the relative contributions of the combined fossil fuel sources *versus* contemporary biomass using a simple isotopic mass balance equation as described elsewhere[14] (Table 3 and Figure 3B).

The compound-specific isotope ratios for every site were combined with literature values for source end members in a mass balance-based source-apportionment scheme. The variability of the isotopic source signatures were accounted for within a Bayesian Markov Chain Monte Carlo framework. Four probability density functions, one for every source, were obtained for every group of PAHs and site (#2, #5, #6, #7, #8 and #10), as is shown at Figure 3A for the group BbF+BjF+BkF and site#7. All samples showed a similar source pattern with the highest contribution coming from the coal combustion at low temperature, ranging from 53 to 75% (61±8%, Table 3 and Figure 3B). Practically equal contributions from liquid fossil fuels and coal combustion at high temperature were also observed for all samples (16 ± 3% and 13 ± 2%, respectively). Biomass combustion was the least important source of PAHs in Czech Republic soils, with contributions ranging between 5 to 16% (9 ± 3%). Only small differences were observed between samples, but those soils with the highest PAH concentrations from the northwestern (#1 and #2) and the eastern border (#5 and #6) regions had slightly higher coal-related contributions (Figure 3B, high + low temperatures coal combustion ~ 74-85% and biomass ~ < 9%). Correspondingly, soils from Kosetice and the southern region had slightly higher biomass contributions (#7, #8 and #10, biomass ~ 10-16% and coal ~ 66-74%). Although some soil sites were placed relatively close to potential PAH point sources and showed higher PAH concentrations, the triple-isotope-based apportionment demonstrated that the contribution from the four different source classes were rather homogeneous for mountainous forest soils across the country. The low observed biomass contributions (9 ± 3%) in Czech background soils are similar to those observed in South Europe, such as in background air from Croatia and Greece[20] (9% and 7%, respectively), but lower than those in North Europe (i.e. Sweden[20], 50%)

Coal combustion at low and high temperatures may be associated to domestic and industrial emissions, respectively. Additionally, combustion of fuels at low temperature has the potential to result in higher PAH emissions than high-temperature combustion sources (i.e. the lower is the combustion temperature, higher are the PAHs emission factors[4]). These high emission factors might explain the high contribution coming from low-temperature coal combustion sources in Czech Republic. However, the household coal usage represents only the 3% of the total coal production in the Czech Republic[68]. Furthermore, the residential coal burning represents one of the most toxic sources of PAHs due to both high emission rates and proximity to population[35]. Emission inventories show a reduction of PAH emissions in recent years in almost all European countries, being the residential sector the most important source of PAHs nowadays[35]. In 2007, residential emissions (including fossil and non-fossil sources) accounted for the 47.5% of the total PAH emissions in Europe[35]. The present study shows like the residential sector in Czech Republic, in particular the residential coal burning, may be more important than the European average. Taken together, PAHs in Czech soils are heavily influenced by coal combustion practices (75%), mainly coming from household emissions (61%).

The present study demonstrates firstly that triple isotope characterization of PAHs is possible and secondly, that this information is useful for source characterization. However, the existing literature on isotope characterization of PAHs is currently limited. We think and hope that the current contribution may encourage researchers to expand the existing source database. Such work should seek to both improve the statistics for the currently investigated sources, but also expand the number of source categories in terms of their geographical prevalence.

REFERENCES

(1) Agency for Toxic Substances and Disease Registry (ATSDR), **1995**. Toxicological profile for polycyclic aromatic hydrocarbons (PAHs). Atlanta, GA: U.S. *Department of Health and Human Services, Public Health Service.*

(2) Gustafsson, Ö.; Buesseler, K. O.; Gschwend, P. M. Using ^{234}Th disequilibria to estimate the vertical removal rates of polycyclic aromatic hydrocarbons from the surface ocean. *Mar. Chem.* **1997**, 57, 11-23.

(3) Lima, A. L .C.; Farrington, J. W.; Reddy, C. M. Combustion-derived polycyclic aromatic hydrocarbons in the environment – a review. *Environ. Forensics* **2005**, *6*, 109-131.

(4) Ravindra, K.; Sokhi, R.; Van Grieken, R. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos. Environ*. **2008**, *42,* 2895-2921.

(5) Beelen, R. *et al.* Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project. *Lancet***2014,** 383, 785-795.

(6) WHO, 2014. Outdoor Air Pollution in the World Cities. World Health Organization, Geneva, Switzerland. http://www.who.int/phe/health_topics/outdoorair/databases/en.

(7) Pedersen, D. U.; Durant, J. L.; Penman, B. W.; Crespi, C. L.; Hemond, H. F.; Lafleur, A. L.; Cass, G. R. Human-cell mutagens in respirable airborne particles in the northeastern United States. 1. Mutagenicity of fractionated samples. *Environ. Sci. Technol*. **2004,** *38,* 682-689.

(8) Nam, J. J.; Thomas, G. O.; Jaward, F. M.; Steinnes, E.; Gustafsson, Ö.; Jones K. C. PAHs in background soils from Western Europe: Influence of atmospheric deposition and soil organic matter. *Chemosphere* **2008**, *70*, 1596-1602.

(9) Galarneau, E. Source specificity and atmospheric processing of airborne PAHs: Implications for source apportionment. *Atmos. Environ.* **2008***, 42,* 8139-8149.

(10) Dvorská, A.; Lammel, G.; Klánová, J. Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. *Atmos. Environ.* **2011***, 45,* 420-427.

(11) Kim, D.; Kumfer, B. M.; Anastasio, C.; Kennedy, I. M.; Young, T. M. Environmental aging of polycyclic aromatic hydrocarbons on soot and its effect on source identification. *Chemosphere* **2009**, *76*, 1075-1081.

(12) O'Malley, V.; Abrajano, Jr. T.; Hellou, J. Determination of the $^{13}C/^{12}C$ ratios of individual PAH from environmental samples: Can PAH sources be apportioned?. *Org. Geochem.* **1994,** *21*, 809-822.

(13) Reddy, C. M.; Pearson, A.; Xu, L.; McNichol, A. P.; Benner, B. A.; Wise, S. A.; Klouda, G. A.; Currie, L. A.; Eglinton, T. I. Radiocarbon as a tool to apportion the sources of polycyclic aromatic hydrocarbons and black carbon in environmental samples. *Environ. Sci. Technol.* **2002,** *36,* 1774-1782.

(14) Mandalakis, M.; Gustafsson, Ö.; Reddy, C. M.; Xu, L. Radiocarbon Apportionment of Fossil versus Biofuel Combustion Sources of Polycyclic Aromatic Hydrocarbons in the Stockholm Metropolitan Area. *Environ. Sci. Technol*. **2004**, *38*, 5344-5349.

(15) Sheesley, R. J.; Kruså, M.; Krecl, P.; Johansson, C.; Gustafsson, Ö. Source apportionment of elevated wintertime PAHs by compound-specific radiocarbon analysis. *Atmos. Chem. Phys*. **2009**, *9*, 3347-3356.

(16) McRae, C.; Snape, C. E.; Sun, C.; Fabbri, D.; Tartari, D.; Trombini, C.; Fallick, A. E. Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived

polycyclic aromatic hydrocarbons in a lagoon sediment. *Environ. Sci. Technol*. **2000**, *34*, 4684-4686.

(17) McRae, C.; Sun, C.; Snape, C. E.; Fallick, A. E.; Taylor, D. δ^{13}C values of coal-derived PAHs from different processes and their application for source apportionment. *Org. Geochem.* **1999***, 30,* 881-889.

(18) Lichtfouse, E.; Budzinski, H.; Garrigues, H. P.; Eglinton, T. I. Ancient polycyclic aromatic hydrocarbons in modern soils: ^{13}C, ^{14}C and biomarker evidence. *Org. Geochem.* **1997**, *26*, 353-359.

(19) Kumata, H.; Uchida, M.; Sakuma, E.; Uchida, T.; Fujiwara, K.; Tsuzuki, M.; Yoneda, M.; Shibata, Y. Compound class specific C-14 analysis of polycyclic aromatic hydrocarbons associated with PM_{10} and $PM_{1.1}$ aerosols from residential areas of suburban Tokyo. *Environ. Sci. Technol*. **2006**, *40*, 3474-3480.

(20) Mandalakis, M.; Gustafsson, Ö.; Alsberg, T.; Egebäck, A. L.; Reddy, C. M.; Xu, L.; Klanova, J.; Holoubek, I.; Stephanou, E. G. Contribution of Biomass Burning to Atmospheric Polycyclic Aromatic Hydrocarbons at Three European Background Sites. *Environ. Sci. Technol*. **2005**, *39*, 2976-2982.

(21) Xu, L.; Zheng, M.; Ding, X.; Edgerton, E.; Reddy, C. M. Modern and fossil contributions to polycyclic aromatic hydrocarbons in PM2.5 from North Birmingham, Alabama in the southeastern U.S. *Environ. Sci. Technol*. **2012**, *46*, 1422-1429.

(22) Zencak, Z.; Klanova, J.; Holoubek, I; Gustafsson, Ö. Source apportionment of atmospheric PAHs in the western Balkans by natural abundance radiocarbon analysis. *Environ. Sci. Technol*. **2007**, *41*, 3850-3855.

(23) Sun, C.; Cooper, M.; Snape, C. E. Use of compound-specific $\delta^{13}C$ and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Commun. Mass Spectrom.* **2003**, *17*, 2611-2613.

(24) Vitzthum von Eckstaedt, C. D.; Grice, K.; Ioppolo-Armanios, M.; Jones, M. $\delta^{13}C$ and δD of volatile organic compounds in an alumina industry stack emission. *Atmos. Environ.* **2011**, *45*, 5477-5483.

(25) Kukucka, P.; Klanova, J.; Sanka, M.; Holoubek, I. Soil burdens of persistent organic pollutants – Their levels, fate and risk. Part II. Are there any trends in PCDD/F levels in mountain soils? *Environ. Pollut.* **2009**, *157*, 3255-3263.

(26) van Drooge, B. L.; Fernández, P.; Grimalt, J. O.; Stuchlík, E.; Torres García, C.J.; Cuevas, E. Atmospheric polycyclic aromatic hydrocarbons in remote European and Atlantic sites located above the boundary mixing layer. *Environ. Sci. Pollut. Res.* **2010**, *17*, 1207-1216.

(27) Mandalakis, M. and Ö. Gustafsson. Optimization of a preparative capillary gas chromatography-mass spectrometry system for the isolation and harvesting of individual polycyclic aromatic hydrocarbons. *J. Chromatogr. A.* **2003**, *996*, 163-172.

(28) Meinert, C. and W. Brack. Optimisation of trapping parameters in preparative capillary gas chromatography for the application in effect-directed analysis. *Chemosphere* **2010**, *78*, 416-422.

(29) Eglinton, T. I.; Aluwihare, L. I.; Bauer, J. E.; Druffel, E. R. M.; McNichol, A. P. Gas chromatographic isolation of individual compounds from complex matrices for radiocarbon dating. *Environ. Sci. Technol.* **1996***, 68,* 5, 904-912.

(30) Zencak, Z.; Reddy, C. M.; Teuten, E. L.; Xu, L.; McNichol, A. P.; Gustafsson, Ö. Evaluation of gas chromatographic isotope fractionation and process contamination by carbon in compound-specific radiocarbon analysis. *Anal. Chem.* **2007**, *79*, 2042-2049.

(31) Pearson, A.; McNichol, A. P.; Schneider, R. J.; von Reden, K. F.; Zheng, Y. Microscale AMS ^{14}C measurement at NOSAMS. *Radiocarbon* **1998,** *40*, 61-75.

(32) McNichol, A. P.; Gagnon, A. R.; Jones, G. A.; Osborne, E.A. Illumination of a Black-Box - Analysis of Gas-Composition During Graphite Target Preparation. *Radiocarbon* **1992,** *34*, 321-329.

(33) Andersson, A. A systematic examination of a random sampling strategy for source apportionment calculations. *Sci. Total Environ.* **2011**, *412-413*, 232-238.

(34) Andersson, A.; Deng, J.; Du, K.; Zheng, M.; Yan, C.; Sköld, M.; Gustafsson, Ö. Regionally-varying combustion sources of the January 2013 severe haze events over eastern China. *Environ. Sci. Technol.* **2015**, *49*, 2038-2043.

(35) Shen, H.; Huang, Y.; Wang, R.; Zhu, D.; Li, W.; Shen, G.; Wang, B.; Zhang, Y.; Chen, Y.; Lu, Y.; Chen, H.; Li, T.; Sun, K.; Li, B.; Liu, W.; Liu, J.; Tao, S. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ. Sci. Technol*. **2013**, *47*, 6415-6424.

(36) Parnell, A. C., Inger, R., Bearhop, S., Jackson, A. L. Source apportionment using stable isotopes: coping with too much variation. *PLOS one 5* **2010**, 1-5.

(37) Ribes, A., van Drooge, B. L., Dachs, J., Gustafsson, Ö., Grimalt, J. O. Influence of Soot Carbon on the Soil-Air Partitioning of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* **2003**, *37,* 2675-2680.

(38) Nam, J. J., Thomas, G. O., Jaward, F. M., Steinnes, E., Gustafsson, Ö., Jones, K. C. PAHs in background soils from Western Europe: Influence of atmospheric deposition and soil organic matter. *Chemosphere* **2008**, *70*, 1596-1602.

(39) Holoubek, I.; Dusek, L.; Sanka, M.; Hofman, J.; Cupr, P.; Jarkovsky, J.; Zbiral, J.; Klanova, J. Soil burdens of persistent organic pollutants – Their levels, fate and risk. Part I. Variation of concentration ranges according to different soil uses and locations. *Environ. Pollut*. **2009**, *157*, 3207-3217.

(40) Grimalt, J. O.; van Drooge, B.; Ribes, A.; Fernández, P.; Appleby, P. Polycyclic aromatic hydrocarbon composition in soils and sediments of high altitude lakes. *Environ. Pollut*. **2004**, *131*, 13-24.

(41) Quiroz, R.; Grimalt, J. O.; Fernandez, P.; Camarero, L.; Catalan, J.; Stuchlik, E.; Thies, H.; Nickus, U. Polycyclic aromatic hydrocarbons in soils from European high mountain areas. *Water Air Soil Pollut.* **2011**, *215*, 655-666.

(42) Dvorska, A.; Lammel, G.; Klanova, J.; Holoubek, I. Košetice, Czech Republic – ten years of air pollution monitoring and four years of evaluating the origin of persistent organic pollutants. *Environ. Pollut.* **2008,** *156*, 403-408.

(43) Behymer, T. D.; Hites, R. A. Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash. *Environ. Sci. Technol.* **1988**, *22,* 1311-1319.

(44) Perraudin, E.; Budzinski, H.; Villenave, E. Kinetic study of the reactions of NO_2 with polycyclic aromatic hydrocarbons adsorbed on silica particles. *Atmos. Environ.* **2005**, *39*, 6557-6567.

(45) Johnsen, A. R.; Karlson, U. Diffuse PAH contamination of surface soils: environmental occurrence, bioavailability, and microbial degradation. *Appl. Microbiol. Biotechnol.* **2007**, *76,* 533-543.(46) Bird, M. I.; Ascough, P. L. Isotopes in pyrogenic carbon: A review. *Org. Geochem.* **2012**, *42*, 1529-1539.

(47) Okuda, T.; Kumata, H.; Naraoka, H.; Takada, H. Origin of atmospheric polycyclic aromatic hydrocarbons (PAHs) in Chinese cities solved by compound-specific stable carbon isotopic analyses. *Org. Geochem.* **2002,** *33*, 1737-1745.

(48) McRae, C.; Sun, C.; McMillan, C. F.; Snape, C. E.; Fallick, A. E. Sourcing of fossil fuel-derived PAH in the environment. *Polycyclic Aromatic Compd.* **2000**, *20*, 97.

(49) Aggarwal, S. G.; Kawamura, K. Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.-Atmos.* **2008**, *113*, D14301, doi:10.1029/2007JD009365.

(50) Pavuluri, C. M.; Kawamura, K. Evidence for 13-carbon enrichment in oxalic acid via iron catalyzed photolysis in aqueous phase. *Geophys. Res. Lett.*, **2012**, *39,* L03802, doi: 10.1029/2011GL050398.

(51) O'Malley, V.; Burke, R.A.; Schlutzhauer, W.S. Using GC-MS/Combustion/IRMS to determine the $^{13}C/^{12}C$ ratios of individual hydrocarbons produced from the combustion of biomass materials – application to biomass burning. *Org. Geochem.* **1997,** *27*, 567-581.

(52) McRae, C.; Love, G. D.; Murray, I. P.; Snape, C. E.; Fallick, A. E. Potential of gas chromatography isotope ratio mass spectrometry to source polycyclic aromatic hydrocarbon emissions. *Anal. Commun.,* **1996**, *33*, 331-333.

(53) Vitzthum von Eckstaedt, C. D.; Grice, K.; Ioppolo-Armanios, M.; Kelly, D.; Gibberd, M. Compound specific carbon and hydrogen stable isotope analyses of volatile organic compounds in various emissions of combustion processes. *Chemosphere* **2012**, *78*, 1407-1413.

(54) Okuda, T.; Kumata, H.; Zakaria, M.P.; Naraoka, H.; Ishiwatari, R.; Takada, H. Source identification of Malaysian atmospheric polycyclic aromatic hydrocarbons nearby forest fires using molecular and isotopic compositions. *Atmos. Environ.* **2002,** *36*, 611-618.

(55) McRae, C.; Snape, C. E.; Fallick, A. E. Variations in the stable ratios of specific aromatic and aliphatic hydrocarbons from coal conversion processes. *Analyst* **1998***, 123,* 1519-1523.

(56) Chen, Y. J.; Cai, W. W.; Huang, G. P.; Li, J.; Zhang, G. Stable Carbon Isotope of Black Carbon from Typical Emission Sources in China. *Environ. Sci.* **2012**, *33,* 673-678 (in Chinese).

(57) Kawashima, H.; Haneishi, Y. Effects of combustion emissions from the Eurasian continent in winter on seasonal $\delta^{13}C$ of elemental carbon in aerosols in Japan. *Atmos. Environ.* **2012,** *46,* 568-579.

(58) Redding, C. E.; Schoell, M.; Monin, J. C.; Durand, B. Hydrogen and carbon isotopic composition of coals and kerogens. *Phys. Chem. Earth* **1980**, *12*, 711-723.

(59) Gleason, J. D. and Kyser, T. K. Stable isotope compositions of gases and vegetation near naturally burning coal. *Nature* **1984**, *307*, 254-257.

(60) Mastalerz, M. and A. Schimmelmann. Isotopically exchangeable organic hydrogen in coal relates to thermal maturity and maceral composition. *Org. Geochem.* **2002***, 33,* 921-931.

(61) Jedrysek, M-O.; Skrzypek, G. Hydrogen, carbon and sulphur isotope ratios in peat: the role of diagenessis and water regimes in reconstruction of past climates. *Environ. Chem. Lett.* **2005**, *2Q*:179–183, doi: 10.1007/s10311-004-0093-4.

(62) Skrzypek, G.; Paul, D.; Wojtun, B. Stable isotope composition of plants and peat from Arctic mire and geothermal area in Iceland. *Pol. Polar Res.* **2008**, *29 (4),* 365–376.

(63) Seki, O.; Meyers, P. A.; Kawamura, K.; Zheng, Y.; Zhou, W. Hydrogen isotopic ratios of plant wax n-alkanes in a peat bog deposited in northeast China during the last 16 kyr. *Org. Geochem.* **2009**, *40*, 671-677.

(64) Holoubek, I.; Caslavsky, J.; Korinek, P.; Kohoutek, J.; Staffova, K.; Hrdlieka, A.; Pokorny, B.; Vancura, R.; Helesic, J. Project Tocoen. Fate of Selected Organic Compounds in the Environment. Part XXVII. Main Sources, Emission Factors and Input of PAHs in Czech Republic. *Polycyclic Aromatic Compd.* **1996**, *9:1-4,* 151-157.

(65) Plachá, D.; Raclavská, H.; Matýsek, D.; Rümmeli, M. H. The polycyclic aromatic hydrocarbon concentrations in soils in the Region of Valasske Mezirici, the Czech Republic. *Geochem. T.* **2009**, *10:12*, doi: 10.1186/1467-4866-10-12.

(66) Zhang, Y.; Tao, S. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos. Environ.* **2009**, *43*, 812-81.

(67) Bergmann, F. D.; Abu Laban, N. M. F. H.; Meyer, A. H.; Elsner, M.; Meckenstock, R. U. Dual (C, H) isotope fractionation in anaerobic low molecular weight (poly)aromatic hydrocarbon (PAH) degradation: Potential for field studies and mechanistic implications. *Environ. Sci. Technol.* **2011***, 45,* 16, 6947-6953.

(68) *OTE, a.s. Czech electricity and gas market operator.* Website; http://www.ote-cr.cz/

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SUPPORTING INFORMATION AVAILABLE

Table S1. Compilation of literature values for isotopic signatures of primary sources

Table S2. Individual PAH concentrations ($\mu g \cdot g^{-1}$ dry weight) in forest soils from Czech Republic

Table S3. $\delta^{13}C$ values of PAHs in forest soils from Czech Republic

Table S4. $\Delta^{14}C$ values of PAHs in forest soils from Czech Republic

Table S5. $\delta^{2}H$ values of PAHs in forest soils from Czech Republic

Figure S1. Relation between the ratio BaA to BaA + CHRY and the $\delta^{13}C$ values of the "chromatographic window": BaA + CHRY (Panel A) and the ratio BaP to BaP + BeP and the $\delta^{13}C$ values of the "chromatographic window": BaP + BeP (Panel B)

Figure S2. GC/MS chromatograms depicting the different PAH traps from Sample #1 isolated by pcGC

Supplemental Text S1. Experimental section

Supplemental Text S2. Calculation of the isotopic signatures (end members) for the primary PAHs sources

Supplemental Text S3. MATLAB script for the Bayesian calculation

This information is available free of charge via the Internet at http://pubs.acs.org.

Table 1. PAH concentrations and average carbon ($\Delta^{14}C$ and $\delta^{13}C$) and hydrogen ($\delta^{2}H$) values of PAHs in forest soils

Sample ID	Site	Longitude	Latitude	Altitude (m a.s.l.[a])	ΣPAH[b] ($\mu g \cdot g^{-1}$ d.w.[c])	$\delta^{2}H$ (‰)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)
#1	Krušné hory-Červená jáma	13° 27.702’	50° 33.804’	840	7.35	-225.8 ± 4.9	-24.18 ± 0.10	-911 ± 87
#2	Lužické hory-Jedlová	14° 33.035’	50° 51.939’	520	5.52	-116.6 ± 3.4	-24.04 ± 0.17	-897 ± 19
#3	Krkonoše-Pašerácký chodník	15° 45.933’	50° 44.416’	1320	2.61		-24.13 ± 0.14	
#4	Jeseníky-Jelení loučky	17° 15.544’	50° 8.867’	1120	2.49		-23.81 ± 0.20	
#5	Beskydy-Kykulka	18° 26.447’	49° 34.523’	930	9.11	-135.5 ± 23.9	-23.94 ± 0.09	-942 ± 24
#6	Javorníky-Kohútka	18° 12.756’	49° 17.713’	811	5.88	-108.6 ± 3.1	-24.04 ± 0.14	-905 ± 18
#7	Košetice	15° 05.476’	49° 34.231’	495	0.872	-99.3 ± 10.6	-24.13 ± 0.17	-819 ± 14
#8	Novohradské hory-Vysoká	14° 44.141’	48° 42.808’	971	3.81	-112.8 ± 3.1	-24.05 ± 0.26	-884 ± 17
#9	Šumava-Boubín	13° 49.018’	49° 0.026’	1120	0.532		-23.97 ± 0.22	
#10	Český les-Čerchov	12° 46.813’	49° 22.946’	985	4.80	-107.0 ± 3.8	-24.19 ± 0.22	-886 ± 14
				Average±stdev	**4.30 ± 2.77**	**-129.4 ± 44**	**-24.05 ± 0.12**	**-892 ± 37**

[a] above sea level

[b] sum of 14 PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, triphenylene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene

[c] dry weight

Table 2. Isotopic signatures (end members) for the primary PAHs sources[a]

Primary Source/ Isotope (mean±stdev, ‰)	$\delta^{13}C$	δ^2H	$\Delta^{14}C$
C3 plant combustion[b]	-28.7 ± 1.4	-94 ± 3	+137.5 ± 21.9
Liquid fossil fuel combustion[c]	-25.3 ± 1.6	-62 ± 7.3	-1000 ± 0
Coal pyrolysis at low temperature (~650 ºC)[d]	-23.2 ± 1.1	-129 ± 20.8	-1000 ± 0
Coal pyrolysis at high temperature (~900 ºC)[e]	-26.8 ± 1.3	-73.2 ± 4.0	-1000 ± 0

[a] See Table S1 and Text S2 with a literature compilation of isotopic signatures and calculation of the primary PAH sources end members, respectively

[b] $\delta^{13}C$ and δ^2H values for biomass were calculated as the average between PAH-specific and bulk signatures found in the literature. Three and one literature sources were used for $\delta^{13}C$ and δ^2H, respectively. $\Delta^{14}C$ for biomass was calculated assuming equal contributions of fresh biomass (+50‰) and wood (+225‰).

[c] $\delta^{13}C$ and δ^2H values were calculated assuming equal contributions from diesel and gasoline sources. Five and two literature sources were used for $\delta^{13}C$ and δ^2H, respectively.

[d] δ^2H and $\delta^{13}C$ values reported for bulk coal were used as δ^2H-PAH and $\delta^{13}C$-PAH signatures for coal combustion at low temperature assuming that the PAHs derived from carbonization processes at low temperatures have isotopic values similar to those of the parent coals. Seven and three literature sources were used for $\delta^{13}C$ and δ^2H, respectively.

[e] Four and one literature sources were used for $\delta^{13}C$ and δ^2H, respectively.

Table 3. Source contributions of liquid fossil fuel combustion, coal combustion at low and high temperature and biomass combustion for the ΣPAH_{14} in forest soils based on a four-source Bayesian Markov Chain Monte Carlo statistical mass-balance model (mean ± stdev)

Sample ID	$f_{liquid\ fossil\ fuel}$ (%)	$f_{low\ T\ coal}$ (%)	$f_{high\ T\ coal}$ (%)	$f_{biomass}$ (%)	f_{coal} ($f_{low\ T\ coal}$ + $f_{high\ T\ coal}$) (%)	f_{fossil} ($f_{low\ T\ coal}$ + $f_{high\ T\ coal}$ + $f_{liquid\ fossil\ fuel}$) (%)
#1				7.9		92.1
#2	15.4 ± 10.3	62.3 ± 10.4	13.2 ± 9.6	9.1 ± 0.2	75.6 ± 10.3	90.9 ± 17.5
#5	9.6 ± 7.3	75.2 ± 8.8	10.1 ± 7.6	5.1 ± 0.1	85.3 ± 7.3	94.9 ± 13.8
#6	17.4 ± 11.6	59.7 ± 11.2	14.5 ± 11.0	8.4 ± 0.2	74.2 ± 11.6	91.6 ± 19.5
#7	17.9 ± 12.3	53.1 ± 12.1	13.2 ± 10.6	15.9 ± 0.3	66.2 ± 12.5	84.1 ± 20.4
#8	15.3 ± 10.6	61.3 ± 10.5	13.2 ± 9.6	10.2 ± 0.2	74.5 ± 10.6	89.8 ± 17.7
#10	17.7 ± 11.9	56.7 ± 11.4	15.6 ± 11.0	10.0 ± 0.2	72.3 ± 11.9	90.0 ± 19.8
Average	**15.6 ± 3.1**	**61.4 ± 7.6**	**13.3 ± 1.8**	**9.5 ± 3.3**	**74.7 ± 6.2**	**90.2 ± 3.5**

FIGURE CAPTIONS

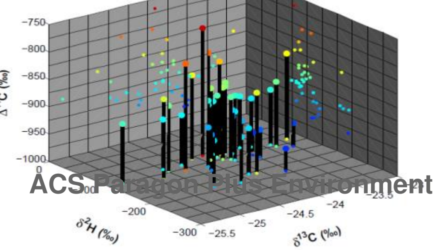
Figure 1. Map depicting bottom-up emission inventory of total 16 PAHs in 2007 (grid 0.1° x 0.1°)[35]. The sampling sites are indicated with white triangles.

Figure 2. Two-dimensional dual-isotope presentation of PAH in forest soils from sites #1 (circles), #5 (diamonds), #6 (triangles) and average of #2, #7, #8 and #10 (squares). Panel (**A**): δ^2H *versus* $\delta^{13}C$, where symbol colors are based on PAH molecular weight: *m/z* 178 (dark blue), *m/z* 202 (light blue), *m/z* 228 (green), *m/z* 252 (yellow and orange), *m/z* 276 (red); Panel (**B**): δ^2H *versus* $\Delta^{14}C$, where symbol colors are based on PAH concentrations. Isotopic signatures of primary sources of PAH are shown: biomass combustion (green), peat (light grey), liquid fossil fuel combustion (black), high temperature coal combustion ("high-T coal", brown) and low temperature coal combustion ("low-T coal", dark grey). Isotopic signatures on primary sources are based on reported literature values (Tables 2 and S1). Abbreviations: phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP).

Figure 3. Probability density functions (pdf) of the relative source contribution of PAHs benzo[b+j+k]fluoranthene for Sample #7 (Panel **A**) and source contributions of fossil (liquid fuel + coal), liquid fossil fuel, coal combustion at low and high temperature and biomass combustion for the sum of PAHs in forest soils from Czech Republic (Panel **B**).

SOURCE APPORTIONMENT OF PAHs

Coal pyrolysis at high temperature (~900 ºC)? **Coal pyrolysis at low temperature (~650 ºC)?**



Liquid fossil fuel combustion? **Biomass combustion?**

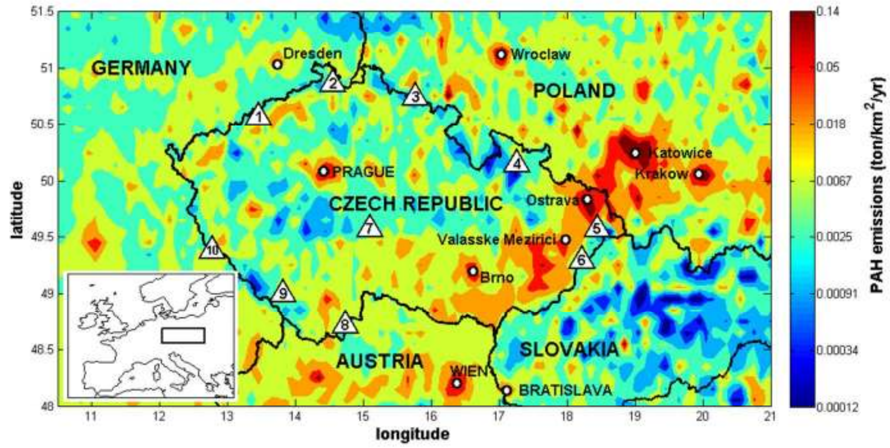


Figure 1. Map depicting bottom-up emission inventory of total 16 PAHs in 2007 (grid 0.1° x 0.1°)35. The sampling sites are indicated with white triangles.
292x164mm (96 x 96 DPI)

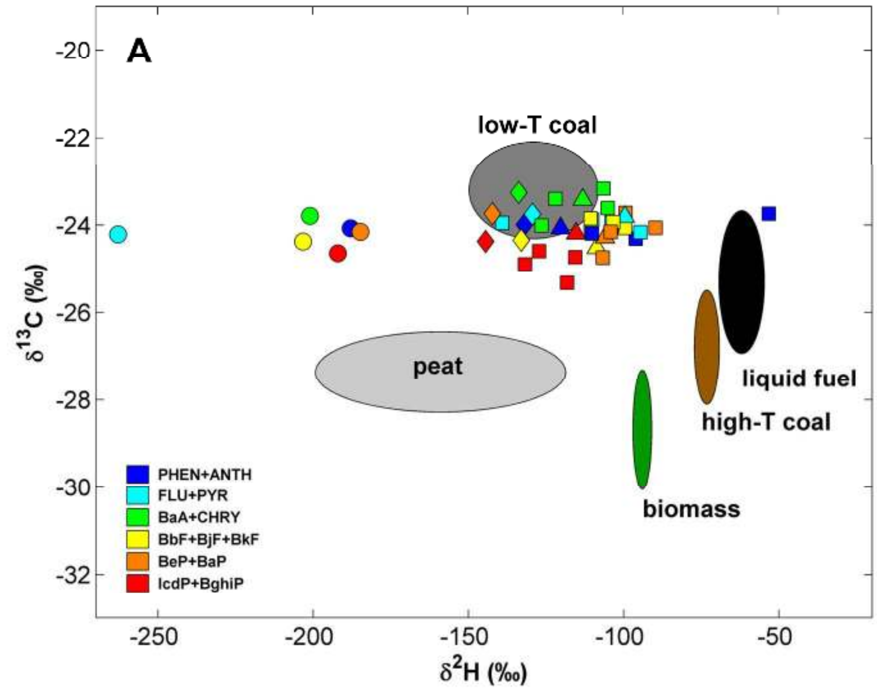
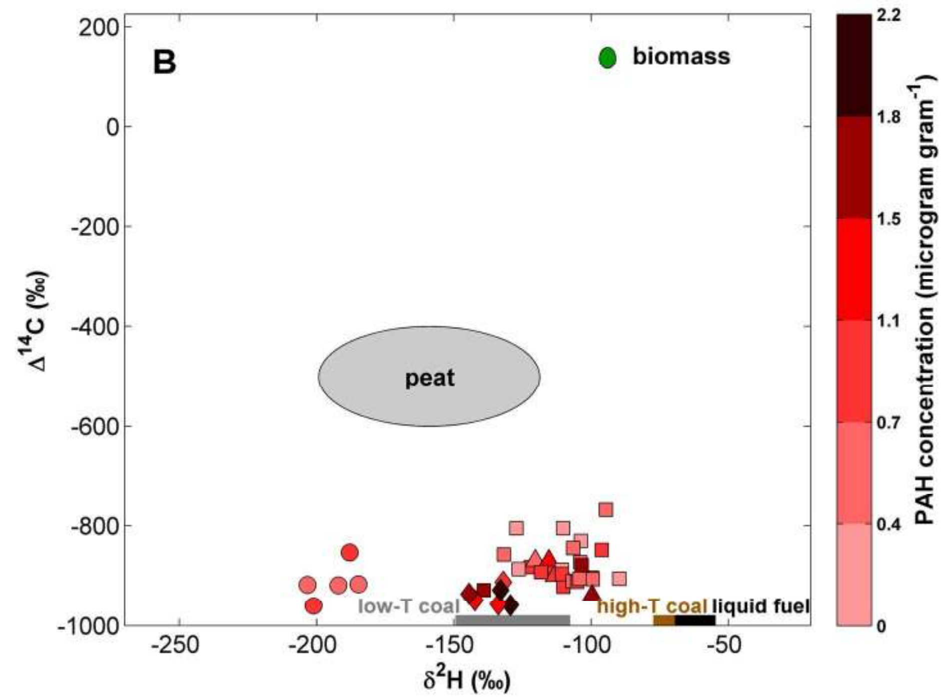


Figure 2. Two-dimensional dual-isotope presentation of PAH in forest soils from sites #1 (circles), #5 (diamonds), #6 (triangles) and average of #2, #7, #8 and #10 (squares). Panel (A): δ2H versus δ13C, where symbol colors are based on PAH molecular weight: m/z 178 (dark blue), m/z 202 (light blue), m/z 228 (green), m/z 252 (yellow and orange), m/z 276 (red); Panel (B): δ2H versus Δ14C, where symbol colors are based on PAH concentrations. Isotopic signatures of primary sources of PAH are shown: biomass combustion (green), peat (light grey), liquid fossil fuel combustion (black), high temperature coal combustion ("high-T coal", brown) and low temperature coal combustion ("low-T coal", dark grey). Isotopic signatures on primary sources are based on reported literature values (Tables 2 and S1). Abbreviations: phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHRY), benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP).
152x114mm (300 x 300 DPI)



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152x114mm (300 x 300 DPI)

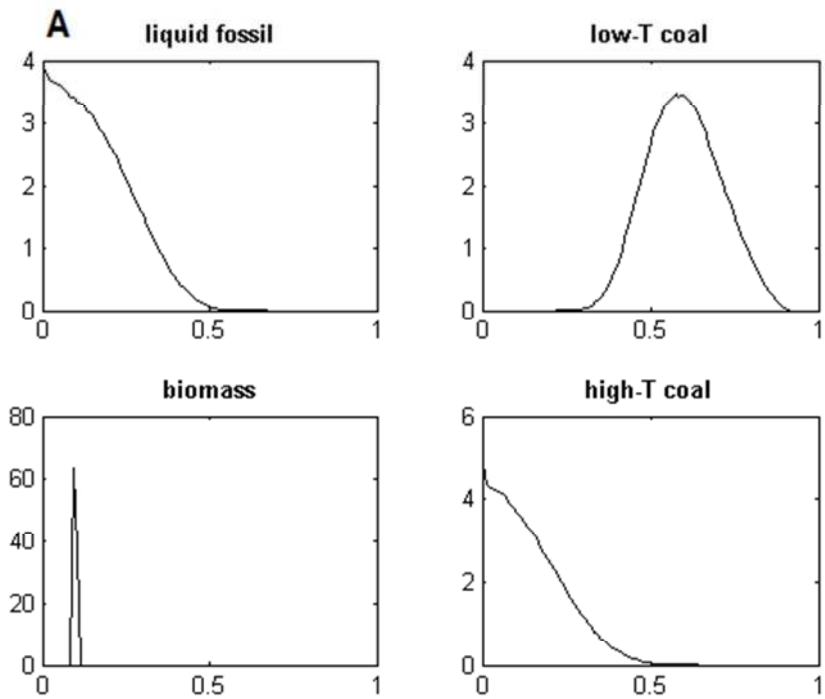

Figure 3. Probability density functions (pdf) of the relative source contribution of PAHs benzo[b+j+k]fluoranthene for Sample #7 (Panel A) and source contributions of fossil (liquid fuel + coal), liquid fossil fuel, coal combustion at low and high temperature and biomass combustion for the sum of PAHs in forest soils from Czech Republic (Panel B).
148x111mm (96 x 96 DPI)

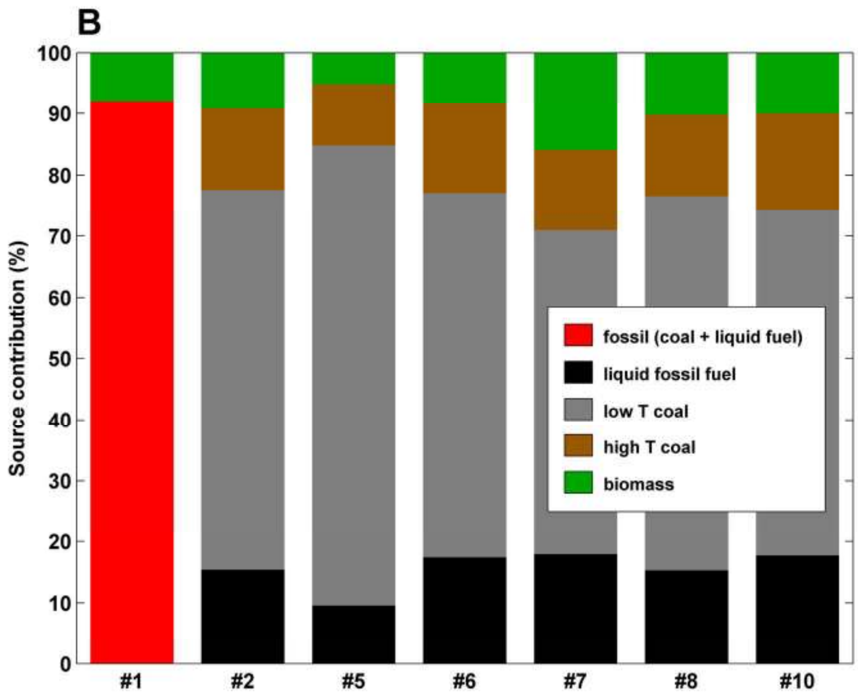

Figure 3. Probability density functions (pdf) of the relative source contribution of PAHs benzo[b+j+k]fluoranthene for Sample #7 (Panel A) and source contributions of fossil (liquid fuel + coal), liquid fossil fuel, coal combustion at low and high temperature and biomass combustion for the sum of PAHs in forest soils from Czech Republic (Panel B).
152x114mm (300 x 300 DPI)