CAN SOURCES OF ENVIRONMENTAL CONTAMINATION WITH PAHS BE IDENTIFIED IN RECIPIENT MATRICES BY CONCOMITANT ANALYSIS OF MOLECULAR MARKERS?

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Introduction

There is a broad range of molecular markers such as hopanes, phytosterols and methylated polycyclic aromatic hydrocarbon (PAH) available for source apportionment of petrogenic and pyrogenic environmental contamination [1-3]. We selected those that are already part of conventional PAH analysis (or could be easily integrated) and applied them to our soil and compost data to see whether source identification is possible in recipient matrices from monitoring studies in combination with PAH analysis. The inconsistent results motivated us to revisit current source literature and examine prevalent characteristic ratios therein. After that, the suitability of the characteristic ratios and selected makers was re-examined in soil and compost data, taking into account possible alterations due to environmental processes.

Materials and Methods

In a first step, characteristic ratios which can be easily included into conventional PAH analysis and allowing to distinguish between: i) petrogenic and pyrogenic origin, ii) different fuels (e.g. gasoline, grass, coal, wood) and iii) traffic and non-traffic sources of PAHs, were selected and commonly suggested numbers/ranges compiled (Table 1, column 1&2). These ratios were applied to PAH emission data collected from the wider literature, i.e. to different soot particles, oil, gasoline etc. (Table 1, column 3&4, n=175, for references see [4]). Differences between the categories were assessed and the data compared with the earlier suggested characteristic ratios. Secondly, ratios were determined in soil[5] (our own earlier data) and source-separated compost[4]. Additional molecular markers suggested for specific sources, i.e. retene (RET) for wood combustion[6], coronene (COR) for traffic sources[7] and perylene (PER) for digenetic origin[8] of PAHs were included. Less established markers (4-H-cylcopenta(*def*)phenanthrene (cPHE) as pyrogenic marker[9] and cyclopenta(*cd*)pyrene (cPYR) for woodburning[2] and/or vehicle emission[10]) were also assigned. If comparing emission ratios with ratios in recipient matrices (e.g. soil and compost), it has to be considered that they could be altered compared to source data due to environmental fractionation and/or possible degradation. Therefore, as a third step, factors accounting for these processes suggested by Zhang et al.[11] were applied to our soil data converting it back to ratios at the source. Degradation/evaporation during composting as well as processes between emission and aerial deposition of PAHs on input material for compositing (presumably the main input pathway to compost) can alter ratios and molecular markers as well. As a fourth step, results obtained from a full-scale composting study[12] and factors accounting for discriminating processes in air[11] were applied to ratios in compost.

Results and Discussion

Anthracene/(Anthracene&Phenanthrene) (ANT/(ANT&PHE))

Although there was a significant difference between ANT/(ANT&PHE) ratios in sources originating from petrogenic and pyrogenic processes in the literature (Table 1, column 3&4), 41% of the values referring to petrogenic origin were above 0.1, which is the current threshold value. This indicates that the discrimination limit is probably too low, as suggested before[13]. According to the ANT/(ANT&PHE) ratio, 90% of the soil and 50% of the compost samples would be dominated by petrogenic origin of PAHs, which is not plausible for the data from Switzerland. After converting soil ratios back to emission ratios, the "petrogenicity" of the data was even more pronounced. ANT/(ANT&PHE) ratios are likely to increase during composting[12] which would, together with conversion, result in high domination of petrogenic PAHs. Overall, we judge this marker as not applicable to monitoring studies.

Benzo(a)anthracene/(Benzo(a)anthracene&Chrysene) (BaA/(BaA&CHR))

As for ANT/(ANT&PHE), BaA/(BaA&CHR) ratios differed significantly in petrogenic and pyrogenic data from the literature. Again more than 45% of the ratios derived from petrogenic matrices were above 0.35, which is the prevalent range characteristic for combustion (Table 1). Even before conversion, BaA/(BaA&CHR) ratios in soil and compost pointed to combustion as a source for PAHs. After conversion, all ratios were above 0.35. This goes in line with the situation in Switzerland, where pollution of soil and compost due to petrogenic sources is marginal.

Ambient levels and trends

Together with the fact that this ratio was more or less stable during composting, it may be more trustworthy then ANT/(ANT&PHE).

Fluoranthene/(Fluoranthene&Pyrene) (FLT/(FLT&PYR))

Ratios of FLT/(FLT&PYR) in matrices originating from combustion were significantly higher than ratios from petrogenic sources (Table 1, Column 3&4). The median of the petrogenic ratios was clearly below the discrimination limit (0.4), suggesting this marker to be suitable for emission source apportionment. The differentiation between fuel and grass/wood/coal combustion could be verified in the literature data. FLT/(FLT&PYR) ratios in soil and compost pointed to grass/wood/coal combustion, whereas conversion shifted them more to fuel combustion, which seems reasonable for the situation in Switzerland. Ratios were slightly higher in compost than in soil, which could point to some PAH input to compost by wood ash. The ratio was stable during composting[12]. In summary, once transformed[11], this ratio seems to preserve its source diagnostic capacity from emission sources to recipient matrices.

Indeno(1,2,3,c,d)pyrene/(Indeno(1,2,3,c,d)pyrene&Benzo(g,h,i)peryleno) (IPY/(IPY&BPE))

More than 50% of the petrogenic literature ratios of IPY/(IPY&BPE) were above 0.2 (Table 1, column 3&4), which was suggested to be characteristic for PAHs originating from pyrogenic processes (Table 1, column 1&2). This indicates that the discrimination level may be too low. The median of the IPY/(IPY&BPE) ratios from wood combustion was above 0.5, however almost 70% of the ratios from coal burning were between 0.2 and 0.5, which is supposed to be characteristic for fuel combustion. It is concluded that IPY/(IPY&BPE) differentiated well between wood and fuel but not between coal and fuel combustion. Median IPY/(IPY&BPE) ratios in soil and compost were 0.5, which marks the limit between fuel and grass/wood/coal combustion. After conversion ratios shifted more to the grass/wood/coal combustion, contradicting with the findings of converted FLT/(FLT&PYR) ratios and the situation in Switzerland, where fuel combustion may be an important PAH source. IPY/(IPY&BPE) ratios were stable during composting[12]. To this end, FLT/(FLT&PYR) appears to provide the more plausible source apportionment.

CombustionPAHs/Σ16PAH (ComPAH/16PAH)

ComPAHs (sum of FLT, PYR, BaA, CHR, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene (not included here), BaP, IPY, and BPE)/16PAH ratios of petrogenic literature data were clearly below the prevailing limit (0.3) differentiating for petrogenic origin of PAHs (Table 1, column 3&4). However, most combustion derived ratios were only slightly above 0.3 and most of them were below the prevalent limit identifying combustion (0.7; Table 1, column 1&2). Ratios in soil and compost clearly identified combustion as the source of PAHs, even though this ratio may be increasing during composting[14]. The problem with this marker may be that the lighter PAHs are gasing out, leading to over-interpretation of pyrogenitcity if the main source was petrogenic, or visa versa, in cold and/or remote areas.

(MethylPHE&ANT)/PHE and (MethylFLT&PYR)/PYR ((MePHE&ANT)/PHE and (MeFLT&PYR)/PYR)

MePHE&ANT)/PHE and (MeFLT&PYR)/PYR ratios pointed to pyrogenic origin of PAHs (Table 1, column l&2) in soil and compost (Table 1), which is in line with the above findings. The development of conversion factors is probably not feasible since this ratio uses sums of methylated isomers with varying individual chemico-physical properties. (MeFLT&PYR)/PYR ratios were found to be stable during composting, whereas (MePHE&ANT)/PHE varied[12], rendering source apportionment with the latter problematic.

1,7- DimethylPHE/(1,7-DimethylPHE&2,6-DimethylPHE) (1,7-/(1,7&2,6)-DimePHE)

1,7-/(1,7&2,6)DimePHE ratios in soil and compost were never below 0.45, which would be characteristic for vehicle emissions (Table 1, column 5&7). One out of 23 soil and five out of 69 compost samples had 1,7-/(1,7&2.6)DimePHE ratios above 0.7 pointing to wood combustion. Only one (compost) sample's FLT/(FLT&PYR) and IPY/(IPY&BPE) ratios were after conversion not above 0.5, which confirmed wood combustion. 1,7-/(1,7&2.6)DimePHE ratio seemed to be stable during composting[12].

Retene/(Retene&Chrysene) (RET/(RET&CHR))

RET/(RET&CHR) ratios in soil were lower (median: 0.04, Table 1) than in compost (median: 0.19). This might be explained by small amounts of wood ash present in compost as indicated by FLT/(FLT&PYR) ratios. However, ratios in soil and compost were clearly below 0.5, identifying fuel combustion as the major PAH source. This contradicts with findings for IPY/(IPY&BPE) and FLT/(FLT&PYR). However, RET can also have petrogenic sources[14]. Together with varying ratios during composting[12], source apportionment is hampered.

Perylene/Σ16 PAH (PER/16PAH)

PER/16PAH ratios suggested only limited diagenic origin of PAH in soil and compost (Table 1, ratios >0.02). However, there is the possibility that PER is formed during organic matter degradation[15] and that it may also have

anthropogenic sources[14]. Combined with the in- and de-creasing concentrations during composting[12], source apportionment applying this marker is problematic.

Benzo(a)pyrene/ Benzo(g,h,i)perylene (BaP/BPE)
There was a significant difference of the BaP/BPE ratios in matrices from traffic and non-traffic origin (Table 1, column 3&4). However, almost 50% of the ratios from traffic sources were lower than 0.6, generally identifying non-traffic PAHs. This limit may need to be reconsidered. Before and even more after conversion BaP/BPE ratios in soil and compost pointed to traffic as the main PAH source, which is an important but not the only source in Switzerland and contradicts with findings for 1,7-/(1,7&2,6)DimePHE. Additionally, this ratio was found to vary during composting[12], and is therefore considered as not suitable for source apportionment in our data.

Coronene/Σ16 PAH (COR/16PAH)
Median COR/16PAHs ratio in soil was 0.02, whereas in Swiss compost it was slightly higher (Table 1, median: 0.03). A possible explanation may be higher contribution of vehicle exhaust in compost compared to soil. Increases of COR/16PAH ratios during composting were observed[12], due to decreasing levels of light PAHs, which calls for a correction factor.

4-H Cyclopenta(def)PHE/ Σ16 PAH (cPHE/16PAH) and Cyclopenta(cd)PYR/ Σ 16PAHs (cPYR/16PAH)
CPHE/16PAHs ratios in Swiss soil were in the same range as in compost (Table 1, column 5&7). During composting a decrease of the ratio was observed[12]. Further research at the source level as well as describing environmental processes is needed to verify if this marker is a suitable pyrogenic tracer. CPYR/16PAH in soil were slightly higher than in compost (Table 1, column 5&7), suggesting that wood and/or traffic combustion contributed more to the PAH concentrations in soil than in compost. This contradicts with findings for COR/16PAH and RET/(RET&CHR). However, the decreasing cPYR/16PAH ratios during composting[12] may account for the difference. However, this still not proves this ratio to be suitable for soil and further research is needed at sources.

Synopsis
Even though for most ratios there was a significant difference between i) petrogenic and pyrogenic ii) fuel and grass/coal/wood combustion and iii) traffic and non-traffic sources, some discrimination levels seemed not to be determined well. Conversion factors accounting for environmental fractionation and possible degradation between sources and recipient matrices seemed to be useful for refined interpretation of the data. However, further research is needed to optimise these factors and to account for other processes.

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Table 1: Characteristic ratios and molecular markers in the emission literature, in soil[5] and compost (own data)

	petrogenic[a]	pyrogenic[a]	petrogenic lit[b]	pyrogenic lit[b]	Swiss soil[c]	soil con[c,d]	Swiss compost[e]	compost con[f]
ANT/(ANT&PHE)	<0.1 [g]	>0.1 [g]	0.04* (0;0.69;53)	0.16* (0;1;139)	0.06 (0.03;0.14)	0.03 (0.02;0.08)	0.10 (0.05;0.19)	<; 0.05 (0.03;0.10)
BaA/(BaA&CHR)	<0.2 [g]	>0.35 [g]	0.34* (0;1;48)	0.44* (0;1;139)	0.36 (0.28;0.45)	0.55 (0.46;0.64)	0.42 (0.27;0.5)	=; 0.55 (0.39;0.63)
FLT/(FLT&PYR)	<0.4 [g]	>0.4 [g]	0.24* (0;0.87;52)	0.53*(0.02;1;139)	0.56 (0.54; 0.63)	0.45 (0.43;0.53)	0.60 (0.45;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	<0.2 [g]	>0.2 [g]	0.22* (0;1;44)	0.48* (0;1;130)	0.51 (0.45;0.54)	0.58 (0.52;0.68)	0.50 (0.44;0.61)	=; 0.58 (0.46;0.63)
ComPAHs/16PAH	0.3 [g]	0.7 [g]	0.07* (0;0.97;53)	0.45* (0;0.98;66)	0.84 (0.57;0.90)	na[h]	0.87 (0.43;0.96)	<; na[h]
(MePHE&ANT)/PHE	5 [g]	0.5 [g]	na	na	0.42 (0.25;0.66)	na[h]	0.47 (0.22;3.07)	>/<; na[h]
(MeFLT&PYR)/PYR	4 [g]	0.3 [g]	na	na	0.43 (0.35;0.53)	na[h]	0.37 (0.23;0.75)	=; na[h]
1,7-/(1,7&2.6)DimePHE	0.45-0.7 [g,i]	<0.45 or 0.7-0.9 [g]	na	na	0.62 (0.60;0.80)	na[h]	0.63 (0.50;0.76)	=; na[h]
	fuel combustion	**biomass combustion[k]**	**fuel combustion lit[a]**	**coal/wood combustion lit[a]**				
FLT/(FLT&PYR)	0.4-0.5 [g]	>0.5 [g]	0.49* (0.14;0.87;46)	0.56* (0.02;1;90)	0.56 (0.54;0.63)	0.45 (0.43;0.53)	0.6 (0.43;0.75)	=; 0.47 (0.31;0.64)
IPY/(IPY&BPE)	0.2-0.5 [g]	>0.5 [g]	0.44 (0; 0.89; 41)	0.5 (0;1;86)	0.51 (0.45;0.54)	0.58 (0.52;0.68)	0.5 (0.44;0.61)	=; 0.582 (0.46;0.63)
RET/(RET&CHR)	0.15-0.5 [l]	0.83 [k]/0.96 [l,m]	na	na	0.04 (0.01;0.44)	na[h]	0.19 (0.03;0.54)	>/=; na[h]
1,7-/(1,7&2.6)DimePHE	<0.45 [n]	0.7-0.9 [m]	na	na	0.62 (0.60;0.80)	na[h]		=; na[h]
	diagenetic	**pyrogenic**						
PER/16PAH	>0.05 [o]	<0.05 [o]	na	na	0.02 (0;0.48)[p]	na[h]	0.02 (0, 0.06)	>/<; na[h]
	non-traffic	**traffic**	**non-traffic lit[a]**	**traffic lit[a]**				
BaP/BPE	<0.6 [g]	>0.6 [g]	1.07* (0;7.7;89)	0.6* (0;7;35)	0.84 (0.57;0.09)	3.74 (1.58;5.94)	0.90 (0.53;1.4)	>/<; 1.50 (0.89;2.34)
1,7-/(1,7&2.6)DimePHE	>0.45 [g]	<0.45 [g]	na	na		na[h]		=; na[h]
Markers								
COR/16PAHs	vehicle exhaust [g]				0.02 (0.01;0.07)	na[h]	0.03 (0.003;0.12)	</=; na[h]
cPHE/16PAH	pyrogenic marker[q]				0.009 (0;0.037)[p]	na[h]	0.01 (0;0.02)	>; na[h]
cPYR/16PAH	wood or traffic marker [r]				0.010 (0;0.092)[p]	na[h]	0.003 (0;0.017)	>; na[h]

a) prevalent discrimination levels, b) literature data, median (min, max, n), c) median (min, max) n=23, d) applying conversion factor for soil suggested by[11], e) median (min, max) n=69, Dibenzo(a,h)anthracene was not determined, instead of Σ16PAHs it is referred to Σ15PAHs f) quantitative alteration during composting[12], < increase, =stable and >decrease during composting, respectively; ratios applying conversion factor for air particles suggested by [11], g) characteristic ratios according to Ref [5] and references therein, h) conversion factor not available, i) also mixed combustion sources, k) grass/coal/wood combustion, l)[16], m) softwood combustion, n) vehicle emission, o)[8], p) own unpublished data (n=87), q) [9], r) [2], Abbreviations: Anthracene (ANT), Phenanthrene (PHE), Benzo(a)anthracene (BaA); Chrysene (CHR); Fluoranthene (FLU), Pyrene (PYR), Indeno(1,2,3,c,d)pyrene (IPY), Benzo(g,h,i)perylene (BPE), Com PAHs (sum of FLT, PYR, BaA, CHR, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene (BaP), IPY, BPE), methylated (Me), dimethylated (dime), Retene (RET), Perylene (PER), Coronene (COR), 4-H CyclopentaPHE (cPHE), Cyclopenta(cd)PYR (cPYR), *significant difference on a 95% level applying the Mann-Whitney-U-Test [10]