Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool.

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Capsule

“PAHs molecular diagnostic ratios which change greatly as a function of distance from the emitting source are improper for source identification purposes.”

Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) molecular diagnostic ratios (MDRs) are unitless concentration ratios of pair-PAHs with the same molecular weight (MW); MDRs have long been used as a tool for PAHs source identification purposes. In the present paper, the efficiency of the MDR methodology is evaluated through the use of a multimedia fate model, the calculation of characteristic travel distances (CTD) and the estimation of air concentrations for individual PAHs as a function of distance from an initial point source. The results show that PAHs with the same MW are sometimes characterized by substantially different CTDs and therefore their air concentrations and hence MDRs are predicted to change as the distance from the original source increases. From the assessed pair-PAHs, the biggest CTD difference is seen for fluoranthene (107
km) vs pyrene (26 km). This study provides a strong indication that MDRs are of limited use as a source identification tool.

Keywords: PAHs, molecular diagnostic ratio, characteristic travel distance, long range transport, fate, source identification.
Introduction

Polycyclic aromatic hydrocarbons (PAHs, or polynuclear aromatic hydrocarbons) are mutagenic organic substances emitted from a variety of anthropogenic sources, mainly as a result of incomplete combustion or pyrolysis of organic material. Such sources include space heating activities, vehicles emissions, industrial activities, almost any combustion process, but also natural emissions (volcanoes, biogenic formation etc.) (Nikolaou et al., 1984; Manoli et al., 2004; Galarneau et al., 2008; Zhang and Tao, 2009; Ratola et al., 2011; Cristale et al., 2012). The large number of sources and the rates and frequency of emissions are said to amount globally to >500 Gg of PAHs, annually (Zhang and Tao, 2009). The aforementioned number of individual sources suggests that the PAHs that occur in the environment are not the result of a single emitting source/episode, but rather a blend of emissions from various sources, characterized by spatial and temporal differences and differences in strength and duration. Especially the seasonality of PAHs emissions is a well demonstrated fact, observed in most monitoring studies, where PAHs air concentrations in winter are much higher than their respective in the summer, due to seasonally variable emission sources like space heating, or cold engine start of vehicles etc. (Cincinelli et al., 2003; Katsoyiannis et al., 2012; Martellini et al., 2012; Tobiszewski and Namiesnik, 2012); nevertheless, the opposite behavior has also been reported (Ohura et al., 2004; Melymuk et al., 2012).

The atmospheric blending of PAHs from different sources makes their source identification a very difficult and challenging task. Various techniques have been proposed as ideal source identification (or apportionment) tools, and much debate exists in scientific literature about the effectiveness of the proposed methodologies. The most common methodology is the use of molecular diagnostic ratios (MDRs), which due to its simplicity is preferred by the vast majority of scientists (e.g., Yunker et al., 2002; Cai et al., 2007; Dai et al., 2007; Usenko et al., 2010);
Tobiszewski and Namiesnik, 2012). The MDRs are unitless concentration ratios of specific individual pair-PAHs (usually of the same molecular weight), and the MDR source identification theory/methodology is based on the assumption that each specific PAHs emitting source will always release individual PAHs at the same ratios. Another assumption of the MDR theory is that PAHs of the same MW will have a similar environmental fate, therefore the concentration ratio of PAH A against PAH B will always remain constant during their entire environmental lifespan. Then, it is claimed by various authors that the MDR value can be used in order to differentiate PAHs originating from a pyrogenic or petrogenic source, or PAHs that derive from fuel vs grass, or coal, or wood combustion, PAHs that come from traffic, fresh PAHs emissions etc. The main ratios used in order to give insight about the responsible sources are given in Table 1.

The efficiency of MDRs as a source identification tool has been questioned by various authors who expressed their concerns about the problems associated with the MDRs methodology. Zhang et al., (2005) used a multimedia fate model to show that MDRs will not be constant “en route from source to receptors”. They also demonstrated that for one specific source, the resulting MDRs at various environmental compartments will not be similar to one another and also proposed factors and ways to “correct” the calculated MDRs. Katsoyiannis et al., (2007), commenting on the use of MDRs for sewage sludge PAHs, suggested that the blending of different-sources-originated PAHs that takes place during the entire wastewater treatment process makes the source understanding unfeasible. Galarneau (2008) used theoretical calculations and simple models to further suggest that even the same sources are not always characterized by the same PAHs emissions profile, or that between different sources there is significant overlapping in MDRs. Dvorska et al., (2011) and Katsoyiannis et al., (2011) used long series of air concentrations and emission inventories to demonstrate that PAHs MDRs are not efficient neither
in depicting the real source, nor in capturing different emission signals. Additionally, Alam et al., (2013) used targeted air sampling to assess the efficiency of MDRs and concluded that from the examined MDRs, only the ratios between heavier PAHs should be further exploited, yet this should always take place with caution. Finally, various studies have presented differences in the reactivity of pair isomer PAHs, supporting indirectly the criticism to MDRs (Perraudin et al., 2005; Esteve et al., 2006).

In a further attempt to assess the MDRs efficiency and robustness, the present study takes into account differences in long-range atmospheric transport (LRT) potential as expressed by the characteristic travel distance (CTD) of individual chemicals in order to estimate the PAHs air concentrations at various distances from an emission source. MDRs are then estimated at various distances from the initial point and the resulting MDR-interpretations are compared. To the best of the author’s knowledge, this is the first scientific paper that tries to quantify the extent to which MDRs are altered as a function of distance from the source. It is expected that our findings could be of interest to all scientists who are interested in applying MDRs, especially in cases where the environmental sampling takes place at remote sites.

Materials and Methods

MDR calculations

As seen in Table 1, the MDRs are easy to calculate, as the only required information are the concentrations of each individual PAH. In monitoring studies, the concentrations are measured by means of chemical analysis, however for a modeling study, a way to estimate the air concentrations at various distances from the emitting source is needed. To address this necessity, and in order to consequently evaluate the impact that differences in environmental fate of individual PAHs can have on MDRs, the parameter of the characteristic travel distance (CTD, or
$L_A$) of chemicals is used. CTD is defined as the distance over which the initial air concentration of a chemical is reduced to $1/e$ (~37%) (Bennett et al., 1998, Beyer et al., 2000, 2003; Breivik et al., 2006). One advantage of using the CTD approach is that the $L_A$ value (in meters) is independent from the chemicals initial concentration, or emission rate.

In a simple form, CTD can be calculated from the Equation 1.

$$L_A = \frac{u \cdot M_A}{[N_{RA} + N_{AS} - N_{SA}]}$$

(1)

where $u$ is the wind speed (m h$^{-1}$), $M_A$ is the amount of chemical in the atmosphere (moles), $N_{RA}$ is the rate of atmospheric reaction (mol h$^{-1}$), $N_{AS}$ is the flux of chemical from the atmosphere to the surface (mol h$^{-1}$) and $N_{SA}$ is the opposite flux from the surface to the atmosphere (mol h$^{-1}$).

After $L_A$ is calculated, then the air concentrations of the chemical of interest can be calculated through Equation 2.

$$C(x) = C_0 \cdot e^{-x/L_A}$$

(2)

where, $C(x)$ is the concentration of the chemical at a distance “$x$” from the emission point, $C_0$ is the initial concentration of the chemical at the point of the emission (distance is 0 km) and $L_A$ is the characteristic travel distance of the chemical.

To calculate the parameters of Equation 1 (except from the wind speed), the Level III (LIII) model (e.g. Mackay, 2001 and references therein) was used. The model software was downloaded from the Trent University, Canada, website: [http://www.trentu.ca/academic/aminss/envmodel/models/VBL3.html](http://www.trentu.ca/academic/aminss/envmodel/models/VBL3.html). The LIII model is a fugacity-based non-equilibrium, steady-state multimedia mass balance model. It estimates the mass balances for four environmental compartments, namely air, water, soil and sediment.

Equilibrium is assumed within each compartment, but not between compartments. The LIII model was selected for this work because it is well documented, transparent, readily available and simple to operate. The LIII model has furthermore been widely tested and used and is often
at the core of more complex environmental fate models (e.g. Arnot et al., 2006; Cowan-Ellsberry et al., 2009). The LIII was also among the various models evaluated in the study of Fenner et al. (2005) where it was found to compare favorably with other examined models.

In order to apply the LIII model, the user needs to specify (i) the environmental and climatic characteristics of the study area, (ii) key physical-chemical properties and environmental half-lives of the chemical in question in all four compartments, and (iii) an emission rate (Mackay and Paterson, 1991). For a detailed account of the LIII model, we refer to the landmark textbook by Mackay (2001).

**Assumptions and model input parameters**

For a consistent estimation of PAHs $L_A$, it is desirable to use consistent physical – chemical properties. Various publications report PAHs properties (e.g. Brubaker and Hites, 1998; Paasivirta et al., 1999; Ma et al., 2010; Wang et al., 2013), and several websites have publicly available PAHs properties datasets. However none reports all the properties that are required by the LIII model estimated for all PAHs. We have therefore used empirical physical-chemical properties (internally consistently), supplemented with data on environmental half-lives, mostly derived from the US-EPA EPI Suite software (EPIWIN Version. 4.1, http://www.epa.gov/opptintr/exposure/pubs/episitedl.htm). The properties used are summarized in Table 2. Water solubility, vapor pressure and log $K_{ow}$ values were taken from the comprehensive analysis by Ma et al. (2010) who reviewed more than 200 publications reporting physical-chemical property data for PAHs. In this study, Ma et al. initially derived so-called literature derived values (LDVs) based on all empirical data published to date, and adjusted them for each compound in order to conform to thermodynamic relationships. The latter finally adjusted values (FAVs) are the primary physical-chemical properties used in the present exercise (Set A), while the initial LDVs were additionally explored for a sensitivity analysis (Set B).
It was further assumed that the exercise took place in Norway and as such the parameters reflecting environmental and climatic conditions used by Katsoyiannis et al. (2013) were selected. These model input parameters are shown in Table S1 (Supporting information). Otherwise, the default values supplied with the LIII model were used. Finally, this exercise represents a simplified condition where we assume primary emissions of individual PAHs occur to air only. This is done in order to evaluate the applicability of various MDRs under the simplest possible conditions.

**Results and discussion**

*Calculation of CTDs*

Table 3 presents the calculated CTDs of the PAHs of interest, for the two datasets used. When derived on the basis of FAVs (Set A), we can see that pair PAHs exhibit much different CTDs, with this difference being up to a factor of four, as in the case of FLT (107 km) against PYR (26.1 km). For the pair ANT vs PHE the difference is also quite substantial (factor of three), while for the pairs IPY vs BPE and BaP vs BPE the calculated CTDs differed at around 20% (26.9 and 22.3 km for IPY and BPE respectively, and 27.2 and 22.3 km, for BaP and BPE, respectively). The only pair of PAHs exhibiting similar CTDs was BaA and CHR, with 26.5 and 26.6 km, respectively. As mentioned, CTD denotes the distance over which the initial air concentration of a chemical is reduced by ~63% and therefore, two chemicals which are emitted at a constant ratio (e.g. 1:1) but have different CTDs, after their emission and environmental transport, their concentrations could be much different than the initial 1:1. Consequently, whenever CTDs are different for pairs of PAHs, their MDRs will also change with increasing distances from a source. As PAHs are able to travel over long distances (Halsall et al., 2001), source apportionment based on MDRs for pairs of PAHs with divergent CTDs could therefore be
problematic. It is therefore important to further explore if differences in characteristic travel
distances for selected PAHs will impact MDRs to such an extent that interpretation of these ratios
could lead to flawed conclusions concerning the responsible sources. In the following paragraphs,
estimated MDRs for various distances from the initial point of release and based on
concentrations calculated from Equation 2 are presented and discussed.

MDR calculations as a function of distance

Anthracene vs Phenanthrene

The ratio ANT/(ANT+PHE) has been suggested as an indicator of petrogenic against pyrogenic
sources (Table 1). This ratio has been criticized in the past (Katsoyiannis et al., 2011; Alam et al.,
2013) because of the fact that ANT is more reactive than PHE, and therefore their environmental
fate is much different. The ratio ANT/(ANT+PHE) is therefore anticipated to change
significantly with increasing distance from a given source. Figure 1a presents the trends for the
ANT/(ANT+PHE) ratio, calculated assuming an initial arbitrary MDR of 0.15. This value would
if measured in the field be attributed to emissions from combustion processes (pyrogenic),
according to the explanation given in Table 1. It can be seen that if sampling takes place at a
distance of ~30 km (practically, within one big city), the same ratio will be <0.10, suggesting a
shift to a predominant influence by a petrogenic source. It is thus evident that comparing
differences in CTD between ANT and PHE may provide useful information on the merit and
limitations of the MDR as a function of distance from a given source.

Benzo[a]anthracene vs Chrysene

The BaA/(BaA+CHR) ratio is supposedly able to discriminate between the same sources as
ANT/(ANT+PHE). A value below 0.20 suggests petrogenic emissions, while a value > 0.35
indicates combustion (pyrogenic emissions). It is assumed again that the initial arbitrary ratio of concentrations falls into the pyrogenic area (0.40). From Figure 1b, it can be seen that the BaA/(BaA+CHR) ratio is not changing significantly over distance, especially when compared to the aforementioned ANT/(ANT+PHE) MDR. In fact, the initial ratio of 0.40 will continue being >0.35 (cut off limit for Pyrogenic emissions) even after 1000 km, which means that the model suggests this can be considered a robust MDR. However, this result is not surprising as some of the key input data for these two PAHs are very similar and in some cases even identical, such as the half-lives in air provided by EPIWIN (Table 2). In the present study, the calculations were all undertaken assuming an ambient temperature of 25°C. Beyer et al., (2003) have previously estimated CTDs for BaA and CHR at different temperatures (0°C, 5°C, and up to 30°C). While they also found that BaA and CHR CTDs would be similar at 25°C, they reported that the predicted CTD of CHR would be twice that of BaA at a temperature of 15°C. If their CTDs at 15°C were used in Equation 2 instead of the values presented in Table 3, it becomes immediately evident that also this MDR should be used with caution. Furthermore, this example also illustrates that environmental and climatic conditions different to the conditions assumed herein are expected to have an impact on the numerical results.

Fluoranthene vs Pyrene

FLT/(FLT+PYR) can also according to the MDRs methodology differentiate between petro- and pyrogenic sources (<0.40 and >0.40, respectively), but can also give insight on whether the pyrogenic emissions are due to fuel combustion (0.4-0.5), or due to combustion of other materials (>0.50). To examine the stability of this MDR, an arbitrary initial value of 0.30 was assumed. The trend is presented in Figure 1c and it is seen that this ratio within less than 20 km has increased to >0.40 and the interpretation has changed from petro- to pyrogenic sources (fuel
Moving further away from the source (30 km), the interpretation changes again from fuel combustion to grass/coal and wood combustion. It is evident that if a monitoring campaign is applied in a trajectory in the same direction as the prevalent wind (e.g., during one sampling period), it is possible that all samples will capture PAHs emitted from the same sources, though, source identification based on MDRs for air samples collected at various distances from the source will provide all three different explanations.

**Indeno[1,2,3-cd]Pyrene vs Benzo[g,h,i]Perylene**

The IPY/(IPY+BPE) ratio is said to offer similar interpretations to FLT/(FLT+PYR). Its trends are presented in Figure 1d, assuming an initial ratio of 0.15. It can be seen that the IPY/(IPY+BPE) ratio is also changing over distance, however at a lower rate than (FLT/FLT+PYR). Again, any inferences about the source on the basis of the calculated IPY/(IPY+BPE) ratios are increasingly at risk of making mistakes as the distance from the primary source increases because of differences in the CTD between the two species considered (Table 3).

From Table 1, one will see that these four MDRs so far discussed can be used to differentiate between petrogenic or pyrogenic sources with the higher values (of all four MDRs) being associated with pyrogenic sources. From our modeling results, it can be seen that as the distance from the source increases (Figures 1a-d), one MDR [(ANT/(ANT+PHE)] has decreasing trends, one remains practically constant [BaA/(BaA+CHR)] and the other two MDRs [FLT/(FLT+PYR) and IPY/(IPY+BPE)] have increasing trends. It is therefore apparent that attempts to interpret PAH sources based on all four MDRs “in concert” are increasingly at risk of failing as the distance from the source increases. Nevertheless, our results also indicate that it could be feasible to identify a petrogenic source if samples are collected in close proximity. Still, as the results
presented are initialized using arbitrary selected MDRs at zero distance, we caution that the
distances discussed in these hypothetical examples should not be used to elucidate a potential
domain of applicability for individual MDRs.

**Benzo[a]Pyrene vs Benzo[g,h,i]Perylene**

In contrast to the other MDRs, the BaP/(BaP+BPE) ratio is said to indicate traffic (>0.60) vs non-
traffic emissions (<0.60; Table 1). The MDR trends are shown in Figure 1e. Assuming an initial
value of 0.50 (non-traffic) it can be seen from this example that the MDR will exceed 0.60 (non-
traffic) within a distance of 20 km.

**Halving and doubling distances**

In the examples discussed earlier (Figure 1), the initial MDRs at zero distance from the source
were all arbitrarily selected. It follows that it is impossible to assess their relative merit and
limitations without standardization with respect to the initial conditions. In an attempt to evaluate
the individual MDRs’ applicability domain against each other, we are therefore introducing the
“halving distance” \( (D_{1/2}) \), and the “doubling distance” \( (D_2) \). The former is the distance until the
initial MDR at zero distance, defined to start at the relevant threshold (e.g. 0.10 in the case of
ANT/(ANT+PHE)), is halved and applies to MDRs with declining trends. Similarly, the latter is
the distance at which the MDR values are doubled, and is applied to MDRs with increasing
trends. The calculated distances are presented in Table 4. It can be seen that within of about 40
km, one MDR is halved [ANT/(ANT+PHE)] while one is doubled [FLT/(FLT+PYR)]. The
IPY/(IPY+BPE) and BaP/BPE MDRs are doubled after longer distances (108 and 87 km,
respectively), and finally the BaA/(BaA+CHR) will be halved after 2000 Km. Distances of 40-
100 km should be considered as very short (regional) knowing that PAHs are detected in air in
very remote areas, far from major source regions (Becker et al., 2006). Nevertheless, based on the model calculations it is evident that the shorter the halving (or doubling) distance, the higher the risk of misinterpreting the actual source. Yet, we caution that these distances (Table 4) are certainly not be considered as a “safe operating space” for continued use of MDRs. Rather, these distances merely give an indication of their relative applicability, given the specific model conditions defined. Yet, our results show that source identification for PAHs based on these MDRs has a rather limited domain of applicability. Even if someone assumes that the large scale environmental blending of PAHs (originating from all possible sources) is not enough to render the use of MDRs inappropriate, it is seen, in the present study, that even a single source is likely to produce continuously changing MDRs during atmospheric transport away from a given source. The approach used in the present study is theoretical and includes various simplifying assumptions. Nevertheless, it may be argued that the trends estimated here are also supported by literature results. Here, it is seen that the ANT/(ANT+PHE) ratio tends to decline as PHE is depleted slower than ANT. If someone takes a close look at the long series of MDRs in the papers of Dvorska et al. (2011) and Katsoyiannis et al. (2011), it is seen that the vast majority of ratios estimated in Kosetice (Czech Republic) and in various cities in the UK were indeed below the 0.1 threshold, which cannot be just a sign of petrogenic sources, but also of the weathering of any pyrogenic signal (>0.1). The reader should note that according to the UK emission inventory presented by Katsoyiannis et al. (2013), the ANT/(ANT+PHE) ratio in direct emissions was always between 0.10 and 0.20 (i.e. pyrogenic). Similar conclusions can be extracted also by comparing the results of Katsoyiannis et al. (2011) for the other MDRs as well, for example the FLT/(FLT+PYR).

MDRs in other environmental compartments
PAHs are mainly emitted in the atmosphere and so, the use of MDRs for PAHs concentrations measured in other environmental compartments (e.g. soil, sediment, sludge, water) can already be wrong in principle as the rate of transfer from air to surface media are likely compound-specific. This was shown by Zhang et al. (2005) who noted that MDRs observed in atmosphere will not be the same in sediments, soils or water and proposed the use of rectification factors to account for such shifts.

The LIII model likewise estimates concentrations in other environmental media, namely water, soil, and sediment, which in turn can be used to calculate MDRs for these three media. This was applied in the present study assuming an initial air concentration of 1 ng m\(^{-3}\) for all PAHs (initial air MDR of 0.50 for all except the BaP/BPE ratio which has a value of 1.0) and the obtained results are presented in Figure 2. As seen, the results show a large variability, and the obtained values are often much different from the initial MDRs values. This confirms the findings of Zhang et al., (2005) that using MDRs as a source identification tool for PAHs found in soils, sediments and water includes a high error probability. One exception is the IPY/(IPY+BPE) ratio, for which the initial value of 0.50 is observed with minor changes in the three additional bulk environmental compartments. This ratio was characterized by Zhang et al. (2005) as the “best diagnostic ratio” and by Alam et al. (2013) as the only that can give reliable results.

Nevertheless, the IPY/(IPY+BPE) MDR was not found similarly robust in air in our study (Table 4). The analysis of Zhang et al. (2005) suggested that FLT/(FLT+PYR) is the most vulnerable MDR because these two chemicals have the biggest differences in their environmental behavior. In the present analysis, this particular result is confirmed by the short doubling distance for this MDR (Table 4) as further rationalized by differences in CTDs as presented in Table 3.

Sensitivity analysis
The results of this modeling exercise are greatly dependent on the selection of input data used for these calculations and in particular whether there are significant different in properties for pairs of related PAHs or not (i.e. physical-chemical properties and half-lives). To further evaluate our results, the MDRs were calculated again as a function of distance, using the LDVs from the study of Ma et al. (2010), instead of the FAVs. The results of the sensitivity analysis showed that the calculated CTDs (Table 3) remained similar for all lighter PAHs, and only for the heavier ones (namely BaP, IPY and BPE), differences up to 10% are observed. This mirrors the findings by Ma et al. (2010) who noted a tight relationship between various physical-chemical properties, e.g. vapor pressure, and molecular mass.

The MDRs obtained by applying the LDVs dataset are shown in Figure 1 (red dots). A first visual comparison of the obtained figures shows that for four of the examined MDRs, the results are similar, confirming the initial hypothesis that MDRs change greatly as a function of distance. The only MDR for which differences are observed for the two datasets is the BaP/BPE. As can be seen in Table 4, the difference in the $D_2$ values is quite significant, being 87 and 55 km for the FAVs dataset and LDVs dataset, respectively. Notwithstanding this important difference, the main conclusion of this study does not change, that is that MDRs are a poor source identification tool.

**Conclusions**

This study calculated the characteristic travel distances of individual PAHs and estimated theoretical MDRs at various distances from an initial point/source. It is demonstrated that differences in characteristic travel distances among pairs of PAHs consequently render improper the use of MDRs for source identification purposes. A simple sensitivity analysis using different sets of physical-chemical properties further confirmed our hypothesis that MDRs has a limited
merit and applicability domain as a source identification tool. From the five MDRs examined, the BaA/(BaA+CHR) was found to be the most robust (for air concentrations). For the other MDRs, it was shown that transport of PAHs over only few km can be enough to cause a change in the source identification interpretation. MDRs that are claimed to show same sources are, according to the present study’s results, following opposite trends over distance. Interpretation of all existing MDRs simultaneously are therefore at increasing risk of failing to discriminate between petrogenic and pyrogenic sources as the distance from the source increases. The estimation of MDRs also in other media (water, soil, sediment) generally confirmed the findings of Zhang et al (2005) that the use of MDRs derived from concentrations in other environmental compartments is conceptually flawed.

The results of this modeling exercise were proven to be coherent with previous scientific evidence and results from existing long-term monitoring campaigns. The present model analysis represents a simplified scenario with constant emissions from one single primary source affecting environmental levels. If in this simplified approach someone adds the arguments used in earlier publications that:

a) There is a large scale mixing of PAHs in the atmosphere

b) The same sources do not always emit PAHs at same rates

c) The climatic and environmental conditions change continuously therefore even MDR will be continuously affected

it can be concluded that MDRs are a limited tool for source identification.

It may be reasonably anticipated that similar results will be obtained even for other pairs of chemicals that are routinely used for source identification purposes as long as source-receptor relationships differs within pairs of related chemicals.
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References


List of Tables:

Table 1: Most commonly used PAH MDRs.

Table 2: Physical - chemical properties and environmental half-lives for selected PAHs (data from EPIWIN unless noted otherwise).

Table 3: Characteristic travel distances for selected PAHs.

Table 4: Distances (km) at which the MDRs are halved, or doubled, reflecting two different sets of property data.
Figure captions:

Figure 1: Molecular diagnostic ratios as a function of distance. 1a) ANT/(ANT+PHE); 1b) BaA/(BaA+Chr); 1c) FLT/(FLT+PYR); 1d) IPY/(IPY+BPE); 1e) BaP/BPE.

Figure 2: MDRs estimated for water, soil and sediment PAHs, assuming an initial air MDR of 0.50 in all cases.
Table 1: Most commonly used PAH MDRs (Yunker et al., 2002; Brandli et al., 2008; Tobiszewski and Namiesnik, 2012).

<table>
<thead>
<tr>
<th></th>
<th>Petrogenic</th>
<th>Pyrogenic</th>
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<tr>
<td>ANT/(ANT+PHE)</td>
<td>&lt;0.1</td>
<td>&gt;0.1</td>
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<tr>
<td>BaA/(BaA+CHR)</td>
<td>&lt;0.2</td>
<td>&gt;0.35</td>
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<tr>
<td>FLT/(FLT+PYR)</td>
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<td>&gt;0.4</td>
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<tr>
<td>IPY/(IPY+BPE)</td>
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<td>&gt;0.2</td>
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<tr>
<th></th>
<th>Fuel combustion</th>
<th>Grass/coal/wood combustion</th>
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<tr>
<td>FLT/(FLT+PYR)</td>
<td>0.4-0.5</td>
<td>&gt;0.5</td>
</tr>
<tr>
<td>IPY/(IPY+BPE)</td>
<td>0.2-0.5</td>
<td>&gt;0.5</td>
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<tr>
<th></th>
<th>Non-traffic</th>
<th>Traffic</th>
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<tr>
<td>BaP/BPE</td>
<td>&lt;0.6</td>
<td>&gt;0.6</td>
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ANT: Anthracene; PHE: Phenanthrene; BaA: Benzo[a]anthracene; CHR: Chrysene; FLT: Fluoranthene; PYR: Pyrene; IPY: Indeno[1,2,3-cd]pyrene; BPE: Benzo[g,h,i]perylene; BaP: Benzo[a]pyrene.
Table 2: Physical - chemical properties and environmental half-lives for selected PAHs.

<table>
<thead>
<tr>
<th>Property</th>
<th>ANT</th>
<th>PHE</th>
<th>BaA</th>
<th>CHR</th>
<th>FLT</th>
<th>PYR</th>
<th>BaP</th>
<th>IPY</th>
<th>BPE</th>
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<td>Molar mass (g mol(^{-1}))</td>
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<td>228.3</td>
<td>228.3</td>
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<td>202</td>
<td>252.3</td>
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<td>Water Solubility (g m(^{-3}))</td>
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<tr>
<td>Set A: FAVs*</td>
<td>2.05</td>
<td>4.28</td>
<td>1.38E-1</td>
<td>8.29E-2</td>
<td>1.04</td>
<td>6.25E-1</td>
<td>2.64E-2</td>
<td>3.64E-3</td>
<td>3.03E-3</td>
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<tr>
<td>Set B: LDVs*</td>
<td>2.40</td>
<td>4.80</td>
<td>1.47E-1</td>
<td>9.97E-2</td>
<td>1.14</td>
<td>7.34E-1</td>
<td>1.45E-2</td>
<td>2.19E-3</td>
<td>2.25E-3</td>
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<tr>
<td>Vapour Pressure (Pa)</td>
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<tr>
<td>Set A: FAVs*</td>
<td>5.89E-2</td>
<td>1.02E-1</td>
<td>3.80E-4</td>
<td>1.35E-4</td>
<td>6.76E-3</td>
<td>4.17E-3</td>
<td>7.94E-6</td>
<td>6.61E-7</td>
<td>4.57E-7</td>
</tr>
<tr>
<td>Set B: LDVs*</td>
<td>5.01E-2</td>
<td>9.12E-2</td>
<td>3.47E-4</td>
<td>1.12E-4</td>
<td>6.17E-3</td>
<td>3.55E-3</td>
<td>1.41E-5</td>
<td>1.07E-6</td>
<td>6.17E-7</td>
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<td>Log (K_{OW})</td>
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<tr>
<td>Set A: FAVs*</td>
<td>4.57</td>
<td>4.47</td>
<td>5.83</td>
<td>5.67</td>
<td>4.97</td>
<td>5.01</td>
<td>6.05</td>
<td>6.57</td>
<td>6.63</td>
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<tr>
<td>Set B: LDVs*</td>
<td>4.63</td>
<td>4.49</td>
<td>5.83</td>
<td>5.67</td>
<td>4.98</td>
<td>5.06</td>
<td>5.99</td>
<td>6.53</td>
<td>6.60</td>
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<tr>
<td>Melting Point (°C)</td>
<td>78.09</td>
<td>78.09</td>
<td>135.96</td>
<td>135.96</td>
<td>119.9</td>
<td>119.9</td>
<td>169.41</td>
<td>199.66</td>
<td>199.66</td>
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<td>Half life in air (h)</td>
<td>6.33**</td>
<td>18.9**</td>
<td>5.13</td>
<td>5.13</td>
<td>21.3**</td>
<td>5.08**</td>
<td>5.08**</td>
<td>3.98</td>
<td>2.95</td>
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<tr>
<td>Half life in water (h)</td>
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<td>1440</td>
<td>1440</td>
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<tr>
<td>Half life in soil (h)</td>
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<td>2880</td>
<td>2880</td>
<td>2880</td>
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<tr>
<td>Half life in sediment (h)</td>
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<td>13000</td>
<td>13000</td>
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</tbody>
</table>

* Ma et al., 2010.
** Brubaker and Hites, 1998.
Table 3: Characteristic travel distances for selected PAHs.

<table>
<thead>
<tr>
<th>PAH</th>
<th>$L_A$ (km)</th>
<th>Set A</th>
<th>Set B</th>
</tr>
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<tbody>
<tr>
<td>ANT</td>
<td>32.6</td>
<td>32.6</td>
<td></td>
</tr>
<tr>
<td>PHE</td>
<td>95.6</td>
<td>95.8</td>
<td></td>
</tr>
<tr>
<td>BaA</td>
<td>26.5</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>CHR</td>
<td>26.6</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>FLT</td>
<td>107</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>PYR</td>
<td>26.1</td>
<td>26.1</td>
<td></td>
</tr>
<tr>
<td>IPY</td>
<td>26.9</td>
<td>24.6</td>
<td></td>
</tr>
<tr>
<td>BPE</td>
<td>22.3</td>
<td>20.5</td>
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<tr>
<td>BaP</td>
<td>27.2</td>
<td>26.8</td>
<td></td>
</tr>
</tbody>
</table>
Table 4: Distances (km) at which the MDRs are halved, or doubled, reflecting two different sets of property data.

<table>
<thead>
<tr>
<th></th>
<th>Set A</th>
<th></th>
<th>Set B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_{1/2}$</td>
<td>$D_2$</td>
<td>$D_{1/2}$</td>
<td>$D_2$</td>
</tr>
<tr>
<td>ANT/(ANT+PHE)</td>
<td>38</td>
<td></td>
<td>38</td>
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</tr>
<tr>
<td>BaA/(BaA+CHR)</td>
<td>1000</td>
<td></td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>FLT/(FLT+PYR)</td>
<td>41</td>
<td></td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>IPY/(IPY+BPE)</td>
<td>108</td>
<td></td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>BaP/BPE</td>
<td>87</td>
<td></td>
<td>55</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Molecular diagnostic ratios as a function of distance from the source. a) ANT/(ANT+PHE); b) BaA/(BaA+Chr); c) FLT/(FLT+PYR); d) IPY/(IPY+BPE); e) BaP/BPE.
Figure 2: MDRs estimated for water, soil and sediment PAHs, assuming an initial air MDR of 0.50 in all cases (initial air MDR for BaP/BPE was 1.0).