1   Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic

2   ratios as a source identification tool.

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10   **Capsule**

11   **"PAHs molecular diagnostic ratios which change greatly as a function of distance from the**

12   **emitting source are improper for source identification purposes."**

13

14   **Abstract**

15   Polycyclic Aromatic Hydrocarbons (PAHs) molecular diagnostic ratios (MDRs) are unitless

16   concentration ratios of pair-PAHs with the same molecular weight (MW); MDRs have long been

17   used as a tool for PAHs source identification purposes. In the present paper, the efficiency of the

18   MDR methodology is evaluated through the use of a multimedia fate model, the calculation of

19   characteristic travel distances (CTD) and the estimation of air concentrations for individual PAHs

20   as a function of distance from an initial point source. The results show that PAHs with the same

21   MW are sometimes characterized by substantially different CTDs and therefore their air

22   concentrations and hence MDRs are predicted to change as the distance from the original source

23   increases. From the assessed pair-PAHs, the biggest CTD difference is seen for fluoranthene (107

24   km) *vs* pyrene (26 km). This study provides a strong indication that MDRs are of limited use as a

25   source identification tool.

26

29

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;

54 Tobiszewski and Namiesnik, 2012). The MDRs are unitless concentration ratios of specific

55 individual pair-PAHs (usually of the same molecular weight), and the MDR source identification

56 theory/methodology is based on the assumption that each specific PAHs emitting source will

57 always release individual PAHs at the same ratios. Another assumption of the MDR theory is that

58 PAHs of the same MW will have a similar environmental fate, therefore the concentration ratio

59 of PAH A against PAH B will always remains constant during their entire environmental

60 lifespan. Then, it is claimed by various authors that the MDR value can be used in order to

61 differentiate PAHs originating from a pyrogenic or petrogenic source, or PAHs that derive from

62 fuel *vs* grass, or coal, or wood combustion, PAHs that come from traffic, fresh PAHs emissions

63 etc. The main ratios used in order to give insight about the responsible sources are given in Table

64 1.

65 The efficiency of MDRs as a source identification tool has been questioned by various authors

66 who expressed their concerns about the problems associated with the MDRs methodology. Zhang

67 et al., (2005) used a multimedia fate model to show that MDRs will not be constant "*en route*

68 *from source to receptors*". They also demonstrated that for one specific source, the resulting

69 MDRs at various environmental compartments will not be similar to one another and also

70 proposed factors and ways to "correct" the calculated MDRs. Katsoyiannis et al., (2007),

71 commenting on the use of MDRs for sewage sludge PAHs, suggested that the blending of

72 different-sources-originated PAHs that takes place during the entire wastewater treatment process

73 makes the source understanding unfeasible. Galarneau (2008) used theoretical calculations and

74 simple models to further suggest that even the same sources are not always characterized by the

75 same PAHs emissions profile, or that between different sources there is significant overlapping in

76 MDRs. Dvorska et al., (2011) and Katsoyiannis et al., (2011) used long series of air

77 concentrations and emission inventories to demonstrate that PAHs MDRs are not efficient neither

78 in depicting the real source, nor in capturing different emission signals. Additionally, Alam et al.,

79 (2013) used targeted air sampling to assess the efficiency of MDRs and concluded that from the

80 examined MDRs, only the ratios between heavier PAHs should be further exploited, yet this

81 should always take place with caution. Finally, various studies have presented differences in the

82 reactivity of pair isomer PAHs, supporting indirectly the criticism to MDRs (Perraudin et al.,

83 2005; Esteve et al., 2006).

84 In a further attempt to assess the MDRs efficiency and robustness, the present study takes into

85 account differences in long-range atmospheric transport (LRT) potential as expressed by the

86 characteristic travel distance (CTD) of individual chemicals in order estimate the PAHs air

87 concentrations at various distances from an emission source. MDRs are then estimated at various

88 distances from the initial point and the resulting MDR-interpretations are compared. To the best

89 of the author's knowledge, this is the first scientific paper that tries to quantify the extent to

90 which MDRs are altered as a function of distance from the source. It is expected that our findings

91 could be of interest to all scientists who are interested in applying MDRs, especially in cases

92 where the environmental sampling takes place at remote sites.

93

94 **Materials and Methods**

95 *MDR calculations*

96 As seen in Table 1, the MDRs are easy to calculate, as the only required information are the

97 concentrations of each individual PAH. In monitoring studies, the concentrations are measured

98 by means of chemical analysis, however for a modeling study, a way to estimate the air

99 concentrations at various distances from the emitting source is needed. To address this necessity,

100 and in order to consequently evaluate the impact that differences in environmental fate of

101 individual PAHs can have on MDRs, the parameter of the characteristic travel distance (CTD, or

5

102   L_A) of chemicals is used. CTD is defined as the distance over which the initial air concentration

103   of a chemical is reduced to 1/e (~37%) (Bennett et al., 1998, Beyer et al., 2000, 2003; Breivik et

104   al., 2006). One advantage of using the CTD approach is that the L_A value (in meters) is

105   independent from the chemicals initial concentration, or emission rate.

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

107   $L_A = u \cdot M_A / [N_{RA} + N_{AS} - N_{SA}]$ (1)

108   where u is the wind speed (m h^{-1}), M_A is the amount of chemical in the atmosphere (moles), N_{RA}

109   is the rate of atmospheric reaction (mol h^{-1}), N_{AS} is the flux of chemical from the atmosphere to

110   the surface (mol h^{-1}) and N_{SA} is the opposite flux from the surface to the atmosphere (mol h^{-1}).

111   After L_A is calculated, then the air concentrations of the chemical of interest can be calculated

112   through Equation 2.

113   $C(x) = C_0 \cdot e^{-x/LA}$ (2)

114   where, $C(x)$ is the concentration of the chemical at a distance "x" from the emission point, C_0 is

115   the initial concentration of the chemical at the point of the emission (distance is 0 km) and L_A is

116   the characteristic travel distance of the chemical.

117   To calculate the parameters of Equation 1 (except from the wind speed), the Level III (LIII)

118   model (e.g. Mackay, 2001 and references therein) was used. The model software was

119   downloaded from the Trent University, Canada, website:

120   http://www.trentu.ca/academic/aminss/envmodel/models/VBL3.html. The LIII model is a

121   fugacity-based non-equilibrium, steady-state multimedia mass balance model. It estimates the

122   mass balances for four environmental compartments, namely air, water, soil and sediment.

123   Equilibrium is assumed within each compartment, but not between compartments. The LIII

124   model was selected for this work because it is well documented, transparent, readily available

125   and simple to operate. The LIII model has furthermore been widely tested and used and is often

126   at the core of more complex environmental fate models (e.g. Arnot et al., 2006; Cowan-Ellsberry

127   et al., 2009). The LIII was also among the various models evaluated in the study of Fenner et al.

128   (2005) where it was found to compare favorably with other examined models.

129   In order to apply the LIII model, the user needs to specify (*i*) the environmental and climatic

130   characteristics of the study area, (*ii*) key physical-chemical properties and environmental half-

131   lives of the chemical in question in all four compartments, and (*iii*) an emission rate (Mackay and

132   Paterson, 1991). For a detailed account of the LIII model, we refer to the landmark textbook by

133   Mackay (2001).

134   *Assumptions and model input parameters*

135   For a consistent estimation of PAHs L_As, it is desirable to use consistent physical – chemical

136   properties. Various publications report PAHs properties (e.g. Brubaker and Hites, 1998;

137   Paasivirta et al., 1999; Ma et al., 2010; Wang et al., 2013), and several websites have publicly

138   available PAHs properties datasets. However none reports all the properties that are required by

139   the LIII model estimated for all PAHs. We have therefore used empirical physical-chemical

140   properties (internally consistently), supplemented with data on environmental half-lives, mostly

141   derived from the US-EPA EPI Suite software (EPIWIN Version. 4.1,

142   http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm). The properties used are summarized

143   in Table 2. Water solubility, vapor pressure and log K_{OW} values were taken from the

144   comprehensive analysis by Ma et al. (2010) who reviewed more than 200 publications reporting

145   physical-chemical property data for PAHs. In this study, Ma et al. initially derived so-called

146   literature derived values (LDVs) based on all empirical data published to date, and adjusted them

147   for each compound in order to conform to thermodynamic relationships. The latter finally

148   adjusted values (FAVs) are the primary physical-chemical properties used in the present exercise

149   (Set A), while the initial LDVs were additionally explored for a sensitivity analysis (Set B).

150 It was further assumed that the exercise took place in Norway and as such the parameters

151 reflecting environmental and climatic conditions used by Katsoyiannis et al. (2013) were

152 selected. These model input parameters are shown in Table S1 (Supporting information).

153 Otherwise, the default values supplied with the LIII model were used.

154 Finally, this exercise represents a simplified condition where we assume primary emissions of

155 individual PAHs occur to air only. This is done in order to evaluate the applicability of various

156 MDRs under the simplest possible conditions.

157

158 **Results and discussion**

159 *Calculation of CTDs*

160 Table 3 presents the calculated CTDs of the PAHs of interest, for the two datasets used. When

161 derived on the basis of FAVs (Set A), we can see that pair PAHs exhibit much different CTDs,

162 with this difference being up to a factor of four, as in the case of FLT (107 km) against PYR

163 (26.1 km). For the pair ANT *vs* PHE the difference is also quite substantial (factor of three),

164 while for the pairs IPY *vs* BPE and BaP *vs* BPE the calculated CTDs differed at around 20%

165 (26.9 and 22.3 km for IPY and BPE respectively, and 27.2 and 22.3 km, for BaP and BPE,

166 respectively). The only pair of PAHs exhibiting similar CTDs was BaA and CHR, with 26.5 and

167 26.6 km, respectively. As mentioned, CTD denotes the distance over which the initial air

168 concentration of a chemical is reduced by ~63% and therefore, two chemicals which are emitted

169 at a constant ratio (e.g. 1:1) but have different CTDs, after their emission and environmental

170 transport, their concentrations could be much different than the initial 1:1. Consequently,

171 whenever CTDs are different for pairs of PAHs, their MDRs will also change with increasing

172 distances from a source. As PAHs are able to travel over long distances (Halsall et al., 2001),

173 source apportionment based on MDRs for pairs of PAHs with divergent CTDs could therefore be

174   problematic. It is therefore important to further explore if differences in characteristic travel

175   distances for selected PAHs will impact MDRs to such an extent that interpretation of these ratios

176   could lead to flawed conclusions concerning the responsible sources. In the following paragraphs,

177   estimated MDRs for various distances from the initial point of release and based on

178   concentrations calculated from Equation 2 are presented and discussed.

179

180   *MDR calculations as a function of distance*

181   **Anthracene *vs* Phenanthrene**

182   The ratio ANT/(ANT+PHE) has been suggested as an indicator of petrogenic against pyrogenic

183   sources (Table 1). This ratio has been criticized in the past (Katsoyiannis et al., 2011; Alam et al.,

184   2013) because of the fact that ANT is more reactive than PHE, and therefore their environmental

185   fate is much different. The ratio ANT/(ANT+PHE) is therefore anticipated to change

186   significantly with increasing distance from a given source. Figure 1a presents the trends for the

187   ANT/(ANT+PHE) ratio, calculated assuming an initial arbitrary MDR of 0.15. This value would

188   if measured in the field be attributed to emissions from combustion processes (pyrogenic),

189   according to the explanation given in Table 1. It can be seen that if sampling takes place at a

190   distance of ~30 km (practically, within one big city), the same ratio will be <0.10, suggesting a

191   shift to a predominant influence by a petrogenic source. It is thus evident that comparing

192   differences in CTD between ANT and PHE may provide useful information on the merit and

193   limitations of the MDR as a function of distance from a given source.

194

195   **Benzo[a]anthracene *vs* Chrysene**

196   The BaA/(BaA+CHR) ratio is supposedly able to discriminate between the same sources as

197   ANT/(ANT+PHE). A value below 0.20 suggests petrogenic emissions, while a value > 0.35

198   indicates combustion (pyrogenic emissions). It is assumed again that the initial arbitrary ratio of

199   concentrations falls into the pyrogenic area (0.40). From Figure 1b, it can be seen that the

200   BaA/(BaA+CHR) ratio is not changing significantly over distance, especially when compared to

201   the aforementioned ANT/(ANT+PHE) MDR. In fact, the initial ratio of 0.40 will continue being

202   >0.35 (cut off limit for Pyrogenic emissions) even after 1000 km, which means that the model

203   suggests this can be considered a robust MDR. However, this result is not surprising as some of

204   the key input data for these two PAHs are very similar and in some cases even identical, such as

205   the half-lives in air provided by EPIWIN (Table 2). In the present study, the calculations were all

206   undertaken assuming an ambient temperature of 25°C. Beyer et al., (2003) have previously

207   estimated CTDs for BaA and CHR at different temperatures (0°C, 5°C, and up to 30°C). While

208   they also found that BaA and CHR CTDs would be similar at 25°C, they reported that the

209   predicted CTD of CHR would be twice that of BaA at a temperature of 15°C. If their CTDs at 15

210   ^{o}C were used in Equation 2 instead of the values presented in Table 3, it becomes immediately

211   evident that also this MDR should be used with caution. Furthermore, this example also

212   illustrates that environmental and climatic conditions different to the conditions assumed herein

213   are expected to have an impact on the numerical results.

214

215   **Fluoranthene vs Pyrene**

216   FLT/(FLT+PYR) can also according to the MDRs methodology differentiate between petro- and

217   pyrogenic sources (<0.40 and >0.40, respectively), but can also give insight on whether the

218   pyrogenic emissions are due to fuel combustion (0.4-0.5), or due to combustion of other materials

219   (>0.50). To examine the stability of this MDR, an arbitrary initial value of 0.30 was assumed.

220   The trend is presented in Figure 1c and it is seen that this ratio within less than 20 km has

221   increased to >0.40 and the interpretation has changed from petro- to pyrogenic sources (fuel

222   combustion). Moving further away from the source (30 km), the interpretation changes again

223   from fuel combustion to grass/coal and wood combustion. It is evident that if a monitoring

224   campaign is applied in a trajectory in the same direction as the prevalent wind (e.g during one

225   sampling period), it is possible that all samples will capture PAHs emitted from the same sources,

226   though, source identification based on MDRs for air samples collected at various distances from

227   the source will provide all three different explanations.

228

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

230   The IPY/(IPY+BPE) ratio is said to offer similar interpretations to FLT/(FLT+PYR). Its trends

231   are presented in Figure 1d, assuming an initial ratio of 0.15. It can be seen that the

232   IPY/(IPY+BPE) ratio is also changing over distance, however at a lower rate than

233   (FLT/FLT+PYR). Again, any inferences about the source on the basis of the calculated

234   IPY/(IPY+BPE) ratios are increasingly at risk of making mistakes as the distance from the

235   primary source increases because of differences in the CTD between the two species considered

236   (Table 3).

237   From Table 1, one will see that these four MDRs so far discussed can be used to differentiate

238   between petrogenic or pyrogenic sources with the higher values (of all four MDRs) being

239   associated with pyrogenic sources. From our modeling results, it can be seen that as the distance

240   from the source increases (Figures 1a-d), one MDR [(ANT/(ANT+PHE)] has decreasing trends,

241   one remains practically constant [BaA/(BaA+CHR)] and the other two MDRs [FLT/(FLT+PYR)

242   and IPY/(IPY+BPE)] have increasing trends. It is therefore apparent that attempts to interpret

243   PAHs sources based on all four MDRs "in concert" are increasingly at risk of failing as the

244   distance from the source increases. Nevertheless, our results also indicate that it could be feasible

245   to identify a petrogenic source if samples are collected in close proximity. Still, as the results

246   presented are initialized using arbitrary selected MDRs at zero distance, we caution that the

247   distances discussed in these hypothetical examples should not be used to elucidate a potential

248   domain of applicability for individual MDRs.

249

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

251   In contrast to the other MDRs, the BaP/(BaP+BPE) ratio is said to indicate traffic (>0.60) *vs* non-

252   traffic emissions (<0.60; Table 1). The MDR trends are shown in Figure 1e. Assuming an initial

253   value of 0.50 (non-traffic) it can be seen from this example that the MDR will exceed 0.60 (non-

254   traffic) within a distance of 20 km.

255

256   *Halving and doubling distances*

257   In the examples discussed earlier (Figure 1), the initial MDRs at zero distance from the source

258   were all arbitrarily selected. It follows that it is impossible to assess their relative merit and

259   limitations without standardization with respect to the initial conditions. In an attempt to evaluate

260   the individual MDRs' applicability domain against each other, we are therefore introducing the

261   "halving distance" ($D_{1/2}$), and the "doubling distance" (D_2). The former is the distance until the

262   initial MDR at zero distance, defined to start at the relevant threshold (e.g. 0.10 in the case of

263   ANT/(ANT+PHE)), is halved and applies to MDRs with declining trends. Similarly, the latter is

264   the distance at which the MDR values are doubled, and is applied to MDRs with increasing

265   trends. The calculated distances are presented in Table 4. It can be seen that within of about 40

266   km, one MDR is halved [ANT/(ANT+PHE)] while one is doubled [FLT/(FLT+PYR)]. The

267   IPY/(IPY+BPE) and BaP/BPE MDRs are doubled after longer distances (108 and 87 km,

268   respectively), and finally the BaA/(BaA+CHR) will be halved after 2000 Km. Distances of 40-

269   100 km should be considered as very short (regional) knowing that PAHs are detected in air in

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270   very remote areas, far from major source regions (Becker et al., 2006). Nevertheless, based on the

271   model calculations it is evident that the shorter the halving (or doubling) distance, the higher the

272   risk of misinterpreting the actual source. Yet, we caution that these distances (Table 4) are

273   certainly not be considered as a "safe operating space" for continued use of MDRs. Rather, these

274   distances merely give an indication of their relative applicability, given the specific model

275   conditions defined. Yet, our results show that source identification for PAHs based on these

276   MDRs has a rather limited domain of applicability. Even if someone assumes that the large scale

277   environmental blending of PAHs (originating from all possible sources) is not enough to render

278   the use of MDRs inappropriate, it is seen, in the present study, that even a single source is likely

279   to produce continuously changing MDRs during atmospheric transport away from a given source.

280   The approach used in the present study is theoretical and includes various simplifying

281   assumptions. Nevertheless, it may be argued that the trends estimated here are also supported by

282   literature results. Here, it is seen that the ANT/(ANT+PHE) ratio tends to decline as PHE is

283   depleted slower than ANT. If someone takes a close look at the long series of MDRs in the

284   papers of Dvorska et al. (2011) and Katsoyiannis et al. (2011), it is seen that the vast majority of

285   ratios estimated in Kosetice (Czech Republic) and in various cities in the UK were indeed below

286   the 0.1 threshold, which cannot be just a sign of petrogenic sources, but also of the weathering of

287   any pyrogenic signal (>0.1). The reader should note that according to the UK emission inventory

288   presented by Katsoyiannis et al. (2013), the ANT/(ANT+PHE) ratio in direct emissions was

289   always between 0.10 and 0.20 (i.e. pyrogenic). Similar conclusions can be extracted also by

290   comparing the results of Katsoyiannis et al. (2011) for the other MDRs as well, for example the

291   FLT/(FLT+PYR).

292

293   *MDRs in other environmental compartments*

294 PAHs are mainly emitted in the atmosphere and so, the use of MDRs for PAHs concentrations

295 measured in other environmental compartments (e.g. soil, sediment, sludge, water) can already be

296 wrong in principle as the rate of transfer from air to surface media are likely compound-specific.

297 This was shown by Zhang et al. (2005) who noted that MDRs observed in atmosphere will not be

298 the same in sediments, soils or water and proposed the use of rectification factors to account for

299 such shifts.

300 The LIII model likewise estimates concentrations in other environmental media, namely water,

301 soil, and sediment, which in turn can be used to calculate MDRs for these three media. This was

302 applied in the present study assuming an initial air concentration of 1 ng m^{-3} for all PAHs (initial

303 air MDR of 0.50 for all except the BaP/BPE ratio which has a value of 1.0) and the obtained

304 results are presented in Figure 2. As seen, the results show a large variability, and the obtained

305 values are often much different from the initial MDRs values. This confirms the findings of

306 Zhang et al., (2005) that using MDRs as a source identification tool for PAHs found in soils,

307 sediments and water includes a high error probability. One exception is the IPY/(IPY+BPE) ratio,

308 for which the initial value of 0.50 is observed with minor changes in the three additional bulk

309 environmental compartments. This ratio was characterized by Zhang et al. (2005) as the "*best*

310 *diagnostic ratio*" and by Alam et al. (2013) as the only that can give reliable results.

311 Nevertheless, the IPY/(IPY+BPE) MDR was not found similarly robust in air in our study (Table

312 4). The analysis of Zhang et al. (2005) suggested that FLT/(FLT+PYR) is the most vulnerable

313 MDR because these two chemicals have the biggest differences in their environmental behavior.

314 In the present analysis, this particular result is confirmed by the short doubling distance for this

315 MDR (Table 4) as further rationalized by differences in CTDs as presented in Table 3.

316

317 *Sensitivity analysis*

318   The results of this modeling exercise are greatly dependent on the selection of input data used for

319   these calculations and in particular whether there are significant different in properties for pairs

320   of related PAHs or not (i.e. physical-chemical properties and half-lives). To further evaluate our

321   results, the MDRs were calculated again as a function of distance, using the LDVs from the study

322   of Ma et al. (2010), instead of the FAVs. The results of the sensitivity analysis showed that the

323   calculated CTDs (Table 3) remained similar for all lighter PAHs, and only for the heavier ones

324   (namely BaP, IPY and BPE), differences up to 10% are observed. This mirrors the findings by

325   Ma et al. (2010) who noted a tight relationship between various physical-chemical properties, e.g.

326   vapor pressure, and molecular mass.

327   The MDRs obtained by applying the LDVs dataset are shown in Figure 1 (red dots). A first visual

328   comparison of the obtained figures shows that for four of the examined MDRs, the results are

329   similar, confirming the initial hypothesis that MDRs change greatly as a function of distance. The

330   only MDR for which differences are observed for the two datasets is the BaP/BPE. As can be

331   seen in Table 4, the difference in the D_2 values is quite significant, being 87 and 55 km for the

332   FAVs dataset and LDVs dataset, respectively. Notwithstanding this important difference, the

333   main conclusion of this study does not change, that is that MDRs are a poor source identification

334   tool.

335

336   **Conclusions**

337   This study calculated the characteristic travel distances of individual PAHs and estimated

338   theoretical MDRs at various distances from an initial point/source. It is demonstrated that

339   differences in characteristic travel distances among pairs of PAHs consequently render improper

340   the use of MDRs for source identification purposes. A simple sensitivity analysis using different

341   sets of physical-chemical properties further confirmed our hypothesis that MDRs has a limited

342   merit and applicability domain as a source identification tool. From the five MDRs examined, the

343   BaA/(BaA+CHR) was found to be the most robust (for air concentrations). For the other MDRs,

344   it was shown that transport of PAHs over only few km can be enough to cause a change in the

345   source identification interpretation. MDRs that are claimed to show same sources are, according

346   to the present study's results, following opposite trends over distance. Interpretation of all

347   existing MDRs simultaneously are therefore at increasing risk of failing to discriminate between

348   petrogenic and pyrogenic sources as the distance from the source increases. The estimation of

349   MDRs also in other media (water, soil, sediment) generally confirmed the findings of Zhang et al

350   (2005) that the use of MDRs derived from concentrations in other environmental compartments is

351   conceptually flawed.

352   The results of this modeling exercise were proven to be coherent with previous scientific

353   evidence and results from existing long-term monitoring campaigns.

354   The present model analysis represents a simplified scenario with constant emissions from one

355   single primary source affecting environmental levels. If in this simplified approach someone adds

356   the arguments used in earlier publications that:

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

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

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

360   continuously affected

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

362   It may be reasonably anticipated that similar results will be obtained even for other pairs of

363   chemicals that are routinely used for source identification purposes as long as source-receptor

364   relationships differs within pairs of related chemicals.

365

References

Alam, M.S., Delgado-Saborit, J.M., Stark, C., Harrison, R.M., 2013. Using atmospheric
measurements of PAH and quinone compounds at roadside and urban background sites to
assess sources and reactivity. Atmospheric Environment 77 (0), 24-35.

Arnot, J.A., Mackay, D., Webster, E., Southwood, J.M., 2006. Screening level risk assessment
model for chemical fate and effects in the environment. Environmental Science and
Technology, 40 (7), pp. 2316-2323.

Becker, S., Halsall, C.J., Tych, W., Hung, H., Attewell, S., Blanchard, P., Li, H., Fellin, P., Stern,
G., Billeck, B., Friesen, S., 2006. Resolving the long-term trends of polycyclic aromatic
hydrocarbons in the Canadian Arctic atmosphere. Environmental Science and Technology,
40 (10), pp. 3217-3222.

Bennett, D.H., McKone, T.E., Matthies, M., Kastenberg, W.E., 1998. General formulation of
characteristic travel distance for semivolatile organic chemicals in a multimedia
environment. Environmental Science and Technology 32 (24), 4023-4030.

Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E., 2000. Assessing long-range
transport potential of persistent organic pollutants. Environmental Science and Technology
34 (4), 699-703.

Beyer, A., Wania, F., Gouin, T., Mackay, D., Matthies, M., 2003. Temperature dependence of the
characteristic travel distance. Environmental Science and Technology 37 (4), 766-771.

Breivik, K., Wania, F., Muir, D.C.G., Alaee, M., Backus, S., Pacepavicius, G., 2006. Empirical
and modeling evidence of the long-range atmospheric transport of decabromodiphenyl ether.
Environmental Science and Technology 40 (15), 4612-4618.

397 Brubaker Jr., W.W., Hites, R.A., 1998. OH reaction kinetics of polycyclic aromatic hydrocarbons

398 and polychlorinated dibenzo-p-dioxins and dibenzofurans. Journal of Physical Chemistry A,

399 102 (6), 915-921.

400 Cai, Q.Y., Mo, C.H., Li, Y.H., Zeng, Q.Y., Katsoyiannis, A., Wu, Q.T., Férard, J.F., 2007.

401 Occurrence and assessment of polycyclic aromatic hydrocarbons in soils from vegetable

402 fields of the Pearl River Delta, South China. Chemosphere 68 (1), 159-168.

403 Cincinelli, A., Mandorlo, S., Dickhut, R.M., Lepri, L., 2003. Particulate organic compounds in

404 the atmosphere surrounding an industrialised area of Prato (Italy). Atmospheric Environment

405 37 (22), 3125-3133.

406 Cristale, J., Silva, F.S., Zocolo, G.J., Marchi, M.R.R., 2012. Influence of sugarcane burning on

407 indoor/outdoor PAH air pollution in Brazil. Environmental Pollution 169, 210-216.

408 Cowan-Ellsberry, C.E., McLachlan, M.S., Arnot, J.A., MacLeod, M., McKone, T.E., Wania, F.,

409 2009. Modeling exposure to persistent chemicals in hazard and risk assessment. Integrated

410 Environmental Assessment and Management, 5 (4), pp. 662-679.

411 Dai, J., Xu, M., Chen, J., Yang, X., Ke, Z., 2007. PCDD/F, PAH and heavy metals in the sewage

412 sludge from six wastewater treatment plants in Beijing, China. Chemosphere 66 (2), 353-

413 361.

414 Dvorská, A., Lammel, G., Klánová, J., 2011. Use of diagnostic ratios for studying source

415 apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central

416 Europe. Atmospheric Environment 45 (2), 420-427.

417 Esteve, W., Budzinski, H., Villenave, E., 2006. Relative rate constants for the heterogeneous

418 reactions of NO_2 and OH radicals with polycyclic aromatic hydrocarbons adsorbed on

419 carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a.

420 Atmospheric Environment, 40 (2), pp. 201-211.

421   Fenner, K., Scheringer, M., Macleod, M., Matthies, M., McKone, T., Stroebe, M., Beyer, A.,

422   Bonnell, M., Le Gall, A.C., Klasmeier, J., Mackay, D., Van De Meent, D., Pennington, D.,

423   Scharenberg, B., Suzuki, N., Wania, F., 2005. Comparing estimates of persistence and long-

424   range transport potential among multimedia models. Environmental Science and

425   Technology, 39 (7), 1932-1942.

426   Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs:

427   Implications for source apportionment. Atmospheric Environment 42 (35), 8139-8149.

428   Halsall, C.J., Sweetman, A.J., Barrie, L.A., Jones, K.C. Modelling the behaviour of PAHs during

429   atmospheric transport from the UK to the Arctic (2001) Atmospheric Environment, 35 (2)

430   255-267.

431   Katsoyiannis, A., Terzi, E., Cai, Q., 2007. On the use of PAH molecular diagnostic ratios in

432   sewage sludge for the understanding of the PAH sources. Is this use appropriate.?

433   Chemosphere 69 (8), 1337-1339.

434   Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to

435   atmospheric sources: a critical evaluation using two decades of source inventory and air

436   concentration data from the UK. Environmental Science and Technology 45 (20), 8897-

437   8906.

438   Katsoyiannis, A., Birgul, A., Ratola, N., Cincinelli, A., Sweetman, A.J., Jones, K.C., 2012. Can

439   car air filters be useful as a sampling medium for air pollution monitoring purposes?

440   Environment International 48, 65-70.

441   Katsoyiannis, A., Breivik, K., Schlabach, M, 2013. Estimating the contribution of long-range

442   transport to the atmospheric deposition of selected organic contaminants over Norway. TA

443   2987/2012, Norwegian Institute for Air Research (NILU), Oslo.

444   Ma, Y.-G., Lei, Y.D., Xiao, H., Wania, F., Wang, W.-H., 2010. Critical review and recommended

445   values for the physical-chemical property data of 15 polycyclic aromatic hydrocarbons at 25

446   °C. (2010) Journal of Chemical and Engineering Data, 55 (2), 819-825.

447   Mackay, D.. 2001. Multimedia Environmental Models. The fugacity approach. Second Edition.

448   Lewis Publishers. ISBN 1-56670-542-8-90000.

449   Mackay, D., Paterson, S., 1991. Evaluating the multimedia fate of organic chemicals: A level III

450   fugacity model. Environmental Science and Technology 25 (3), 427-436.

451   Manoli, E., Kouras, A., Samara, C., 2004. Profile analysis of ambient and source emitted particle-

452   bound polycyclic aromatic hydrocarbons from three sites in northern Greece. Chemosphere

453   56 (9), 867-878.

454   Martellini, T., Giannoni, M., Lepri, L., Katsoyiannis, A., Cincinelli, A., 2012. One year intensive

455   PM 2.5 bound polycyclic aromatic hydrocarbons monitoring in the area of Tuscany, Italy.

456   Concentrations, source understanding and implications. Environmental Pollution 164, 252-

457   258.

458   Melymuk, L., Robson, M., Helm, P.A., Diamond, M.L., 2012. PCBs, PBDEs, and PAHs in

459   Toronto air: Spatial and seasonal trends and implications for contaminant transport. Science

460   of the Total Environment, 429, pp. 272-280.

461   Nikolaou, K., Masclet, P., Mouvier, G., 1984. Sources and chemical-reactivity of polynuclear

462   aromatic-hydrocarbons in the atmosphere - a Critical-Review. Science of the Total

463   Environment 32 (2), 103-132.

464   Ohura, T., Amagai, T., Fusaya, M., Matsushita, H., 2004. Polycyclic Aromatic Hydrocarbons in

465   indoor and outdoor environments and Factors Affecting their Concentrations.

466   Environmental Science and Technology, 38 (1), 77-83.

467   Oliveira, C., Martins, N., Tavares, J., Pio, C., Cerqueira, M., Matos, M., Silva, H., Camões, F.,

468   2011. Size distribution of polycyclic aromatic hydrocarbons in a roadway tunnel in Lisbon,

469   Portugal. Chemosphere 83 (11), 1588-1596.

470   Paasivirta, J., Sinkkonen, S., Mikkelson, P., Rantio, T., Wania, F., 1999. Estimation of vapor

471   pressures, solubilities and Henry's law constants of selected persistent organic pollutants as

472   functions of temperature, Chemosphere, 39 (5), pp. 811-832.

473   Perraudin, E., Budzinski, H., Villenave, E., 2005. Kinetic study of the reactions of NO_2 with

474   polycyclic aromatic hydrocarbons adsorbed on silica particles, Atmospheric Environment,

475   39 (35) 6557-6567

476   Ratola, N., Alves, A., Lacorte, S., Barceló, D., 2012. Distribution and sources of PAHs using

477   three pine species along the Ebro River. Environmental Monitoring and Assessment 184 (2),

478   985-999.

479   Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution

480   emission sources. Environmental Pollution 162, 110-119.

481   Usenko, S., Simonich, S.L.M., Hageman, K.J., Schrlau, J.E., Geiser, L., Campbell, D.H.,

482   Appleby, P.G., Landers, D.H., 2010. Sources and deposition of polycyclic aromatic

483   hydrocarbons to western U.S. national parks. Environmental Science and Technology 44

484   (12), 4512-4518.

485   Wang, Y.L., Xia, Z.H., Liu, D., Qiu, W.X., Duan, X.L., Wang, R., Liu, W.J., Zhang, Y.H., Wang,

486   D., Tao, S., Liu, W.X., 2013. Multimedia fate and source apportionment of polycyclic

487   aromatic hydrocarbons in a coking industry city in Northern China. Environmental Pollution,

488   181, pp. 115-121.

489   Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of

490   polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach.

491   Environmental Science and Technology, 39 (23), 9109-9114.

503 **Figure captions:**

504

505 Figure 1: Molecular diagnostic ratios as a function of distance. 1a) ANT/(ANT+PHE); 1b)

506 BaA/(BaA+Chr); 1c) FLT/(FLT+PYR); 1d) IPY/(IPY+BPE); 1e) BaP/BPE.

507

508 Figure 2: MDRs estimated for water, soil and sediment PAHs, assuming an initial air MDR of

509 0.50 in all cases.

510   Table 1: Most commonly used PAH MDRs (Yunker et al., 2002; Brandli et al., 2008;

511   Tobiszewski and Namiesnik, 2012).

	Petrogenic	Pyrogenic
ANT/(ANT+PHE)	<0.1	>0.1
BaA/(BaA+CHR)	<0.2	>0.35
FLT/(FLT+PYR)	<0.4	>0.4
IPY/(IPY+BPE)	<0.2	>0.2

	Fuel combustion	Grass/coal/wood combustion
FLT/(FLT+PYR)	0.4-0.5	>0.5
IPY/(IPY+BPE)	0.2-0.5	>0.5

	Non-traffic	Traffic
BaP/BPE	<0.6	>0.6

512   ANT: Anthracene; PHE: Phenanthrene; BaA; Benzo[*a*]anthracene; CHR: Chrysene; FLT: Fluoranthene; PYR:
513   Pyrene; IPY: Indeno[*1,2,3-cd*]pyrene; BPE: Benzo[*g,h,i*]perylene; BaP: Benzo[*a*]pyrene.
514

515 Table 2: Physical - chemical properties and environmental half-lives for selected PAHs.

Property	ANT	PHE	BaA	CHR	FLT	PYR	BaP	IPY	BPE
Molar mass (g mol^{-1})	178	178	228.3	228.3	202	202	252.3	276	276
Water Solubility (g m^{-3})									
Set A: FAVs*	2.05	4.28	1.38E-1	8.29E-2	1.04	6.25E-1	2.64E-2	3.64E-3	3.03E-3
Set B: LDVs*	2.40	4.80	1.47E-1	9.97E-2	1.14	7.34E-1	1.45E-2	2.19E-3	2.25E-3
Vapour Pressure (Pa)									
Set A: FAVs*	5.89E-2	1.02E-1	3.80E-4	1.35E-4	6.76E-3	4.17E-3	7.94E-6	6.61E-7	4.57E-7
Set B: LDVs*	5.01E-2	9.12E-2	3.47E-4	1.12E-4	6.17E-3	3.55E-3	1.41E-5	1.07E-6	6.17E-7
Log K_{OW}									
Set A: FAVs*	4.57	4.47	5.83	5.67	4.97	5.01	6.05	6.57	6.63
Set B: LDVs*	4.63	4.49	5.83	5.67	4.98	5.06	5.99	6.53	6.60
Melting Point (°C)	78.09	78.09	135.96	135.96	119.9	119.9	169.41	199.66	199.66
Half life in air (h)	6.33**	18.9**	5.13	5.13	21.3**	5.08**	5.08**	3.98	2.95
Half life in water (h)	1440	1440	1440	1440	1440	1440	1440	1440	1440
Half life in soil (h)	2880	2880	2880	2880	2880	2880	2880	2880	2880
Half life in sediment (h)	13000	13000	13000	13000	13000	13000	13000	13000	13000

516 * Ma et al., 2010.
517 ** Brubaker and Hites, 1998.

518   Table 3: Characteristic travel distances for selected PAHs.

PAH	L_A (km)	
	Set A	Set B
ANT	32.6	32.6
PHE	95.6	95.8
BaA	26.5	26.5
CHR	26.6	26.5
FLT	107	107
PYR	26.1	26.1
IPY	26.9	24.6
BPE	22.3	20.5
BaP	27.2	26.8

519

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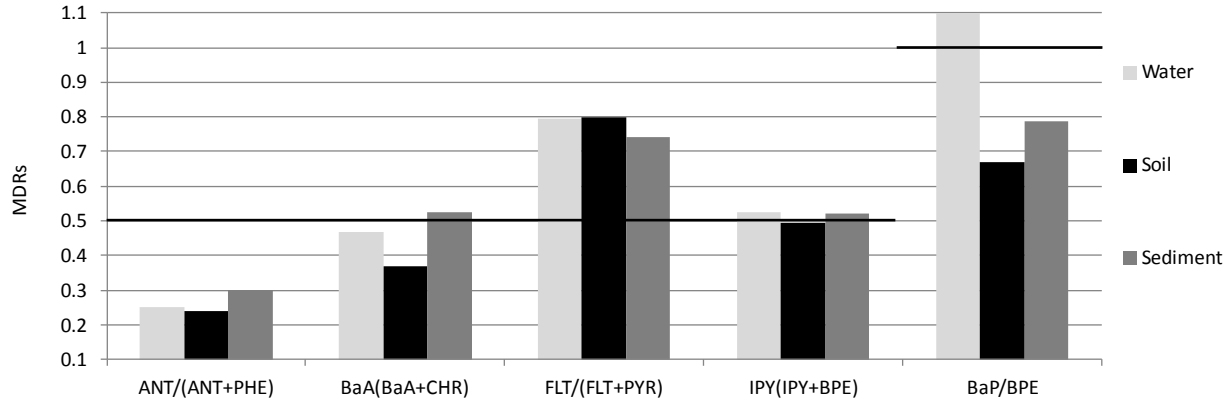
521   of property data.

	Set A		Set B	
	$D_{1/2}$	D_2	$D_{1/2}$	D_2
ANT/(ANT+PHE)	38		38	
BaA/(BaA+CHR)	1000		2000	
FLT/(FLT+PYR)		41		41
IPY/(IPY+BPE)		108		107
BaP/BPE		87		55

522
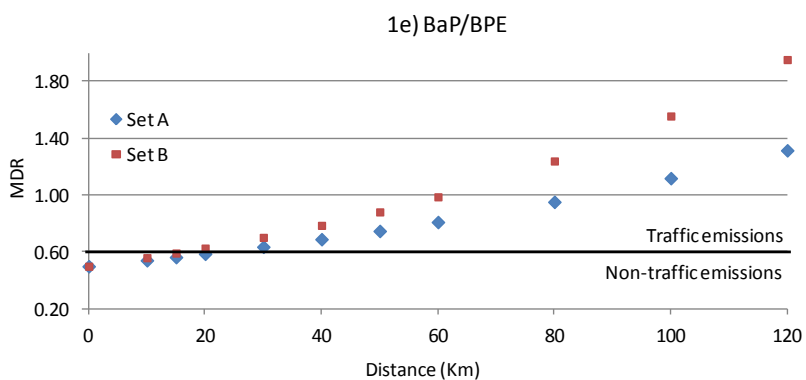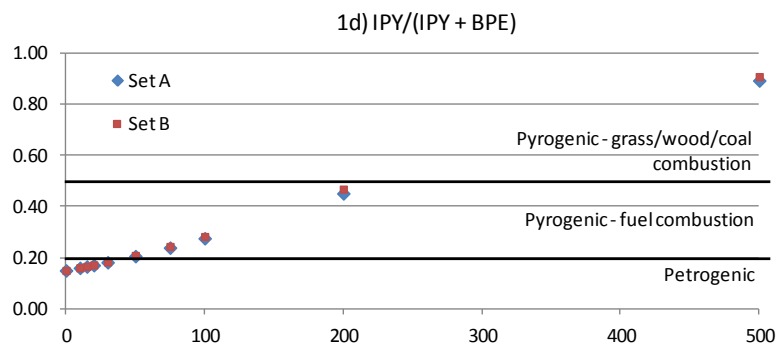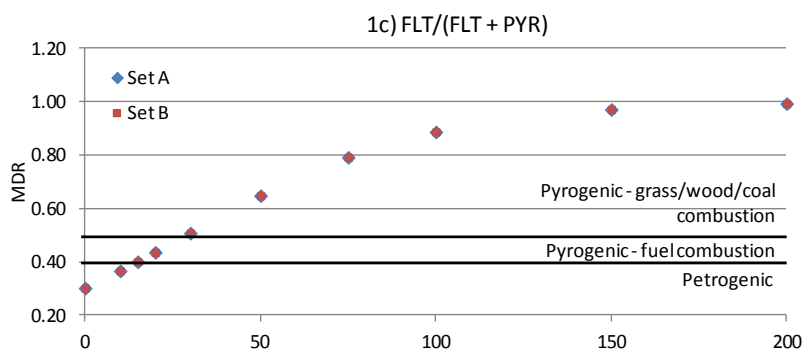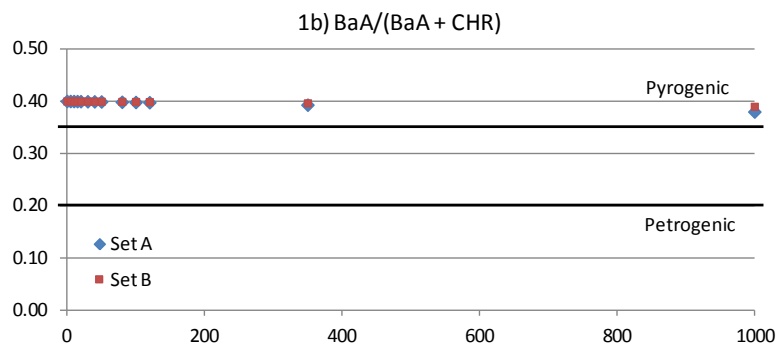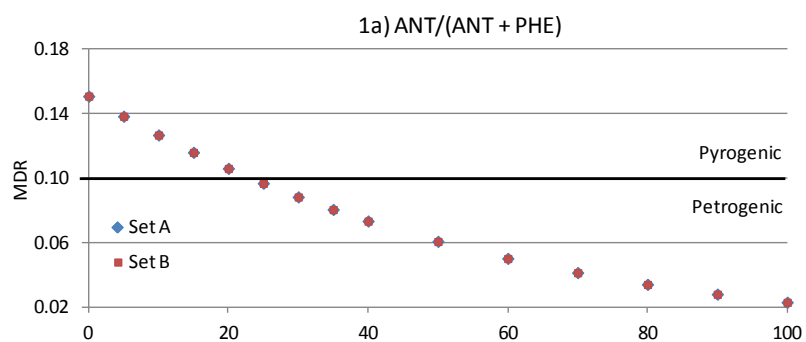
Figure 1: Molecular diagnostic ratios as a function of distance from the source. a) ANT/(ANT+PHE); b) BaA/(BaA+Chr); c) FLT/(FLT+PYR); d) IPY/(IPY+BPE); e) BaP/BPE.

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).