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13 **Analyzing hydrocarbons in sewer to help in PAH source**
14 **apportionment in sewage sludges**

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Analyzing hydrocarbons in sewer to help in PAH source apportionment in sewage sludges

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Abstract

A multi-molecular approach for polycyclic aromatic hydrocarbons (PAH) source apportionment in sewage sludge was tested. Three simple catchment areas with corresponding wastewater treatment plants (WWTP) were chosen. Sewage sludges of these WWTPs chronically exceeded the French guide values of PAHs. Aliphatic and aromatic hydrocarbons were quantified in sediments or wastewater suspended particulate matter sampled in different locations of the sewer as well as in sewage sludges. Various molecular indices including PAH ratios were calculated. The results showed that the ratios calculated from sewage sludge analyses provided a rather unspecific hydrocarbon fingerprint where combustion input appear as the main PAH sources. The complexity of the inputs as well as degradation occurring during wastewater treatment prevent any detailed diagnosis. Coupled to the analyses of samples collected in the sewer, the multi-molecular approach becomes more efficient especially for the identification of specific petroleum inputs such as fuel or used lubricating oils which can be important PAH sources. Indeed, the sampling in the sewer allows a spatial screening of the hydrocarbon inputs and facilitates the PAH source apportionment by avoiding the dilution of specific inputs with the whole wastewater inputs and by limiting the degradation of the molecular fingerprint that could occur during transfer and treatment in the WWTP. Then, the combination of PAH ratios and aliphatic distribution analyses is a very valuable approach that can help in sewer and WWTP management.

Keywords : sewage sludges, sewer, PAHs, aliphatic hydrocarbons

1. Introduction

PAHs in sewage sludges have many sources related to the intense use of petroleum products (automobile fuels, lubricating oils...) or to combustion processes (fuel, wood and coal burning, automobile exhaust, heat and power generation ...). They end up in sewage sludges (i) by runoff on urbanized surfaces and (ii) by direct introduction into the sewer by industrial effluents, accidents or individual spillage. They are diluted with organic compounds brought with wastewater, partially degraded in the wastewater treatment plant (WWTP) and eventually accumulate in sewage sludges.

High PAH contamination can be recorded all along the year or chronically in sewage sludges produced by the WWTPs of some cities or even small rural districts. The French regulation allows sludge amendments on agricultural soils when fluoranthene, benzo[b]fluoranthene and benzo[a]pyrene are respectively lower than $5 \mu\text{g.g}^{-1}$ dry weight (dw), $2.5 \mu\text{g.g}^{-1}\text{dw}$ and $2 \mu\text{g.g}^{-1}\text{dw}$. The other ways of elimination of sludges are much more expensive and this cost is sometimes unbearable for small villages. Thus, the knowledge of the main PAH sources is crucial information to help improving the management of effluents that enter the sewer network, to better define the type of wastewater treatment, or to better inform citizens about what should not be dumped into the sewer.

There are several ways to identify PAH sources. The most common is to study PAH distributions and to use specific PAH ratios to differentiate pyrogenic sources from petrogenic sources. This has been mainly applied to river or marine sediments (Colombo et al., 1989; Budzinski et al., 1997; Yunker et al., 2002), atmospheric particles (Aboul-Kassim and Simoneit, 1995; Motelay-Massei et al., 2007), soils (Wilcke, 2000; Bucheli et al., 2004), in sewers, sewage sludges or in compost (Blanchard et al., 2001; Rocher et al., 2004a,b; Brandli et al., 2007; Dai et al., 2007). Recently, Zhang et al. (2005) and Katsoyiannis et al. (2007)

questioned the pertinence of PAH ratios for source apportionment especially in sewage sludge arguing the dilution and the degradation of paired chemicals are not similar during transfer from sources to receptors. Some authors consider PAH profiles and ratios as insufficiently specific to identify petroleum pollution and suggest to support PAH diagnosis with the analyses of other hydrocarbon fingerprints such as alkanes and hopanes in order to narrow down the sources (Fernandes and Brooks, 2003; Yunker and Macdonald, 2003; Jardé et al., 2005; Jeanneau et al., 2008).

This study discusses the approach of molecular indices calculated from hydrocarbon analysis to help in identifying prevailing sources of PAH in sewage sludges. Three WWTPs in small rural districts have been selected for their chronic or permanent PAH contamination, for the simple network of their sewer and the low complexity of the inputs in their sewer. Samples were collected in the sewer and in the WWTP and their hydrocarbon contents analyzed by gas chromatography-mass spectrometry. Parent and alkylated PAHs and alkanes were quantified. The study also checks the preservation of specific hydrocarbon fingerprints from the sewer to sewage sludge despite biological degradation in the sewer and the WWTP.

2. Materials and methods

2.1. Sites

Three sites A, B and C in rural districts of Lorraine, North East of France have been selected for this study based on several criteria (Table 1 and details in Figure 1 of supplementary information). First, all the sludges produced by the WWTPs presented a recurring PAH contamination of their sludges based on French regulation. Second, small rural districts were preferred to important urban cities because of the limited number of suspected PAH sources (low traffic, low industrialization). Finally, small and simple sewer networks were chosen in order to facilitate the sampling and to limit the sample number.

107 Site A gathers three villages with 1000 inhabitants in a rural environment. The district is
108 not industrialized except for a sawmill which is not connected to the sewer. Its WWTP is
109 made up of a primary treatment (sand, grit and grease removal), an aeration basin, a clarifier
110 and the sludges are finally stored in a silo which is emptied every year. Despite this rural
111 context, the sewage sludges have recorded PAH contamination for four successive years. In
112 December 2003, two samples of sewage sludge were collected in the silo A0-Slu1 and in the
113 aeration basin A0-Slu2. Six samples were taken in the sewer at five different locations (A1 to
114 A5) allowing to differentiate the effluents from the three villages. According to the
115 accessibility of the sewer and water flow (null in some parts), approximately 3 L of
116 wastewater (abbreviated "ww") or sediments accumulated in the sewer (abbreviated "sed")
117 were sampled.

118 Site B is a small village of 400 inhabitants in the northern part of Lorraine which is highly
119 industrialized (coking plants and steel industries). The WWTP has a very simple treatment
120 system made up of a sedimentation tank with a sand bed filter. In March 2004, three samples
121 (B1-sed to B3-sed) were collected in the sewer delimitating three areas of the village. At the
122 time of the sampling, a fuel storage tank was leaking in the village and a smell of fuel could
123 be clearly noticed when sampling the sewer at location B1. The wastewaters were sampled at
124 the entrance of the WWTP (B0-ww). Finally, four samples of sludge were collected in
125 different parts of the sedimentation tank to check the homogeneity of the sediments in the
126 tank (B0-slu1 to B0-slu4).

127 Site C consists of three villages 20 km far from a big city and gathers 2 500 inhabitants.
128 The WWTP treats wastewaters from a large watershed with diversified activities: agriculture,
129 forestry, industries including trucking companies, printing works and other unidentified
130 activities. The WWTP is quite similar to that of site A with a screening process, an aeration
131 basin and a clarifier. In July 2004, five samples (C1 to C5) were taken in different locations of

the sewer in order to differentiate the effluents generated in the industrial park (C1), and in residential areas (C2 to C5). Two wastewater samples (3 L) were collected at the entrance of the WWTP serving two villages (residential areas) plus an industrial zone (C1-ww1) as well as the third village with agricultural activity (C0-ww2). Finally, two sludges were sampled (C0-slu1 and C0-slu2).

Water and sludge samples were collected with aluminum pans and stored in glass containers. Utensils and containers were carefully washed with solvents before use to avoid contamination.

2.2. Sample preparation and extraction

The sediments and sludges were preserved in a freezer before their extraction within a few weeks after their collection. Wastewater samples (approximately 3 L) were filtered on glass fiber filters (0.45 μm) using a pump in order to collect suspended matters. Suspended matters on filters, sediments and sewage sludges were freeze-dried. Freeze-dried sediments and sewage sludges were crushed and sieved (250 μm).

The protocol used was a modification of Li et al. (2002). Five grams of each freeze-dried sample were extracted with an accelerated solvent extractor (ASE; ASE200 Dionex[®]) using dichloromethane. Prior to extraction, the samples were spiked with a recovery surrogate containing 2-fluorobiphenyle, d14-p-terphenylene and d14-dibenzo[ah]anthracene in order to monitor the quality of the quantification method. The conditions of extraction by ASE were: 11-mL cells, 80 °C, 100 bar, 5-min heat-up time, two cycles of 5-min static time, 50 % flush, 200 seconds purge with nitrogen. The extracts obtained were concentrated to 1 ml under N₂ using a TurboVap[®] Evaporation System.

The organic extract was fractionated into aromatic, aliphatic and polar compounds by liquid chromatography on alumina and silica previously washed with 200 mL of each solvent (cyclohexane and dichloromethane) and activated at 150 °C for 4 h.

The concentrated extracts were transferred to a 5 g-alumina column (6 mm i.d. × 20 cm in length) and eluted with dichloromethane to obtain a hydrocarbon fraction (aromatic + aliphatic). Dichloromethane was then exchanged with cyclohexane without evaporation to dryness. The concentrated hydrocarbon fraction in 1 mL of cyclohexane was then transferred to a 5 g-silica gel column (6 mm i.d. × 200 mm in length) and eluted with 12 mL of hexane to recover the aliphatic fraction. The silica gel column was then eluted with a hexane/dichloromethane mixture (65:35, v:v). The two hydrocarbon fractions were concentrated to 1 mL under N₂.

2.3. Analysis and quantification

The GC-MS analyses of the aliphatic and aromatic fractions were performed in an Agilent Technologies 6890 GC coupled to an Agilent Technologies 5973 mass spectrometer, using an injector in splitless mode, a 60 m DB-5 J&W, 0.25 mm id; 0.1 µm film fused silica column. The temperature program was 70 -130°C at 15°C.min⁻¹, then 130 - 315°C at 3°C.min⁻¹, followed by an isothermal stage at 315°C during 15 min (constant helium flow of 1mL.min⁻¹). Injection volume was 1 µl.

Quantifications of parent PAHs (26) and alkylated PAHs were performed using single ion monitoring mode and were based on the application of perdeuterated compounds as internal standards (acenaphthene-d₁₀, chrysene-d₁₂, naphthalene-d₈, perylene-d₁₂ and phenanthrene-d₁₀) (Jeanneau et al., 2008). Peak areas were converted into concentration using response factors determined from multiple injections of a certified PAH calibration mixture at

various concentrations (0.5 to 8 ppm). Alkylated PAH compounds were quantified using the response factor of the parent PAHs.

Cholestane-d₆ and *n*-tetracosane-d₅₀ were added to the aliphatic fraction as internal standards in order to quantify the *n*-alkanes, the Unresolved Complex Mixture (UCM) and the hopanes. Quantitative data were calculated by comparison of the peak areas in the extracted ion current chromatogram (*m/z* = 57 for *n*-alkanes, *m/z* = 191 for hopanes ; *m/z* = 183 for isoprenoids ; *m/z* = 95 for UCM)) with the peak areas of the internal standards.

2.4. Organic geochemical ratios

Molecular ratios were calculated from the different hydrocarbon concentrations. Their significance is presented as supplementary information (Table 1). Moreover, the Carbon Preference Index (CPI) that measures the ratio of odd to even carbon numbered *n*-alkanes was calculated as :

$$CPI = \frac{1}{2} \times \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right)$$

The low/high molecular weight *n*-alkanes (LMW/HMW_{Ali}) was quantified by the ratio C₁₂-C₂₀ / C₂₁-C₄₀ *n*-alkanes (LMW/HMW_{ali}) (Colombo et al., 1989).

3. Results

3.1. Polycyclic aromatic hydrocarbons

The sum of 16 EPA priority PAHs ranged between 17 and 73 µg.g⁻¹dw in the sewage sludges (Table 2) and no sludge was found to comply with the French regulation (for detailed analyses of 16 PAH, see Table 2 of supplementary information). The distributions of the 16 PAHs (Figure 1 and Table 2) were quite similar from one sludge to another: dominated by Benzo(b+j)fluoranthene (B(b+j)F), enriched in HMW PAHs (LMW/HMW_{PAH} ranging between 0.1 and 0.24) and depleted in alkylated PAHs (Alk/Par ranging between 0 and 1.29).

204 Sediments collected in the sewers showed PAH concentrations ranging between 5 and 118
205 $\mu\text{g.g}^{-1}\text{dw}$ and generally higher than in the sludges. They were generally enriched in LMW and
206 alkylated PAHs compared to sludges (Figure 1 and Table 2). Suspended matters in
207 wastewater usually showed lower PAH concentrations (0.8 to 45 $\mu\text{g.g}^{-1}\text{dw}$) with higher
208 LMW/HMW_{PAH} ratio (0.18 to 3.41) and higher Alk/Par ratio (0.16 to 8.57) than sediments
209 settled in the sewer (respectively 0.08 to 0.78 and 0 to 2.36). B0-ww, C1-ww and C2-ww
210 showed the highest values of the LMW/HMW_{PAH} ratio (above 1.5). B1-sed, B0-ww, C5-ww
211 and C5-sed were characterized by the predominance of alkylated PAHs (Alkyl/Par ratio above
212 1). The presence of LMW PAHs (2-3 rings) and the abundance of alkylated derivatives can be
213 characteristic of petroleum sources (Masclet et al., 1987; Yan et al., 2005).

214 The cross-correlation of several PAH ratios (Table 2 and figure 2) allowed inferring the
215 sources of PAH in the sewers and the sludges according to the work of Yunker et al. (2002).
216 Most of the PAH ratios proposed by Yunker et al. (2002) were tested and provided results
217 relatively consistent with the results proposed by the cross-plot Fl/(Fl + P) vs. C0/(C0+C1) P-
218 A (Figure 2). The PAHs of most of the samples originated from combustion. Only four
219 samples, C5-ww, C5-Gr, B0-ww and C5-sed had a C0/(C0+C1) Phen-Ant ratio below 0.5
220 indicating a petroleum source of PAHs. Four samples, C5-ww, C5-Gr, C0-Slu1 and C0-Slu2
221 had a Fl/(Fl + Py) ratio below 0.4 also implying a petroleum source.

222 From the detailed examination of PAHs for each sampling site, it arises that PAHs
223 measured in the samples of site A were only from pyrogenic sources.

224 The site B showed the highest PAH concentrations. Suspended matter at the entrance of
225 the WWTP (B0-ww) clearly contained petrogenic PAHs according to LMW/HMW_{PAH},
226 Alk/Par and C0/(C0+C1)P-A. Fl/(Fl+P) did not provide such a clear conclusion and rather
227 indicated a petroleum combustion source. All the ratios calculated for sludges B0-Slu2 to B0-
228 Slu4 as well as for sediments B2-sed and B3-sed showed a clear combustion source. B1-sed

had an intermediate position and most of the ratios (figure 2 and Table 3). They were between those obtained for B0-ww (representing a petroleum influence) and those calculated for B0-Slu2 to Slu4 (representing an unequivocal combustion input). This petroleum input is consistent with the observation made on the site B1 where a smell of fuel was noticed at the time of the sampling. B0-slu1, the closest to the entrance was slightly influenced as indicated by the Alkyl/Par, LMW/HMW_{PAH} ratio slightly higher than in B0-Slu2 to Slu4 and C0/(C0+C1)P-A slightly lower.

At the site C, the PAH distribution in the sludges was dominated by several compounds identified as diisopropylnaphthalenes which were not quantified. These compound mixtures are used as solvents in the manufacturing of printing materials or in agriculture as plant growth regulators (Brzozowski et al., 2002). Their abundance in the sewer at C1 and in the sludges is probably related to the important printing activities developed in the industrial park. Besides these compounds, the PAH distribution and the different aromatic ratios clearly identified a petroleum contribution in the sample C5 (corresponding to the village with agricultural activities). In the other parts of the sewer (C1 and C2), low molecular weight PAHs (Figure 1) were significantly abundant (LMW/HMW_{PAH} > 3) but the other aromatic ratios did not allow to conclude to a petrogenic contribution (Table 3). This specific PAH distribution is probably related to the industrial activity developed at the site C. Fl/(Fl + Py) and BaA/ (BaA+Chr) were the only ratios to suggest a petrogenic input in sludges with values in the same range as in the samples C5.

3.2. Aliphatic hydrocarbons

The detailed analysis of aliphatic hydrocarbons and the calculation of simple ratios provided complementary information on PAHs and other hydrocarbon contributions (Table 2 and figure 3). In all samples, *n*-alkane concentrations were higher than PAH concentrations (1

to 10 times higher). *n*-Alkane concentration was the highest at the site B with an average value of 684 $\mu\text{g.g}^{-1}\text{dw}$, in lower concentration at site C (245 $\mu\text{g.g}^{-1}$) and the lowest at site A (162 $\mu\text{g.g}^{-1}$). The *n*-alkane concentration generally decreased from the sewer to the sewage sludge. Hopanes were present in all the samples and their distributions typical from mature fossil fuels were rather identical from one sample to another. Their presence attests to the general contamination by petroleum products such as road asphalt imported into the sewer through run-off that is also observed in aquatic sediments (Faure et al., 2000).

The three sites offered contrasted alkane distributions. At the site A (figure 3, table 2), the *n*-alkane distributions were quite similar from one sample to another with the predominance of HMW *n*-alkanes (LMW/HMW_{ali} ratios between 0.04 and 0.4) and high CPI ratios (1.6 to 3.9). This is typical of the contribution of terrestrial plants in the sewer which is dominant for samples A4, A5 and the two sludges (Wakeham, 1996). The LMW/HMW_{ali} ratio remained low in all samples.

At the site B (Figure 3, table 2), the predominance of LMW *n*-alkanes and the presence of the two isoprenoids, pristane and phytane in the sample B1 were assigned to an important input of fuel. This petroleum input was already evidenced with the PAH ratios and is confirmed and better identified thanks to its specific *n*-alkane distribution. The CPI of *n*-alkanes in the sewer was close to 1.5 and confirmed the predominance of petroleum input over terrestrial plant input. Finally, the low abundance of hopanes was another element to conclude to a fuel input. A very specific distribution was observed in the sample B0-ww at the entrance of the WWTP. It was dominated by pristane and phytane and no LMW *n*-alkane was identified. This distribution is typical of weathered oils (Palmer, 1993) and could be the result of the biodegradation of a fuel. This suggests the presence of an old contamination that entered the sewer near the entrance of the WWTP. We have no clear evidence of the relationship between the fuel identified at B1 and this weathered fuel. These very specific

fingerprints in the sewer were also evidenced in the sewage sludges although they were less pronounced. The fuel contribution was important in the sludge B0-Slu1 close to the entrance of the WWTP but decreased in the sludges sampled further from the entrance (B0-Slu2 to Slu4). The weathered fuel also influenced the composition of the sludge B0-Slu1 by decreasing its ratios C_{17} /pristane or C_{18} /phytane compared to B0-Slu2 to B0-Slu4 (only the chromatogram of B0-Slu3 is shown).

The site C (Figure 3, table 2) offered a wide variety of *n*-alkane distributions revealing complex inputs of hydrocarbons. Samples C1 located in the industrial park showed an uncommon *n*-alkane distribution dominated by the even-numbered high molecular weight *n*-alkanes in the range *n*-C20-*n*-C40. This specific distribution, although diluted by the other inputs was also observed in the sludges and it lowered significantly their CPI which were the lowest of any sludge (1.2-1.3). We could relate this contamination to the presence of diisopropylnaphthalenes in the aromatic fraction although we have no further evidence. It was observed in the suspended matters in the sewer but largely attenuated C1-sed. The abundance of low molecular weight *n*-alkanes in samples C5 allowed identifying a contribution of refined petroleum products similar to the one observed at site B and assigned to an input of fuel. This petroleum contribution was very important in the samples C5-ww and C5-Gr but diluted by a terrestrial plant input in the sample C5-sed as indicated by the high CPI and a quite low LMW/HMW_{ali} ratio. The sample C5-ww was also characterized by the abundance of the hopanes (236 $\mu\text{g}\cdot\text{g}^{-1}\text{dw}$). The sample C2-ww was characterized by a low CPI (1.27), the predominance of HMW *n*-alkanes (LMW/HMW_{ali} = 0.0) and the abundance of the hopanes (106 $\mu\text{g}\cdot\text{g}^{-1}\text{dw}$). This distribution suggests a contribution of heavy petroleum products. The samples C3-ww and C4-ww showed *n*-alkanes distributions dominated by terrestrial plant inputs (chromatograms not shown).

3.3. Unresolved Complex Mixture (UCM)

The UCM concentrations varied from one sample to another. They were generally high (average of 6400 $\mu\text{g.g}^{-1}$ dw with a standard deviation of 7925 $\mu\text{g.g}^{-1}$ dw) but consistent with results previously published by other authors (Moreda et al., 1998; Rocher et al., 2004a). They were attributed to the presence of weathered crude oils and some refined products such as lubricating oils or biodegraded petroleum residues. They were positively correlated to the hopane concentration with a Pearson correlation coefficient of 0.89. Three samples showed high UCM concentrations, C2-ww, C5-ww and C5-gr. The important HMW UCM of C5-ww and C5-gr is associated with a specific distribution of *n*-alkanes and the abundance of hopanes which strongly suggests an important contamination by lubricating oil. These features are less pronounced in sample C2-ww but could indicate a small contamination by these petroleum products.

Another important point to consider is the shape of the UCM which is very characteristic of the inputs (Supplementary information, Figure 2)(Kaplan et al., 2001; Wang et al., 2004). The absence of specific input or the dominance of terrestrial plant input is characterized by a flat UCM shape such as in sample A3-sed. The presence of fuel oil is marked by a LMW UCM with a typical bell shape such as in sample B1-sed and B0-ww. The presence of HMW hydrocarbons from lubricating oil results in a HMW UCM with a bell shape as observed in C5 samples. Finally, most of the samples and more specifically A5-sed and C3-ww show an UCM classically observed in urban dust and road asphalt (Kaplan et al., 2001; Fernandes and Brooks, 2003).

4. Discussion

Significance and pertinence of molecular indices for PAH source apportionment in sludges

The complexity of the inputs in the sewers and the degradation of organic matter that takes place in the sewer and the WWTP make PAH source apportionment difficult. Based on the strict significance of PAH ratios (figure 2), most of the samples have an unambiguous combustion fingerprint which is confirmed by the analysis of the aliphatic hydrocarbons. The best example is probably the site A where all the PAH ratios indicate pyrogenic PAHs. The *n*-alkane distributions as well as the UCM abundances and other ratios do not provide any supplementary information on the different contributions except an important dilution by terrestrial plants. Only two samples have an unambiguous petroleum fingerprint (C5-Gr and C5-ww) according to PAH ratios. In this case, hydrocarbon analysis provides crucial information on the nature of the petroleum contributions. High UCM and hopane concentrations, low CPI (<1.5), high LMW/HMW (>0.3) allow inferring inputs of lubricating oil (or heavy petroleum residues) and fuel. Used lubricating oil commonly contains PAHs and unburned fuel (Kaplan et al., 2001).

In several samples (B0-ww, B1-sed and B0-slu1), an obvious fuel contribution is identified based on the aliphatic distribution but it is not clearly evidenced by the strict interpretation of PAH ratios. It suggests either that the petrogenic input is not as important as the combustion one or that biodegradation has altered the significance of molecular ratios.

Interest of sampling in the sewer – persistence of molecular indices in the sludges

The molecular indices calculated exclusively from sludge analyses are quite difficult to interpret for two reasons: (i) they are the result of a mixture of multiple sources more or less diluted with other organic matters and (ii) they have undergone a rather severe biodegradation. Thus, molecular indices in sludges generally show the same molecular fingerprint: most of the PAH ratios indicate mainly pyrogenic inputs and sometimes a mixed petroleum and combustion contribution ; *n*-alkanes distributions are most of the time

unimodal, UCM have generally the same shape turned toward HMW. The indices of a specific and unusual input are very weak and it appears difficult to interpret a slight deviation from the average sludge composition in terms of specific inputs.

The analyses of samples from the sewer give a more comprehensive insight of the inputs and allow strengthening PAH source apportionment. Moreover, it provides a spatial screening of the different inputs and can then help in identifying accidental inputs, contaminated area or polluting activities. Sampling in the sewer also allows to obtain less degraded organic matter and thus limits the change in molecular indices from source to receptors. When it was possible to sample wastewater and sediments in the sewer at the same site, the comparison of the composition of sediments and suspended particulate matter in wastewater showed a systematic enrichment in LMW hydrocarbons suggesting less degraded hydrocarbons in suspended particulate matter. Several authors (Zhang et al., 2005; Brandli et al., 2007; Katsoyiannis et al., 2007) pointed out the instability of PAH ratios in different processes such as biodegradation or composting. Our data show a systematic decrease of LMW/HMW_{PAH} and Alk/Par from the sewer to the sludge also observed by Blanchard et al. (2001). This suggests that the petroleum contribution is minimized in sludge because of its dilution and more probably because of its preferential degradation during the transfer and the degradation processes in the WWTP.

5. Conclusions

The first conclusion of this study is that, although questionable, PAH ratios provide at least some leads to distinguish combustion from petroleum PAHs. But, they do not allow going further into the interpretation of the origin of the petroleum or combustion inputs. The identification of the different inputs can only be performed thanks to the aliphatic hydrocarbons that will help in narrowing down the origin of petroleum products. In this way,

LMW/HMW_{ali} ratio, CPI and the abundance and the shape of the UCM are good source indicators. However, there is a lack of indices to perform the same distinction between multiple combustion sources since carbonaceous residues are generally depleted in aliphatic hydrocarbons or do not have an unequivocal aliphatic distribution. Although Fernandes and Brooks (2003) showed that every black carbon has its own molecular fingerprint, this distinction becomes very difficult in the context of complex inputs, mixing petroleum and combustion sources such as in sewer or sludge.

The second conclusion is that the multi-molecular approach can only be very efficient when calculated from suspended matter or sediments sampled in the sewer and sludges. Indeed, sewer samples allow spatial screening of the different inputs. When carefully chosen, the sampling sites in the sewer integrate a lower number of hydrocarbon sources and data are then easier to interpret. Moreover, the hydrocarbon fingerprints are better preserved from biodegradation, water-washing and volatilization than in the sludge since they are close to the emission source.

This study shows the pertinence of a multi-molecular approach combining PAH and aliphatic ratios to identify the different hydrocarbon contributions in a sewer that end up in the WWTP and finally in sewage sludges. It is particularly useful to point out the accidental inputs of petroleum derivatives such as fuel or lubricating oils that overlap the diffuse inputs of combustion PAHs brought by the run-off of the surfaces drained by the sewer. It can then provide useful tools to manage the inputs in a sewer, improve the efficiency of a WWTP and then lower PAH concentrations in sludges. The application of this multi-molecular approach to samples collected with auto-samplers or sediment traps placed into the sewer would improve the methodology and provide not only qualitative information on PAH sources but also a better quantification of these inputs.

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CAPTIONS

Table 1: Sample names and main characteristics of the three sampling sites. See Figure 1 of supplementary information for locations of sampling points on a map.

Table 2: PAH and alkane concentrations and main molecular ratios calculated from hydrocarbon concentrations. Max PAH = major PAH ; LMW/HMW_{PAH} is the ratio of the 2-3 rings PAHs to the 4-6 rings PAHs ; Alk/Par is the ratio of the sum of the alkyl-PAH (C1-C4 Na ; C1-C3P/A ; C1-C2F/P) to the sum of the parent PAHs with masses 128, 178, 202 ; $C0/(C0+C1)$ P-A is the ratio of parent PAHs with mass 178 (P, A) to PAHs with mass 178 (A; P) plus their C1 alkyl homologues ; Max n-alkane = major aliphatic hydrocarbon ; UCM/R is the ratio of the concentration of unresolved complex mixture (UCM) to resolved alkanes ($R = n\text{-alkanes} + \text{hopanes} + \text{isoprenoids}$).

Figure 1: PAH distribution normalized to the sum of the 16 PAH. The left column gathers samples of suspended particulate matter from the wastewaters collected in the sewer, the central column gathers sediments settled in the sewer, and the right column gathers sewage sludges. Na: Naphthalene; Acy: Acenaphthylene; Ace: Acenaphthene; F: Fluorene; P : Phenanthrene; A : Anthracene; Fl : Fluoranthene; Py : Pyrene; BaA: Benzo(a)anthracene; Ch: Chrysene; B(b+j)F: Benzo(b)fluoranthene; BkF: Benzo(k)fluoranthene; BaP: Benzo(a)pyrene; DhA: Dibenzo(ah)anthracene; Bghi: Benzo(ghi)perylene; IP: Indeno(123-cd)pyrene

Figure 2: PAH cross plot for the ratio $Fl/(Fl+Py)$ vs $C/(C0+C1)$ P-A.

Figure 3: Alkane distributions ($m/z=57$) of selected samples at the 3 sites. Pr = Pristane ; Ph= Phytane.

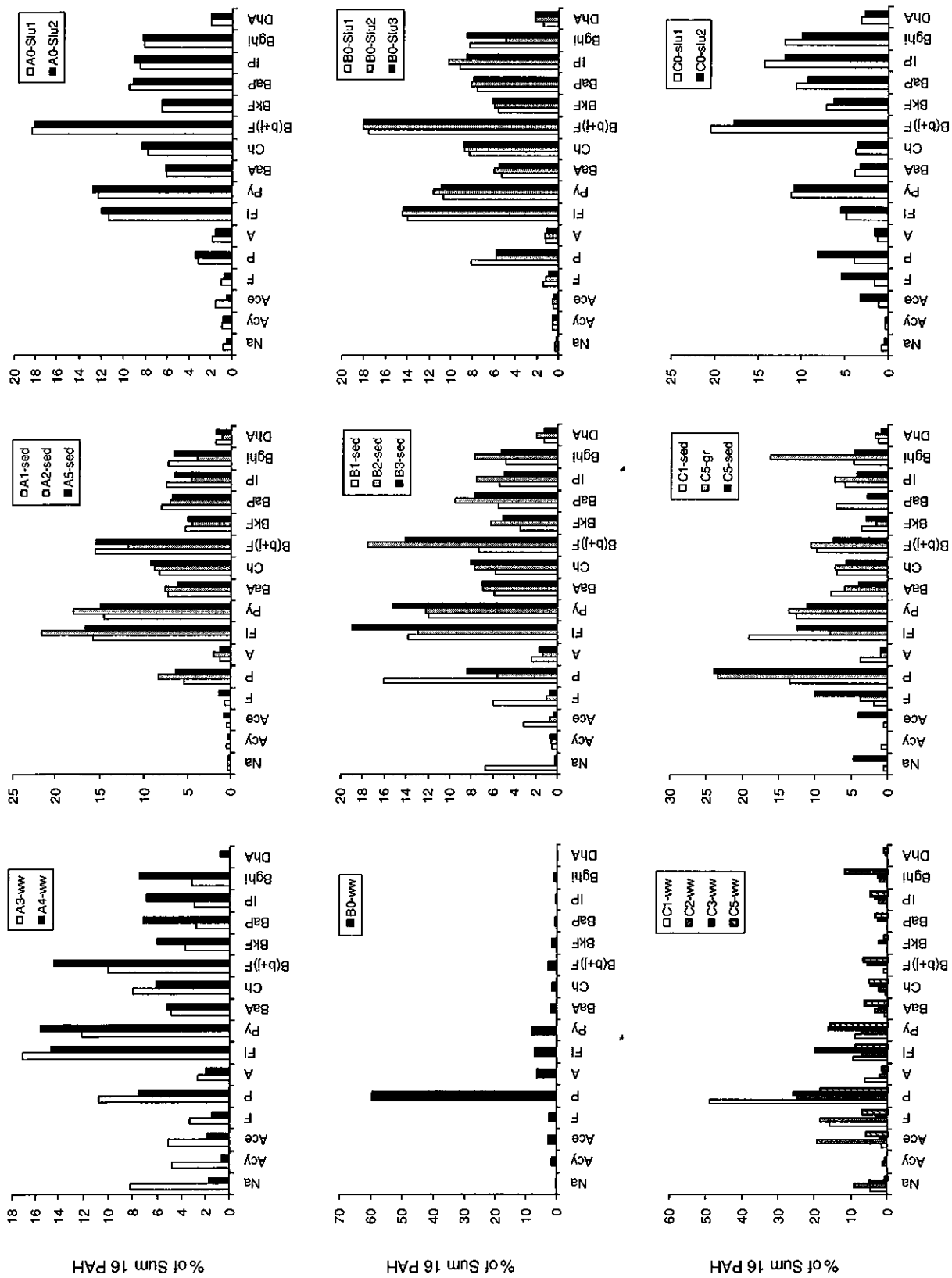


Figure 1

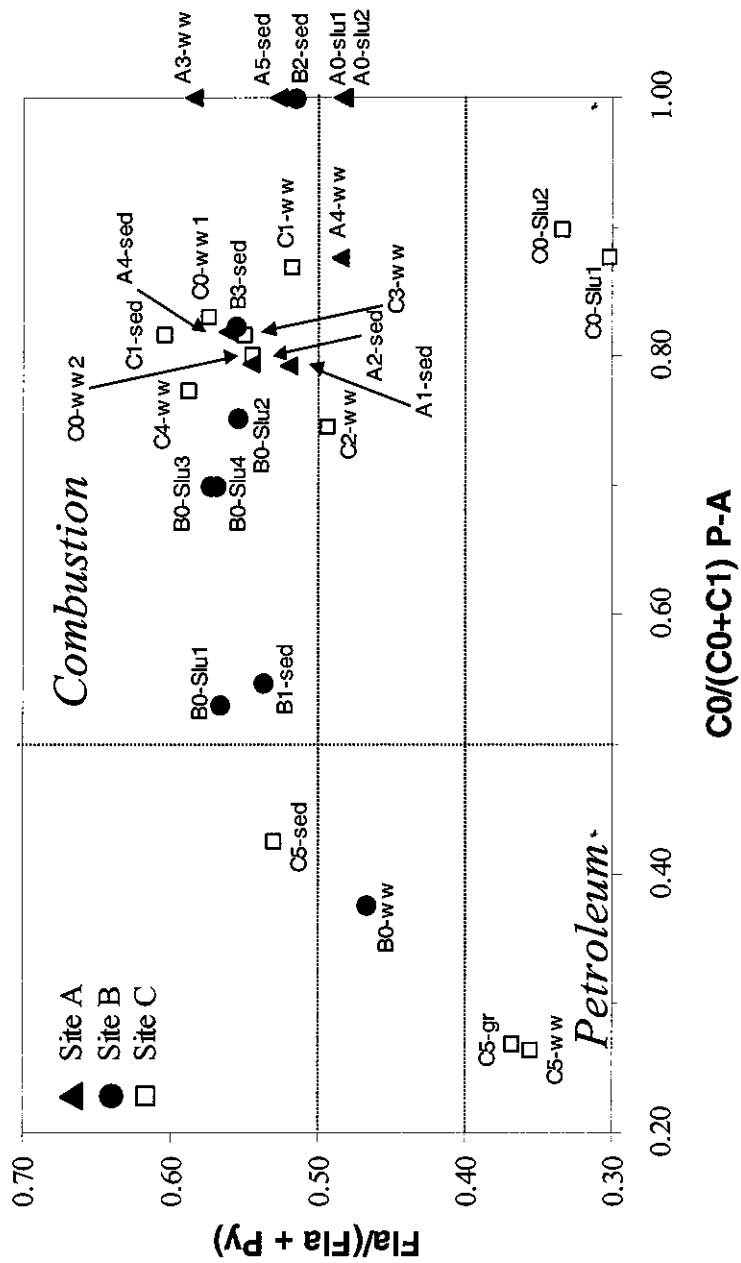


Figure 2

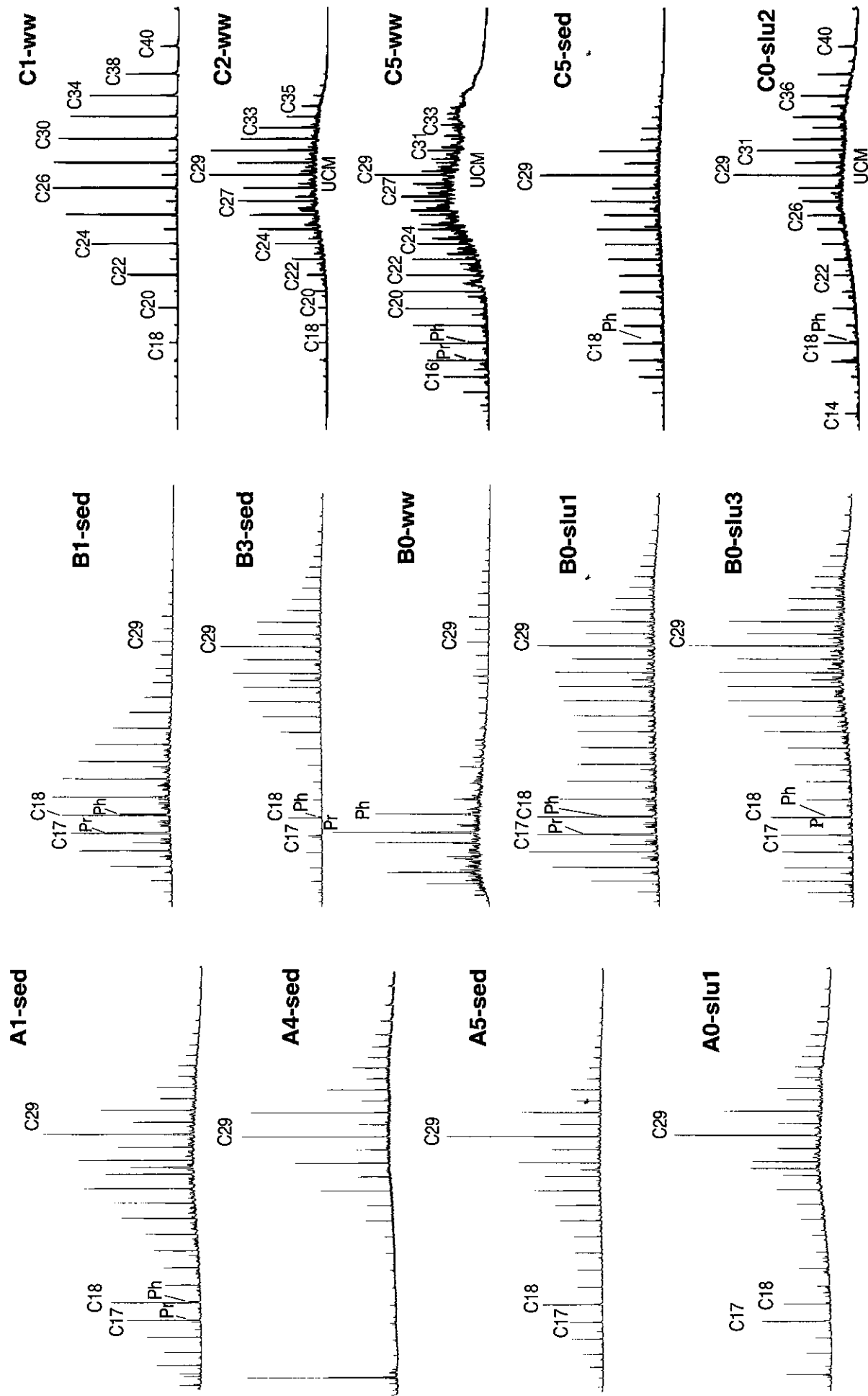


Figure 3

Table 1

Abbreviation	Location	Main characteristics
A0-Slu1	Site A - WWTP	Sewage sludge in the WWTP Silo
A0-Slu2	Site A - WWTP	Sewage sludge in the WWTP aeration basin
A1-sed	Site A - Sewer	Sediments in the manhole at the confluence of villages 1 and 2
A2-sed	Site A - Sewer	Sediments in the manhole of the village 3 collecting wastewater and runoff
A3-ww	Site A - Sewer	Wastewater in the manhole of the newest residential part of village 1
A4-ww	Site A - Sewer	Wastewater in the manhole of the oldest residential part of village 1
A4-sed	Site A - Sewer	Sediments in the manhole of the oldest residential part of village 1
A5-sed	Site A - Sewer	Sediments in the manhole of the whole village 1
B0-ww	Site B - WWTP	Wastewater at the entrance of the WWTP
B0-Slu1	Site B - WWTP	Sewage sludge in the sedimentation tank
B0-Slu2	Site B - WWTP	Sewage sludge in the sedimentation tank
B0-Slu3	Site B - WWTP	Sewage sludge in the sedimentation tank
B0-Slu4	Site B - WWTP	Sewage sludge in the sedimentation tank
B1-sed	Site B - Sewer	Manhole of the village
B2-sed	Site B - Sewer	Manhole of the village
B3-sed	Site B - Sewer	Manhole of the village
C0-ww1	Site C - WWTP	Wastewater from villages 1 and 2 at the entrance of the WWTP
C0-ww2	Site C - WWTP	Wastewater from village 3 at the entrance of the WWTP
C0-slu1	Site C - WWTP	Sewage sludge in the aeration basin
C0-slu2	Site C - WWTP	Sewage sludge in the silo
C1-ww	Site C - Sewer	Wastewater in a manhole of the industrial park
C1-sed	Site C - Sewer	Sediments in a manhole of the industrial park
C2-ww	Site C - Sewer	Wastewater in a manhole of a residential area
C3-ww	Site C - Sewer	Wastewater in a manhole of villages 1 and 2
C4-ww	Site C - Sewer	Wastewater in a manhole of villages 1 and 2
C5-ww	Site C - Sewer	Wastewater in a manhole of village 3
C5-gr	Site C - Sewer	Grease in a manhole of village 3
C5-sed	Site C - Sewer	Sediments in a manhole of village 3

	A1-sed	A2-sed	A3-ww	A4-sed	A4-ww	A5-sed	A0- Slu1	A0- Slu2	B1-sed	B2-sed	B3- sed	B0-ww	B0- Slu1	B0- Slu2	B0- Slu3	B0- Slu4	C1-ww	C1- sed	C2-ww	C3-ww	C4-ww	C5-ww	C5-gr	C5- sed	C0- ww1	C0- ww2	C0- slu1	C0- slu2
Σ16 PAH (μg.g ⁻¹ dw)	31.4	65.4	0.8	71.0	7.3	21.6	25.3	22.6	60.2	49.6	118.2	14.1	59.6	70.4	72.6	43.7	0.8	82.1	1.4	2.8	11.3	45.0	4.9	5.2	2.6	1.7	16.8	18.7
Alkyl PAH (μg.g ⁻¹ dw)	4.6	12.1	0.1	1.6	0.5	<DL	<DL	<DL	64.3	4.9	12.6	99.4	26.5	12.0	13.6	7.9	0.1	12.9	0.7	0.7	1.7	74.8	3.2	6.5	0.4	0.4	2.1	2.2
Max PAH	FI	FI	FI	B(b+h)F	Py	FI	B(b+h)F	B(b+h)F	P	B(b+h)F	FI	P	B(b+h)F	B(b+h)F	B(b+h)F	B(b+h)F	P	FI	P	P	FI	P	P	P	P	P	B(b+h)F	B(b+h)F
LMW/HMW _{PAH}	0.09	0.12	0.54	0.08	0.18	0.12	0.10	0.08	0.53	0.10	0.14	2.85	0.14	0.11	0.10	0.11	3.41	0.27	3.03	0.63	0.17	0.52	0.39	0.78	0.57	1.69	0.10	0.24
Alk/Par	0.39	0.37	0.29	0.16	0.09	0.00	0.00	0.00	2.09	0.30	0.24	8.57	1.29	0.51	0.58	0.54	0.17	0.32	0.93	0.36	0.33	3.63	1.44	2.36	0.36	0.40	0.57	0.45
Co/(Co+C1) P-A	0.79	0.79	1.00	0.82	0.88	1.00	1.00	1.00	0.55	1.00	0.82	0.38	0.53	0.75	0.70	0.70	-	0.82	0.75	0.82	0.77	0.27	0.27	0.43	0.83	0.80	0.88	0.90
FI/(FI+Py)	0.52	0.55	0.59	0.56	0.49	0.53	0.48	0.48	0.54	0.52	0.56	0.47	0.57	0.55	0.57	0.57	-	0.60	0.49	0.55	0.59	0.36	0.37	0.53	0.57	0.54	0.30	0.33
BaA/(BaA+Ch)	0.42	0.41	0.31	0.37	0.36	0.33	0.35	0.34	0.44	0.41	0.40	0.53	0.32	0.34	0.32	0.33	-	0.48	0.48	0.28	0.41	0.50	0.37	0.35	0.35	0.39	0.34	0.34
IP/(IP+Bghi)	0.51	0.53	0.49	0.54	0.48	0.50	0.51	0.52	0.53	0.49	0.49	0.33	0.52	0.67	0.50	0.52	-	0.56	0.54	0.56	0.53	0.29	0.31	0.48	0.57	0.46	0.55	0.54
Σn-alkanes (μg.g ⁻¹ dw)	239	82	44	31	24	507	158	207	908	409	1309	92	956	397	726	677	45	131	593	152	21	464	560	447	121	191	112	107
ΣHopanes (μg.g ⁻¹ dw)	18.4	11.1	<DL	25.6	<DL	14.4	29.0	29.6	7.5	17.9	44.7	5.2	38.9	28.9	38.6	47.9	<DL	31.2	106	11.8	7.5	236	41.8	20.1	6.7	5.5	33.2	31.1
UCM (μg.g ⁻¹ dw)	3101	914	530	252	446	4032	4963	5055	3859	2447	6451	6624	7435	3940	6147	7595	166	4558	11302	2946	809	40612	21568	5086	1518	1372	6558	6239
CPI	1.80	1.62	1.73	3.27	3.87	2.42	2.55	2.15	1.67	1.39	1.30	1.01	1.43	1.70	1.62	1.50	-	1.14	1.27	2.11	2.24	-	1.40	2.07	2.08	1.48	1.21	1.33
Max n-Alkane	C29	C29	C29	C29	C29	C29	C29	C29	C18	C29	C29	Pr	C29	C29	C29	C29	C26	C22	C31	C29	C29	C22	C20	C29	C29	C29	C29	C29
LMW/HMW _{ALU}	0.3	0.1	0.0	0.0	0.4	0.2	0.2	0.1	2.0	0.1	0.1	0.0	0.5	0.4	0.4	0.2	0.0	0.3	0.0	0.1	0.2	1.2	0.5	0.2	0.0	0.0	0.1	0.1
UCM/R	11.8	9.7	11.8	4.5	18.2	7.5	26.3	21.2	3.7	5.6	4.7	19.2	7.0	9.0	7.8	10.3	3.7	26.9	16.1	17.9	27.9	54.2	33.8	10.6	11.8	7.0	44.5	44.3
C ₁₇ /Pristane	4.3	4.4	2.9	-	20.8	2.0	8.9	8.6	0.9	2.2	3.0	0.0	0.8	2.9	2.4	2.4	-	1.5	2.4	-	3.5	1.8	2.0	1.9	3.5	-	1.1	1.3

Table 2

Ratio	Description	Petrogenic	Petroleum burning or mixed contribution	Coal, wood and grass combustion	References
$\text{LMW}/\text{HMW}_{\text{PAH}}$	Ratio of the 2-3 rings PAHs to the 4-6 rings PAHs	>1,5	<0.65		(Yan et al. 2005)
Alk/Par	Ratio of the sum of the alkyl-PAH ((C1-C4 Na; C1-C3P/A; C1-C2F/P) divided by the sum of the parent PAHs with masses 128, 178, 202	>2	<1		(Yan et al. 2005)
$\text{C0}/(\text{C0}+\text{C1})$ A-P	Ratio of parent PAHs with mass 178 (P, A) to PAHs with mass 178 (A; P) plus their C1 alkyl homologues	<0.5	>0.5		(Yunker et al. 2002)
BaA/ (BaA+Chy)	Ratio of benzo[a]anthracene to the sum of benzo[a]anthracene + chrysene	<0.2	>0.35		(Yunker et al. 2002)
Fl/(Fl+Py)	Ratio of fluoranthene to the sum of fluoranthene and pyrene	<0.4	0.4 to 0.5	>0.5	(Yunker et al. 2002)
IP/(IP+Bghi)	Ratio of indeno[1,2,3-cd]pyrene to the sum of indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene (Bghi)	<0.2	0.2 to 0.5	>0.5	(Yunker et al. 2002)
UCM/R	Concentration of unresolved complex mixture (UCM)/ resolved alkanes ($R = n$ -alkanes + hopanes + isoprenoids)	>4.0	>6.0	<4	(Yan et al. 2005)

Table 1: Main molecular indicators calculated in this study and their respective diagnostic ratios

	A1-sed	A2-sed	A3-ww	A4-ww	A5-sed	A4-sed	A0- Slu1	A0- Slu2	B1-sed	B2-sed	B3- sed	B0-ww	B0- Slu1	B0- Slu2	B0- Slu3	B0- Slu4	C1- ww	C1- sed	C2-ww	C3-ww	C4-ww	C5-ww	C5-gr	C5- sed	C0- ww1	C0- ww2	C0- slu1	C0- slu2
Na	0,1	0,2	0,1	0,1	0,1	0,1	0,2	0,1	4,0	0,1	0,2	0,1	0,2	0,2	0,1	0,1	<DL	0,5	0,1	<DL	0,1	0,1	0,4	<DL	0,2	0,2	0,3	0,1
Acy	0,1	<DL	0,0	<DL	0,1	0,5	0,2	0,2	0,3	0,3	0,8	0,2	0,3	0,4	0,4	0,3	<DL	0,7	<DL	<DL	0,1	0,0	<DL	<DL	<DL	<DL	0,1	0,1
Acen	0,1	<DL	0,0	0,1	0,2	0,6	0,4	0,1	1,9	0,4	0,4	0,4	0,3	0,4	0,3	0,2	<DL	0,4	0,3	0,1	<DL	2,7	<DL	0,2	0,1	0,1	0,2	0,6
Fluo	0,2	<DL	0,0	0,1	0,3	0,6	0,2	0,2	3,6	0,5	0,8	0,4	0,9	0,8	0,6	0,5	0,1	1,5	0,3	0,1	0,1	3,2	0,2	0,5	0,1	0,2	0,3	1,0
Phe	1,7	5,5	0,1	0,5	1,4	2,7	0,8	0,8	9,7	2,8	9,9	8,4	4,8	4,1	4,2	2,6	0,4	11,1	0,3	0,7	1,1	8,4	1,1	1,2	0,4	0,5	0,7	1,5
An	0,4	1,3	0,0	0,1	0,3	1,1	0,5	0,3	1,4	0,7	2,0	0,9	0,7	0,9	0,8	0,6	<DL	3,1	<DL	<DL	0,2	0,7	<DL	<DL	<DL	<DL	0,2	0,3
Fl	4,9	14,2	0,1	1,1	3,6	8,1	2,9	2,7	8,3	6,4	22,5	1,0	8,3	10,2	10,4	6,6	0,1	15,7	0,1	0,6	2,2	4,0	0,4	0,6	0,2	0,2	0,8	1,0
Py	4,5	11,8	0,1	1,1	3,2	6,3	3,1	2,9	7,2	6,0	18,0	1,2	6,4	8,2	7,9	4,9	0,1	10,3	0,1	0,5	1,5	7,2	0,7	0,6	0,2	0,1	1,9	2,0
BaA	2,3	5,0	0,0	0,4	1,3	3,7	1,5	1,4	3,5	3,4	8,4	0,3	3,1	4,2	4,0	2,5	<DL	6,4	<DL	0,1	0,8	2,9	0,3	0,2	0,1	0,1	0,6	0,6
Chy	2,6	5,8	0,1	0,4	2,0	4,3	2,0	1,9	3,5	3,9	9,7	0,2	4,9	6,1	6,4	3,7	<DL	5,8	<DL	0,1	0,9	2,4	0,4	0,3	0,2	0,1	0,6	0,7
B(b+)]F	4,9	7,7	0,1	1,0	3,3	12,7	4,7	4,1	4,4	8,7	16,7	0,4	10,5	12,8	13,1	7,7	<DL	8,0	<DL	0,2	1,4	3,1	0,5	0,4	0,3	0,1	3,4	3,3
BkF	1,7	2,9	<DL	0,4	1,1	3,8	1,7	1,5	2,1	3,1	6,0	0,2	3,3	4,2	4,5	2,5	<DL	3,0	<DL	0,1	0,5	0,5	0,1	0,2	0,1	<DL	1,2	1,2
BaP	2,5	4,6	<DL	0,5	1,5	6,0	2,4	2,1	3,3	4,8	9,2	0,1	4,5	5,7	5,8	3,4	<DL	5,8	<DL	0,1	0,8	1,7	<DL	0,1	0,2	<DL	1,8	1,7
IP	2,4	3,0	<DL	0,5	1,4	10,2	2,2	2,1	3,3	3,8	5,9	0,1	5,5	7,2	6,2	3,9	<DL	4,8	<DL	0,1	0,8	2,2	0,4	0,2	0,2	<DL	2,4	2,2
Bghi	2,3	2,6	<DL	0,5	1,4	8,6	2,1	1,9	2,9	3,9	6,3	0,1	5,0	3,5	6,2	3,5	<DL	3,8	<DL	0,1	0,7	5,3	0,8	0,2	0,2	<DL	2,0	1,9
DhA	0,6	0,6	<DL	0,1	0,4	1,8	0,5	0,4	0,8	1,0	1,5	0,0	0,8	1,6	1,6	0,8	<DL	1,1	<DL	<DL	0,2	0,5	0,1	<DL	<DL	<DL	0,5	0,5
Σ16 PAH (ug.g ⁻¹ dw)	31,4	65,4	0,8	7,3	21,6	71,0	25,3	22,6	60,2	49,6	118,2	14,1	59,6	70,4	72,6	43,7	0,8	82,1	1,4	2,8	11,3	45,0	4,9	5,2	2,6	1,7	16,8	18,7

Table 2: Concentrations of the 16 PAH in mg.g⁻¹dw in the samples of the three sites.

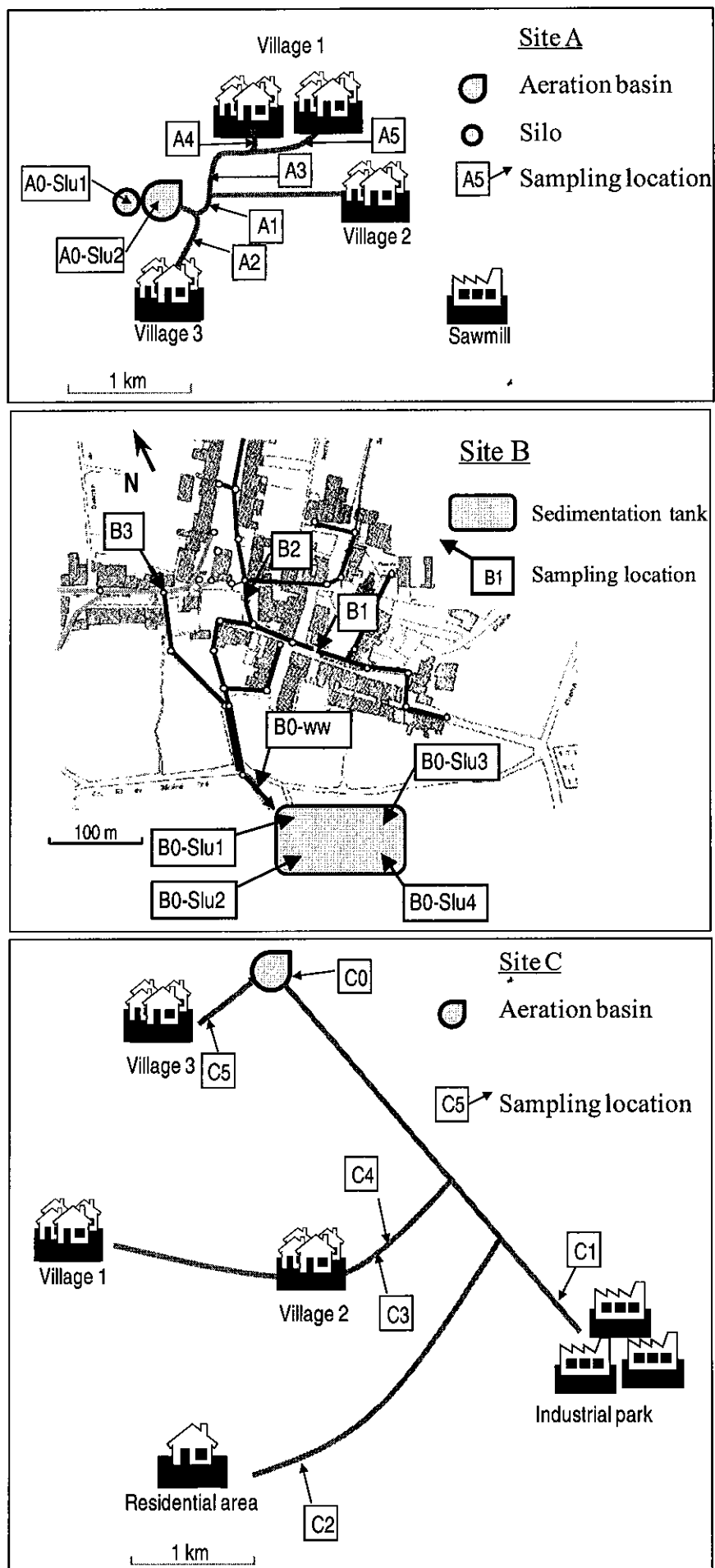


Figure 1: Detailed map of the three sampling sites

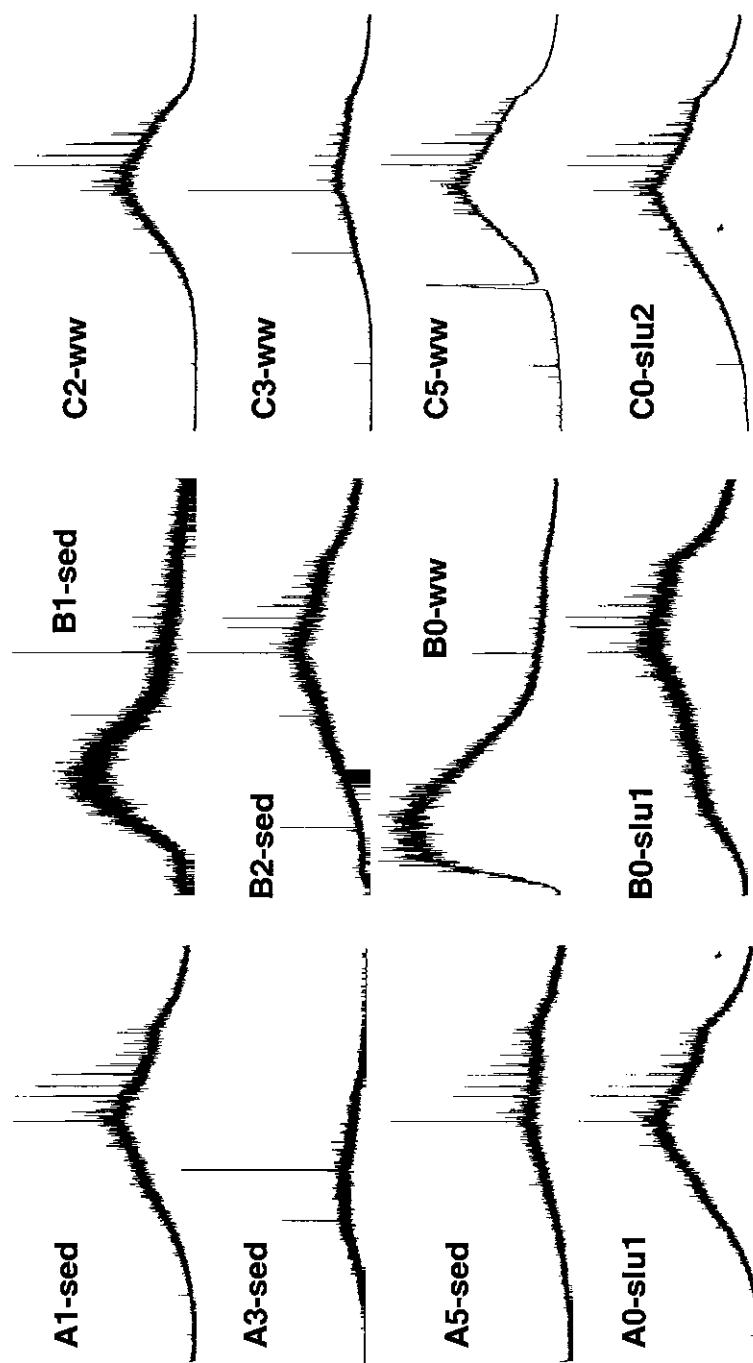


Figure 2: UCM distributions ($m/z=95$) of selected samples at the three sites.