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To cite this version:
A. Motelay-Massei, Donatienne Ollivon, Brigitte Garban, M. Chevreuil. Atmospheric deposition of toxics onto the Seine Estuary, France: example of polycyclic aromatic hydrocarbons. Atmospheric Chemistry and Physics Discussions, European Geosciences Union, 2002, 2 (5), pp.1351-1369. hal-00327799

HAL Id: hal-00327799
https://hal.archives-ouvertes.fr/hal-00327799
Submitted on 17 Sep 2002

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Atmospheric deposition of toxics onto the Seine Estuary, France: example of polycyclic aromatic hydrocarbons

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Received: 23 May 2002 – Accepted: 10 July 2002 – Published: 17 September 2002

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Abstract

Concentrations of Polycyclic Aromatic Hydrocarbons (PAH) were measured in precipitation samples on a weekly basis between March and October 2001, at four sites in the Seine Estuary (France). Mean concentrations of total PAHs (Σ14 PAHs) ranged from 38 to 141 ng L\(^{-1}\). Fluoranthene, phenanthrene and pyrene were the dominant PAH compounds and were detected in each sample. The six potential carcinogenic PAHs accounted for 20 to 25% of the total PAH concentration in bulk deposition. The PAH signatures in bulk (wet and dry) deposition and surface water were also compared to investigate source/sink relationships. Seasonal patterns were observed with maximum loading occurring during the colder months of the studied period (March and April). Mean values of daily flux reported for Σ14 PAHs ranged from 108 to 267 ng m\(^{-2}\) d\(^{-1}\). Spatial influences were also observed, indicating both localized and long-range atmospheric source inputs (controlled by hydroclimatic parameters).

1. Introduction

The evolution of industry and the increase of population have resulted in deep changes in quality of our environment. Nowadays much more often the attention of analysts is focused on the presence of organic pollutants in precipitation. These studies showed the presence of more than 600 chemicals like polycyclic aromatic hydrocarbons, organohalogen compounds, pesticides or polychlorinated biphenyls for example in the most of countries (Gryniewicz et al., 2002; Kawamura and Kaplan, 1986; Kiss et al., 1997; Leuenberger et al., 1988; Manoli et al., 2000; Simcik et al., 2000). Atmospheric inputs (wet and dry) play a significant role in semivolatile chemicals cycling (Offenberg and Baker, 1997). Then, atmospheric depositions represent respectively 90%, 78% and 58% of inputs of organic contaminants to the surface of Superior, Michigan and Huron Lakes (Strachan and Eisenreich, 1988). Atmospheric deposition consists of both wet (vapour and particle washout) and dry (particle settling). Polycyclic aromatic hydrocar-
bons (PAHs) are class of compounds referred to as semi-volatile organic contaminants (SOCs). There are two to eight ring compounds of great environmental concern because of their carcinogenic and mutagenic properties (Menzie et al., 1992; Tsai et al., 1995; Valberg et al., 1996; Valerio et al., 1992). PAHs are formed primarily during incomplete combustion of fossil fuels and wood. Major sources of PAHs to urban atmosphere can include automobile traffic, home heating, municipal incinerators and industrial emissions. Despite their production in urban and industrial sites, PAHs occur at high concentrations in rural areas due to their persistence and ability to be transported over long distances.

The aim of this investigation was to obtain information about the occurrence of organic trace components in precipitation in the Seine Estuary. It was also of interest to investigate the spatial and temporal variability of PAHs in the bulk (wet and dry) deposition occurring in the estuary region and to estimate PAH deposition flux. Moreover, it seemed to be interesting to check the potential differences between the various sites (urban, industrial or rural).

2. **Experimental**

2.1. **Sampling sites**

Precipitation samples were collected at four locations in the Seine Estuary. Figure 1 shows a map of the sampling sites. These one were chosen so as to be able to establish the effect of sampling location on the contents of the PAHs analysed. Historically, the Seine Estuary, like most of European estuaries, has been the centre of the development of an important economic activity. Intensive development of human activities (petrochemical industries, thermal power-station, incinerators, domestic heating, automobile traffic) in the alluvial plains and in the estuary is the cause of the important flow of contaminants in these ecosystems. The following locations were selected:

- **Site 1 Rouen**, representative of urban area influenced by heavy traffic.
Site 2 Notre-Dame de Gravenchon (NDG), representative of urban area, subjected to an industrial pressure.

Site 3 Le Havre, representative of typical industrial areas in the estuary.

Site 4 Evreux, rural site

Sites were chosen to be as far away as possible from buildings, large trees and roads to keep contamination at a minimum.

2.2. Sampling procedure and analytical methods

Bulk atmospheric deposition (wet and dry) were collected weekly from March to October 2001 (88 samples). Thus it is possible to pinpoint qualitative and quantitative changes in the occurrence of PAHs. Moreover, the weekly sampling period makes it possible to avoid the uncertainties. A longer sampling period could be especially detrimental to PAH deposition measurements, as heat and light may cause evaporation, revolatilization and deterioration of the PAH species.

Meteorological data (temperature, precipitation amount and wind direction) were obtained from the nearest Mto France stations. Three meteorological stations at the sampling stations were used. The same station was used to Le Havre and NDG because of their climatic similarities. As regards typical circulation of air masses, the prevailing wind direction was generally West and Northwest (Fig. 2). Meteorological data on the sampling period are summed up in Table 1.

Samples were collected using a simple apparatus consisting of a 25 L aluminium bottle equipped with a polished stainless steel funnel (collection area = 0.36 m²). After a sampling period, the receiving bottles are brought to the laboratory for PAHs analysis and also for the analysis of organochlorine contaminants. On the total volume of precipitation, 3.6 L were extracted. Fallout extractions were performed using a liquid-liquid technique. Samples were shaken 3 times and for 20 min in a glass bottle, using 100 mL of a hexane/methylene chloride mixture (v/v 85/15) for each litre of sample (Ollivon et
al., 1999). Extracts were combined and reduced to about 3 ml on a rotary evaporator; after removal of sulphides by adding mercury, no further purification was performed. As elution solvent for HPLC is acetonitrile/water, hexane had to be exchanged with acetonitrile. For this purpose, methylene chloride and acetonitrile were added to the reduced extract in a 3/1/1 proportion for hexane/methylene chloride/acetonitrile, respectively. Then the mixture was concentrated on a rotary evaporator to about 0.5 mL and subjected to liquid chromatographic analysis.

A solution of a standard mixture (PAH-Mix 9 in acetonitrile from Dr. Ehrenstorfer GmbH, Augsburg, Germany) containing the 16 PAHs recommended by the EPA method # 610 was used: naphthalene (NAP), acenaphthalene (ACY), acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FTH), pyrene (PYR), benz(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), dibenz(a,h)anthracene (DBA), benzo(g,h,i)perylenne (BGP), indeno(1,2,3-cd)pyrene (IND). When extracted in the same conditions, the recovery efficiency ranged from 91% to 113%.

Chromatography of the extracts was performed on a Dionex 4500i chromatograph, equipped with a Vydac 201TP5415 column and two detectors, UV/visible and fluorimetric. The instrumental conditions have been described more precisely elsewhere (Ollivon et al., 1995). Replicate analyses of standards gave relative standard deviation (RSD) from ±4% to ±8%, and detection limits, in our analytical conditions, ranged from 0.06 to 0.6 ng L\(^{-1}\), depending on the PAH analysed. Blanks extracted in the same conditions were below detection limits and results were displayed without blank correction. Naphtalene, which is highly volatile, and acenaphththalene, which is weakly fluorescent, were not quantified; therefore, “total PAHs” included 14 compounds.

3. Results and discussion

The following results bring together data from 5 March to 1 October 2001. Analytical results indicated that polynuclear aromatic hydrocarbons were present in precipitation...
in frequent basis. For the 88 samples, concentrations were indeed greater than the
limit of detection (L.D.).

3.1. Bulk deposition concentrations

Concentrations of selected PAHs measured in the Seine Estuary are summarized in
Table 2. These values showed bulk deposition, such means both wet and dry de-
position. 14 PAHs were identified and quantified. For sum of total PAHs, concentrations
ranged from 3.45 to 234 ng L\(^{-1}\) at Evreux, from 8.7 to 672 ng L\(^{-1}\) at Le Havre, from
3.45 to 129 ng L\(^{-1}\) at Rouen and from 9.6 to 184 ng L\(^{-1}\) at NDG. Mean concentrations
of total PAHs were, respectively, 77.8, 141, 49.6 and 38 ng L\(^{-1}\). Usually, levels mea-
sured in rainwater of the Seine estuary were close to those reported in the literature.
However, their comparison is not easy because (i) measured PAHs may differ and (ii)
measurements may concern only wet instead of bulk deposition. Nevertheless, or-
ders of magnitude can be compared. Bulk deposition concentrations of \(\Sigma 14\) PAHs in
Switzerland were 210 ng L\(^{-1}\) in Spring and 130 ng L\(^{-1}\) in Summer (Leuenberger et al.,
1988). Kiss et al. (1997) estimated relatively higher bulk deposition concentrations
of PAHs near Lake Balaton in Hungary. Mean values reported for \(\Sigma 12\) PAHs were
324 ng L\(^{-1}\) (March to May) and 164 ng L\(^{-1}\) (June to August). Phenanthrene, fluoro-
anthene and pyrene together accounted for 50–65% of the total PAH concentrations in
the precipitation (Fig. 3). The dominance of these three compounds may be explained
by their higher water solubility, higher emission rates and/or lower reactivity in atmo-
sphere. The sum of the six potential carcinogenic PAHs (\(\Sigma PAH_{\text{carc}}\)) as described by the
International Agency for Research on Cancer (IARC, 2001), i.e. BAA, BBF, BFK, BAP,
DBA and IND, was found to be in large amount concentrations at Le Havre, represent-
ing 25% of total PAHs.

The PAH signatures in bulk deposition and surface water were compared to investi-
gate source/sink relationships. Figure 4 shows this average signature of the concen-
trations both in rainwater (Rouen) and in surface water. Surface water concentrations
data were taken from Ollivon et al. (1999) in the Seine River. The PAH signature in
surface waters was correlated with the signature of bulk precipitation ($r^2 = 0.70$), supporting the hypothesis that atmospheric deposition are among the major PAH sources into surface waters.

3.2. Bulk deposition fluxes

Highest fluxes were measured in Le Havre precipitations, with flux of 56 $\mu$g m$^{-2}$ during the studied period. Fluxes in Rouen and Evreux were, respectively, 30.8 and 28.2 $\mu$g m$^{-2}$. The lowest value was found in NDG with 22.7 $\mu$g m$^{-2}$. At the four sites, daily fluxes were 0.27 $\mu$g m$^{-2}$ d$^{-1}$, 0.15 $\mu$g m$^{-2}$ d$^{-1}$, 0.13 $\mu$g m$^{-2}$ d$^{-1}$, and 0.11 $\mu$g m$^{-2}$ d$^{-1}$, for Le Havre, Rouen, Evreux, and NDG. Halsall et al. (1997) reported higher bulk deposition fluxes of PAHs in Manchester and Cardiff: median values reported for 13 PAHs were 5.2 and 4.1 $\mu$g m$^{-2}$ d$^{-1}$, respectively. The lower range obtained in our case may be due to the fact that the sampling period did not include the colder months, during which fluxes are usually known to be greater (Brun et al., 1991; Golomb et al., 1997).

As PAH production is associated with anthropogenic activities such as home heating and industry, the distance from potential source may explain the differing observations. The total PAHs deposition fluxes for the studied period were not found to differ significantly between Rouen (urban site) and Evreux (rural site). The latter site is actually located at the periphery of the city of Evreux, more exactly at the North of the town. Prevailing southeasterly winds (Fig. 5) would then indicate that PAHs fluxes measured at this rural site originate the city of Evreux (e.g. essentially home heating and automobile traffic).

NDG seemed to be less affected by PAHs contamination, which phenomenon appears fairly unexpected. One could explain this effect by prevailing northern winds that avoid PAHs fluxes originating the south of NDG (location of the industrial site) to reach the city. Moreover, great chimney height on the industrial site also prevent the town from contaminants deposition: falling of PAHs would then affect neighbouring towns.
Bulk deposition fluxes of the sum of 14 PAH species decreased in summer when the lowest values reached 43 ng m\(^{-2}\) week\(^{-1}\) (Rouen, 10–17 September 2001). At Rouen (Fig. 6), the mean for the heating season was 2766 ng m\(^{-2}\) week\(^{-1}\), for the non-heating season was 619 ng m\(^{-2}\) week\(^{-1}\), indicating deposition fluxes were higher in cold period than in summer, due to the greater use of fossil fuels and wood for space heating in the colder months.

The seasonal change in deposition total PAH fluxes can be attributed to different phenomena. During the colder months (March and April), large amounts of PAHs are emitted from residential heating (Lohmann et al., 2000; Ollivon et al., 2002.). Moreover the low-temperature driving conditions results in a 4–10 fold increased emission from motor vehicles (Grimmer, 1983). Finally, in addition to the higher emission rates, the meteorological conditions in cold period (lower intensity of sunshine and consequently less efficient photochemical decomposition) favour the increase of PAH concentration in atmosphere and therefore PAH deposition fluxes. Higher deposition of PAHs in winter compared to summer has been reported by several investigators, as we already mentioned above. Hart et al. (1993) found the spring:summer ratio of total PAH concentrations in rain in Switzerland to be about 2:1.

4. Conclusions

PAH concentrations in bulk deposition were measured at different sites in the Seine Estuary during the period of March to October 2001. PAHs were present in rain in such levels as to give rise to great concern. The concentrations of PAHs in this study were comparable to the range of concentrations reported for other locations. Bulk depositional fluxes of these contaminants had been directly determined from the data. Le Havre received more atmospheric deposition of PAHs than the other sites, indicating the influence of industrial activities. Notable seasonal variability in the deposition fluxes of total PAHs was observed. During the heating season there is more deposition. Further, deposition fluxes of PAHs were found to vary spatially in Seine Estuary, likely
due to the location of the site (urban, rural or industrial area) and to the influence of meteorological parameters. Atmospheric deposition appears to be an important phenomenon for the introduction of organic pollutants in terrestrial and aquatic ecosystems (surface- and groundwater).

Acknowledgements. Special thanks are expressed to Air Normand for collecting the Evreux and Le Havre samples. The technical help of C. Chesterikoff, J. Rolet and L. Hanselin was highly appreciated. This work was supported by Seine Aval scientific programme and by the “Agence pour l'Environnement et la Maîtrise de l'Energie”.

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Table 1. Meteorological data during the sampling period at the 3 sites

|                          | Le Havre | Rouen | Evreux |
|--------------------------|----------|-------|--------|
| Mean temperature (°C)    | 13.7     | 14.1  | 14.2   |
| Mean precipitation (mm)  | 645      | 565.6 | 421.6  |
| Prevailing wind direction| W        | SW    | W      |

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Table 2. PAH concentrations (ng L\(^{-1}\)) in bulk deposition

|           | Le Havre | Evreux | Rouen | NDG |
|-----------|----------|--------|--------|-----|
|           | Mean (min–max) | Mean (min–max) | Mean (min–max) | Mean (min–max) |
|           | \(n = 22\) | \(n = 21\) | \(n = 22\) | \(n = 21\) |
| ACE       | 2.12 (0.25–5.9) | 0.68 (0.01–2.85) | 1.06 (<D.L.–5.02) | 0.56 (0.13–1.18) |
| FL        | 3.19 (0.5–9.1) | 2.31 (<D.L.–6.71) | 2.36 (<D.L.–8.84) | 1.95 (0.63–3.93) |
| PHE       | 19.6 (2.2–82.8) | 16.8 (0.23–69.6) | 8.01 (0.15–25.63) | 7.13 (1.89–18.3) |
| ANT       | 0.61 (0.01–2.68) | 0.62 (<D.L.–2.69) | 0.31 (<D.L.–0.97) | 0.22 (0.02–1.5) |
| FTH       | 23.9 (1.06–120.2) | 16.4 (0.55–58.4) | 9.08 (<D.L.–24.7) | 6.02 (1.36–26.2) |
| PYR       | 21.1 (1.27–86.95) | 10.6 (0.36–32.5) | 6.76 (<D.L.–21.6) | 5.22 (0.36–35.9) |
| BAA       | 5 (0.03–29.5) | 2.08 (0.07–7.91) | 1.82 (<D.L.–8.09) | 0.98 (<D.L.–7.35) |
| CHR       | 14.3 (0.31–59.9) | 4.51 (<D.L.–15.2) | 3.78 (<D.L.–13.4) | 3.11 (<D.L.–25.5) |
| BBF       | 13.5 (0.1–76.0) | 4.96 (0.06–20.1) | 3.33 (0.06–12.6) | 2.64 (0.34–17.6) |
| BKF       | 5.6 (0.04–37.6) | 2.18 (0.01–10.4) | 1.52 (0.01–6.76) | 1.01 (0.1–5.99) |
| BAP       | 5.8 (0.01–76.0) | 2.34 (<D.L.–12.4) | 1.70 (<D.L.–9.78) | 1.10 (0.01–10) |
| DBA       | 1.30 (<D.L.–13) | 0.68 (<D.L.–4.04) | 0.31 (<D.L.–1.64) | 0.32 (<D.L.–2.12) |
| BGP       | 12.3 (0.1–83.1) | 4.34 (0.05–19.3) | 2.72 (0.05–12.4) | 2.04 (<D.L.–16.5) |
| IND       | 5.9 (<D.L.–35.6) | 2.50 (<D.L.–12.1) | 1.14 (<D.L.–4.47) | 1.36 (<D.L.–9.79) |

\[\Sigma PAH = 141.21 (8.7–672)\] \[\Sigma PAH_{CARC} = 37.01 (0.17–237)\]

acenaphthene (ACE), fluorene (FL), phenanthrene (PHE), anthracene (ANT), fluoranthene (FTH), pyrene (PYR), benz(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)pyrene (BAP), dibenz(a,h)anthracene (DBA), benzo(g,h,i)perylene (BGP), indeno(1,2,3-cd)pyrene (IND).

PAH\(_{CARC}\): BAA, BBF, BFK, BAP, DBA and IND (IARC, 2001)
Fig. 1. Location of the monitoring sites in the Seine Estuary.
Fig. 2. Compass roses related to the sampling sites.
Fig. 3. Mean contribution of compounds to $\Sigma$PAH.
Fig. 4. Average signatures of the concentrations of PAHs in bulk deposition and surface water.
Fig. 5. PAH flux (ng m\(^{-2}\) week\(^{-1}\)) according to wind direction at Evreux.
Fig. 6. Bulk deposition fluxes of the sum of 14 PAH species. Segregated by heating and non-heating seasons. Solid lines are averages.