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PAHs in the bulk atmospheric deposition of the Seine river basin: Source identification and apportionment by ratios, multivariate statistical techniques and scanning electron microscopy

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Abstract

The origin of polycyclic aromatic hydrocarbons (PAH) contamination in bulk atmospheric deposition at two sites of the Seine estuary, one urban and one industrial, has been investigated. The PAH profiles indicate that PAHs mainly have a pyrolytic origin, both in urban and industrial areas. PAH sources vary during the year with an increase of high molecular weight PAH proportions (especially for carcinogenic PAHs) in winter, that means an increase of combustion processes such as domestic heating. Ratios of indicator PAHs (FTH/FTH + PYR and IcdP/IcdP + BghiP) confirm the pyrolytic origin of PAHs. In summer, ratios show the presence of industrial sources. In addition to these two methods, a factor analysis/multiple linear regression model was applied and gave an approximation of PAH source apportionment. PAH were found to be associated predominantly with emissions from road traffic (gasoline and diesel), that accounts for 17–34%. Domestic heating is a very important PAH source in urban areas and accounts for up to 85% of PAHs in winter. Industrial emissions (refineries...) account for 25% in the industrial area in summer. Each is an identified source category for the region and these results are consistent with fly-ashes identified by scanning electron microscopy. This study demonstrates that a combination of source identification methods is a far more efficient than one method alone.

Keywords: PAHs; Sources; Ratios; Factor analysis; Scanning electron microscopy

1. Introduction

During the past century, the Seine basin has experienced rising contaminant inputs due to increasing population and industry. Nowadays, this watershed that covers approximately 78 650 km^2, represents 16 million inhabitants (including 10 million for Paris and its suburbs) and almost 40% of the French economic activity. Various studies have shown high levels of organic contaminants such as polycyclic aromatic hydrocarbons (PAHs) in the Seine estuary, causing a degradation of the environment and leading to a danger for the local population (Fernandes et al., 1997a; Fernandes et al., 1997b). PAHs are ubiquitous environmental pollutants and include some of the most carcinogenic material (IARC, 2004). In the atmosphere, PAHs are produced (i) by the incomplete combustion of coal, oil, petrol and wood (=pyrolytic origin) which is the main way of formation (McElroy et al., 1989; Wild and Jones, 1995) and (ii) during the formation of fossil fuels (=petrogenic origin). In the Seine estuary, natural sources of PAHs

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are insignificant and PAHs in urban and industrial air are almost exclusively of anthropogenic origin (automobile traffic, domestic heating or industrial emissions).

Dry and wet atmospheric depositions are considered as one of the major pathways for contaminants into aquatic ecosystems. In some coastal environments, atmospheric deposition, waste water discharges and river inputs are of the same order of magnitude (Webber, 1983; Clark, 1997; Larsson et al., 2000; Axelman et al., 2001). In Europe, a few studies were carried out about the PAH contamination in atmospheric deposition (Brorstrom-Lunden, 1996; Gevao et al., 1998; Manoli et al., 2000; Grynkiewicz et al., 2002), notably in the very urbanized area of Paris (Ollivon et al., 2002).

In order to adjust emission control strategy in the Seine basin, it is essential to identify PAH sources in atmospheric deposition. However, the number of production processes and their transport in the atmosphere leads to the presence in the environment of a mixture of compounds, which is sometimes difficult to associate with a specific source. The PAH origin can be assessed by different methods. First, numerous studies used molecular indices based on ratios of individual PAH concentrations for source identification in sediments (Budzinski et al., 1997; Mitra et al., 1999; Adami et al., 2000; Didyk et al., 2000; Hong et al., 2000; Savinov et al., 2000; Notar et al., 2001; Yunker et al., 2002; Zheng et al., 2002; Doong and Lin, 2004), in soils (Nam et al., 2003) and in ambient air (Khalili et al., 1995; Simcik et al., 1999; Didyk et al., 2000; Li and Ro, 2000; Kendall et al., 2001; Oda et al., 2001). This method allows to identify the origin of the contamination by comparing PAH ratios with well-known references and thus to distinguish qualitatively petrogenic and pyrolytic sources. Secondly, multivariate analyses can be very useful, especially in areas with numerous pollutant sources (Harrison et al., 1996; Simcik et al., 1999; Savinov et al., 2000; Bixiong et al., 2006). When coupled with a multiple regression model, they can be used to identify PAH sources and to calculate their contribution to the total contamination. Lastly, fly-ash particles from fossil fuel combustion have received considerable attention in recent years. The morphology of these particles is actually to some extent indicative of organic matter burnt, and it has been suggested that scanning electron microscopy could be used to identify combustion sources in atmospheric deposition (Griffin and Goldberg, 1981; Hurt and Gibbins, 1995; Hurt et al., 1995; Alliksaar et al., 1998; Alliksaar and Punning, 1998). Therefore, when combined with other methods such as multivariate analyses, electron microscopy could be a powerful tool for the identification of PAH sources.

PAHs were measured in bulk (wet + dry) deposition for one year in two urban and industrial sites of the Seine basin. The objectives of this work was to identify PAH emission sources by means of various methods such as distribution patterns, ratios, factor analysis/multiple linear regression (FA/MLR) and less-commonly used scanning electron microscopy.

2. Experimental

2.1. Sampling

Samples were collected weekly from March 2001 to March 2002 at two sites in the Seine estuary (Fig. 1). The

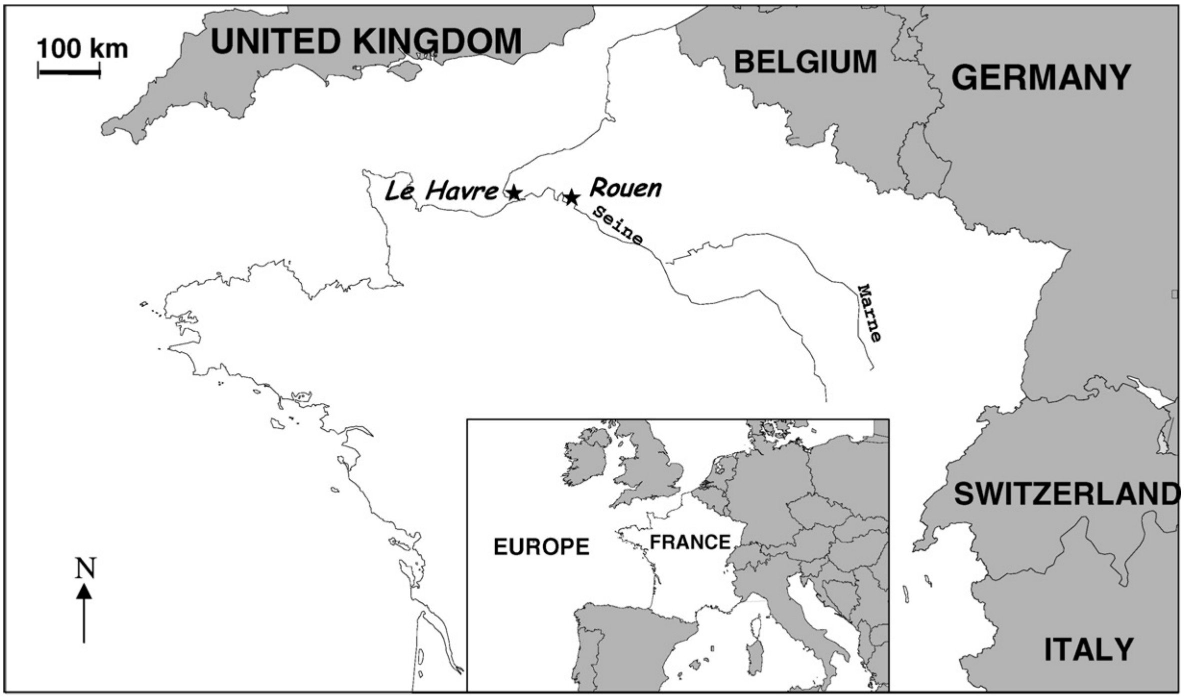

Fig. 1. Location of the sampling sites.