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Characterisation and seasonal variations of particles in the atmosphere of rural, urban and industrial areas: Organic compounds

Fabrice Cazier[1,*], *Paul Genevray*[1], *Dorothée Dewaele*[1], *Habiba Nouali*[1], *Anthony Verdin*[2], *Frédéric Ledoux*[2], *Adam Hachimi*[3], *Lucie Courcot*[4], *Sylvain Billet*[2], *Saâd Bouhsina*[2], *Pirouz Shirali*[2], *Guillaume Garçon*[2,5], *Dominique Courcot*[2]

1. *Common Center of Measurements (CCM), Univ. Littoral Côte d'Opale, F-59140 Dunkirk, France. E-mail* Fabrice.Cazier@univ-littoral.fr
2. *Unit of Environmental Chemistry and Interactions with Life, UCEIV-EA4492, Univ. Littoral Côte d'Opale, F-59140 Dunkirk, France*
3. *MicroPolluants Technologie SA, 4 Rue de Bort Les Orgues, F-57070 Saint Julien Les Metz, France*
4. *Oceanology and Geosciences Laboratory, LOG UMR 8187, Univ. Littoral Côte d'Opale, F-62230 Wimereux, France*
5. *Impact of Chemical Environment on Human Health, Univ. Lille, CHU Lille, Institut Pasteur de Lille, EA4483-IMPECS, 59000 LILLE, France*

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ABSTRACT

Atmospheric aerosol samples ($PM_{2.5–0.3}$, *i.e.*, atmospheric particles ranging from 0.3 to 2.5 μm) were collected during two periods: spring–summer 2008 and autumn–winter 2008–2009, using high volume samplers equipped with cascade impactors. Two sites located in the Northern France were compared in this study: a highly industrialised city (Dunkirk) and a rural site (Rubrouck). Physicochemical analysis of particulate matter (PM) was undertaken to propose parameters that could be used to distinguish the various sources and to exhibit seasonal variations but also to provide knowledge of chemical element composition for the interpretation of future toxicological studies. The study showed that $PM_{2.5–0.3}$ concentration in the atmosphere of the rural area remains stable along the year and was significantly lower than in the urban or industrial ones, for which concentrations increase during winter. High concentrations of polycyclic aromatic hydrocarbons (PAHs), dioxins, furans and dioxin like polychlorinated biphenyls (DL-PCBs), generated by industrial activities, traffic and municipal wastes incineration were detected in the samples. Specific criteria like Carbon Preference Index (CPI) and Combustion PAHs/Total PAHs ratio (CPAHs/TPAHs) were used to identify the possible sources of atmospheric pollution. They revealed that paraffins are mainly emitted by biogenic sources in spring–summer whereas as in the case of PAHs, they have numerous anthropogenic emission sources in autumn-winter (mainly from traffic and domestic heating).

Introduction

The knowledge on atmospheric pollutants, particularly on their origin and concentration, is essential to assess their impact on environment and on human health. While the evidence for the health adverse effects of air pollution related to particulate matter (PM) has been growing these last decades, outdoor air pollution and fine PM were recently

* *Corresponding author.*

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classified as carcinogenic to humans by the International Agency for Research on Cancer, (Loomis et al., 2013), there is still uncertainty about constituents within PM that are the most harmful. It is likely that PM mass concentration alone might not be able to explain the health outcomes, because PM is chemically nonspecific. Growing evidences appeared that PM-size, composition related also to emission sources and sampling seasons, interact in a complex manner to produce $PM_{2.5–0.3}$-induced human adverse health effects (Lu et al., 2008). One of the most striking observation is that some chemical compounds are preferentially associated with early oxidative and/or inflammatory events whereas others are involved in the later oxidative damage, genotoxic alterations or epigenetic modifications (Dergham et al., 2012; Lepers et al., 2014; Borgie et al., 2015; Dergham et al., 2015; Manzano-León et al., 2015).

It is also proposed that the mixture of components in PM could show some seasonal differences in association between health outcomes and PM in epidemiologic studies. Some evidences have linked seasonal changes in PM levels and chemical composition with health outcomes in industrialised countries (Bentayeb et al., 2015; Tenailleau et al., 2015; Toscano et al., 2011). The Nord-Pas-de-Calais Region (France) is one of the regions with the highest number of cancers in France. Moreover, it is also a region with a high population density but also numerous industrial areas. Therefore, the diversity of the emission sources (industrial and urban) makes the identification of specific tracers an issue of major interest. This work deals with characterisation of Dunkirk (North of France) atmospheric $PM_{2.5–0.3}$ sampled during spring–summer 2008 and autumn–winter 2008–2009 under urban or industrial influence compared to a rural area (Rubrouck, France). A comparison of the PM chemical characteristics according to the three influences (urban, industrial, rural) and the two seasons will be led in order to find specific physicochemical parameters for selected urban or industrial activities and also to validate compounds selected as possible tracers (Cazier et al., 2007; Bouhsina et al., 2008).

Up to date only few studies have focused on the organic characterisation of atmospheric particles in the area regarding to the inorganic fraction (Alleman et al., 2010; Kfoury, 2013; Ledoux et al., 2006). Therefore, the results presented here especially concerning the characterisation of fine particles for organic constituents like PAHs, paraffins, dioxins, furans and dioxin like polychlorinated biphenyls (DL-PCBs) are of great interest.

1. Materials and methods

1.1. Site description

Atmospheric aerosol samples were collected at Dunkirk (France) under industrial or urban wind influence (West to North vs Northeast to Southwest wind sectors respectively) and at a rural site (Rubrouck, France) (Fig. 1) in spring–summer 2008 (February to September 2008) and autumn–winter 2008–2009 (October 2008–March 2009). Dunkirk is located along the North-Sea coast close to the Strait of Dover. This medium size city (210,000 inhabitants) is affected both by human activities (traffic due to two major motorways (A16, A25), domestic heating) and by heavy industrial activities (metallurgy, refineries, cement plant, chemistry) but also by marine influence (sea spray, algae bloom, maritime traffic). The Dunkirk sampling point is located at the edge of the town centre and the industrial area. The second sampling point is located in Rubrouck, a rural site 20 km from Dunkirk and the North-Sea coastline.

1.2. Sampling methods

The samplings of fine particles ($PM_{2.5–0.3}$) were based on continuous collection using high volume samplers (80 m^3/hr)

Fig. 1 – Sampling sites under urban, industrial and rural influence (modified from http://www.geoportail.gouv.fr website).