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Fine particles sampled at an urban background site and an industrialized coastal site in Northern France — Part 1: Seasonal variations and chemical characterization

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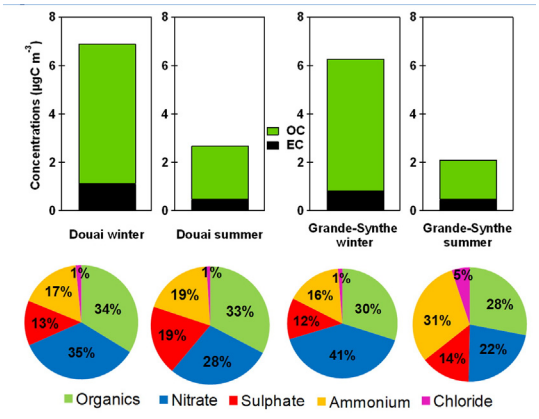
HIGHLIGHTS

- Two summer and winter field campaigns were performed at two sites in Northern France.
- Chemical characterization of $PM_{2.5}$ was performed by offline and online analyses.
- Concentrations of polycyclic aromatic hydrocarbons, dicarboxylic acids are reported.
- Particulate sulfate and chloride emitted by industries were observed at one site.

GRAPHICAL ABSTRACT



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ABSTRACT

The chemical composition of particulate matter sampled at two French Northern sites (Douai, DO – urban background; Grande-Synthe, GS – industrialized coastal site) was investigated during two summer and winter field campaigns at each site. Measurements of the major chemical species (organic, sulfate, nitrate, ammonium, chloride) in the non-refractory submicron aerosols (NR-PM_1) were carried out by a High Resolution Time-of-Flight Aerosol Mass Spectrometer. Black Carbon in $PM_{2.5}$ was monitored using an Aethalometer, while the OC and EC fractions and some targeted chemical organic families (polycyclic aromatic hydrocarbons, PAHs; dicarboxylic acids, DCAs) were quantified by the simultaneous collection of $PM_{2.5}$ on filters followed by offline analyses. The seasonal trends and winter-to-summer (W/S) concentration ratios are discussed in this paper. Results indicate that the total average mass concentrations of $PM_{2.5}$ varied between 20.5 µg m^{-3} and 32.6 µg m^{-3} in DO and between 10.6 µg m^{-3} and 29.9 µg m^{-3} in GS during summer and winter, respectively. Similar concentration patterns were found for PAHs and Organic Carbon (OC, representing ~80% of the total carbon) with highest concentrations in winter at the urban site. DCA concentrations showed less seasonal variations, although the highest value also appeared during winter. Total NR-PM_1 presented concentrations in summer lower by a factor of 4 (for DO) and 10 (for GS) than those observed in winter. Organics and nitrates dominated

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HR-ToF-AMS
Industrial sources

the NR-PM_1 in DO for both seasons and during winter in GS while sulfates and nitrates were the most dominant species in summer in GS. Average chloride concentrations were slightly more important in GS than those in DO related to its use in industrial processes and no significant seasonal trend was observed. The size-resolved chemical composition showed that aerosols sampled in DO in winter are more aged than those collected in GS where fresh emissions of sulfate from the industrial sector were observed.

1. Introduction

Northern France belongs to the North-West European Megalopolis which is the most populated area in Europe. In this particular French region, the high concentration of industries, together with heavy traffic, is responsible for 40% of $PM_{2.5}$ emissions (CITEPA, 2005) and leads to a significant release of fine aerosols into the atmosphere. Furthermore, recent reviews (Riffault et al., 2015; Taiwo et al., 2014) have highlighted the need to collect more data on the chemical composition, concentration levels and source identification in areas heavily impacted by industrial emissions.

Several studies have already investigated particulate pollution in this area (Boyouk et al., 2011, 2010; Cazier et al., 2011; Flament et al., 2008; Ledoux et al., 2006a, 2006b, 2004; Mattielli et al., 2009; Mirivel et al., 2011, 2009a). In particular, Volatile Organic Compounds (VOCs — see list of acronyms and abbreviations in Table 1) (Badol et al., 2008a, 2008b; Roukos et al., 2011; Xiang et al., 2012), as well as heavy metals (Alleman et al., 2010; Mbengue et al., 2014) and inorganic species in PM_{10} particles (Rimetz-Planchon et al., 2008) have been quantified at the most industrialized site, Dunkirk. The fast evolution of urban aerosol properties (size and elemental compositions) collected in stable atmospheric conditions was evaluated during an episode of industrial pollution plume from this site using a non-destructive technique based on single-particle analysis (Choël et al., 2010). It was shown that the presence of steelworks in the vicinity plays an important role in the rapid changes of the chemical composition of aerosols highlighting a rapid change of pollution sources and dilution of pollutants. The fast evolution of aerosol composition has also been confirmed with $PM_{2.5}$ sampling near chimneys (Marris et al., 2012). At the Douai (DO) urban background site, literature data are very scarce (Mirivel et al., 2011, 2009a) and consist only of some organic speciation (PAHs and some nitro- and oxy-derivatives, carboxylic acids) with poor time resolution (typically 24 h) over short periods of time. Consequently, and despite numerous occurrences of exceedance episodes, the speciation of particulate organic material in Northern France, and the contribution and temporal variability of particulate chemical species in particular for fine particles with an aerodynamic diameter smaller than 2.5 μm, are not clearly assessed. In the DO area, the three main contributors to $PM_{2.5}$ emissions (PM_1, respectively) have been estimated to be the residential sector for 60% (64%), the road traffic for 19% (17%) and the industry for 15% (14%) (Inventaire régional des émissions de polluants, 2008). The same study reports emissions in the area of Dunkirk mainly due to the industrial sector (67% and 61%), residential sources (19% and 24%) and the road traffic (12% and 13%) for $PM_{2.5}$ and PM_1, respectively.

This work has targeted compounds or families present in $PM_{2.5}$ particles to study their seasonal variations, such as (i) carbonaceous material, which is commonly classified into Organic Carbon (OC) and Elemental (EC) or Black Carbon (BC); (ii) dicarboxylic acids (DCAs), emitted primarily by motor vehicles and biomass burning, or as the result of air mass chemical aging, which generally appear significant in terms of concentrations (Pol et al., 2006) and can represent up to 10% of the total mass (Pöschl, 2005); (iii) polycyclic aromatic hydrocarbons (PAHs) emitted by incomplete combustion of organic matter (Ravindra et al., 2008), besides presenting a major impact on human health due to their specific toxicity (Billet et al., 2008; Saint-Georges et al., 2008). This paper describes and compares the concentration levels and chemical characterization of fine particles at two sites – an urban background site (DO) and an industrialized coastal site (Grande-Synthe, a suburb of Dunkirk, hereafter "GS") – and during two contrasted seasons. A companion paper will specifically compare the results obtained by offline and online methods for carbonaceous aerosols (Crenn et al., 2016a). A more detailed analysis of the source apportionment for submicron particles will be presented in a forthcoming article (Crenn et al., 2016b).

2. Material and methods

2.1. Sampling area and field campaign description

Four field campaigns have been conducted at two sites and during two seasons: the first one is an urban background site located in DO

Table 1
List of acronyms and abbreviations used in the text.

Acronyms		
ASE	Accelerated Solvent Extraction	
BC	Black Carbon	
CE	Collection Efficiency	
DCAs	Di-Carboxylic Acids	
DO	Douai	
DRE	Dynamic Range Enhancement	
EC	Elemental Carbon	
ESI	ElectroSpray Ionization	
FID	Flame Ionization Detector	
GS	Grande-Synthe	
HPLC	High-Performance Liquid Chromatography	
MCP	Micro Channel Plates	
NR-PM	Non-Refractory Particulate Matter	
OC	Organic Carbon	
PAHs	Polycyclic Aromatic Hydrocarbons	
P-ToF	Particle Time-of-Flight	
HR-ToF-AMS	High Resolution Time-of-Flight Aerosol Mass Spectrometer	
UPLC	Ultra-high Performance Liquid Chromatography	
VOC	Volatile Organic Compounds	
W/S	Winter-to-summer	
PAH abbreviations		
FLA	Fluoranthene	
PYR	Pyrene	
BaA	Benzo[a]anthracene	
CHR	Chrysene	
BbF	Benzo[b]fluoranthene	
BkF	Benzo[k]fluoranthene	
BaP	Benzo[a]pyrene	
DahA	Dibenzo[ah]anthracene	
BghiP	Benzo[ghi]perylene	
IP	Indeno[1,2,3-cd]pyrene	
DCA abbreviations	IUPAC name	Common name
M	Cis butenedioic acid	Maleic acid
F	Trans butenedioic acid	Fumaric acid
C_4	Butanedioic acid	Succinic acid
iC_4	Methylpropanedioic acid	Methylmalonic acid
C_5	Pentanedioic acid	Glutaric acid
iC_5	Methylbutanedioic acid	Methylsuccinic acid
C_6	Hexanedioic acid	Adipic acid
iC_6	2-Methylpentanedioic acid	2-Methylglutaric acid
Ph	1,2-Benzenedicarboxylic acid	Phthalic acid
C_7	Heptanedioic acid	Pimelic acid
iPh	1,3-Benzenedicarboxylic acid	Isophthalic acid
C_8	Octanedioic acid	Suberic acid
C_9	Nonanedioic acid	Azelaic acid
C_{10}	Decanedioic acid	Sebacic acid
C_{11}	Undecanedioic acid	
C_{12}	Dodecanedioic acid	

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