

# "ORIGINE DES AÉROSOLS INORGANIQUES SECONDAIRES DANS LE NORD DE LA FRANCE ET ÉVOLUTION PRÉVISIBLE"

P. Espina, C. Debevec; E. Perdrix, L. Y. Alleman, A. Bourin, S. Sauvage et P. Coddeville

Centre d'Enseignement, de Recherche et d'Innovation Energie et Environnement (CERI EE), IMT Lille  
Douai,  
Université de Lille, 59000 Lille, France  
pablo.espina-martin@imt-lille-douai.fr

**“Origin of secondary inorganic aerosols in the north of France and how they may evolve in the future”**

## RESUME

Une comparaison des concentrations et de la composition chimique des  $PM_{2.5}$  entre des sites périurbains, ruraux et naturels a été menée dans le Nord de la France. Elle montre une faible différence des concentrations massiques en  $PM_{2.5}$  entre les sites périurbain/rural (+1,8  $\mu g m^{-3}$ ), qui contraste avec les différences plus élevées pour les sites périurbain/naturel et rural/naturel (+6,7 et +4,9  $\mu g m^{-3}$ , respectivement). Quelle que soit la typologie du site, les aérosols inorganiques secondaires (AIS) représentent environ 50% de la masse des  $PM_{2.5}$ , le nitrate d'ammonium ( $NH_4NO_3$ ) étant le principal constituant. Cette pollution à l'échelle régionale s'explique en partie par le transport de masses d'air en provenance du Benelux et de l'Allemagne, ces zones étant connues comme émettrices de gaz précurseurs d'AIS. Bien qu'il y ait une tendance à la baisse des concentrations en  $PM_{2.5}$  au cours des dernières années, l'impact sur la santé pourrait ne pas diminuer en raison d'une évolution de la composition des AIS vers des aérosols enrichis en sulfates.

## ABSTRACT

A comparison of the concentrations and chemical composition of  $PM_{2.5}$  between suburban, rural and remote sites located in the North of France was carried out. It shows little  $PM_{2.5}$  mass concentration differences between suburban/rural (+1.8  $\mu g m^{-3}$ ), contrasting with higher ones between suburban/remote and rural/remote sites (+6.7 and +4.9  $\mu g m^{-3}$ , respectively). Whatever the site typology, Secondary Inorganic Aerosols (SIA) account for about 50% of  $PM_{2.5}$  mass, with ammonium nitrate ( $NH_4NO_3$ ) being the major component. This pollution at the regional scale may be partly explained by the transport of air masses from Benelux and Western Germany, given that these areas are well-known hotspots of SIA precursor gases. Although there is a decreasing trend of  $PM_{2.5}$  concentrations in the past years, other potential hazardous effects could arise in the future due to the changes in the composition of SIA towards more sulfate-based aerosols.

**MOTS-CLES :**  $PM_{2.5}$ , Aérosols Inorganiques Secondaires, acidité des aérosols / **KEYWORDS:**  $PM_{2.5}$ , SIA, aerosol acidity

## 1. INTRODUCTION

Benelux and the north of France areas have been recognized as hotspots for inorganic precursor gases of secondary inorganic aerosols (SIA), and particulate matter (PM). The high population densities, intensive agricultural practices maintaining consistent high  $NH_3$  levels, the large number of industries and power plants emitting high levels of  $NO_2$  and the favorable meteorological conditions promote the occurrence of several pollution episodes during winter and spring seasons. The annual mean levels of  $PM_{2.5}$  in past years have ranged from 10-20  $\mu g m^{-3}$ , in between of the 10  $\mu g m^{-3}$  recommended value by the WHO and the 20  $\mu g m^{-3}$  limit value established for 2020 by the Directive 2008/50/EC (EEA, 2019). As a consequence, the populations located in the Northwestern area of Europe have average losses of lifespan estimated between 3.6 to 7 months (Pascal et al. 2013). Although the levels of  $PM_{2.5}$  show a decreasing trend in the past years (LCSQA, 2020), the physico-chemical evolution of the atmosphere due to climate change may modify the speciation of the aerosols, affecting their acidity. Aerosol acidity is known to catalyze the formation of potentially hazardous secondary organic aerosols and to increase the bioavailability of several metals potentially toxic for human health (Fang et al. 2017).

Long term observations of  $PM_{2.5}$  and precursor gases using high temporal resolution measurements provide valuable information to understand the nature and variability of sources, secondary aerosol formation processes, fate and evolution of these complex pollutants. Therefore, a comparison of the  $PM_{2.5}$  levels and chemical composition between 3 sites with different typologies in the north of France was conducted to better understand the contribution of the regional sources, and investigate what may be the possible evolution of  $PM_{2.5}$  health impacts on northern French populations in function of future changes in the PM level and chemical composition, in a context of a predicted climate change.

## 2. METHODS

Three field campaigns in northern French sites were compared: Douai (suburban site in Nord department, Atmo Hauts de France (HdF) air quality monitoring station; (Roig et al (2019)), Caillouël-Crépigny (C-C) (temporal rural site in the Aisne department), and Revin (MERA-EMEP remote station in the Ardennes department (Oliveira, 2017)). They present an increasing density of population, from Revin (0 inh km<sup>-2</sup>) to C-C (66 inh km<sup>-2</sup>) and Douai (2347 inh km<sup>-2</sup>). PM<sub>2.5</sub> mass concentrations, inorganic precursor gases and chemical speciation data were obtained for different time periods during the last 10 years (Table 1).

Table 1. Variables measured and instrumentation used in each site

	Remote (Revin)	Rural (C-C)	Suburban <sup>1</sup> (Douai)
Campaign duration	2011-2018	03/2018-02/2019	08/2015-07/2016 2018 (Only PM <sub>2.5</sub> )
PM <sub>2.5</sub> mass	BAM 1020 (1h)	TEOM-FDMS (1h)	
NH <sub>3</sub> , HCl, HONO, HNO <sub>3</sub> , SO <sub>2</sub>	Not measured		MARGA (1h)
NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	HVS + offline IC (24h every 6 days)		
EC	HVS + offline OCEC (24h every 6 days)	Online OC-EC (1 h)	2λ-Aethalometer (1h)
OC			Not measured

2λ-Aethalometer : aerosol absorption at 270 and 880 nm

BAM: Beta Attenuation Monitoring

HVS: High Volume Sampler (filter sampling)

IC: Ion Chromatography

MARGA: monitor for aerosol and gases in ambient air (based on wet denuder sampling and IC analysis)

OC-EC: thermo-optical analysis of organic and elemental particulate carbon

TEOM-FDMS: Tapered Element Oscillating Microbalance - Filter Dynamics Measurement System

Chemical composition, ionic balance, mass closure of the PM<sub>2.5</sub> and statistical analysis were performed to validate the three databases and determine the levels and main correlations of the measured species. The three campaigns were carried out at different time periods, therefore the comparisons between sites were adjusted to the matching periods (Table 2).

Table 2. Common time periods of the different sites.

Site typology	Remote (Revin)	Rural (C-C)	Suburban (Douai)
Comparison period of PM <sub>2.5</sub> levels	2018		
Comparison periods of PM <sub>2.5</sub> chemical speciation	08/2015-07/2016		08/2015-07/2016
	03/2018-02/2019	03/2018-02/2019	

The local PM<sub>2.5</sub> sources were assessed by means of Non-Parametric Wind Regression (NWR) analysis which combines pollutant concentrations with wind speed and direction, while the regional sources were evaluated by using the Potential Source Contribution Function (PSCF) model which combines pollutant concentrations with air mass back-trajectories and gives information on the regions responsible of the highest concentrations impacting the measuring sites (Petit et al., 2017).

The thermodynamic model ISORROPIA II was used to calculate the pH of the aerosols of the rural site, running the model in "forward" mode and considering deliquescent aerosols (Fountoukis and Nenes, 2007).

## 3. MAIN FINDINGS

### 3.1. Comparison of PM<sub>2.5</sub> levels and chemical composition

The PM<sub>2.5</sub> levels of the three sites show an increasing gradient from the remote to the rural sites ( $\Delta = +4.9 \mu\text{g m}^{-3}$ ; +56%) and from rural to suburban ( $\Delta = +1.8 \mu\text{g m}^{-3}$ ; +13%) (Figure 1). All sites had maximum concentrations during spring and winter, while minimum concentrations were observed in summer.

This points out to similar drivers in all sites: in winter, the meteorological conditions favor the emissions from domestic heating sources and the condensation of semi-volatile species while in spring, high pollution episodes occur periodically due to continental transport and the impact of both regional and local agricultural activities.

The influence of local sources decreases from the suburban site to the remote one (Figure 1b). Minimum PM<sub>2.5</sub> levels occurred when the winds came from the SW sector (Atlantic Ocean). However, all sites have higher concentrations from the NE sector (continental Europe), pointing to medium to long range transport as a major driver of PM<sub>2.5</sub> concentrations in the HdF region.

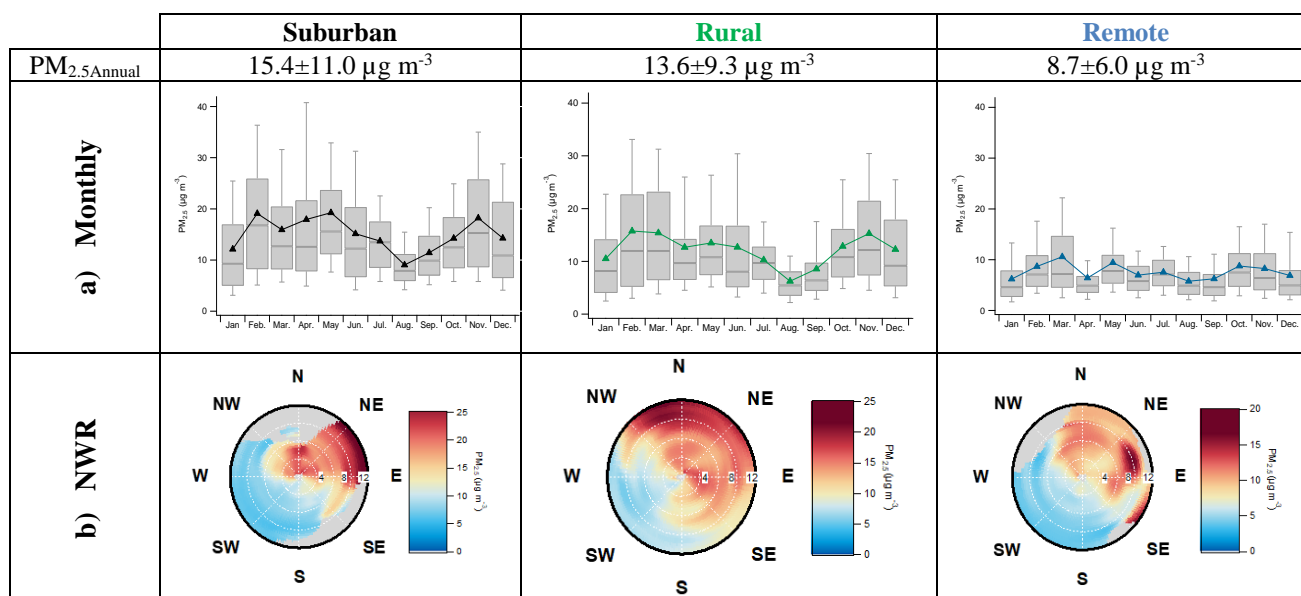


Figure 1. a) Temporal variability at monthly scale b) NWR plots of PM<sub>2.5</sub> (µg m<sup>-3</sup>) at a suburban, rural and remote sites during 2018

### 3.2. Comparison of PM<sub>2.5</sub> chemical composition

The main differences in the chemical composition between the remote and the anthropogenized sites are the SIA concentrations, responsible for more than 50% of the ΔPM<sub>2.5</sub> between sites (Figure 2). The levels of NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> are very similar regardless of the site typology, as SO<sub>4</sub> aerosols are mostly coming from continental transport processes. The variations in SIA concentrations were mostly attributed to nitrate in the form of neutralized NH<sub>4</sub>NO<sub>3</sub>, which is higher in the suburban and rural sites. This is likely to occur due to higher NO<sub>x</sub> sources in the anthropogenized sites and the high NH<sub>3</sub> levels from agricultural sources, which combined with the favorable weather conditions promote the formation of secondary NO<sub>3</sub><sup>-</sup>. The small differences between the rural and suburban sites are related to the strong contribution of the secondary processing of aerosols in this region, rather than primary emissions.

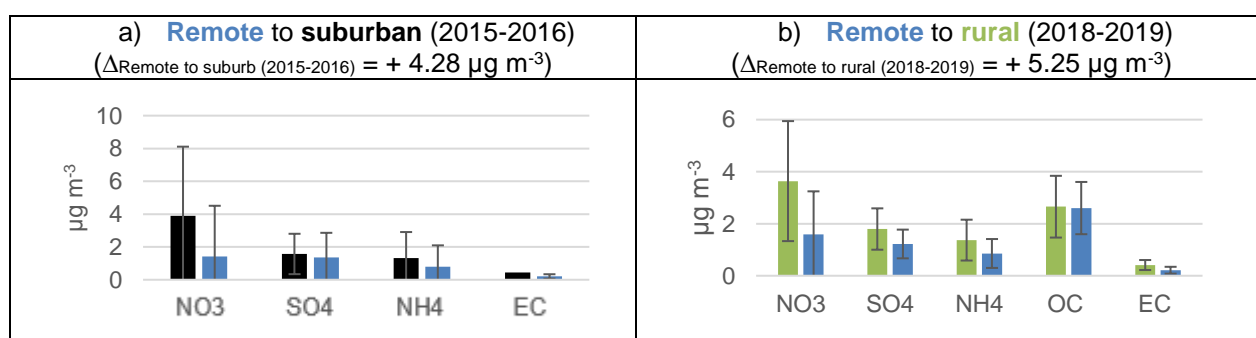


Figure 2. Annual average concentrations of the main chemical PM<sub>2.5</sub> species at (a) remote and suburban (b) rural and remote sites.

### 3.3. Evolution of the SIA distribution in the north of France

The mass relative contribution to SIA of each species (NO<sub>3</sub>-SO<sub>4</sub>-NH<sub>4</sub> in %) for the rural and remote sites is displayed in the triangular diagrams (Figure 3). The measuring period average mass composition shows distributions of 50-30-20 % for the rural site and 31-47-22 % for the remote site. There is a distinct seasonal dispersion; with spring being NO<sub>3</sub>-rich and summer being more deviated towards SO<sub>4</sub>-rich at both sites, most likely due to the volatilization of the semi-volatile NH<sub>4</sub>NO<sub>3</sub> and favored photochemical oxidation of SO<sub>2</sub> and subsequent formation of sulfate.

As the meteorological conditions are expected to change towards warmer and dryer due to the climate change, this may point out to a change of the current  $\text{NO}_3$ -rich aerosols towards  $\text{SO}_4$ -rich. This change may potentially acidify the aerosols of the region. The pH of the rural aerosols was estimated with ISORROPIA II, with acidic aerosols on an annual basis ( $\text{pH}_{\text{annual}}=3.25$ ), further decreasing during the summer season ( $\text{pH}_{\text{summer}}=2.8$ ) and reaching values below 1 when heatwave conditions occurred. Despite of a possible temperature effect (reduction of aerosol pH by water evaporation), the lower pH in the warm months was correlated to the monthly average concentrations of  $\text{SO}_2$ ,  $\text{HNO}_3$ , and  $\text{SO}_4$  ( $R^2= 0.78, 0.68$  and  $0.75$ ), which happened to be at their maximum during summer.

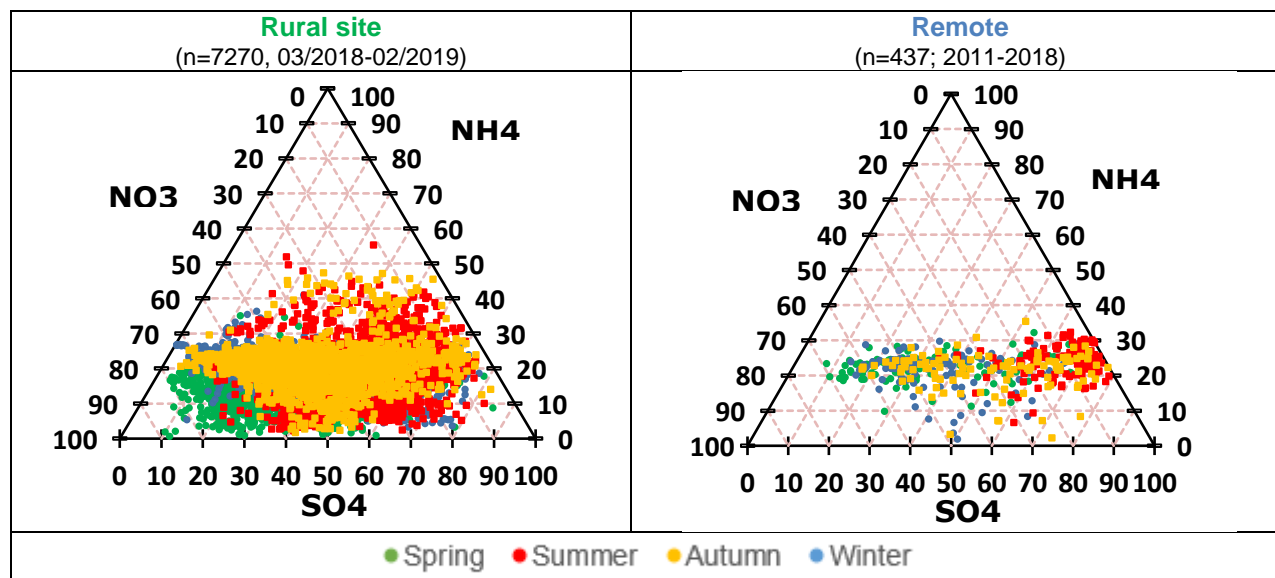


Figure 3. Ternary diagram of the seasonal SIA composition in relative mass % of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  at the rural (C-C) and remote (Revin) sites for their respective measured periods.

These findings may prove useful to determine the potential risk over the health of the HdF population due to the effects of very acidic aerosols, even if  $\text{PM}_{2.5}$  concentration levels decrease.

#### 4. ACKNOWLEDGEMENTS AND REFERENCES

**Acknowledgements** to the Conseil Régional HdF and IMT Lille Douai for funding the doctoral grant, to Conseil Régional HdF, Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation (CPER Climibio), Ministère de la Transition Ecologique et Solidaire (LCSQA), ANR and European Regional Development Fund (Labex CaPPA) for their financial support. To ATMO Grand Est and ATMO HdF for the technical support in the measuring sites of Revin and Cailloüel-Crépigny, respectively.

EEA: Air quality in Europe 2019, Publication. [online] Available from: <https://www.eea.europa.eu/publications/air-quality-in-europe-2019> (Accessed 11 December 2019), 2019.

Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A. and Weber, R. J.: Highly Acidic Ambient Particles, Soluble Metals, and Oxidative Potential: A Link between Sulfate and Aerosol Toxicity, *Environ. Sci. Technol.*, 51(5), 2611–2620, doi:10.1021/acs.est.6b06151, 2017.

Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for  $\text{K}^+$ ;  $\text{Ca}^{2+}$ ;  $\text{Mg}^{2+}$ ;  $\text{NH}_4^+$ ;  $\text{Na}^+$ ;  $\text{SO}_4^{2-}$ ;  $\text{NO}_3^-$ ;  $\text{Cl}^-$ ;  $\text{H}_2\text{O}$  aerosols, *Atmospheric Chemistry and Physics*, 7(17), 4639–4659, doi:https://doi.org/10.5194/acp-7-4639-2007, 2007.

LCSQA; Evolution sur le long terme des concentrations massiques en  $\text{PM}_{2.5}$  et  $\text{PM}_{10}$ ; [https://www.lcsqa.org/system/files/documents/2.7.2-FicheMERA\\_SpeciationPM25\\_202006.pdf](https://www.lcsqa.org/system/files/documents/2.7.2-FicheMERA_SpeciationPM25_202006.pdf); 2020.

Oliveira, D.: Identification of the main sources and geographical origins of  $\text{PM}_{10}$  in the northern part of France, IMT-Lille-Douai. [online] Available from: <https://ori-nuxeo.univ-lille1.fr/nuxeo/site/esupversions/225a6d5c-9d98-48c6-bea0-713e0d1aacc7> (Accessed 11 October 2018), 2017.

Pascal, M., Corso, M., Chanel, O., Declercq, C., Badaloni, C., Cesaroni, G., Henschel, S., Meister, K., Haluza, D., Martin-Olmedo, P., Medina, S. and Aphekom group: Assessing the public health impacts of urban air pollution in 25 European cities: results of the Aphekom project, *Sci. Total Environ.*, 449, 390–400, doi:10.1016/j.scitotenv.2013.01.077, 2013.

Petit, J.-E., Favez, O., Albinet, A. and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind and trajectory analyses, *Environmental Modelling & Software*, 88, 183–187, doi:10.1016/j.envsoft.2016.11.022, 2017.

Roig Rodelas, R., Perdrix, E., Herbin, B. and Riffault, V.: Characterization and variability of inorganic aerosols and their gaseous precursors at a suburban site in northern France over one year (2015–2016), *Atmospheric Environment*, 200, 142–157, doi:10.1016/j.atmosenv.2018.11.041, 2019