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Sampling analysis and characterization of particles in the atmosphere of rural, urban and industrial areas

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Abstract

This work concerns atmospheric particles (PM 2.5) collected in the surroundings of rural, urban and industrial areas. The investigation zone chosen for the study is Dunkirk (North of France), a highly industrialised city located along the North sea, where various activities are present such as metallurgy, petrol refineries and other chemical companies but also an important city with 210 000 inhabitants and two highly loaded motorways. Comparisons with a rural area were carried out. Physicochemical analysis of particulate matter was undertaken to propose parameters that could be used to distinguish the various sources and also to provide chemical elements for interpretation of future toxicological studies. This paper focuses on both organic and inorganic pollutants: Polycyclic Aromatic Hydrocarbons (PAH), paraffins, Volatile Organic Compounds (VOC), heavy metals and major soluble compounds (anionic and cationic).

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1. Introduction

The knowledge of the atmospheric pollutants, their origin and concentration is essential to assess their impact on environment and on human health. Because of its small diameter, PM_{2.5} can be deposited in lung and due to its large surface area, toxins including polycyclic aromatic hydrocarbons (PAH) and heavy metals are absorbed onto the surface. Organs such as lung and heart, cells and DNA can be damaged by these toxins. Therefore, fine airborne particles (PM_{2.5}) are regarded to be more toxic than coarse particles (PM₁₀) [1].

This work deals with characterisation of Dunkirk (North of France) atmospheric PM_{2.5} sampled during spring and summer 2008 under urban or industrial influence compared to a reference rural area (Rubrouck, France).

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Comparisons among the three samples will be used to find specific physicochemical parameters for selected urban or industrial activities and also to validate compounds selected as possible tracers in a previous study [2,3]. Composition and concentrations of the various organic and inorganic compounds will also be used to assess their impact on health in a complementary toxicological study. This toxicological study will be the continuation of a previous one that was performed on a global multisource PM_{2.5} sample (all wind directions included) collected near Dunkirk [4].

The results presented here concern the physicochemical characterisation of fine particles for organic pollutants (VOC, PAH, paraffins) using GC-MS, metals analyzed by ICP-MS and major soluble compounds (anionic and cationic) by IC. Particles were also studied by Scanning Electron Microscopy coupled to X-ray emission (SEM-EDX). Dioxins, furans and PCB analysis, elementary analysis (CHONS), specific surface area measurements and thermal analyses by DTA-TGA (Differential Thermal Analysis – Thermo Gravimetric Analysis) were also performed but are not presented here.

2. Materials and methods

2.1 Sites description

Atmospheric aerosol samples were collected in Dunkirk (France) under industrial or urban wind influence (North-West and North East - South-West respectively) and at a rural site (Rubrouck, France). Dunkirk is a medium size city (210 000 inhabitants), located along the Côte d'Opale coast which is strongly affected by urban (domestic heating and traffic of two major motorways: A16, A25) and heavy industrial activities (metallurgy, refineries, cement plant, ...) but also marine environment. The Dunkirk sampling point is located at the edge of the town centre and the beginning of the industrial area. It is also near the shore. The second sampling point is in Rubrouck, a rural small size city (702 inhabitants) situated at 20 km from Dunkirk and the coastline.

2.2 Sampling methods

The samplings are based on continuous field collection made in two locations with two different aerosols sampling devices (Figure 1). Fine particles (PM_{2.5}) were collected during the spring and summer 2008 using high volume sampling pumps (80 m³ .h⁻¹) equipped with impactors (high volume Sierra model 235 cascade impactor (Sierra Anderson, Smyrna, GA, USA)).



Figure 1: Sampling sites and equipments (source: fr.mappy.com)

The impactor's plates were mounted without any filters and no back up filter was used to maintain a constant aspiration flow rate. The lowest stage was doubled to increase the efficiency of smallest particle sampling.

In Dunkirk, two sampling pumps (one for urban influence and the other one for industrial influence) were placed at a height of approximately 5 meters from the ground as the systems were placed on the roof of a one story building. Urban and industrial samplings were automatically started and controlled by meteorological conditions using a rain detector and a weather cock connected to an electronic device. This device has two main functions: first it activates one of the two high volume sampling pumps depending on the wind direction (urban influence sampling if the wind direction is between 60 to 225° - industrial influence sampling if wind direction is between 250 and 345° - no sampling for the other wind directions or if it rains). Secondly it collects and saves the meteorological data (wind direction and speed, rain and humidity, temperature and atmospheric pressure). The rural sampling system was placed on a telescopic mast at Rubrouck in a grassland at 50 meters from the closest street. Only the rain detection signal stops the sampling as we were considering all wind directions.

After exposure, impactors were stored at room temperature under laminar flow bench during at least 24 hours to dry the particles and allow their collection. Particles were then divided into two size fractions: fine particles and coarse particles. After collection the impaction substrates were kept in cleaned vials and stored frozen until analysis. Particles characterisation and analyses were only performed on the PM_{2.5} fraction.

2.3 Analytical methods

2.3.1 PM physical characterization

Scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX; LeoTM 438 VP microscope and IXRF analysis system; Zeiss SAS, Le Pecq, France) was used to perform single particle analysis and also to determine the PM size. Prior to the analysis, PM was suspended in an n-hexane solution using ultrasonic treatment, and then filtered through a nucleopore filter to obtain well distributed and dispersed PM, without agglomerates, as suitable for the SEM-EDX analysis. The filter was then coated with carbon before analysis.

2.3.2 Organic compounds

The analytical methods used for volatile and semi-volatile hydrocarbons analysis were based on those described in previous works [5]. However, the analysis of the VOC using the thermal desorption preconcentration method followed by quantification with GC/MS (Combi Injector/Desorber module - EM640 Brüker) required some modifications to obtain optimal conditions for particles thermal desorption of the compounds from C₆ to C₁₅. Extraction of the VOC was carried out by thermal desorption (180°C) to attain the most volatile compounds. Desorption lasted 1.5 min (optimal conditions to desorb the VOC without attaining the semi-volatile compounds extracted in a second time with solvent). After thermal desorption, the same particles were submitted to a soxhlet extraction with dichloromethane (100 ml, 24 hours) to attain the semi-volatile compounds such as polycyclic aromatic hydrocarbons and paraffins. The extract obtained was concentrated under nitrogen flux and analysed by GC/MS (model VARIAN 1200 TQ). Materials used for compound identification and quantification were purchased from Sigma-Aldrich. Hydrocarbons identifications were assigned by comparing retention times of chromatographic peaks from samples with those from standard mixtures and by comparing mass spectra with those contained in NIST and/or WILEY libraries.

2.3.3 Major soluble compounds

The water soluble ions were extracted by ultrasonic agitation in 10 ml deionised water for 30 min. This was performed six times on the same aliquot. All extracts were filtered using a cellulose acetate filter (Millipore; 0,45 µm). Inorganic species were analyzed using ion chromatography (IC, Dionex 500) with a conductivity detector (Dionex ED40) and a gradient pump (Dionex GP40). Anions were evaluated with a Dionex Ion Pack AG 14 guard column and a Dionex Ion Pack AS14 analytical column, whereas the cations were examined with a Dionex Ion Pack

CG12A guard column and a Dionex Ion Pack CS12A analytical column. Eluants for anions and cations analysis were 3,5 mM Na₂CO₃ + 1 mM NaHCO₃ and 2 mM methane sulfonic acid (HMSA) respectively.

2.3.4 Trace elements

For trace element analysis, 15 to 25 mg of sample were treated by microwave digestion (CEM MSP 1000 – 950W) using HNO₃ and HClO₄ (JT Baker for trace metal analysis) in 1:2 ratio. After filtration on cellulose filters (Whatman 1) and dilution up to 25 ml with ultrapure water, the solutions were analysed by ICP-MS (Varian 820 MS). ICP/MS calibration solutions were prepared by dilution of a commercial 10 ppm multi-element standard (SCP33MS, SCP Science-Quebec, Canada) in a HClO₄ / HNO₃ matrix.

3. Results and discussion

Ambient PM_{2.5} concentrations measured for the rural, urban and industrial influences were respectively 2.8, 9.9 and 11.5 µg/m³. Urban and industrial atmospheres have quite similar PM_{2.5} concentrations even if the industrial one is slightly more concentrated, and they are 3 to 4 times more concentrated in PM_{2.5} than the rural area. This urban concentration is coherent with the urban PM_{2.5} average concentrations of 12 µg/m³ measured in urban French areas [6] and 8 to 30 µg/m³ in other European urban cities depending on the seasons [7]. The main wind directions for the sampling period were NE and SW.

3.1 PM physical characterization

The rural sample contained the higher proportion of particles having a size below 1 µm (87%) while the urban one contained a quite high proportion of particles higher than 1µm (Table 1). The rural site may be less exposed to local source emissions or resuspension linked to human activities or road traffic.

Table 1: Size distribution

Sample	Rural	Urban	Industry
Number of particles studied	1781	2545	1722
< 1 µm	87 %	35 %	53 %
< 2.5 µm	98 %	84 %	97 %
< 5 µm	99 %	98 %	99 %

The SEM-EDX individual analysis of the particles showed that all the samples were influenced by littoral and coastal natural sources. Si-rich particles (containing more than 75% of Si) were present and correspond to the smallest size fractions of sand particles. We also saw other types of naturally occurring particles well known in suspended particulate matter: terrestrial particles containing mostly Al, Si, Ca and Fe and gypsum particles (Ca,S).

The industry sample contained 16 % of Fe-rich particles and also nearly 5% of particles containing Fe as main element (> 50%) associated to Ca and Si. These two types of particles are linked to the close metallurgic site as shown in a previous study [2].

3.2 Organic compounds

It should be noticed that the collection technique used (drying during 24 hours under laminar flow bench of the impactor's plates before particles collection) does not allow reliable quantification of the most volatile elements such as BTEX and short chain paraffins. Volatile organic compounds were detected in the industry sample and in the urban one in a lower amount whereas they seem to be negligible in the rural sample.

As we can see in Figure 2, for alkanes: I (industry) > R (rural) > U (urban). In the industrial sample we detected lighter paraffins (C13 to C18) than in the urban and rural ones where the lightest paraffin was C22. The presence of the chain paraffins in the industry sample is in agreement with the results of a previous study [2,3] where paraffins below C20 were detected in the source samples of the industry studied.

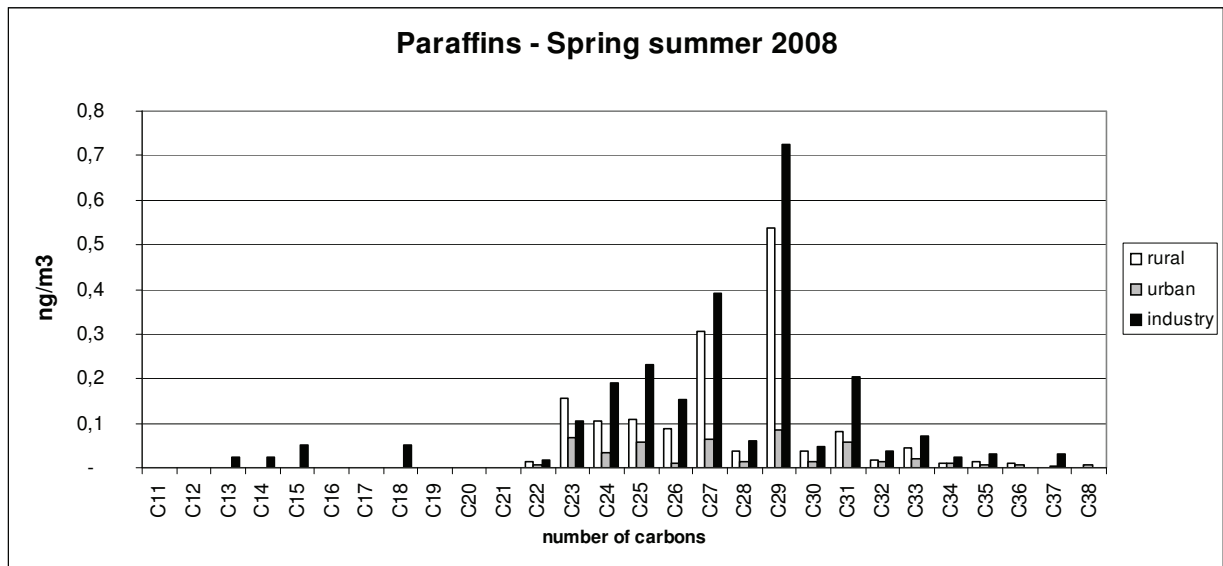


Figure 2: Alkanes profile in the spring-summer 2008 samples

These remarks are in agreement with Aboul-Kassim [8], as alkanes are petroleum components and have also terrestrial biogenic origins.

In rural area, alkanes could come from trace input of terrestrial plant wax. More precisely, C13-C19 can have microbiota origin and are also present in volatile fossil fuels (diesel).

C20-C37 are present in plant waxes and in fossil fuel detritus of urban areas. In the study of Gogou [9], a comparison between rural and urban aerosols was made: maximum alkanes contribution from rural area were odd carbon n-alkanes C27, C29 and C31, and for urban area the same profile was observed plus lighter alkanes as C23, C24 and C25. We have the same tendency in our study for industry or urban influence in comparison with rural area.

Concerning PAH (Table 2), they are more concentrated in the samples collected under urban and industrial influence than in the rural one.

Furthermore even if fluoranthene, pyrene and benzo[a]pyrene were more concentrated in the urban sample than in the industrial one, urban and industrial samples showed similar profiles for heaviest PAH. We detected an important peak of Naphtalene in urban and industrial samplings. This compound is probably linked to a close industrial source that has to be investigated in future works.

Combustion PAHs (pyrolytic origin) were the major components in rural aerosols in comparison to urban ones, where petrogenic PAHs were very abundant. Similar conclusions are given by Yassaa [10] in a study performed in Algiers urban and rural areas and by Ladji [11] in urban, industrial and forest atmospheres of Northern Algeria.

The (FluT/FluT+Py) mean value, in our study, was 0.55 for all samples. This value is very similar to vehicular emissions of 0.61 for diesel engines [12]. The (Ind/Ind+BghiP) values were 0.49 for rural and 0.54 for industrial and urban influence. These values are very similar to diesel, coal or wood burning: respectively 0.37, 0.56, 0.62 which is to compare to gasoline (< 0.5) [13].

The (Bap/Bap+Chr) values decreased (0.56, 0.53, 0.5) from rural, urban to industrial influence and the mean value was very similar to diesel emission (0.5). In each case, we could note a stronger contribution of gasoline emissions (0.7) on rural area than in both other areas.

Table 2: PAH results

ng/m ³		rural	urban	industry
Naphtalene	Nap	0.0009	0.3716	0.7316
acenaphtylene	AcPy	0.0003	0.0009	0.0034
Fluorene	Flu	0.0006	0.0008	0.0009
phenanthrene	PA	0.0034	0.0128	0.0102
Anthracene	Ant	0.0007	0.0043	0.0019
fluoranthene	FluT	0.0078	0.0250	0.0182
other 202		0.0015	0.0022	0.0010
Pyrene	Py	0.0062	0.0206	0.0140
benzo(a)anthracene	BaA	0.0125	0.0199	0.0176
Chrysene	Chr	0.0133	0.0263	0.0221
benzo(b)fluoranthene	BbF	0.0353	0.0709	0.0717
benzo(k)fluoranthene	BkF	0.0078	0.0148	0.0189
other 252		0.0019	0.0020	0.0034
other 252		0.0186	0.0409	0.0407
benzo(a)pyrene	BaP	0.0169	0.0299	0.0224
other 252		0.0102	-	0.0134
other 276		0.0099	0.0220	0.0236
indeno(123cd)pyrene	Ind	0.0185	0.0451	0.0430
dibenzo(ah)anthracene	DahA	0.0038	0.0077	0.0083
other 276		-	0.0078	0.0053
benzo(ghi)perylene	BghiP	0.0189	0.0391	0.0372
<i>Total PAH</i>		<i>0.1891</i>	<i>0.7645</i>	<i>1.1090</i>

3.3 Major soluble compounds

Significant differences of ion concentration levels were observed between the rural sample and the two others (Figure 3). The rural site showed the lowest concentrations for all the ions suggesting that local sources and anthropogenic activities have high contributions in urban and industrial samplings. Secondary sulphates and nitrates formed from gaseous oxides of nitrogen and sulphur dioxide emissions and primary calcium are dominant constituents in PM_{2.5} for urban and industrial sites.

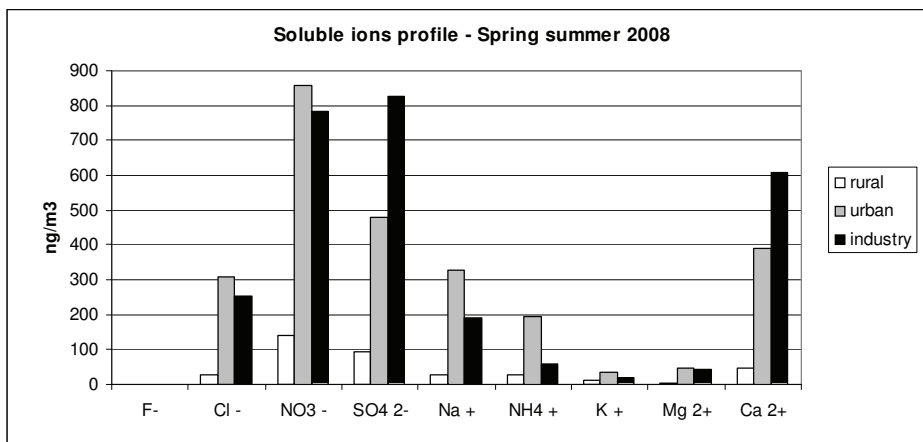


Figure 3: Soluble ion profile

High concentrations of Cl^- , Na^+ and Mg^{2+} were also observed for particles sampled under urban and industrial influence compared to the rural area which shows a real impact of marine environment on the first sampling location due to its geographical position (along the North Sea Coast).

Na^+ , K^+ and NH_4^+ were more concentrated in the urban sample than in the industrial one. Cl^- , NO_3^- and Mg^{2+} were in equivalent amounts and only SO_4^{2-} and Ca^{2+} were more concentrated in the industrial sample than in the urban one. This observation is in good agreement with previous observations [2,3].

The city of Dunkirk being surrounded by highways, the urban nitrate could be attributed to vehicular traffic emission as there is no domestic heating during this period. Surprisingly, an equivalent concentration of NO_3^- was observed in the industry sample. The observation of high levels of nitrate in the industry sample is coherent with the large combustion processes take place in the study zone (they also generate sulphate as we will see below): 6907 t of NO_x emitted by the close metallurgic site during year 2008 (biggest NO_x emitting unit of the Nord-Pas de Calais region), 2175 t of NO_x emitted by the refinery in 2008 (second biggest emitting unit of the Nord-Pas de Calais region) [14]. An explanation of this equivalent level of nitrate observed in urban and industry sample could be that the nitrate traffic source in urban sample is equivalent to the industrial sources of nitrate in the industry sample during summer. This hypothesis will have to be confirmed by further samplings and analysis that will be performed in identical conditions in autumn and winter for seasonal variation studies.

For Ca^{2+} in particles collected under industrial influence, the identified sources are the cement factories and the steel works located in the industrial site at the north west of Dunkirk. Different processes take place in the steelworks industry, among others a production unit where important amounts of CaCO_3 are handled to carry out the desulphuration of ores. This could explain the high level of calcium observed in the industry sample.

The presence of elevated SO_4^{2-} level in the industry sample is coherent with the close industrial sources as the refinery, which is the biggest SO_2 emitting unit of the Nord-Pas de Calais region, emitted 8152 t of SO_2 during year 2008 and the close metallurgic site, which is the second biggest emitting unit of the Nord-Pas de Calais region, emitted 6348 t of SO_2 in 2008 [14].

Cl^-/Na^+ ratios show that there is a strong marine influence in the industrial sample ($\text{Cl}^-/\text{Na}^+ = 1.3$ compared to 1.5 for pure NaCl). It also shows a possible crustal contribution for Na in the urban and rural samples (ratio of 0.9 for these two samples). Ionic analysis of the three samples shows a concentration level of ammonium aerosol decreasing in following order: $[\text{NH}_4^+]_{\text{urban}} > [\text{NH}_4^+]_{\text{rural}} > [\text{NH}_4^+]_{\text{industry}}$. Further investigations have to be conducted to explain the urban ammonium concentrations

3.4 Trace elements

Rural sample was the less concentrated for all the trace elements analysed and we always had: $\text{I} > \text{U} > \text{R}$ except for Se ($\text{U} = \text{I}$), Na and Mo ($\text{U} > \text{I}$).

For the three types of sources the major trace elements were (Table 3): Fe, Al, Mn, Zn, Ca, K, Mg, Na (concentrations above 10 ng/m^3). Then Cu, Ti, Pb, Ba, Cr, Ni, Sr, Sn showed concentrations between 1 and 10 ng/m^3 . The other elements analysed were below 1 ng/m^3 (Mo, Rb, Ce, La, Sb, Se, Co, As, Cd, Bi, Tl, Ag). This trace element profile is similar to the one described by Deboudt [15] and Huston [16].

Atmospheric Se particulate mostly comes from naturally released sea salts but can also be issued by coal combustion and refuse incineration dust from metal melting [17]. The Se content being equal in urban and industry sample (0.27 and 0.28 ng/m^3 , compared to 0.06 at rural site), a main sea salt origin seems to be logical. This is coherent with Se particulate concentrations ranging from 0.15 to 0.4 ng/m^3 observed in North Atlantic [18]. As Se may vary between summer and winter as a result of coal or oil combustion during the winter season, this hypothesis will have to be confirmed by the future winter sampling campaign.

The sea salt origin of Na proposed in the soluble ionic species discussion seems to be confirmed as we have 325 ng/m^3 for the soluble part (analysed by ionic chromatography) and 359 ng/m^3 for the total Na (analysed by ICP/MS). The marine influence is the same for industry and urban sample (as seen with the Cl^-/Na^+ ratios previously studied) but the Na content in the urban one is reinforced by a crustal contribution.

Further investigations have to be performed to explain the Mo origin in urban aerosol as there are numerous local metallurgical activities that should lead to higher concentrations in the industry sample.

For the major trace elements for which $\text{I} > \text{U} > \text{R}$, Al and Fe are known as being crustal elements (8.1% and 5% in Earth's crust respectively) especially in particles $> 2.5 \mu\text{m}$ [19] but in our sampling zone and for the size of particles

we are studying ($<2.5 \mu\text{m}$), Fe can also have a strong anthropogenic origin due to the large metallurgic industries that are close to the industrial influence sampling site. It should be noticed that these industrial sources also slightly affect the urban sample. This has already been illustrated in a previous study [2,3]. For Al, we also observed a strong anthropogenic influence on the industry sample (cement plant and ores handling sites near the sampling site).

Table 3: Trace element concentrations

ng/m ³	rural	urban	industry	ng/m ³	rural	urban	industry
Ag	0.004	0.017	0.027	Mg	14.14	91.0	150.4
Al	57.2	140	453	Mn	3.05	18.02	70.3
As	0.057	0.205	0.251	Mo	0.099	0.658	0.570
Ba	0.65	3.04	5.77	Na	37.43	359	284
Bi	0.021	0.055	0.065	Ni	0.30	1.89	2.82
Ca	55.2	439	699	Pb	1.16	3.72	5.34
Cd	0.028	0.082	0.226	Rb	0.065	0.360	0.480
Ce	0.086	0.292	0.469	Sb	0.081	0.266	0.338
Co	0.026	0.183	0.264	Se	0.062	0.266	0.282
Cr	0.60	3.85	4.76	Sn	0.17	1.34	1.77
Cu	1.10	8.65	19.22	Sr	0.24	2.09	2.60
Fe	73.4	415	1 234	Ti	0.98	7.24	9.41
In	< 0.0015	< 0.005	< 0.006	Tl	0.004	0.018	0.040
K	13.55	61.8	79.7	V	0.25	1.05	1.80
La	0.044	0.273	0.410	Zn	3.14	17.58	32.43

For Mn, the metallurgic influence on the industry sample is evident (Fe-Mn production unit near the sampling site) and results are in agreement with a previous study [2,3].

For Zn, the metallurgic influence on the industry sample was also present but was weaker than the one observed for Fe and Mn. This observation is coherent with the fact that Zn has possible other anthropogenic origins. It has for example also been proposed as tracer of the vehicular emissions, this element being present in tire wears [16, 19]. The I/U concentration ratio for Zn (1.84) is thus lower than the ones for Al (3.23), Fe (2.97) and Mn (3.90). Other metals such as Cd, Cu and Tl have also I/U ratios >2 .

For Ca, the explanations for the predominant industrial concentration is given in the soluble ionic species discussion as important amounts of CaCO₃ are handled to carry out the desulphuration of ores in the steelworks industry [2,3]. Origin of the high Ca content in the urban sample has to be investigated as the crustal contribution does not seem enough to explain it (in the rural sample, where Ca has mainly crustal origin, we only measure 55.2 ng/m³). Marine origin assumption seems neither not viable.

Like Ca, elements such as Mg and K can come from crustal sources (3.6%, 2.1% and 2.6% in Earth's crust respectively), naturally released sea salts and also from anthropogenic activities in our case. In urban and industrial samples, K and Mg amounts are coherent with marine aerosol concentration levels [20], but we observe at least a 1:2 ratio between soluble and total concentrations of Mg and K in most of the cases (except in the rural one for K). Marine origin is thus not the only one in these cases and a more mixed influence has to be considered especially for Mg (I/U = 1.6 (as for Ca) compared to K for which I/U = 1.3).

For minor trace elements ($<10 \text{ ng/m}^3$), as for some of the major ones, a strong anthropogenic influence is observed in most of the cases. The seasonal study information will be precious for source attribution and explanations between rural, urban and industrial samples variability.

4. Conclusion

For most of the compounds studied except paraffins, the urban and industrial samples were more concentrated than the rural one. Paraffins in rural sample are mainly attributed to terrestrial plant wax whereas in industry they were also linked to petroleum products. Combustion PAHs were the major components in rural aerosols in

comparison to urban ones, where petrogenic PAHs were very abundant. For chloride ion we found a major marine influence on the industrial and urban samples whereas sodium, magnesium and potassium ions seem to have at least mixed marine and crustal origins especially in the urban sample. Calcium, sulphate and nitrate have an anthropogenic urban-industrial origin. Ammonium source identification in the urban samples has to be completed. Most of the metals showed a strong anthropogenic origin in urban and industrial sample, iron and manganese being for example clearly linked to the local metallurgic activities. Zinc was also partly linked to the metallurgic activities. For the minor trace elements further investigations have to be conducted to propose reliable source identification.

In the industry sample, we have found good correlations for some of the tracers of the local metallurgic activities found in a previous study such as Fe-rich particles, Fe, Mn and Ca contents, sulphate levels, gypsum, short chain paraffins (>C20), ... [2,3]. For contribution assessment of the other industrial activities in the industry sample, further point source analysis will have to be performed in these industries to find specific tracers.

The rural sample is clearly different from the urban and industrial ones as shown with the concentrations levels of PM_{2.5}, the particles size, but also the trace elements, major soluble compounds, organic compounds profiles and concentrations. The Dunkirk sampling point being located at the edge of the town centre and the beginning of the industrial area exhibited quite mixed influences in the source attributions due to the urban-industrial site situation compared to a rural exposition. Further samplings and analysis will be performed in identical conditions in autumn and winter. They will allow seasonal variation studies and will give more elements to complete source attribution especially for the urban influence. Complementary toxicological studies will also be conducted.

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References

- [1] S. Lu, Z. Yao, X. Chen, M. Wu, G. Sheng, J. Fu, P. Daly, *Atmospheric Environment*, 42, 31 (2008), 7205-7214
- [2] S. Bouhsina, F. Cazier, H. Nouali, D. Dewaele, A. Delbende, D. Courcot, A. Aboukais, AAAS08 (Advanced Atmospheric Aerosol Symposium), Naples, Italy, 2008
- [3] F. Cazier, D. Dewaele, H. Nouali, A. Vasseur, S. Bouhsina, H. Laversin, F. Ledoux, D. Courcot, A. Aboukais, 6th International Conference on Urban Air Quality, Cyprus, 2007
- [4] S. Billet, G. Garçon, Z. Dagher, A. Verdin, F. Ledoux, F. Cazier, D. Courcot, A. Aboukais, P. Shirali, *Environmental Research*, 105, 2 (2007) 212-223
- [5] I. Caplain, F. Cazier, H. Nouali, A. Mercier, J.C Déchaux, V. Nollet, R. Joumard, J.M. André, R. Vidon, *Atmospheric Environment*, 40 (2006) 5954–5966
- [6] AFSSE, 2005 (<http://www.afsset.fr> - last access : May 2010)
- [7] M. Sillanpää, R. Hillamo, S. Saarikoski, A. Frey, A. Pennanen, U. Makkonen, Z. Spolnik, R. Van Grieken, M. Braniš, B. Brunekreef, M.C. Chalbot, T. Kuhlbusch, J. Sunyer, V.M. Kerminen, M. Kulmala, R.O. Salonen, *Atmospheric Environment*, 40, 2 (2006), 212-223
- [8] T.A.T Aboul-Kassim., B.R.T. Simoneit, *Environmental Science & Technology*, 29, 10 (1995), 2473-2483
- [9] A. Gogou, N. Stratigakakis, M. Kanakidou, E. G. Stephanou, *Organic Geochemistry*, 25, 1/2 (1996), 79-96
- [10] N. Yassaa, B.Y.Meklati, A.Cecinato, F. Marino, *Atmospheric Environment*, 35 (2001) 4
- [11] R. Ladjji, N. Yassaa, C. Balducci, A. Cecinato, B. Y. Meklati, *Science of the total environment*, 408 (2009) 415-424
- [12] M. Mandalakis, M. Tsapakis, A. Tsoga, E.G. Stephanou, *Atmospheric Environment*, 36, 25 (2002) 4023-4035
- [13] K. Ravindra, L. Bencs, E.Wauters, J. de Hoog, F. Deutsch, E. Roekens, N. Bleux, P. Berghmans, R. Van Grieken, *Atmospheric Environment*, 40, 4 (2006) 771-785
- [14] IRE Report (DREAL), 2009 (www.nord-pas-de-calais.developpement-durable-gouv.fr - last access in May 2010)
- [15] K. Deboudt, P. Flament, M.L. Bertho, *Water, air and soil pollution*, 151, 1-4 (2004) 335-359

- [16] R. Huston, Y.C. Chan, T. Gardner, G. Shaw, H. Chapman, *Water Research*, 43, 6 (2009) 1630-1640
- [17] H. Wen, J. Carignan, *Atmospheric environment*, 41 (2007) 7151-7165
- [18] M.L. Godoy, J. Godoy, L. Roldão, D. Soluri, R. Donagemma, *Atmospheric Environment*, 43, 14 (2009) 2366-2374
- [19] X. Huang, I. Olmez, N. Aras, G. Gordon, *Atmospheric Environment*, 28, 8 (1994) 1385-1391
- [20] M. Claeys, W. Wang, R. Vermeylen, I. Kourtchev, X. Chi, Y. Farhat, J.D. Surratt, Y. Gómez-González, J. Sciare, W. Maenhaut, *Journal of Aerosol Science*, 41 (2010) 13-22