Characteristics of suspended particulate matter emitted from an iron and steel company – A multi technique approach for search of tracers

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This paper describes our multi technique approach to determine the origin of particles collected in Dunkirk (North of France), a strongly industrialised city. Sampling, analysis and characterisation of point-source and diffuse particles emissions were performed in an industrial site and its surroundings to determine physicochemical parameters that could be used as tracers for the evaluation of fallout fluxes. Organic, metallic, soluble inorganic compounds were analysed by GC-MS, ICP-MS and IC. Particles morphology and individual composition were studied by scanning electron microscopy coupled to X-ray microanalysis (SEM-EDX). Complementary investigation of the inorganic fraction was undertaken by X-ray diffraction (XRD).

1. INTRODUCTION

The knowledge of the atmospheric pollutants, their origin and concentrations is essential to assess their impact on environment. This work concerns the development of a multi technique approach using physicochemical parameters in order to determine the origin of atmospheric particulate pollutants that can be found in the area of Dunkirk (North of France), a strongly industrial city having huge metallurgic (steel, ferro-manganese, ...) and chemical (refineries, petrochemistry ...) activities but also cement plants ... . In a previous work (Cazier, 2005), sampling, analysis and characterisation of point-source particles were performed in the steel-making industrial site with a particular focus on some specific sectors: a coke work plant, a sintering unit and a steelwork unit. Specific chemical characteristics (PAHs ratios, lead isotopic ratios, major soluble inorganic compounds) were defined and possible organic and mineral tracers were selected. The analysis of the selected sources was completed by SEM-EDX to study the morphology of particles and their individual composition. Complementary investigation of the mineral fraction of particles has been undertaken with the use of XRD which allow the determination of the structure and chemical environment of some major metallic elements while ICP/MS analyses trace metals and allows isotopic ratios determination. Then, to validate the possible tracers selected for this industrial activity, twenty diffuse particles samples were collected in the surroundings of the site under specific wind direction. Among these environmental samplings, some were performed, the same day, upwind and downwind of the industrial site studied to exhibit the site influence. The individual advantages of each technique used were then combined to develop a multi technique approach able to differentiate the various possible origins of the particles collected it the environment.

2. METHODOLOGY

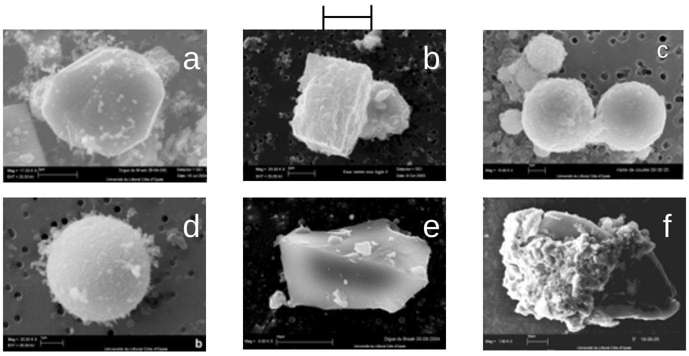
Different reference samples were analyzed. Manual samplings of coals, iron ores, and particles from the baghouse filtration system of the blast furnace and the steel plant were performed. Particles from the sintering plant chimney were also sampled in the stacks using an isokinetic sampler equipped with heated probe and filter. In the surrounding environment, samplings were performed between 300 and 500 meters downwind of some particulate emissaries. These samplings were realised by global filtration of the atmosphere at 80 m^3/h. Fiberglass filters were used for organic compounds sampling, cellulose filters for metallic and soluble inorganic compounds and polycarbonate filters for SEM-EDX study (5 m^3/h). The organic compounds were analysed by GC-MS after soxhlet extraction. For metals, samples were analysed by ICP-MS after microwave digestion. Soluble inorganic compounds were analysed by IC after an ultrasonic extraction. Morphology and automated single particle analysis were performed with a Scanning Electron Microscope equipped with an Energy Dispersive X-ray spectrometer (SEM-EDX). For each sample, 1000 particles were analysed and a hierarchical cluster analysis (HCA) was made to determine the different types of particles in the sample. X-ray diffraction (XRD) analyses were directly performed on glass fibre filters using $CuK\alpha$ radiation generated at 40 kV and 40 mA.

3. RESULTS AND DISCUSSION

3.1 – Source samples

To determine the major soluble inorganic compounds, the individual particle composition of different processes of the industrial site was investigated. By ion chromatography (CI), specific profiles for different sources were established. $CaCl_2$ seems to be specific to the steel plant, whereas $MgSO_4$, K_2SO_4 and $CaSO_4$ are related to blast furnace activities except for its baghouse filtration system part. The high Ca^{2+} percentage (53 -55%) in the steel plant can be linked to the addition of $CaCl_2$ for sulphur removal at this step of the process. For the sintering plant, no specific fingerprint can be established, but we characterised NH_4^+, which is not detected in the other sources. This latter result is coherent with the XRD study (Laversin,2006). Particles collected in these chimneys shows different crystallized phases containing Cl: KCl (Fig. 1.b), (JCPDS 41-1476); NaCl (05-0628) and NH_4Cl (JCPDS 07-0007). These salts, which belong to a fine fraction (< 5 µm), are released upon thermal treatment in a gas phase whereas the elements as K, Cl, Na can form aggregates with primary particles (Fe-rich, Fe-Ca-Si-Al and others). The analysis of sources samples was completed by SEM-EDX study. A proportion of Fe-rich particles (19 to 71%), appearing as spheres, was detected (Figs. 1c and 1d) in the blast furnace and steel plant samples. This is coherent with recent studies, which propose the presence of a relatively high proportion of iron spherules in airborne particles as a characteristic of steel plant emissions (Moreno, 2004; Sammut, 2005). Such particles result from the condensation of iron released into the atmosphere after a high temperature process and could be used as a tracer of the iron and steel plant.

Figure 1: Secondary Electron images of particles collected downwind of various iron and steelworks sources



a) angular shape of Fe ores (scale:4 µm); b) K and Cl rich particles (scale:5µm); c) and d) Spherical iron oxide (scale:3µm); e) graphite flake (scale:10µm); f) graphite flake (scale:25µm) covered by Fe-Ca-Si aggregates (left side)

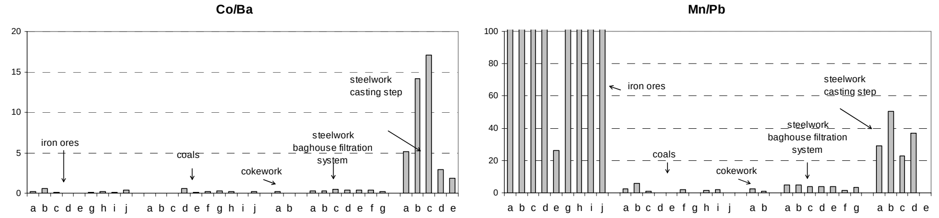
Table 1: Crystalline phases in reference samples particles from the iron and steel works

Sector	Type	Sample	Crystalline phase
Iron ores	powder fraction	1	α-Fe$_2$O$_3$, α-FeOOH, SiO$_2$, (Mg$_5$Al)(Si,Al)$_4$O$_{10}$(OH)$_8$
	(< 50 µm)	2	α-Fe$_2$O$_3$, [α-FeOOH, SiO$_2$]
		3	Fe$_3$O$_4$, SiO$_2$
		4	α-Fe$_2$O$_3$, α-FeOOH
Sintering plant	TSP inside	1	KCl, α-Fe$_2$O$_3$, NH$_4$Cl, NaCl, SiO$_2$, CaCO$_3$
	the chimneys	2	KCl, α-Fe$_2$O$_3$, CaCO$_3$, SiO$_2$
Blast furnace	baghouse filtration system	1	α-Fe$_2$O$_3$, Fe$_3$O$_4$, [graphite]
Steel plant	baghouse filtration system	1	C graphite, α-Fe$_2$O$_3$, Fe$_3$O$_4$
Slag heap	TSP in storage area	1	C graphite, CaCO$_3$, Ca$_2$Al$_2$SiO$_7$, [α-Fe$_2$O$_3$, Fe$_3$O$_4$]

Minor phases given in brackets

Organic compounds were also measured. The organic content of the particles collected on various processes of the plant selected exhibit mainly paraffin, PAH and methylated PAH. Paraffins were well identified in the coke work samples whereas not found or at trace level in the sintering and steelwork samples. The organic compounds at the coke work unit (cogeners PAHs and associated methyled PAHs) exhibit strong changes as the methylated PAHs disappear all along the combustion process. For the parent PAHs, all of them are detected in the raw materials and coke work samples but only the heaviest ones are found in the hot processes and the sintering unit (mass 252, 276, 302) and PAHs such as coronene appear. Possible organic tracers could be selected using ratios of concentration between specific PAHs: Fla/Pyr, Chry/BaA, BghiP/IND, BaP/BkF and BeP/BkF. Fla/Pyr may be used as tracers for the hot processes of the coke work unit whereas BaP/BkF could be used for the sintering unit. The steelwork unit may be traced by Fla/Pyr or BeP/BkF (Cazier, 2005, 2007). The metal analysis exhibited specific characteristics for most of the process samples, being either metallic content profile, metal ratios (Fig.2) or lead isotopic ratios: iron ores have high content of Mn and specific Mn/Pb (>200) and Mn/Cu (17-260) ratios ; coals have low content of metals and Mn/Pb<2.2; baghouse filtration system of the steelwork unit have specific lead isotopic ratios and Zn/Cu>10 ; particles collected at the steel casting step have specific profile and metallic ratios : Mn/Pb>20 and 1.9<Co/Ba<17 ; sintering has low Zn content and Ba/Cu>1 ; blast furnace samples have, as for steelwork unit, Zn/Cu>10, but pig iron pouring particles have also specific Mn/Cu ratio (970-1300) and low amount of Al. Blast furnace baghouse filtration system is noticeable by its lead isotopic ratio (Fig. 4) and Pb/Cd ratio (60-70). The sources isotopic results are discussed further with the surroundings ones.

Figure 2: Metal ratios of the different activities of the industrial site



3.2 – Samples collected in the surroundings of the site

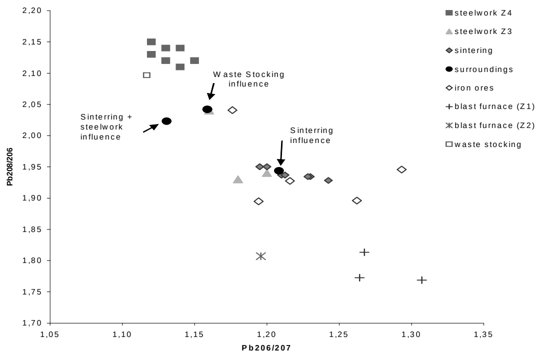
The close surroundings of the site encompass, in the west part, a ferro-manganese metallurgic site, a cement production unit and a petroleum refinery and at the east site, a refinery specialised in lubricant production. The North Sea runs all along the north of the site and the south of the site is strongly urbanised.

3.2.1 – Comparison between the sources and the surroundings

Some results can be correlated to the ones found in the sources.

Metal profiles give indications on sources and can also reveal other contribution. For example, samples collected under the sintering unit influence have coherent profile with the source but one of them has higher content of copper that may indicate a steelwork unit contribution (Fig. 4). The origin of particles can be confirmed more precisely using Pb isotopic ratios (Fig. 3). For the metallurgic site of interest, the samples performed under its influence are coherent with the Pb isotopic ratio of the sources investigated: ^{208}Pb/^{206}Pb for the sintering influence (1,94) is very close from the sintering sample one

Figure 3: Isotopic ratios repartition in the samples



blast furnace:
- *dust generated during the reaction between coke and sinter (Z1)*
- *pig iron pouring (Z2)*

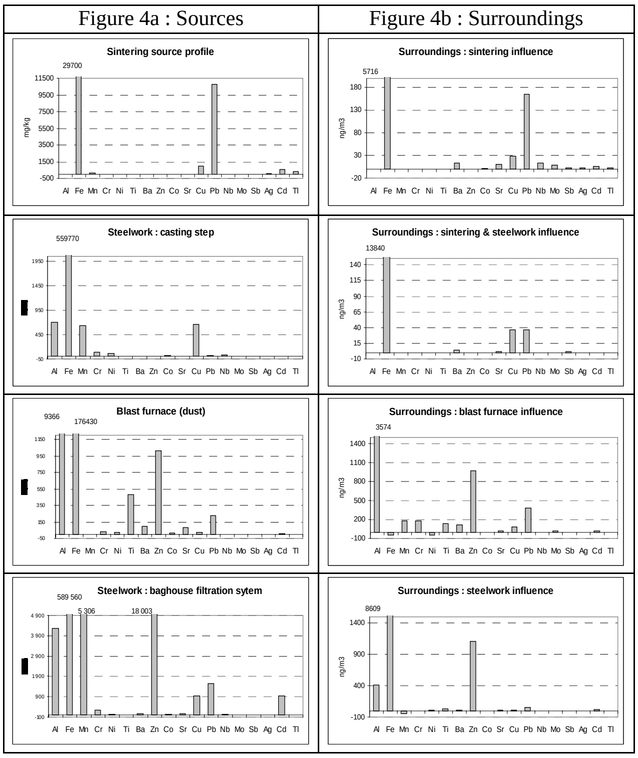
steelwork unit:
- *baghouse filtration system (Z4)*
- *casting steps (Z3)*

waste stocking zone:
non-intentional products generated during the process

(1,84 – 1,93). For the influence of the waste stocking zone, the characteristic of the source are also coherent: $^{208}Pb/^{206}Pb$ = 2,04 and $^{206}Pb/^{207}Pb$ = 1,16 (waste stocking zone : $^{208}Pb/^{206}Pb$ = 2,10 and $^{206}Pb/^{207}Pb$ = 1,12). Samples performed under the ferro-manganese site, urban or refineries influences are either at the edge or different ($^{206}Pb/^{207}Pb$ < 1,12) from the ratios of the site sources (Fig. 3).

As we can see, generally, Pb isotopic ratios of samples performed under the influence of the metallurgic site are located between the ones of the sources, which confirms the site influence and also indicate a mix of various site sources.

Figure 4: Profile comparison between source and environment



For SEM results, particles sampled under the irons ores, blast furnace and steelwork influence can be distinguished one from each others: an angular shape (Fig. 1a) with high Fe content shows the iron ores influence confirmed by the presence of a majority of hematite form, blast furnace and steelwork contain spherical shape particles having a size bellow 1 to 3 µm with hematite and magnetite phase present which is in good correlation with the observations mentioned in Table 1. Pb and Zn levels and Pb isotopic ratio found under blast furnace influence and steelwork influence (Fig. 4b) are also coherent with the sources characteristics (Fig. 4a).

Tendencies for organic compounds (Table 2) show that Fla/Pyr (0,88-1,83) is quite constant whatever influence samples are submitted to which make it unusable as a tracer. The same is observed for Chry/BaA (2,9-3,5), BghiP/IND (0,8-1,3) and Pyr/BaP (0,78-1,25). BaP/BkF is about 0,39 to 0,5 when the sample is taken under urban influence and about 0,58 to 0,67 when submitting a global metallurgic influence (steelwork, coke work, blast-furnace), allowing it to be a good tracer. These results can be correlated to the ones found in the sources: BaP/BkF of 0,6 to 0,7 mostly represents the coke work unit, where quite high amount of PAHs are found which can strongly contribute to the ratio found in the particles downwind of the steelmaking site. We also observe ratios close from the ones found at the sources: Fla/Pyr (0,7 -1,7), BghiP/IND

Table 2: PAHs ratios in diffuse particle samples collected under specific wind direction

Influence	*Urban*			*Coke work*		*Blast Furnace*		*Steelwork*		*Mix**	*refinery*	
Fla/Pyr	1.3	1.18	1.46	1.73	1.44	0.88	1.4	1.06	1.27	1.22	1.83	1.11
Chry/BaA	nd	3.47	nd	nd	nd	nd	nd	nd	nd	3.22	nd	nd
BaP/BkF	0.49	0.5	0.39	0.63	0.67	0.48	0.6	0.58	0.63	0.66	nd	nd
BghiP/IND	nd	0.82	nd	nd	1.3	nd	nd	nd	0.97	nd	nd	nd
Pyr/BaP	0.93	2.44	6.4	nd	0.79	0.96	1.13	nd	0.78	1.25	nd	nd

nd : not detected ** mixed sources of the steel making site of interest*

around 1 for hot processes and >1 for coals, Pyr/BaP >> 1. At the opposite, the Fla/Pyr of 0.35 is never observed whereas expected when having a steelwork unit influence; it may be linked to the low amount of PAHs in the steelwork effluents.

However, some values determined in the environment are more difficult to correlate to sources values that's why we decided to compare upwind to downwind profiles to exhibit possible evolutions.

3.2.2 Upwind and downwind samplings

Upwind and downwind samplings have been performed under the metallurgic site of influence. No contribution of the blast furnace source is observed as no change in PAHs ratios (BaP/BkF stays near 0.49), soluble ions profile (Fig. 5a) and metal profile. Possible explanations can be the weather conditions or the altitude of the air masses influenced by the site too high, compared to the sampling mast height. At the opposite, the influence of the metallurgic industrial site is observed on the aerosol composition: BaP/BkK evolves from 0.39 to 0.66, respectively determined as tracers for urban and metallurgical influence, a modification of Ca^{2+}, K^+ and SO_4^{2-} rates (Fig. 5b) is observed (according to the source's ion analysis, the blast furnace seems to be the most influencing unit) and strong modification of the metal profile is also noted. In this case, profiles can be used to determine the source at the origin of the influence.

Figure 5: Measured weight percentages of ions upwind and downwind of the site

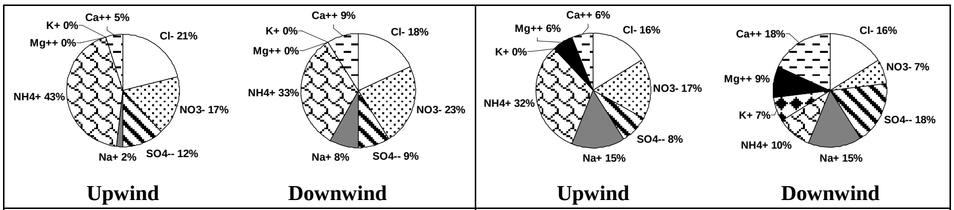


Fig 5a : Blast furnace influence

Fig 5b : Site mixed sources influence

3.3.3 Environmental characteristics

For IC analysis of environmental samples, NH_4^+ is the main cationic species found (23-46%), and is only emitted, in our sources, by the sintering unit. NH_4^+ is found in all the environmental samples but as this element can also be affected by the marine influence it should be carefully used in the identification method. Direct comparison with the sources profiles shows that, results for soluble inorganic compositions in environmental

Table 2: Weight percentages of soluble ions in source and environmental blast furnace samples

Source		%Cl$^-$	%NO$_3^-$	%SO$_4^{2-}$	%Na$^+$	%NH$_4^+$	%K$^+$	%Mg^{2+}	%Ca^{2+}
Blast furnace	baghouse filtration system	**37**	-	6	6	-	17	1	**33**
	Pig iron pouring	3	1	**43**	5	-	**32**	-	16
	coal	3	1	**11**	6	-	-	**37**	**42**
Environment		**%Cl$^-$**	**%NO$_3^-$**	**%SO$_4^{2-}$**	**%Na$^+$**	**%NH$_4^+$**	**%K$^+$**	**%Mg^{2+}**	**%Ca^{2+}**
Blast furnace influence	bf1	**18**	**23**	9	8	**33**	-	-	9
	bf2	**16**	**16**	10	12	**23**	1	6	16
	bf3	**18**	**23**	9	8	**33**	-	-	9
	bf4	7	8	10	3	**32**	1	2	**37**

samples can’t be correlated to the ones found in the sources as shown with the sample collected under blast furnace influence (Table 2). In fact, the profiles determined in the on-site samples are affected in the environment by mixture with other sources (domestic heat, vehicles ...). To complete this latter approach, ratios between soluble ions have been calculated for samples collected in the surroundings of the industrial site, as done for PAHs and metals. A relationship can be established between the following ratios: Cl^-/NH_4^+, NO_3^-/NH_4^+, Ca^{2+}/SO_4^{2-} and the sources. The Cl^-/ NH_4^+ ratio seems to be a more specific tracer: aerosols sampled under influence of refinery and cement factory (0,124 – 0,26), city (0,491 – 0,497) and steel industry (0,542–0,681) could be differentiated by ratio values comparison. For the samples collected close to the ferro-manganese metallurgic site, we notice a high Cl^-/NH_4^+ ratio value (1,6) which seems to discriminate this metallurgic source from the steel making one. Using these observations, it is possible to define specific ratios and the upwind and downwind profiles as tracers of specific sources.

For metallic ratios, the values determined in the environment are more difficult to correlate to sources values, but specific ratios have been found in the environmental samples and can be used to differentiate the metallurgic site of interest from the other industrial activities: $1.14<Pb/Cu<4.65$ and $Mn/Cu >2$ for the site influence (urban and refineries influences having $Pb/Cu <2.5$ and $Mn/Cu<2$) whereas ferro-manganese site influence shows a Pb/Cu ratio around 8, this ratio being around 10 for the cement producer. For cement and ferromanganese site, $Ba/Cu>1.3$ whereas <1 for all the other influences. Cement site influence exhibit also an Al/Zn ratio of 44 whereas <15 for all the other influences.

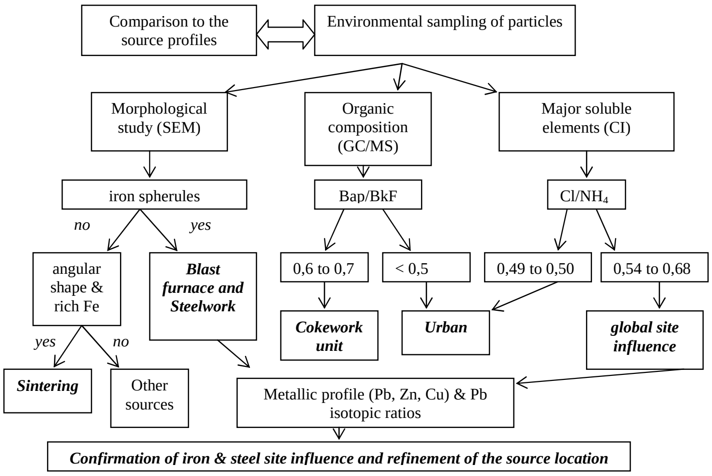
3.3.4 Multi technique origin determination

Using the various exploitation (profiles, ratios …) of the multi techniques results collected a preliminary diagram for source identification of the particles collected in the environment could be proposed (Fig. 6).

4. CONCLUSION

The multi-technique analysis show that the exact profiles and ratios determined in the on-site samples were affected in the environment by mixture with other sources (domestic heat, vehicles ...). However, we exhibit that is was possible to get, in the environment, new specific ratios and profiles resulting from the specific sources (steelwork, coke work, sintering, coke oven, urban, maritime). None of the individual

Figure 6: multi technique approach for search of tracers



techniques used is able to differentiate the various possible origins of the particles collected it the environment. Nevertheless, the combination of these techniques (Fig. 6) allows a quite accurate determination of the sources implicated. A new approach using organic, metallic and ionic ratios determined in samples collected in the surroundings of the industrial site was then developed in order to determine the aerosols origin.

5. ACKNOLEDGMENTS

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