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ATMOSPHERIC AEROSOLS BEHAVIOUR AT AN INDUSTRIAL AREA IN NORTHERN FRANCE

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ABSTRACT

Aerosols samplings were performed taking into account wind directions simultaneously at an urban and a rural site in Northern France. Major and trace elements were studied after sampling by use of a high volume cascade impactor, to follow the behaviour of particles between the coarse particles (> 1 µm) and the fine particles (< 1 µm). The behaviour of the different elements is determined by the evolution of the mass median diameters and the mass size distribution according to the wind. The kind of compounds under which some ions are, is determined by calculation of neutralization ratios.

Key Words : Urban and Rural Aerosols, Mass Median Diameter, Mass Size Distribution, Neutralization Ratio.

1. INTRODUCTION

The Northern France, Nord – Pas de Calais, is one of the most industrialized county of France, and in 2001, it was estimated that it was responsible of 13% of the total French particulate matter emission. In this region, 60% of this kind of emissions are originated from the high industrialized Dunkerque area which has an important local as well as on a large scale, influence.
The aim of this work is the characterization of particulate aerosols in a heavy industrialized area such as the Northern France, counting a lot of heavy metals emissaries (metallurgic industries, smelters, waste incinerators...).
If a great number of studies have been lead on the coast of the North Sea, among which (Bruynseels et al., 1988 ; Injuk et al., 1992 ; Rojas et al. 1993), can be cited, few of them concern this area (Flament et al., 1987). The present study attempts to determine the composition of particles in selected size fractions according to source contribution and the behaviour of some elements in the air.

2. METHODOLOGY

2.1. Study area

The sampling sites are located at Dunkerque an important urban city with roughly 220000 inhabitants with its suburbs, and where important industrial activities are concentrated, and at a rural area, Les Moëres, a village with 860 inhabitants, situated approximately 15 km ESE of the urban site (Fig. 1).

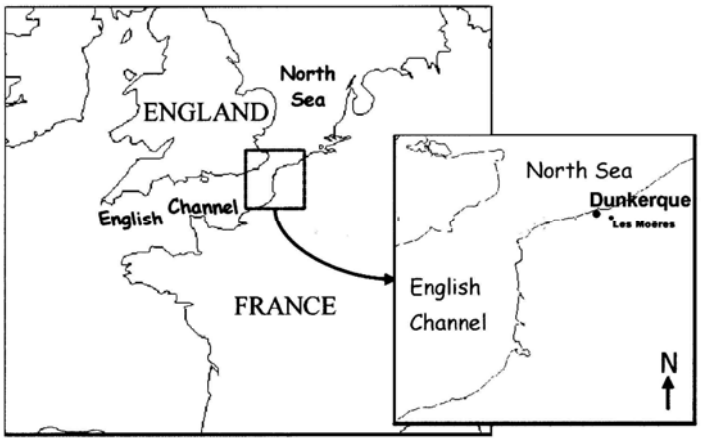


Fig. 1. Sampling location

The sampling site at Dunkerque is under the important influence of numerous aerosols sources, as urban origins, as well as particularly westside industrial sources (metallurgical plants, oil refineries, organic chemistry), and also marine sources under the northside marine influence of the North Sea. Three wind sectors are taken into account from the different wind directions with respectively the marine sector (340-60°), the continental and urban sector (60–240°) and the industrial sector (240-340°). For the rural sampling site, these three wind sectors are also used, with the difference that the 60–240° sector is only under the continental influence, and the 240–340° sector is under the complete influence of Dunkerque area.

2.2. Sampling methods

Aerosol samples were collected from January 15th 2001 to February 23rd 2001. Size-fractionated atmospheric particulate matter are sampled on Whatmann 41® cellulosic filters by use of a 5 stage plus back-up filter high volume cascade impactor (Sierra Instruments, Model 235). For each impaction stage, experimental values for the aerodynamic 50% cut-off particle diameter ($D_{p,50}$) as recommended by Willeke (1975) and used by Bayens et al. (1990) and Flament et al. (1996) in similar studies with same collection substrat and nominal flow rate (68 $m^3.h^{-1}$), are indicated in table 1.

The particles were divided in coarse particles (> 1 µm) sampled on the stages 1, 2 and 3, and fine particles (< 1 µm) collected on the stages 4, 5 and 6 (back-up).

Table 1. Calculated 50% cut-off particle diameters $D_{p,50}$ (µm) under a nominal flow rate of 68 $m^3.h^{-1}$ for the cascade impactor Sierra Model 235

Stages	1	2	3	4	5	6
$\mathbf{D_{p,50}}$	5.08	2.10	1.04	0.64	0.33	0.04

A meteorological station was set up at each sampling site to obtain local wind speed and direction, atmospheric pressure, temperature, hygrometry, rain fall.

2.3. Filters preparation

Unwashed cellulose filters present varying trace metals contents and especially for Fe, up to 5 µg per filter. So this kind of filters are treated as described by Obata et al. (1997) for Fe analysis. Filters are then dried under a laminar flow hood (Class 100, US Federal Standard 209a), and then hermetically kept in clean plastic bags and stored in a freezer (-20°C) before using. Such a treatment lowers the Fe contamination under 0.1 µg per filter, and contents of all other analysed elements are lower than limit detection.

2.4. Chemical analysis

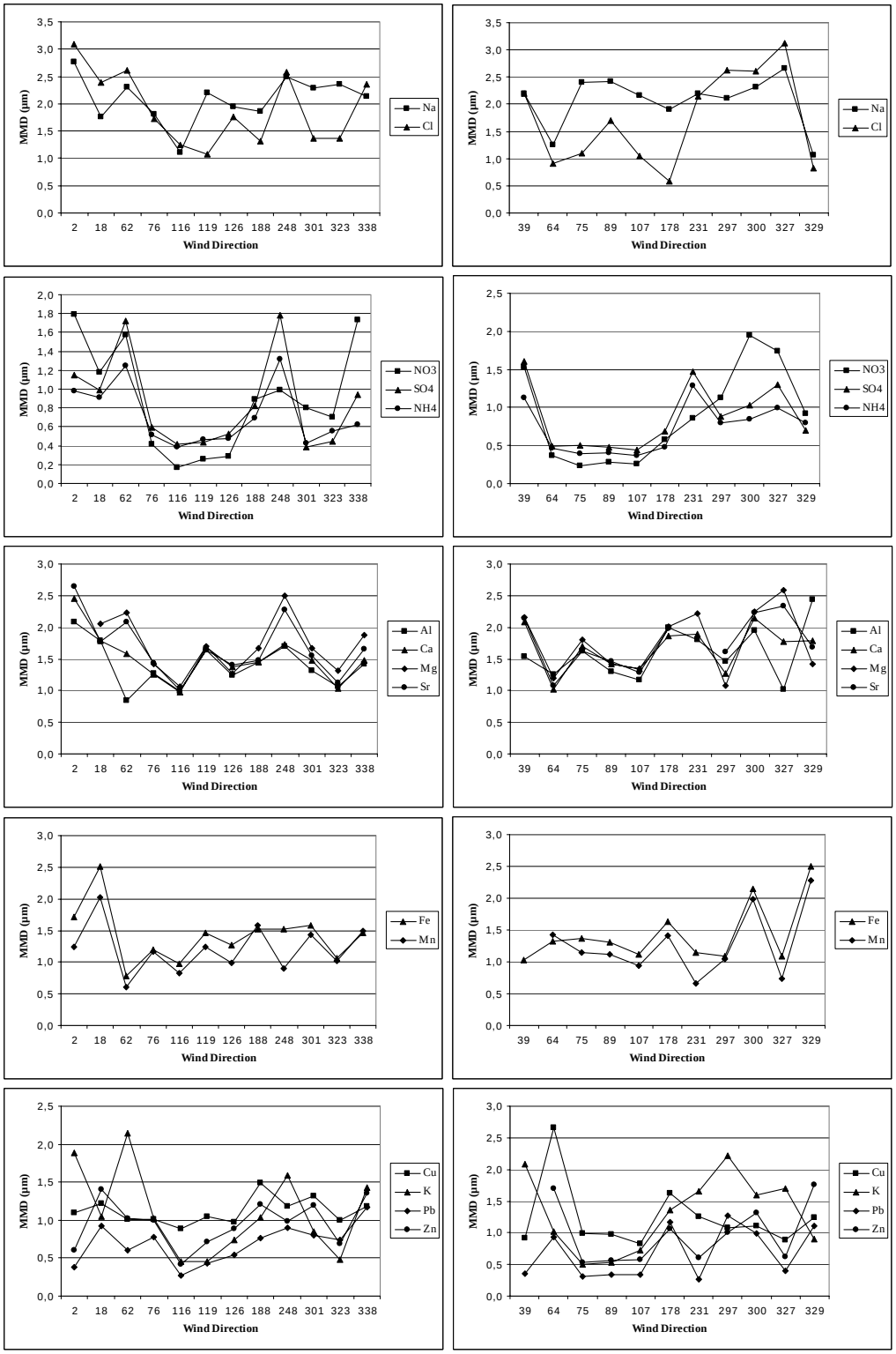
Major elements (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na, Mg and Ca), and trace elements (Al, Cu, Fe, K, Mn, Pb, Sr, and Zn) were taken into account and analysed. ICP-AES (Varian Liberty II) was used to quantify Al, Ca, Fe, K, Mg, Mn, Na, Sr, and Zn, whereas Cu and Pb concentrations were determined with the GFAAS technique (Perkin Elmer, Aanalyst 600, Zeeman background correction). Water soluble ions were analysed by ion chromatography (Cl^-, NO_3^-, SO_4^{2-}) and indophenol-blue spectrophotometry (NH_4^+).

3. RESULTS AND DISCUSSION

3.1. Mass Median Diameter (MMD)

The evolution of the behaviour of the different elements was followed by their calculated (MMD) according to the wind direction (Fig. 2).

Elements with similar profiles are gathered on the same graph, but Cu, K, Pb and Zn with their particular profiles cannot be superimposed with the other elements. Na and Cl are shown separately just for considering their behaviour, since they have a great and important affinity. If at the both sampling sites, the size of the particles related to these two elements are very well correlated for the marine sector (340–60°), on the other hand these particles present different profiles especially for the 60–240° sector which is strictly continental for the rural site, and continental with urban area influence for the urban site.



A – Urban site **B – Rural site**

Fig. 2. Evolution of MMD for elements at each sampling site *versus* wind directions

At the urban site, three groups of elements with identical profiles have been identified : (i) NO_3^-, SO_4^{2-} and NH_4^+, (ii) Al, Ca, Mg and Sr , (iii) Fe and Mn. At the rural site, these elements are gathered in exactly the same way as at the urban area, but with notably differences for the 240–340° sector, corresponding to the important influence of the industrialized area of Dunkerque, especially for NO_3^-, Al and Ca.

3.2. Mass Size Distribution (MSD)

Table 1 and Table 2 present the distribution of fine and coarse particles for the sampled elements according to the different wind sectors at the both sampling sites.

Table 1. Size distribution of particles at the urban site according to wind directions

Wind sector	Particles	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Pb	Sr	Zn	Cl	NO3	SO4	NH4
340 - 60	% > 1 µm	46	50	38	51	53	73	46	83	26	67	38	82	45	31	25
marine	% < 1 µm	54	50	62	49	47	27	54	17	74	33	62	18	55	69	75
60 - 240	% > 1 µm	48	48	41	49	20	53	41	57	15	50	29	41	12	16	14
continental	% < 1 µm	52	52	59	51	80	47	59	43	85	50	71	59	88	84	86
240 - 340	% > 1 µm	41	44	40	40	24	61	44	82	27	50	35	70	33	17	17
industrial	% < 1 µm	59	56	60	60	76	39	56	18	73	50	65	30	67	83	83

Table 2 . Size distribution of particles at the rural site according to wind directions

Wind sector	Particles	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Pb	Sr	Zn	Cl	NO3	SO4	NH4
340 - 60	% > 1 µm	52	56	51	54	31	72	51	80	14	63	27	70	14	19	15
marine	% < 1 µm	48	44	49	46	69	28	49	20	86	37	79	30	86	81	85
60 - 240	% > 1 µm	56	57	47	53	29	61	44	65	19	60	31	25	11	15	11
continental	% < 1 µm	44	43	53	47	71	39	56	35	81	40	69	75	89	85	89
240 - 340	% > 1 µm	58	56	34	53	49	66	50	80	34	71	43	77	49	29	32
industrial	% < 1 µm	42	44	66	47	51	34	50	20	66	29	57	23	51	71	68

The 340–60° wind sector represents correctly the marine sector for the sampling sites with Ca, Mg, Na, Sr and Cl which are in majority coarse particles (> 1 µm), with the higher percentage in this mode whatever the sector may be for Mg, Na and Sr, and also for Al at the rural site.

On the other hand, for the urban site, the other trace elements have their main percentage in the fine mode (< 1 µm) especially in the continental sector (60–240°) under the important influence of the city and in the industrial sector (240–340°), source of main anthropogenic elements. This mode is also found at the rural site for the trace elements except for Al and Fe.

The mass size distribution allows us to determine the behaviour of the different aerosols according to their size distribution, and it is well known (Safai et al., 1993) that this size distribution is generally similar and often bimodal with differences in the percentage contributions of particles present in the two modes (Horvath et al., 1996).

The MSD of the sampled elements at the both sampling sites, for a precise wind direction at each sector, are presented respectively for the major elements (Fig. 3) and for the trace metals (Fig. 4).

The major elements are characterized (Fig. 3) by a unimodal distribution for both sampling sites for the marine sector, and these ions dominate in the coarse mode (2.1-5.08 µm) except NH_4^+ with a peak in the fine mode (0.64-1.04 µm),

and SO_4^{2-} having a bimodal distribution for the urban site with a peak between 0.33 and 0.64 µm.

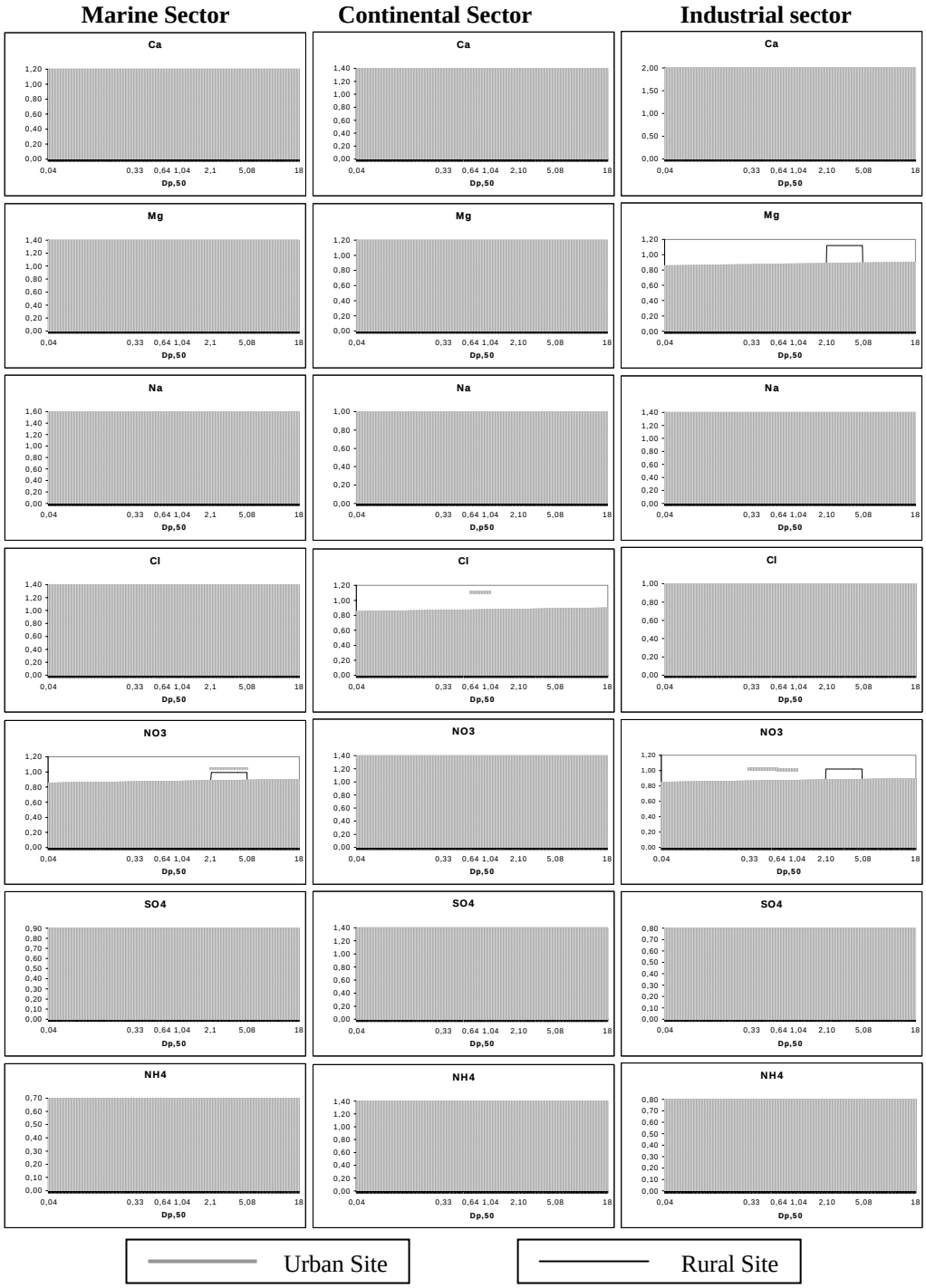


Fig. 3. MSD of major elements at the sampling sites according to wind directions

All these major aerosols have a bimodal distribution in the continental sector for the urban site, and only Ca, Cl^- and NO_3^- have the same kind of distribution for

Fig. 4 . MSD of trace elements at the sampling sites according to wind directions

the rural site. It can be noted that the elements characterized by a bimodal distribution have common peaks between 0.64-1.04 µm and 2.1-5.08 µm, but Cl^-, NO_3^-, SO_4^{2-} and NH_4^+ from the rural site, present a peak between 0.33-0.64 µm instead of 0.64-1.04 µm. This difference between the two sampling sites results probably of the importance of the influence of the urban area on the urban site. For the industrial sector, the same peaks are always present for the bimodal distribution, with the difference that for the rural site, Cl^-, NO_3^- and SO_4^{2-} have a peak at 2.1-5.08 µm and NH_4^+ with a unimodal distribution, dominates with a peak at 0.64 and 2.1 µm.

Taking into account the trace elements, (Fig. 4), we see that their distribution can be unimodal or bimodal according to wind sectors.

For the marine sector, Al, Mn, Pb, Sr and Zn at the urban site, and K and Sr at the rural site, present a unimodal distribution. Al, K and Sr dominate in the coarse mode with diameters of the particles between 2.1 and 5.8 µm. The diameters of the other particles are between 0.33 and 0.64 µm and 0.64 and 1.04 µm respectively and a wide range for Zn (0.33-1.04 µm).

For the continental and industrial sectors, all these trace elements present a bimodal distribution at the urban site. In that case, the diameters of the particles in the two modes are between 0.64 and 1.04 µm and 2.1 and 5.08 µm. The fine mode is the main result of the important influence of the industrial area, and this is particularly shown by the slipping peak from 0.64-1.04 µm to 0.33-0.64 µm for Pb and above all K and Zn. For the same sectors for the rural site, the diameters of the particles are the same in the two modes, very important between 2.10 and 5.08 µm for all elements except Zn, for the continental sector. The influence of the industrial sector appears with most particles submicrometer sized (0.64-1.04 µm).

3.3. Neutralization of Particles

From the analytical results, we have observed that most molar ratios of NH_4^+/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/Cl^- are widely higher than theoretical values which are respectively 2, 1 and 1. This shows that a noticeable amount of NH_4^+ is combined with organic compounds as well with coarse particles as with fine particles. In coarse particles, the molar ratio NH_4^+/Cl^- is often below 1, and by this way it is possible to say that ammonium chloride is also present with coarse particles (Zuhang et al. 1999). This observation easily allows the explanation of neutralization ratios (NR) obtained during the two sampling campaigns, using the following formula :

$$NR = \frac{NH_4^+(nmol.m^{-3})}{2.nssSO_4^{2-}(nmol.m^{-3}) + NO_3^-(nmol.m^{-3})} \quad \text{(nss = non-sea-salt)}$$

The amounts of NH_4^+ are much higher in the submicronic field, and this ratio increases when the particles are in the fine mode. Fig. 5 shows that, for fine particles, this ratio is higher than 1 at the both sampling sites, and in this case, it can be supposed the presence of NH_4Cl or other forms of NH_4^+ compounds,

because lowest temperatures in winter could stabilize this compound and limit its volatilization.

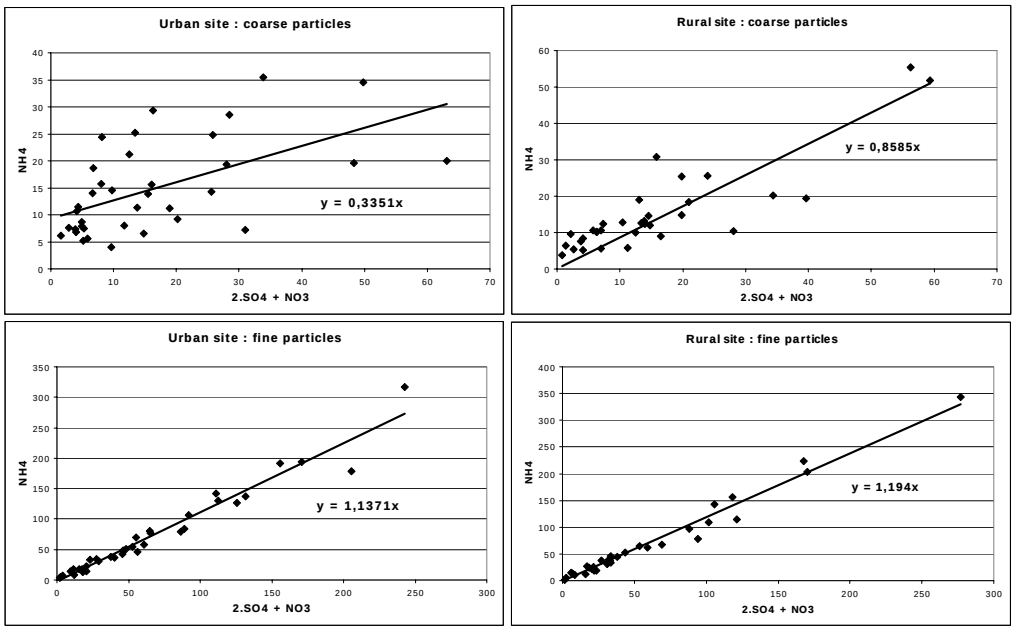


Fig. 5. Neutralization ratios (NR) at each sampling site

On the other hand, a ratio close to 1, indicates that NH_4^+ is mainly present as $(NH_4)_2SO_4$ and NH_4NO_3. For each sampling site this ratio for coarse particles is lower than 1 and indicates that SO_4^{2-} and NO_3^- are associated with other elements like Na and Ca (Harrison et al., 1994; Wakamutsu et al., 1996).

4. CONCLUSION

Mass Median Diameter reveals that the elements have different profiles according to the wind sectors, and for each sampling site, elements having industrial profiles can be classified in three groups: (1) NO_3^-, SO_4^{2-}, NH_4^+, (2) Al, Ca, Mg, Sr (3) Fe and Mn. The influence of the industrialized area on the rural site appears very well because of differences in the profiles of some trace elements. The mass size distribution study shows for most of the elements a bimodal mode, corresponding to several sources. One peak occurred between 0.33-0.64 µm or 0.64-1.04 µm, and the second between 2.10-5.08 µm. Aerosols exist in the fine and the coarse mode, but differ in percentage contribution according to the origin of the winds. Anthropogenic elements, fine particles, are identified by the industrial wind sector, and coarse particles, notably major elements, are characterized by the marine wind sector. NO_3^-, SO_4^{2-} and NH_4^+, at the urban sampling site, are mainly originated from gaz-particle conversion because they present a unimodal distribution especially in the fine mode.

According to the importance of the neutralization ratio study between NH_4^+ and $SO_4^{2-} + NO_3^-$, the behaviour of NH_4^+ in the aerosols can be explained.

5. ACKNOWLEDGEMENTS

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