

Chemical and mineralogical composition and sources of urban atmospheric particles, specially sulphates – A study at Tours (France)

Composition chimico-minéralogique et sources d'émissions des particules atmosphériques urbaines, spécialement des sulfates – Le cas de la ville de Tours (France)

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Abstract

In order to reconstruct the formation mechanism of the sulphated black crusts found on the tuffeau and stained glass windows of Saint-Gatien Cathedral in Tours, a study was performed on the particulate content of the atmosphere in the town, based on two sampling campaigns that took place during December 1994 and July-August 1995. The Black Carbon (BC) in air was continuously measured by means of an aethalometer. Total suspended particles were sampled both day and night by air filtration through Nuclepore membranes. The analysis of eight filters by Analytical Scanning Electronic Microscopy (ASEM) allowed the classification of particles of more than 1 μm into six categories (marine, terrigenous, mixture of marine and terrigenous, S bearing terrigenous, anthropogenic, biogenic) (+ "undetermined").

Aethalometry and analysis of filters by X-Ray Fluorescence (XRF) indicated S, BC and Na to be the main elements present in the particles of Tours: S in summer, BC and Na in winter. Geochemical calculations show S to be of dual origin, mainly anthropogenic (S_{excess}) and, to a lesser extent, marine (S_{marine}). The unexpected contribution of the marine natural source is confirmed by the high levels of Na, a typical marine element, also measured sporadically on the site. This phenomenon is linked to the arrival of oceanic air masses in low pressure conditions from the south-western sector and is characterised by a significant amount of marine particles in the form of crystals of halite (NaCl) and polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) containing S_{marine} . The contribution of the anthropic source is most frequently predominant, particularly in periods of strong atmospheric stability characterised by the absence of wind and in winter, in strongly anticyclonic conditions. Such pollution episodes are characterised by the abundance of anthropogenic particles and S_{excess} is present in the form of ammonium sulphates, principally mascagnite ($(\text{NH}_4)_2\text{SO}_4$). The BC is emitted primarily by automobiles and, when present, is mainly in the typical form of microsoot particles.

Thus, the sulphates deposited on the tuffeau and stained glass windows and accumulating in the areas sheltered from rainwater must be taken into account in determining the mechanism of formation of the gypsum cement of the black crusts.

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Résumé

Afin de reconstituer le mécanisme de formation des croûtes noires sulfatées recouvrant le tuffeau et les vitraux de la cathédrale Saint-Gatien de Tours, une étude du contenu particulaire de l'atmosphère de cette ville a été réalisée à partir de deux campagnes de prélèvements atmosphériques effectuées en décembre 1994 et juillet-août 1995. La concentration de l'air en Black Carbon (BC) a été mesurée en continu au moyen d'un aethalomètre. L'échantillonnage des particules totales a été réalisé le jour et la nuit par filtration d'air au travers de membranes Nucléopore. L'analyse de huit filtres par microscopie électronique analytique en balayage a permis d'établir un classement des particules supérieures à 1 µm en six catégories (marines, terrigènes, marines + terrigènes, terrigènes + S, anthropogéniques, biogéniques) (+ « indéterminées »).

L'aethalométrie et l'analyse des filtres par spectrométrie de fluorescence X indiquent que S, BC et Na sont les éléments majeurs dans les aérosols de Tours : S en été, BC et Na en hiver. Les calculs géochimiques indiquent que S a une double origine, principalement anthropique ($S_{\text{excès}}$) et dans une moindre mesure marine (S_{marin}). La contribution inattendue de cette source naturelle marine est confirmée par les fortes teneurs en Na, élément typiquement marin, mesurées ponctuellement. Ce phénomène est lié à l'arrivée de masses d'air océaniques en situation dépressionnaire de secteur sud-ouest et se caractérise par une proportion importante de particules marines sous forme de cristaux de halite (NaCl) et de polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$) contenant le S_{marin} . La contribution de la source anthropique prédomine le plus souvent, particulièrement en période de forte stabilité atmosphérique caractérisée par l'absence de vent et en hiver, en situation fortement anticyclonique. Ces épisodes de pollution sont caractérisés par l'abondance des particules anthropogéniques et $S_{\text{excès}}$ se présente sous la forme de sulfates d'ammonium, principalement de la mascagnite $((NH_4)_2SO_4)$. Le BC est émis principalement par les automobiles et se présente sous la forme typique de microsues.

Ainsi ces sulfates, qui se déposent sur le tuffeau et les vitraux et qui s'accumulent dans les zones abritées des pluies, doivent être pris en compte pour déterminer le mécanisme de formation du ciment gypseux des croûtes noires.

Introduction

On the surface of buildings in areas sheltered from rainwater, one generally observes the presence of black crusts, which result from the successive deposition of atmospheric particles, followed by their cementation by gypsum. Among the diverse particles encountered, industrial fly ash originating from heavy fuel and/or coal combustion have been evidenced by Del Monte et al. [1], and subsequently systematically detected in numerous black crusts sampled in polluted urban environments [2-6], as well as in marine regions [7, 8]. According to Camuffo et al. [2], the fly ash play an active role in the formation of gypsum cement, since they transport metals such as Fe, Ni, V, that catalyse to heterogeneous oxidation of SO_2 into sulphate, in the presence of H_2O . This hypothesis was accordingly adopted by other authors [1, 2, 7, 9] and was experimentally verified, in particular by Cheng et al. [10], Ausset et al. [11] and Sabbioni et al. [12]. Preliminary studies conducted at Tours highlighted the presence of typical fly ash within the black crusts on tuffeau and windows of the Saint-Gatien Cathedral and also in the air and rainwater sampled on the said Cathedral [13-15]. Without disputing the catalytic role of fly ash, we believe it is important not to neglect the other particles present in the atmosphere.

Thus, the aim of the present article is to characterise the particulate content of the atmosphere in Tours and, in particular, to establish, apart from fly ash, the sources and nature of the particles contributing to the formation of the gypsum cement of

the black crusts, such as the sulphates which are generally abundant in urban particles.

Description of the site, sampling and analysis

Description of the site

The city of Tours is situated in the Loire Valley at 230 km from the Atlantic Ocean. The west-east orientation of the valley favours the penetration of oceanic winds.

Sampling

Atmospheric particles were sampled in the city centre, on the first floor of the Psalette Cloister, located on the northern side of the Saint-Gatien Cathedral, at a height of 5 m above the ground. Two sampling campaigns were carried out, one in winter from 3 December to the night of 20 December 1994, the other in summer from 3 July to the night of 5 August 1995.

Black Carbon (BC) concentrations in the air were continuously measured by means of an aethalometer (Magee Scientific, model AE-9) [16]. The pump rate was set at 20 l min^{-1} and measurements were performed every five minutes. BC concentrations measured by aethalometer method agreed well with particulate elemental carbon measured by thermo/optical reflectance [17, 18].

The particles were collected by air filtration through polycarbonate membranes of 0.4 µm porosity (Nuclepore®) placed in a filter support linked

to an electric pump (Reciprotor Sweden AB) and to a volumetric counter (Gallus 2000). Thus, all the particles having a diameter superior to $0.4\ \mu\text{m}$ are theoretically collected.

Two air filtration units functioning simultaneously permitted particles to be collected on two series of membranes. The first was employed for global chemical analysis by X-Ray Fluorescence (XRF), the second for the observation and chemical analysis of individual particles by Analytical Scanning Electron Microscopy (ASEM). Two samples were collected every 24 hours, the first during the day (from 7.00 to 21.00 h), the second during the night (from 21.00 to 7.00 h the next morning). The initial pump rate was $5\ \text{l min}^{-1}$ in winter and $8\ \text{l min}^{-1}$ in summer.

The concentrations of particulates (PM_{10}) are now currently measured on five stations in Tours by the air quality network survey Lig'Air [19, 20]. The concentrations of NO_x were measured in the city centre, at approximately 800 m south-west of the Cathedral, by the Laboratoire Départemental de Touraine (LDT).

There being no meteorological station within the town walls, the meteorological parameters employed were those measured by the Météo-France station at the Tours-Saint-Symphorien Airport, located 6 km north of the city centre. Wind speed and direction were measured every 3 hours, the duration and density of precipitation every 6 hours and atmospheric pressure reported to sea level every 12 hours.

The trajectographies of the air masses were calculated at Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) using the current version of the TM2 model of atmospheric transport initially developed at the Max Planck Institute in Hamburg and modified by Ramonet [21].

Analysis methods

The measurement of the BC concentrations in air is based on the optical measurement of the black body properties of the particles. The aethalometer pumps the air through a quartz fibre filter, measuring at regular intervals the attenuation of the light beam transmitted (530 nm) through the filter. The mass of deposited BC was estimated, after which the concentration was calculated by dividing the mass by the volume of filtered air.

The overall elemental concentrations of the particles were measured by XRF (SIEMENS SRS 303) with wavelength dispersion over all the first series of membranes (104 filters). This method permits a quantitative elemental analysis of particles since the intensity of fluorescence of an element is proportional to its mass deposited on the filter, provided that the samples constitute a thin layer. This hypothesis has been confirmed experimentally by the measurement of filter transmission using the "radiator" technique [22]. The masses of the 15 chemical elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Fe, Cu, Zn, Pb) were

determined on each filter according to the procedure defined by Quisefit and al. [23].

The individual analysis of particles was carried out on 8 filters (4 for winter, 4 for summer), on the second series of membrane, by SEM (JEOL JSM 840 A) coupled with an X-Ray energy dispersive spectrometer (TRACOR TN 5400) allowing the detection of elements with atomic number higher than 6 (carbon). However the presence of C can be assumed by the presence of an important background in the spectra. The operative conditions were as follows: accelerating voltage: 15 kV; probe current: $6.10^{-10}\ \text{A}$; working distance: 39 mm; measurement time: 100 s; spectrum acquisition from 0 to 10 keV; dead time between 20 and 25%. The study of the filters, previously made conductors by the deposition of a carbon film, was performed following the protocol described by Chabas and Lefèvre [24] and consisted of observing, measuring and analysing the particles larger than $1\ \mu\text{m}$ present in randomly chosen areas under an enlargement of X1000. The mineralogical classification of the particles is performed starting from a semi-quantitative analysis of their chemistry and elemental composition, and of their morphology.

Certain particles underwent specific study by means of low intensity field effect SEM (JEOL JSM-6301-F) and Transmission Electron Microscopy (TEM) (JEOL 100 CX II) coupled with a X-Ray energy dispersive spectrometer (respectively, Link ISIS 300 and TRACOR TN 421), which allowed the detection of elements with atomic number greater than 5. The operating conditions chosen for the field effect ASEM were the following: accelerating voltage: 20 kV; probe current: $6.10^{-10}\ \text{A}$; working distance: 15 mm; measurement time: 100 s; spectrum acquisition from 0 to 20 keV; dead time between 20 and 30%. The operating conditions chosen for the ATEM were: accelerating voltage: 100 kV; working distance: 28 mm; tilt: 35° ; measurement time: 100 s; spectrum acquisition from 0 to 10 keV; dead time between 20 and 25%.

Results and discussion

Global chemical and elemental composition of particles

Geometric means and standard deviations

The geometric concentration means and their associated standard deviations were calculated for the BC measured by aethalometry and for 12 elements out of 15 determined by XFS on the 104 filters (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, Fe, Zn and Pb). In fact, V, Cr and Cu frequently present levels that are below the detection threshold of the spectrometer.

The results presented in Table 1 p. 106 indicate that S, BC and Na are the predominant elements (relative abundance $> 10\%$) and that Si, Ca, Fe, K, Al, Cl and Mg are the minor elements ($1\% < \text{relative}$

abundance < 10%). The elements Ti, Zn and Pb, which were present in trace (relative abundance < 1%) are not studied below. The geometric standard deviations calculated for each major and minor element are close (variation between 1.85 and 2.94), with the exception of Cl, whose value of 5.22 highlights a strong temporal variability in its concentration.

The mean concentrations measured in Tours are of the same order of magnitude as those measured in other towns in France (Figure 1) and the higher level of S and BC confirms the predominance of anthropic sources in urban sites. The levels of BC in Tours and Arles are, however, far lower than those measured in Paris (4600 ng m⁻³ according to Brémond et al. [25]; 7900 ng m⁻³ according to Delumyea and Kalivretanos [26]). Conversely, the concentration of Na, almost identical to that encountered in Arles, is double in Tours compared to Paris. Thus, the town of Tours seems to undergo, like Arles (some 30 km from the Mediterranean Sea), an oceanic influence, in spite of its relatively great distance from the Atlantic Ocean (230 km).

Table 1.
Geometric means (ng m⁻³), standard deviations and relative abundance (%) of major and minor elements of the particles sampled in Tours.

Moyennes géométriques (ng m⁻³),
écarts types géométriques des concentrations
et abondance relative (%) en éléments majeurs et mineurs
des aérosols prélevés à Tours.

	Geometric mean	Standard deviation	Relative abundance
BC	1432	2.44	24
Na	853	2.54	15
Mg	126	1.99	2
Al	184	2.61	3
Si	578	2.94	9
S	1662	2.32	28
Cl	169	5.22	3
K	213	1.85	3
Ca	495	2.88	8
Fe	240	2.11	4
Ti, Zn, Pb	24, 42, 86	1.74, 2.60, 1.62	< 1, < 1, < 1

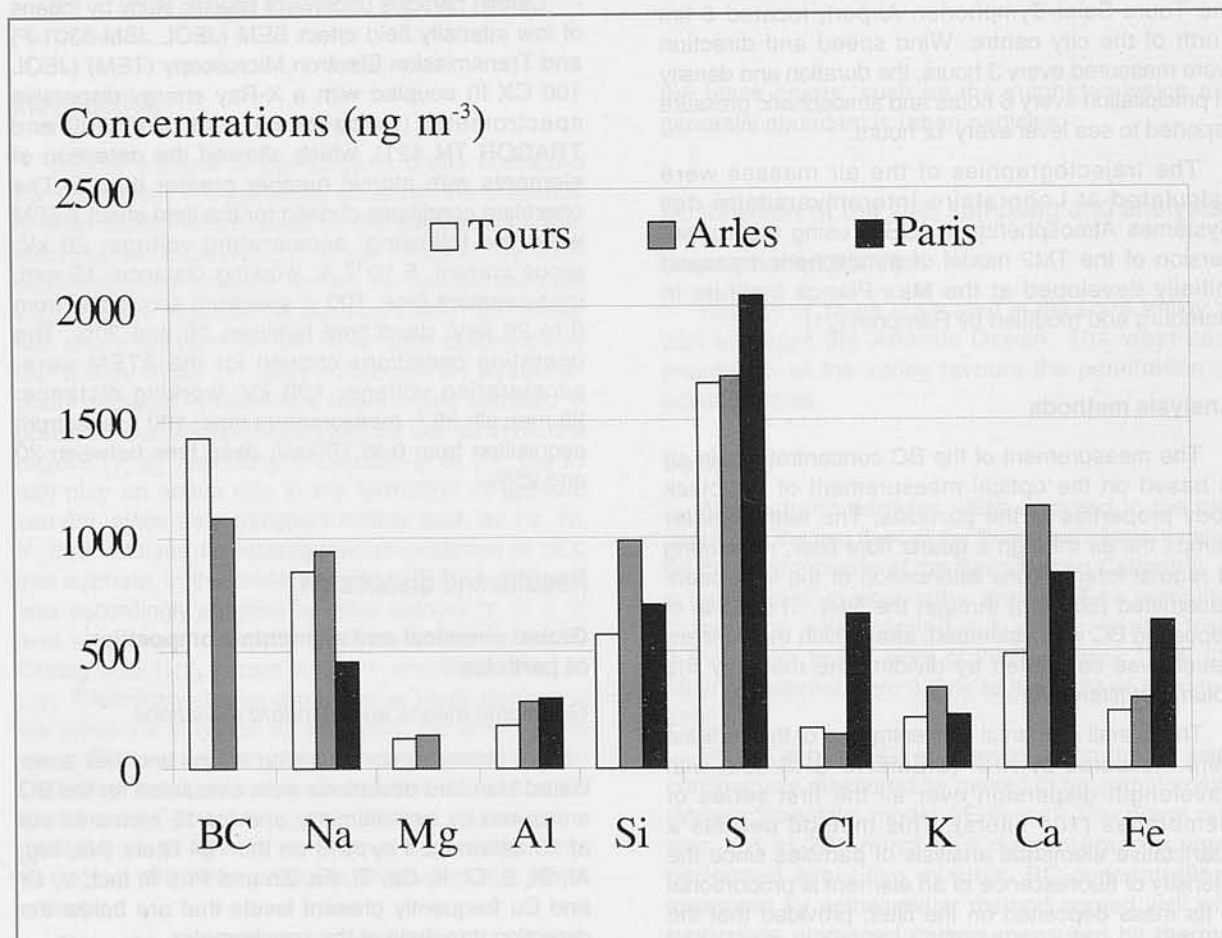


Figure 1.

Comparison of geometric means of elemental concentrations (ng m⁻³) in particles sampled in Tours [27], Arles [28] and Paris [29].

Comparaison de la moyenne géométrique des concentrations élémentaires (ng m⁻³) des particules prélevées à Tours [27], en Arles [28] et à Paris [29].

Enrichment factors

Enrichment factors (EF) allow one to establish the probable origin (marine, terrigenous or other) of the major and minor elements present in the particles, except for BC, which is emitted mainly by anthropogenic sources (fossil fuel or biomass combustion). The EF are calculated according to Mason's earth crust model [30] (1) and Brewer's seawater model [31] (2). Al is taken as reference element for the crustal model and Na_{marine} (Na corrected for its crustal contribution) for the seawater model (3).

$$EF_{\text{terrigenous}}(X) = \frac{(X/Al)_{\text{aerosol}}}{(X/Al)_{\text{crustal rock}}} \quad (1)$$

$$\text{and } EF_{\text{marine}}(X) = \frac{(X/Na)_{\text{aerosol}}}{(X/Na)_{\text{seawater}}} \quad (2)$$

$$Na_{\text{marine}} = Na_{\text{aerosol}} - Na_{\text{terrigenous}}$$

$$\text{with } Na_{\text{terrigenous}} = Al_{\text{aerosol}} \times (Na/Al)_{\text{crustal rock}} \quad (3)$$

In the results reported in Table 2, one can distinguish three groups of chemical elements:

- Al, Si and Fe where $EF_{\text{terrigenous}}$ is close to 1 and EF_{marine} high, are exclusively of terrigenous origin;
- Na, Mg and Cl, where EF_{marine} is close to 1 (except for Cl) and $EF_{\text{terrigenous}}$ high, are mainly of marine origin. According to Eriksson [32], the depletion of Cl in relation to seawater ($EF_{\text{marine}} = 0,1$) indicates that marine particles such as halite (NaCl) react strongly with the acid compounds present in the air (H_2SO_4 and HNO_3). This chemical reaction leads to the release of HCl to the gaseous state and the enrichment of the particles by sulphates and nitrates;
- S, K and Ca present high EF regardless of the reference, resulting from the contribution of different sources (terrigenous, marine and others). S is mainly emitted by "other" sources and partly by the marine source, while K and Ca tend to be of mixed origin (terrigenous, marine) and "other".

Seasonal and diurnal evolution of concentrations

Generally speaking, and with the exception of BC, Na and Cl, the concentrations are 2 to 3 times lower in winter than in summer (Figure 2, p. 108). This is due to the abatement effect of rain, which diminishes the number of suspended particles, a phenomenon more active in winter, when the rainy days are more numerous

(68% in winter against 23% in summer) and the ratio of precipitations to the number of days higher ($2,5 \text{ mm j}^{-1}$ in winter against $1,2 \text{ mm j}^{-1}$ in summer).

The high winter concentrations of Na and Cl are linked to the presence of winds arriving mainly from the southwesterly sector (Figure 3, p. 108), i.e. of oceanic winds transporting marine particles. In summer, winds are more frequently continental and follow a northeast to southwest trajectory, corresponding to the direction of the Loire Valley towards Tours.

Element concentrations show two types of diurnal evolution in both seasons: day/night cycle with higher day concentrations for terrigenous chemical elements (example in winter Figure 4, p. 109) and sporadic evolution for marine chemical elements and S (example in winter Figures 5 and 6, p. 109 and 110). Day/night variations seem dependent on the human activity because day variations correspond to the remobilization of deposited dust at night when human activities slow down.

Concentrations of BC are generally higher in winter due to the decrease in the mixing layer height [25] and to the contribution of supplementary sources such as heating plants [33]. The latter hypothesis cannot apply in the present case since the BC, in Tours, is mainly emitted by automobile traffic. In fact, the profile of its hourly mean concentrations (Figure 7, p. 110) reveals two maxima (9.00 h and 19.00 h) corresponding to automobile rush hour times. Finally, there is a good correlation ($R = 0.83$) between BC and NO_x (Figure 8, p. 111), with the nitrogen oxides in Tours mainly originating from automobiles [27].

Specific study of S

Calculations of contributions

The respective contribution of natural (marine and terrigenous) sources responsible for the measured levels of S is calculated following the method of Marchal [34] using the above-mentioned models.

$$S_{\text{marine}} = Na_{\text{marine}} \times (S/Na)_{\text{seawater}}$$

$$\text{and } S_{\text{terrigenous}} = Al_{\text{aerosol}} \times (S/Al)_{\text{crustal rock}}$$

The contribution of the "other" or "excess" source in relation to the previous sources is calculated from the difference:

$$S_{\text{excess}} = S - (S_{\text{marine}} + S_{\text{terrigenous}})$$

Table 2.
Enrichment factors (EF) of the particles sampled in Tours compared with the crustal model of Mason [30] and the seawater model of Brewer [31].

Facteurs d'enrichissement (FE) par rapport au modèle de croûte de Mason [30] et au modèle d'eau de mer de Brewer [31] des particules prélevées à Tours.

	Na	Mg	Al	Si	S	Cl	K	Ca	Fe
EF terrigenous	13	3	1	1	2825	573	4	6	2
EF marine	1	2	1442534	4528	29	0,1	9	19	1830336

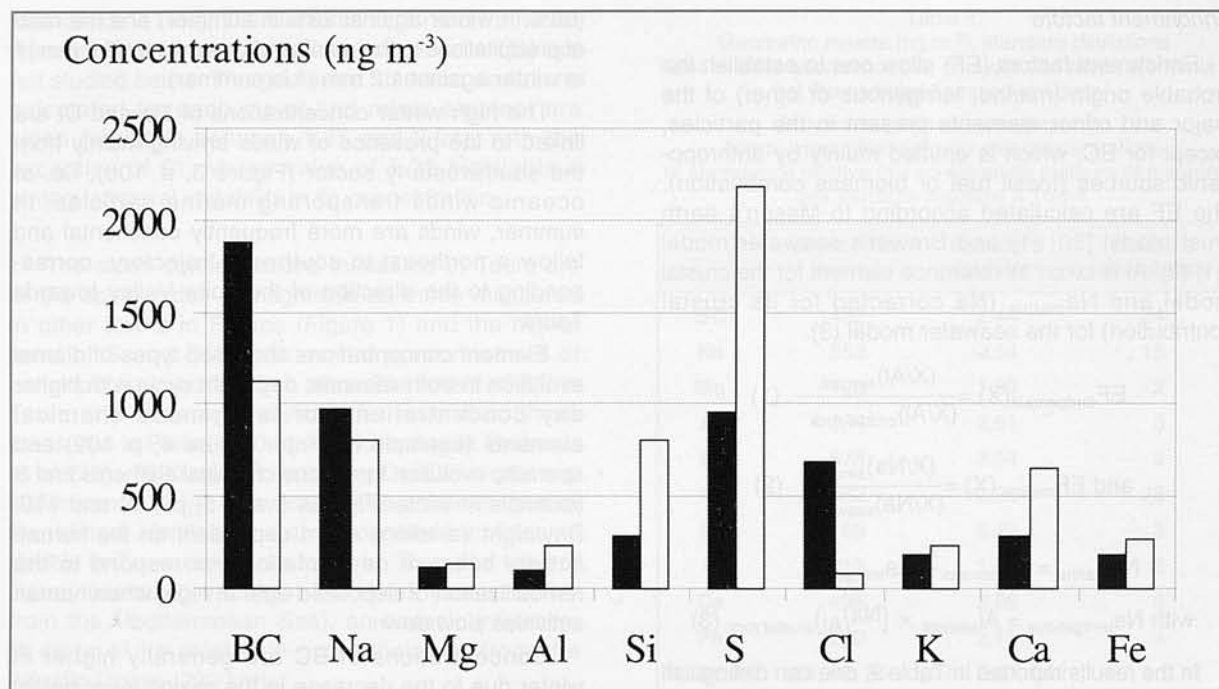


Figure 2.

Geometric means of elemental concentrations (ng m^{-3}) of particles sampled in Tours in December 1994 (■) and July-August 1995 (□).

Moyennes géométriques des concentrations élémentaires (ng m^{-3}) des particules prélevées à Tours en décembre 1994 (■) et en juillet-août 1995 (□).

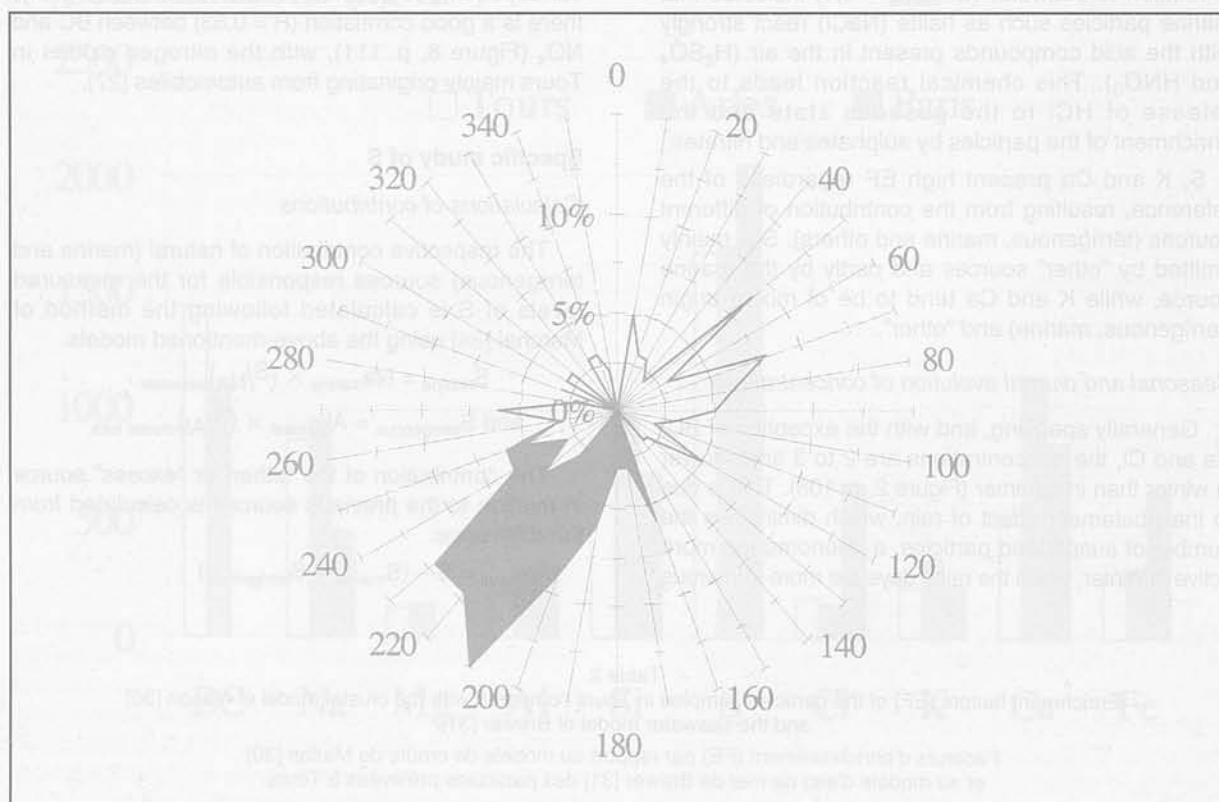


Figure 3.

Means frequencies of wind directions (°) in Tours in December 1994 (■) and July-August 1995 (□) (Météo-France Data).

Fréquences moyennes des directions des vents (°) à Tours en décembre 1994 (■) et en juillet-août 1995 (□). (Données Météo-France).

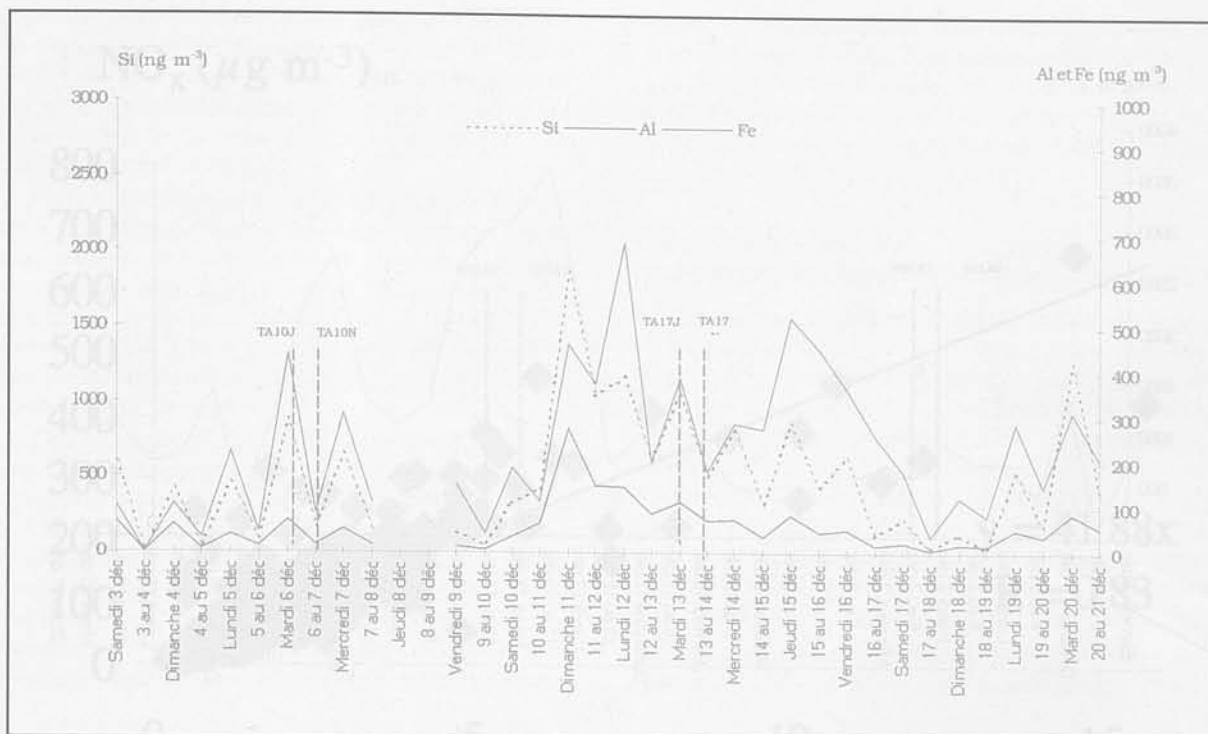


Figure 4.
Day-night variation of terrigenous elements concentrations (ng m⁻³) in Tours in December 1994.
Variation jour-nuit des concentrations (ng m⁻³) en éléments terrigènes à Tours en décembre 1994.

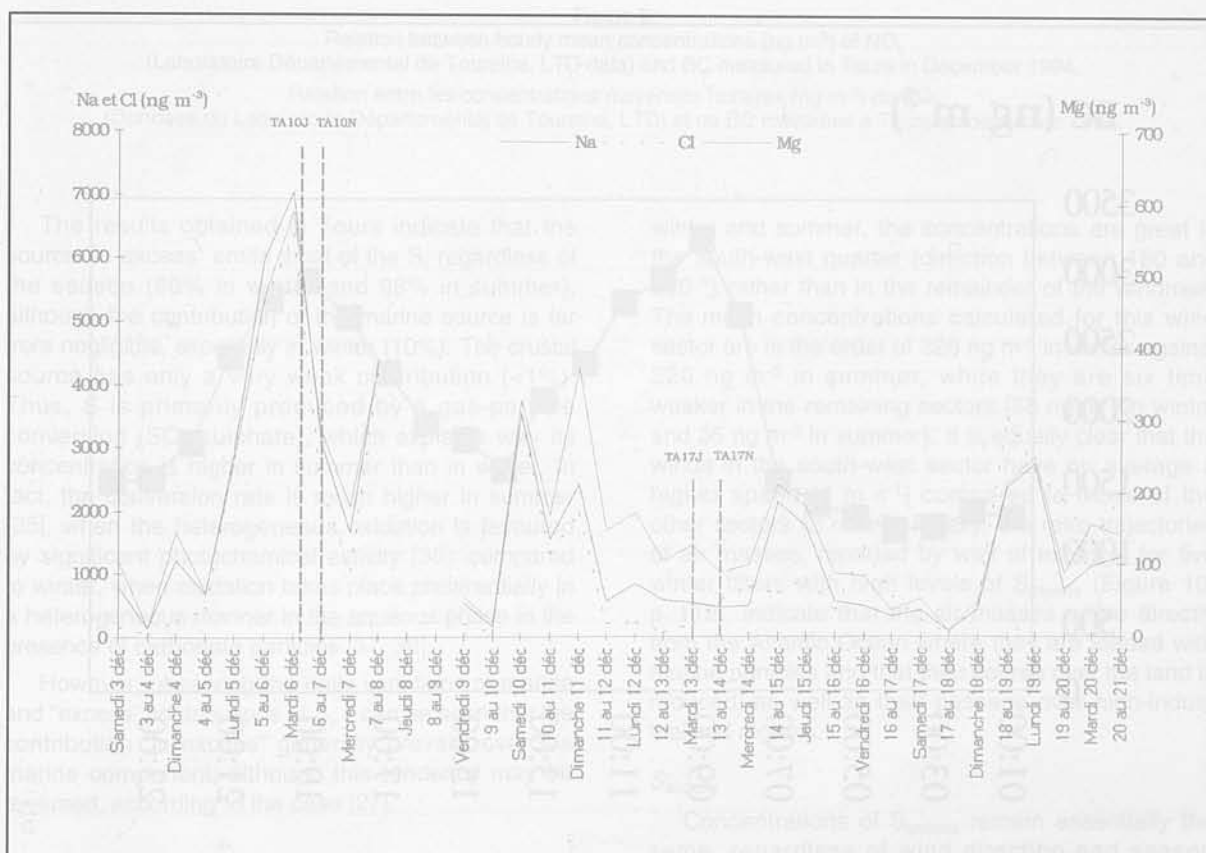


Figure 5.
Day-night variation of marine elements concentrations (ng m⁻³) in Tours in December 1994.
Variation jour-nuit des concentrations (ng m⁻³) en éléments marins à Tours en décembre 1994.

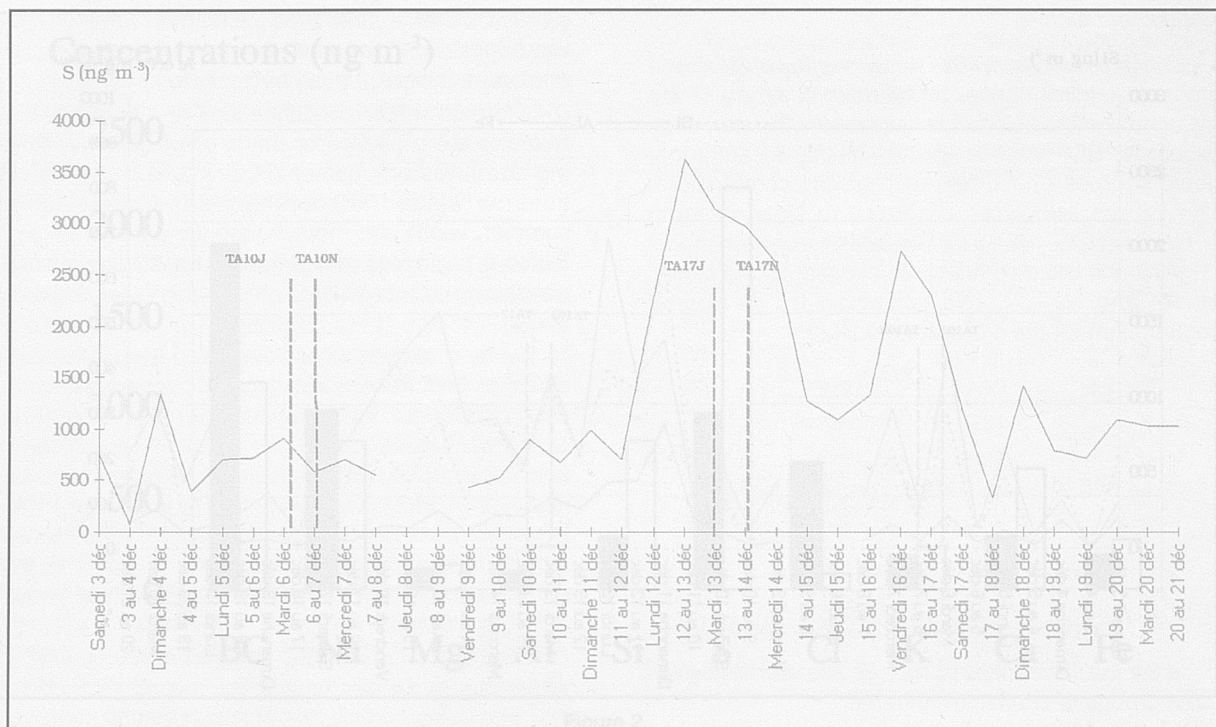


Figure 6.
Day-night variation of S concentrations (ng m⁻³) in Tours in December 1994.
Variation jour-nuit des concentrations (ng m⁻³) en S à Tours en décembre 1994.

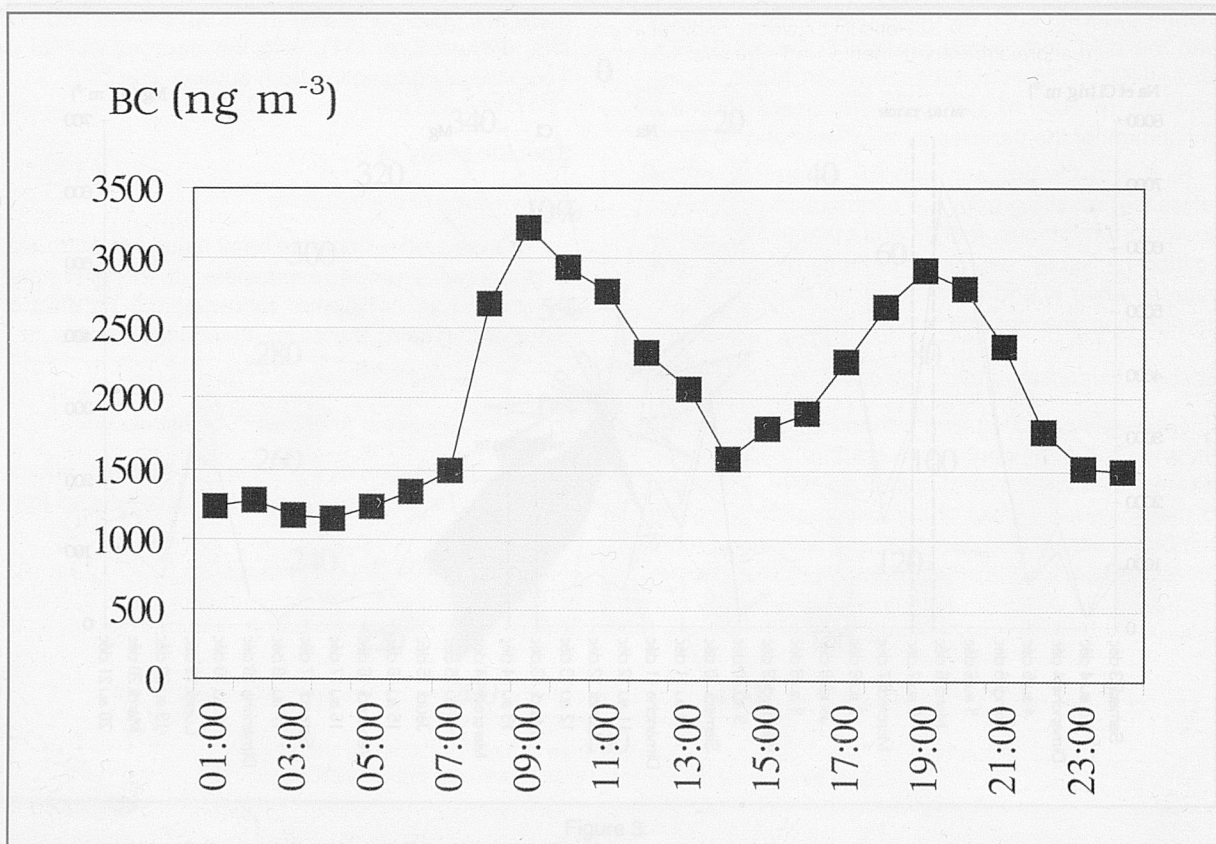


Figure 7.
Profile of hourly mean concentrations of BC (ng m⁻³) measured in Tours in December 1994.
Profil des concentrations moyennes horaires en BC (ng m⁻³) mesurées à Tours en décembre 1994.

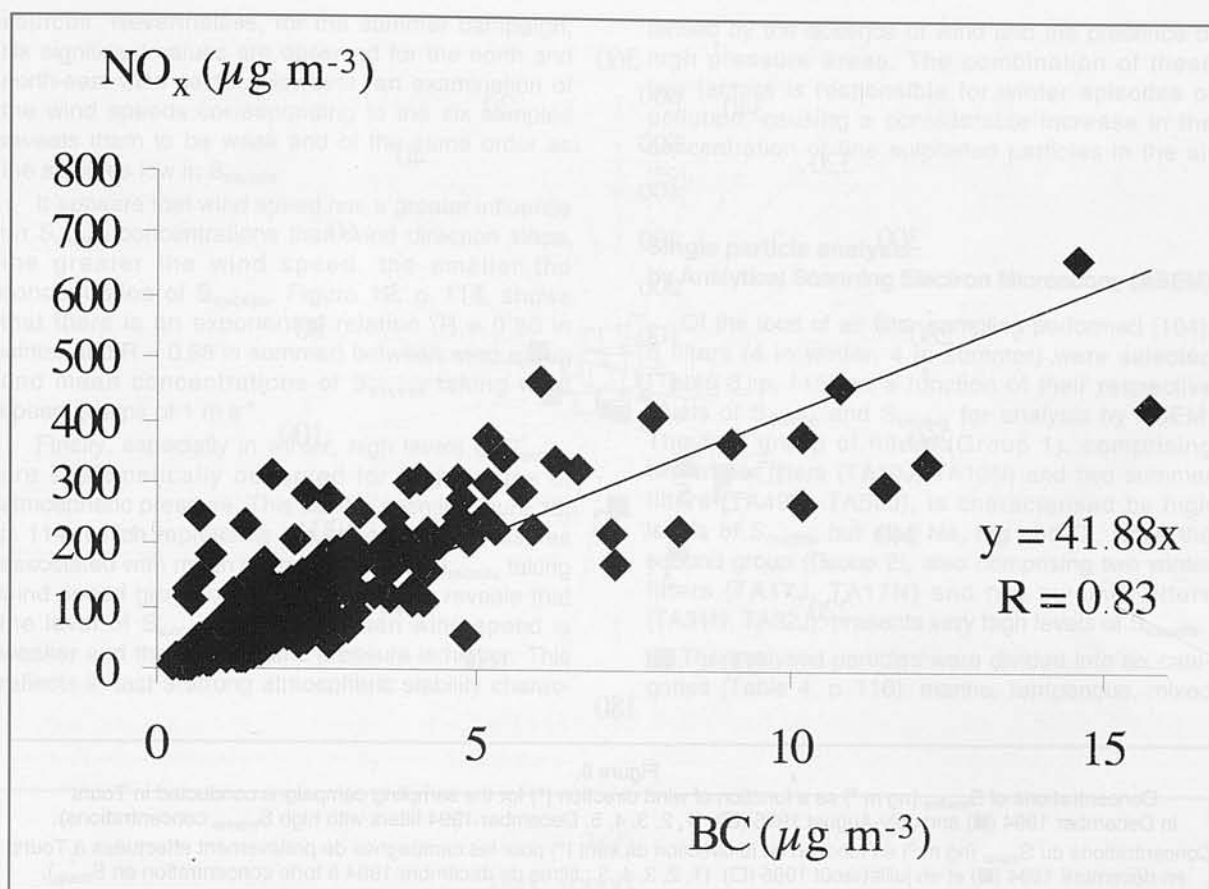


Figure 8.

Relation between hourly mean concentrations (ng m^{-3}) of NO_x
(Laboratoire Départemental de Touraine, LTD data) and BC measured in Tours in December 1994.

Relation entre les concentrations moyennes horaires (ng m^{-3}) de NO_x
(Données du Laboratoire Départemental de Touraine, LTD) et de BC mesurées à Tours en décembre 1994.

The results obtained in Tours indicate that the source "in excess" emits most of the S, regardless of the season (90% in winter and 98% in summer), although the contribution of the marine source is far from negligible, especially in winter (10%). The crustal source has only a very weak contribution (<1%). Thus, S is primarily produced by a gas-particle conversion (SO_2 -sulphate), which explains why its concentration is higher in summer than in winter. In fact, the conversion rate is much higher in summer [35], when the heterogeneous oxidation is favoured by significant photochemical activity [36], compared to winter, when oxidation takes place preferentially in a heterogeneous manner in the aqueous phase in the presence of carbonate particles [37, 38].

However, observing the daily variations of marine and "excess" contributions of S, it can be seen that the contribution "in excess" generally prevails over the marine component, although this tendency may be reversed, according to the case [27].

S_{marine}

Representing S_{marine} concentrations on a compass card (Figure 9, p. 112), it is clearly seen how, both in

winter and summer, the concentrations are great in the south-west quarter (direction between 180 and 270 °) rather than in the remainder of the windrose. The mean concentrations calculated for this wind sector are in the order of 326 ng m^{-3} in winter against 220 ng m^{-3} in summer, while they are six times weaker in the remaining sectors (56 ng m^{-3} in winter and 35 ng m^{-3} in summer). It is equally clear that the winds in the south-west sector have on average a higher speed (4 m s^{-1}) compared to those of the other sectors (3 m s^{-1}). Finally, the retro-trajectories of air masses, reported by way of example for five winter filters with high levels of S_{marine} (Figure 10, p. 112), indicate that the air masses arrive directly from the Atlantic Ocean where they are loaded with marine particles and that their course over the land is reduced, as well as their passage over high-industrialised regions.

S_{excess}

Concentrations of S_{excess} remain essentially the same, regardless of wind direction and season (Figure 11, p. 113), indicating that there are no contributions of S_{excess} from any particular wind sector and that there are no particular anthropogenic

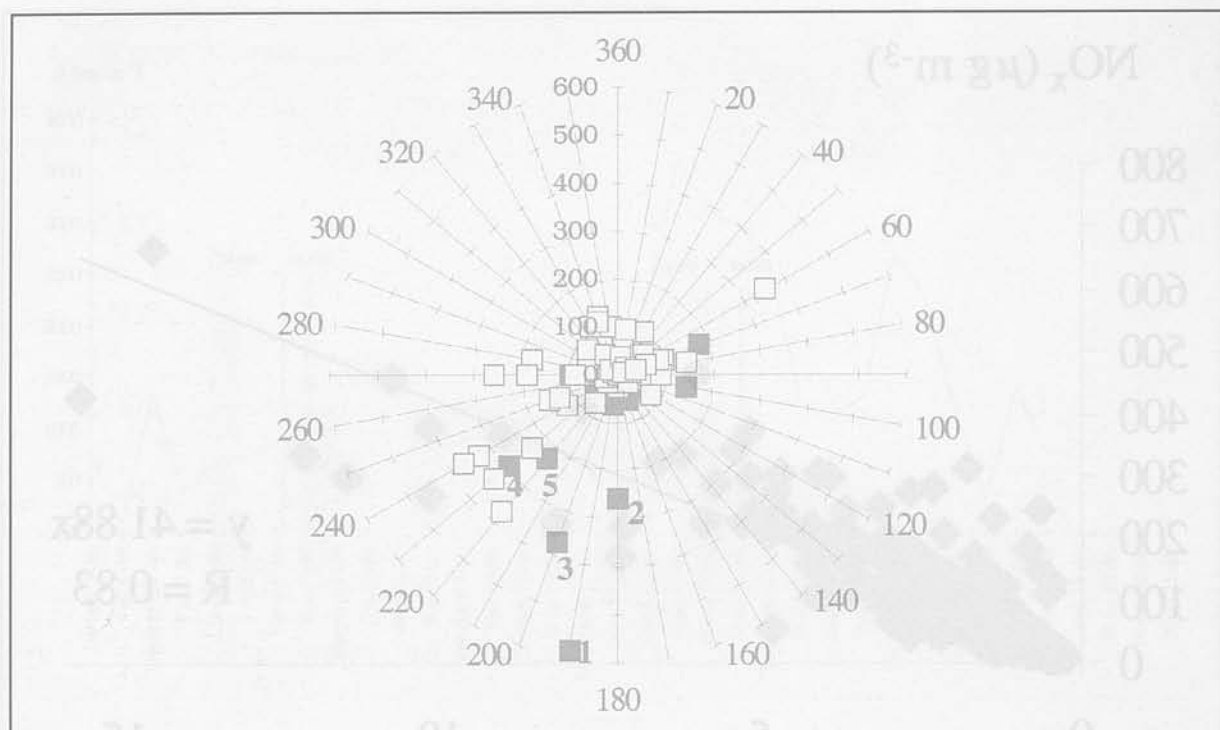


Figure 9.

Concentrations of S_{marine} (ng m^{-3}) as a function of wind direction ($^{\circ}$) for the sampling campaigns conducted in Tours in December 1994 (■) and July-August 1995 (□). (1, 2, 3, 4, 5: December 1994 filters with high S_{marine} concentrations).
 Concentrations du S_{marin} (ng m^{-3}) en fonction de la direction du vent ($^{\circ}$) pour les campagnes de prélèvement effectuées à Tours en décembre 1994 (■) et en juillet-août 1995 (□). (1, 2, 3, 4, 5 : filtres de décembre 1994 à forte concentration en S_{marin}).

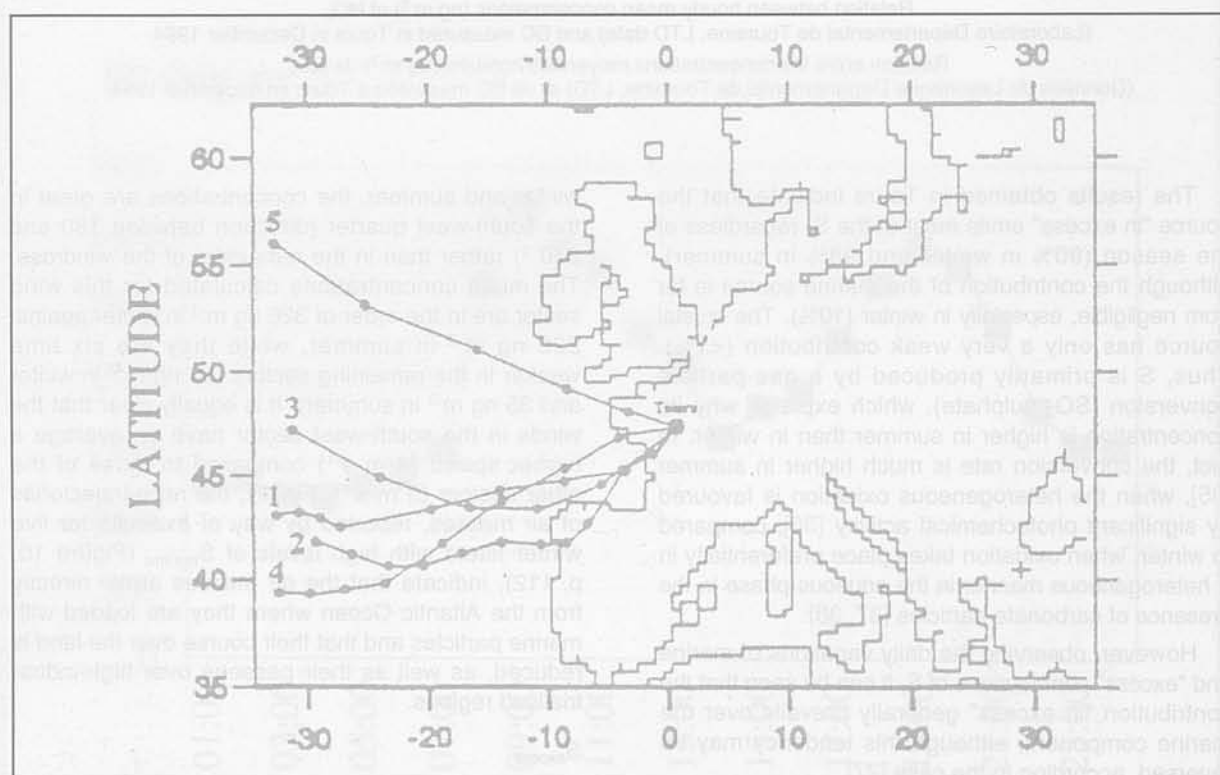


Figure 10.

Retro-trajectories of air masses (at 934 hPa) associated with the December 1994 filters (1, 2, 3, 4 and 5) presenting the highest S_{marine} concentrations sampled in Tours.

Rétrotrajectoires des masses d'air (à 934 hPa) associées aux filtres de décembre 1994 (1, 2, 3, 4 et 5) présentant les concentrations en S_{marin} les plus fortes relevées à Tours.

sources. Nevertheless, for the summer campaign, six significant values are observed for the north and north-east wind sector. However, an examination of the wind speeds corresponding to the six samples reveals them to be weak and of the same order as the samples low in S_{excess} .

It appears that wind speed has a greater influence on S_{excess} concentrations than wind direction since, the greater the wind speed, the smaller the concentration of S_{excess} . Figure 12, p. 114, shows that there is an exponential relation ($R = 0.80$ in winter and $R = 0.98$ in summer) between wind speed and mean concentrations of S_{excess} taking wind speed groups of 1 m s^{-1} .

Finally, especially in winter, high levels of S_{excess} are systematically observed for high values of atmospheric pressure. This can be seen in Figure 13, p. 114, which represents the atmospheric pressures associated with mean concentrations of S_{excess} taking wind speed group of 1 m s^{-1} . The figure reveals that the level of S_{excess} is higher, when wind speed is weaker and the atmospheric pressure is higher. This reflects in fact a strong atmospheric stability charac-

terised by the absence of wind and the presence of high pressure areas. The combination of these two factors is responsible for winter episodes of pollution, causing a considerable increase in the concentration of fine sulphated particles in the air [39].

Single particle analysis by Analytical Scanning Electron Microscopy (ASEM)

Of the total of air filter sampling performed (104), 8 filters (4 in winter, 4 in summer) were selected (Table 3, p. 115) as a function of their respective levels of S_{marine} and S_{excess} for analysis by ASEM. The first group of filters (Group 1), comprising two winter filters (TA10J, TA10N) and two summer filters (TA49N, TA50J), is characterised by high levels of S_{marine} but also Na, Mg and Cl, while the second group (Group 2), also comprising two winter filters (TA17J, TA17N) and two summer filters (TA31N, TA32J), presents very high levels of S_{excess} .

The analysed particles were divided into six categories (Table 4, p. 116): marine, terrigenous, mixed

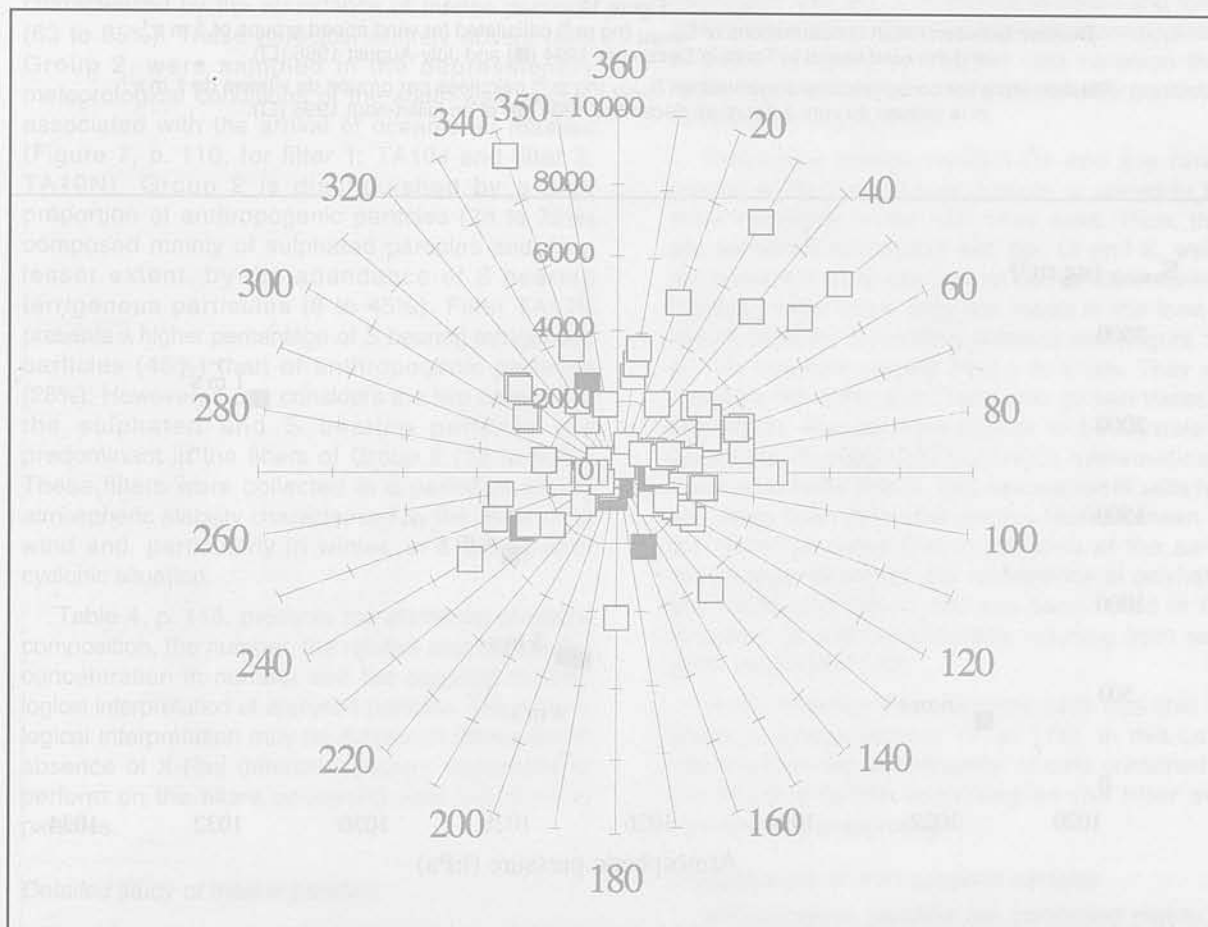


Figure 11.

Concentrations of S_{excess} (ng m^{-3}) as a function of wind direction ($^{\circ}$) for the sampling campaigns conducted in Tours in December 1994 (■) and July-August 1995 (□).

Concentrations du $S_{\text{excès}}$ (ng m^{-3}) en fonction de la direction du vent ($^{\circ}$) pour les campagnes de prélèvement effectuées à Tours en décembre 1994 (■) et en juillet-août 1995 (□).

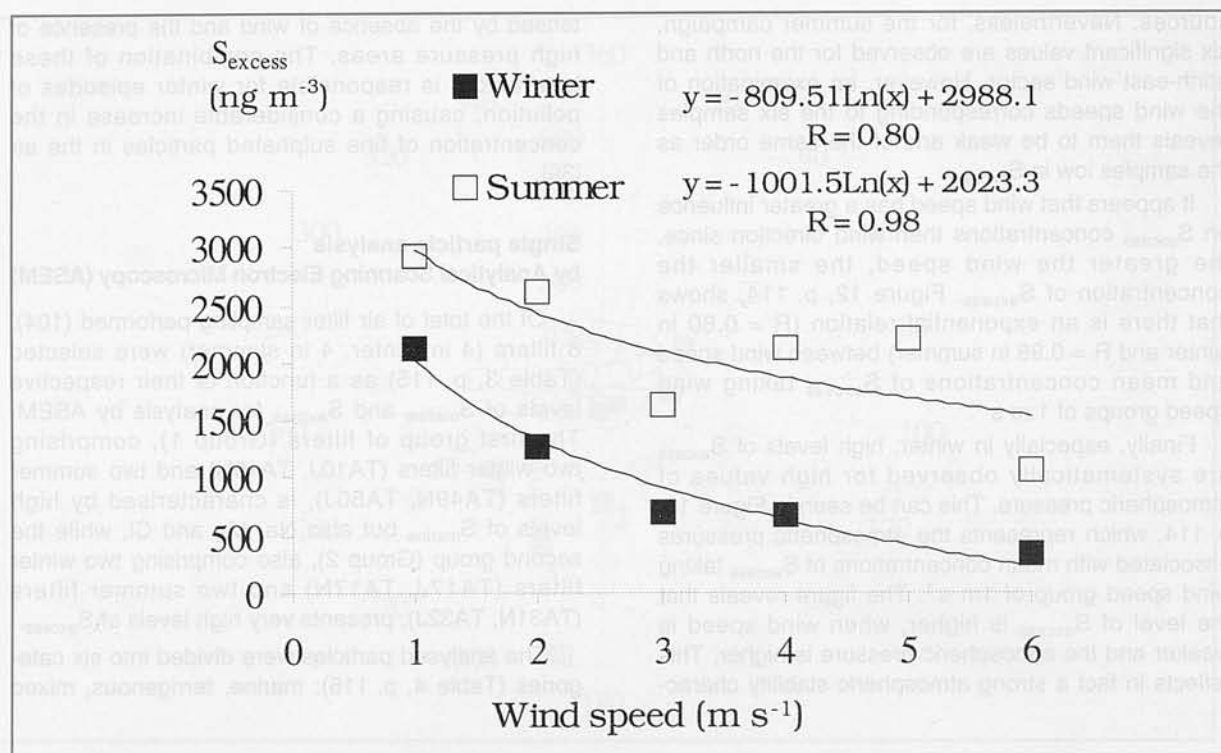


Figure 12.

Relation between mean concentrations of S_{excess} (ng m^{-3}) calculated for wind speed groups of 1 m s^{-1} and the wind speed in Tours in December 1994 (■) and July-August 1995 (□).

Relation entre les concentrations moyennes en $S_{\text{excès}}$ (ng m^{-3}) calculées par groupe de vitesse de 1 m s^{-1} et la vitesse du vent à Tours en décembre 1994 (■) et en juillet-août 1995 (□).

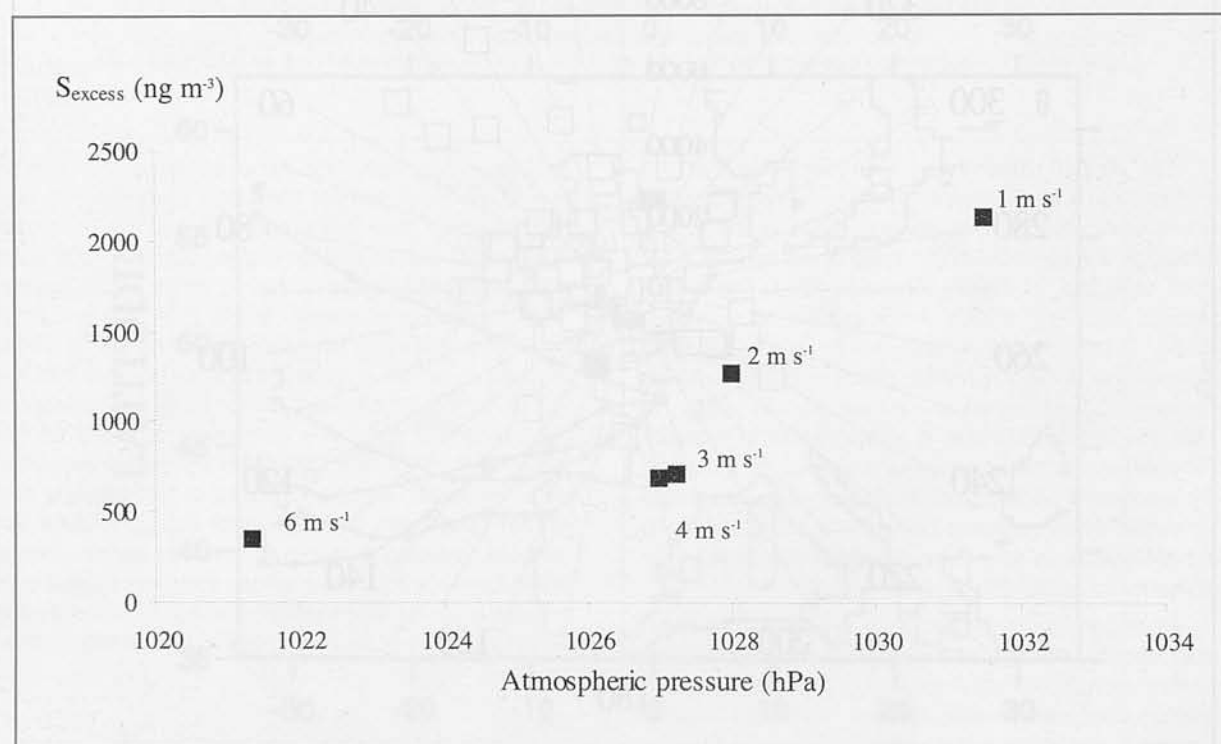


Figure 13.

Relation between S_{excess} concentration (ng m^{-3}) and atmospheric pressure (hPa) (reduced to sea level) in Tours in December 1994 (■) taking groups of wind speed 1 m s^{-1} .

Relation entre la concentration en $S_{\text{excès}}$ (ng m^{-3}) et la pression atmosphérique (hPa) (réduite au niveau de la mer) à Tours en décembre 1994 (■) par groupe de vitesse de 1 m s^{-1} .

Table 3.
Sampling conditions and concentrations of S_{marine} and S_{excess} of the eight filters selected for study by Analytical Scanning Electron microscopy (ASEM).
Conditions de prélèvement et concentrations en S_{marin} et $S_{\text{excès}}$ des huit filtres sélectionnés pour l'étude en microscopie électronique analytique en balayage (MEAB).

	Filters	Sampling Date	Wind direction (°)	Wind speed (m s ⁻¹)	Atmospheric pressure (hPa)	S_{marine} (ng m ⁻³)	S_{excess} (ng m ⁻³)
Group 1	TA10J	6/12/94	187	3	1022	585	325
	TA10N	6-7/12/94	183	6	1022	258	328
	TA49N	26-27/7/95	220	5	1017	372	550
	TA50J	27/7/95	242	6	1017	368	486
Group 2	TA17J	13/12/94	240	2	1031	35	3083
	TA17N	13-14/12/94	246	2	1028	32	2920
	TA31N	8-9/7/95	50	2	1015	63	8090
	TA32J	9/7/95	116	2	1015	21	2486

marine and terrigenous, S bearing terrigenous, anthropogenic, biogenic (+ undeterminate).

The relative proportion of these categories for each filter is reported in Figure 14, p. 117. Group 1 is characterised by the abundance of marine particles (63 to 85%). These particles, entirely absent from Group 2, were sampled in the depressionary meteorological conditions of the south-west sector, associated with the arrival of oceanic air masses (Figure 7, p. 110, for filter 1: TA10J and filter 2: TA10N). Group 2 is distinguished by a high proportion of anthropogenic particles (28 to 79%) composed mainly of sulphated particles and, to a lesser extent, by the abundance of S bearing terrigenous particles (8 to 45%). Filter TA17N presents a higher percentage of S bearing terrigenous particles (45%) than of anthropogenic particles (28%). However, if one considers the two categories, the sulphated and S bearing particles are predominant in the filters of Group 2 (72 to 90%). These filters were collected in a period of strong atmospheric stability characterised by the absence of wind and, particularly in winter, in a strong anti-cyclonic situation.

Table 4, p. 116, presents the elemental chemical composition, the number, the relative abundance, the concentration in number and the possible mineralogical interpretation of analysed particles. The mineralogical interpretation may be subject of discussion in absence of X-Ray diffraction pattern impossible to perform on the filters containing very low mass of particles.

Detailed study of marine particles

Marine particles are composed of equal proportions of chlorides and sulphates (Table 4).

Chlorides are invariably associated with Na and are present in the form of halite (NaCl) crystals which are frequently cubic (Figure 15, p. 118). The crystals

are sometimes associated with S and Ca and constitute a mixture of salts composed partly by halite and partly by gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) or anhydrite (CaSO_4). Sometimes the halite is associated with Mg, S, K and Ca in traces and forms a mixture which is difficult to interpret mineralogically. Another type of chlorides, far less common than halite, has also been identified as probably consisting of bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$).

Sulphates always contain Ca and are rarely present in the form of pure gypsum or anhydrite but more frequently mixed with other salts. Thus, they are sometime associated with Na, Cl and K, which are present in trace and cannot be identified mineralogically. More often, they are found in the form of oblong particles resembling grains of rice (Figure 16, p. 118) of length varying from 1 to 2 μm . They are therefore rich in Na and Cl and also contain traces of Mg and K. The particles appear to be crystals of polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) systematically mixed with halite (NaCl). This association of salts has also been observed in the eastern Mediterranean on the island of Delos [24] in particles of the same morphology. Moreover, the coexistence of polyhalite and halite is common and has been noted in the sequence of salt crystallisation resulting from seawater evaporation [40].

These chlorites and sulphates salts can also be found in groups (Figure 17, p. 119), in this case resulting from the crystallisation of salts contained in the liquid droplets impacting on the filter and subsequently evaporating [41].

Detailed study of anthropogenic particles

Anthropogenic particles are composed mainly of sulphated particles (Table 4) of diameter less than or equal to 1 μm . Such isolated particles can be either spherical or bean-like in shape (Figure 18, p. 119). The superposition of the chemical analysis spectra of the particle and that of the filter reveals the absence of

carbon and the presence of sulphur in the particle (Figure 18). The peak of C is due to the metallisation by carbon and to the polycarbonate filter membrane. Under ATEM, these particles turn out to be little opaque to the electrons and very instable under the electronic beam (Figure 19, p. 120). Very quickly, under the effect of the beam, bubbles appeared inside the particle, which is completely emptied of its

contents. Once it has totally vaporised, all that remains is an imprint whose shape is identical to that of the initial particle. Because of this particularity, it was not possible to identify their electron micro-diffraction pattern.

This type of micronic sulphated particles has already been observed and account for the greater part of the fine aerosol fraction of very many urban

Table 4.

Elemental chemical composition, number, relative abundance, number concentration and possible mineralogical interpretation of analysed particles by ASEM on eight filters sampled in Tours.

Composition chimique élémentaire, nombre, abondance relative, concentration en nombre et identification minéralogique possible des particules analysées par MEAB et recueillies par filtration de l'air à Tours sur huit filtres.

Elemental analysis	TA10J (247)	TA10N (70)	TA49N (60)	TA50J (95)	TA17J (250)	TA17N (60)	TA31N (92)	TA32J (71)	Possible mineralogical interpretation
	155 63%	58 83%	52 87%	62 65%					Marine particles
	32	58	52	24					Isolated salts
									CHLORIDES
Na Cl	27	56	21	9					Halite
Na Cl (Mg S K Ca)	4	1	8	7					Halite + (?)
Mg Cl (Na S K)			2						Bischofite and (?)
									SULPHATES
S Ca	1	1							Gypsum or anhydrite
S Ca Na Cl (Mg K)			21	8					Polyhalite + halite
	123			38					Salts in clusters
									CHLORIDES
Na Cl	40			6					Halite
Na Cl (S Ca)	3								Halite + (gypsum or anhydrite)
Na Cl (Mg S K Ca)	3								Halite + (?)
									SULPHATES
S Ca (Na Cl K)	1								Gypsum or anhydrite + (?)
S Ca Na Cl (Mg K)	76			32					Polyhalite + halite
	10 4%	2 3%		14 15%	18 7%	3 5%	5 5%	4 6%	Terrigenous particles
									SILICEOUS PARTICLES
Si	2		1	4	2			2	Silica
Si Ca (Mg Al K)	1		2						Silica and calcite + impurities
									CALCIUM PARTICLES
Ca	1	2	6	1			1		Calcite
Ca (Si Al)	2		3					1	Calcite + (?)
									ALUMINO-SILICATED PARTICLES
Si Al				1					Kaolinite
Si Al K (Fe)	2			5	1	1			Illite-muscovite-orthoclase
Si Al Mg K Ca (Ti)	1								Smectite
Si Al (Na Ca)	1		1	5			1		Plagioclase
Si Al Mg Fe			1	1				1	Chlorite
Si Al Mg K Fe (Ti)				1			2		Biotite
Na Cl S Ca Si Al	14 6%	1 1%	3 5%	7 7%					Mixtures marine-terrigenous particles
Si Al Ca S					47 19%	27 45%	7 8%	8 11%	S bearing terrigenous particles

(): total number of analysed particles, **majors**, minors and (traces) elements.

Table 4 (continued).

Elemental chemical composition, number, relative abundance, number concentration and possible mineralogical interpretation of analysed particles by ASEM on eight filters sampled in Tours.

Composition chimique élémentaire, nombre, abondance relative, concentration en nombre et identification minéralogique possible des particules analysées par MEAB et recueillies par filtration de l'air à Tours sur huit filtres.

Elemental analysis	TA10J (247)	TA10N (70)	TA49N (60)	TA50J (95)	TA17J (250)	TA17N (60)	TA31N (92)	TA32J (71)	Possible mineralogical interpretation
	48 19%	2 3%	4 7%	3 3%	132 53%	17 28%	59 64%	56 79%	Anthropogenic particles
C S					103	11	47	55	SULPHATED PARTICLES Ammonium sulphates
C	14			3	2	4	6	1	CARBONACEOUS PARTICLES Microsoot
C Cl (Na S)	27								Microsoot + marine salts
C S					20	2			Sulphated microsoot
Fe (Si S Cl Cu Zn Ba)	6		4		3		4		METALLIC DEBRIS Fe-rich debris
Cu Zn (S Cl)		2							?
Si Al K Ti Fe					2		1		SPHERICAL PARTICLES Smooth alumino-silicated fly ash
Fe (Al Si Ca S Ti)	1				2		1		Smooth hyper-ferriferous fly ash
C P S K (Cl)	9 4%				10 4%	3 5%	8 9%		Biogenic particles
	11 4%	7 10%	1 1%	9 10%	43 17%	10 17%	13 14%	3 4%	Undetermined particles

(): total number of analysed particles, **major**s, minors and (traces) elements.

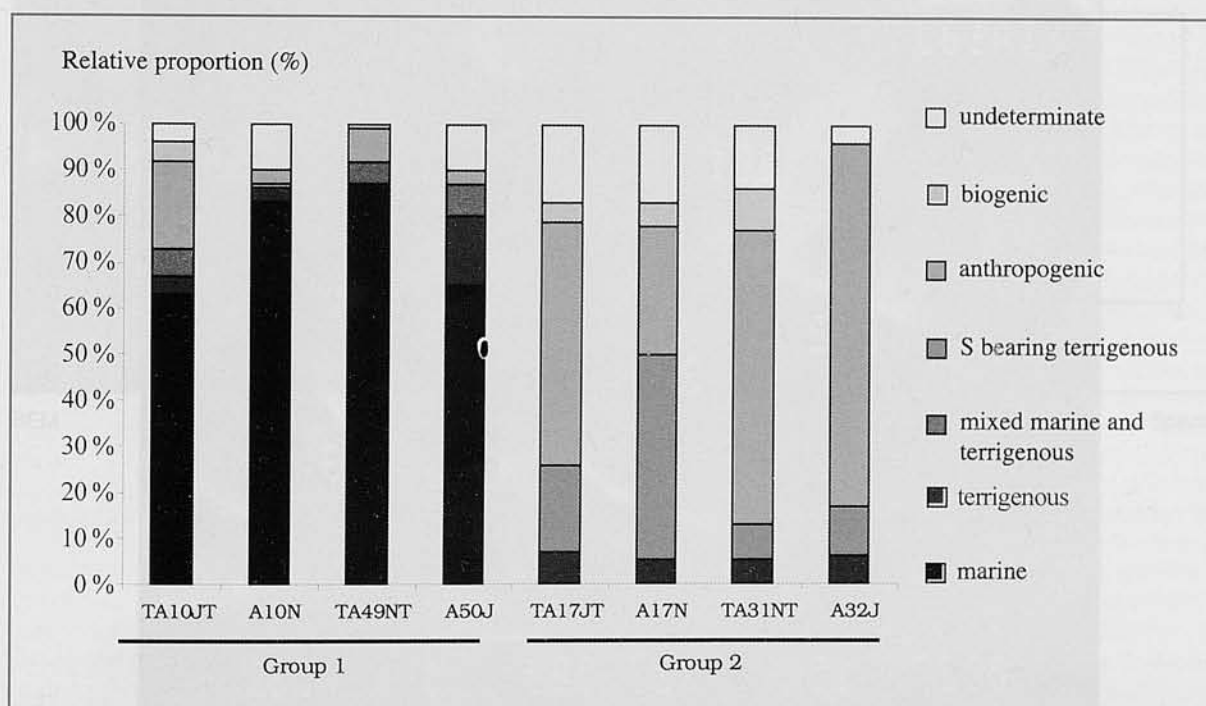


Figure 14.

Comparison of the proportion of particles according to category for the two groups of filters collected in Tours in December 1994 and July-August 1995 (Group 1: strong concentrations of S_{marine} ; Group 2: strong concentrations of S_{excess}).

Comparaison de la proportion de particules selon la catégorie sur les deux groupes de filtres prélevés à Tours en décembre 1994 et en juillet-août 1995 (Groupe 1 : fortes concentrations en S_{marin} ; Groupe 2 : fortes concentrations en $S_{\text{excès}}$).

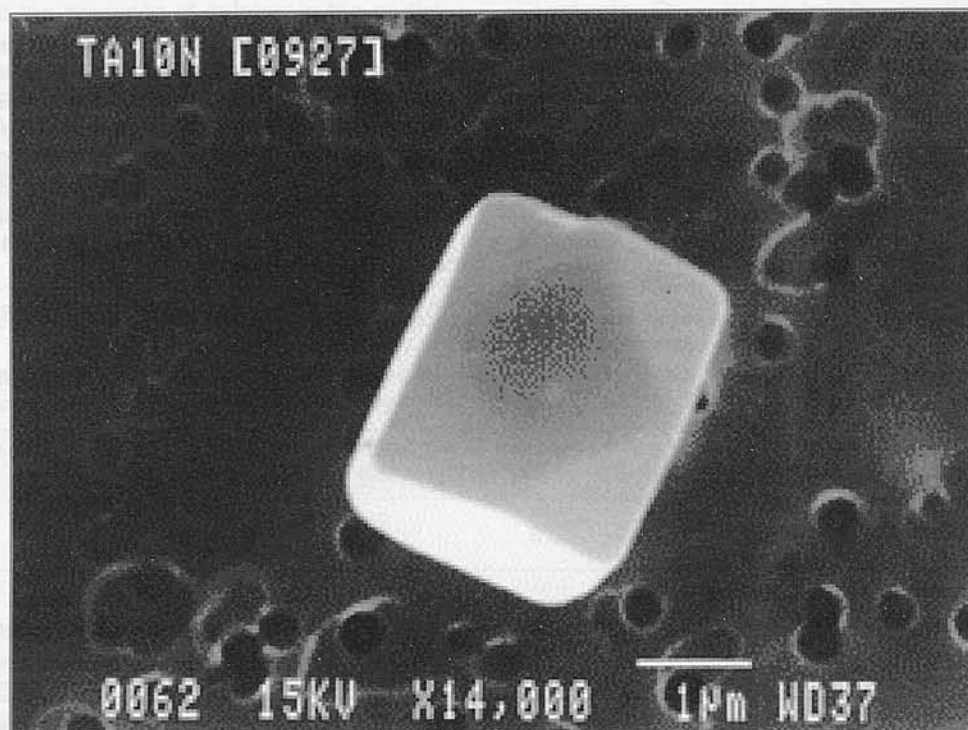


Figure 15.
Cubic halite crystal observed by ASEM.
Photo: M. Derbez (LISA).
Cristal de halite de forme cubique observé par MEAB.
Photo : M. Derbez (LISA).

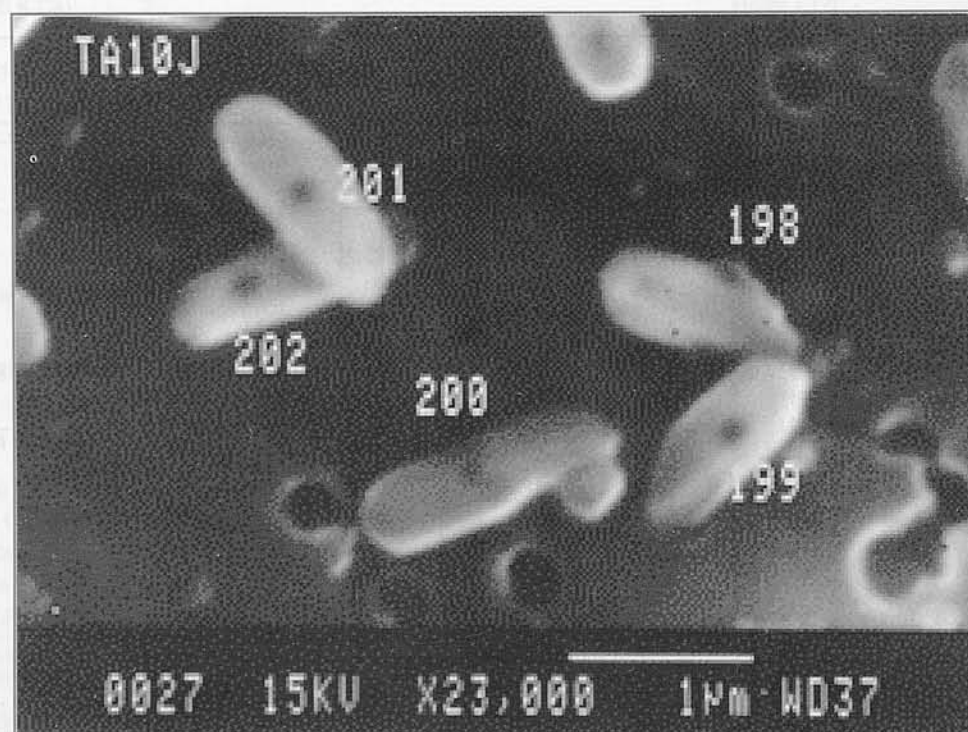


Figure 16.
Polyhalite crystal with rice-grain shape observed by ASEM.
Photo: M. Derbez (LISA).
Cristaux de polyhalite en forme de grains de riz observés par MEAB.
Photo : M. Derbez (LISA).

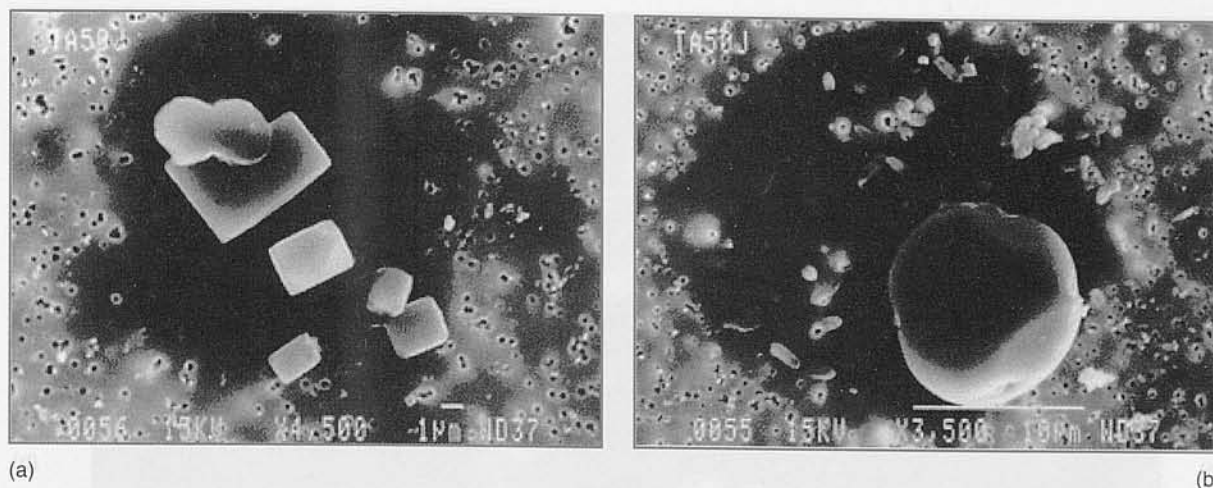
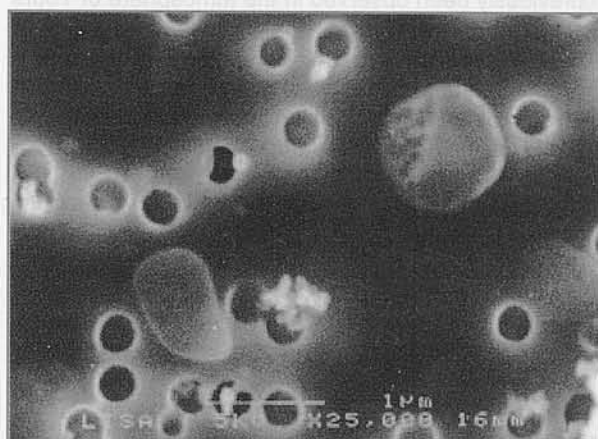


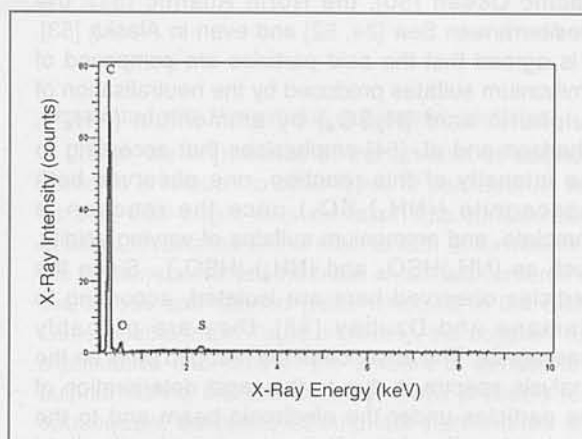
Figure 17.
Accumulation (a) of cubic halite crystals
and (b) of oblong polyhalite crystals juxtaposed to a rounded halite particle.

This accumulation results
from the evaporation of seawater droplets deposited on the filters.
Photo: M. Derbez (LISA).

Amas (a) de cristaux cubiques de halite
et (b) de cristaux oblongs de polyhalite juxtaposés à une particule arrondie de halite.
Ces amas sont issus de l'évaporation de gouttes d'eau de mer
déposées sur les filtres.
Photo : M. Derbez (LISA).



SEM



Spectre

Figure 18.

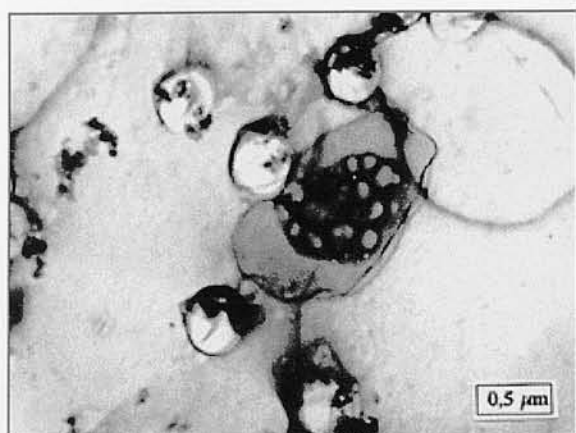
Micronic particles observed by field effect ASEM
and superposition of chemical analytical spectra
of the top right-hand particle (grey line) and of the filter
obtained using a light element detector (black line).
The analytical spectra indicate that the particle is sulphated
but does not contain carbon.

The carbon ray originates from the metallisation and filter.
Photo: M. Derbez (LISA).

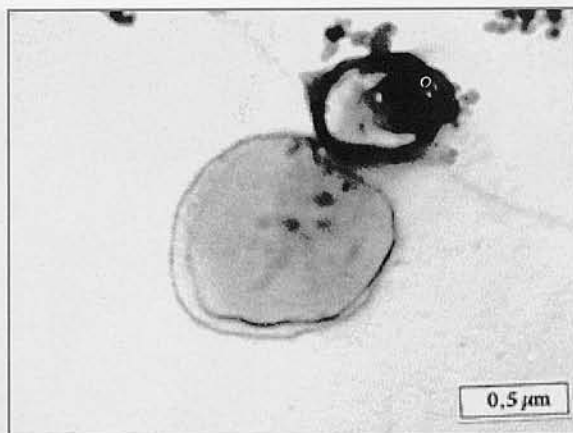
Particules microniques observées par MEB à effet de champ
et superposition des spectres d'analyse chimique
de la particule située en haut à droite (en gris) et du filtre
obtenus à l'aide d'un détecteur à éléments légers.

Les spectres d'analyse indiquent que la particule est soufrée
mais qu'elle ne contient pas de carbone.

La raie du carbone est issue de la métallisation et du filtre.
Photo : M. Derbez (LISA).



(a)



(b)

Figure 19.

(a) Micronic particle observed by ATEM sublimated under the electronic beam and (b) imprint left on the filter after vaporisation of its contents.

Photo : M. Derbez (LISA).

(a) Particule micronique observée par MEAT se sublimant sous le faisceau électronique et (b) empreinte laissée sur le filtre après vaporisation de son contenu.

Photo : M. Derbez (LISA).

sites, such as Antwerp [42], Arles [28], Brest [43], Khartoum [44], Philadelphia [45] and Phoenix [46], but also in rural sites, such as Arizona [47], Maryland [48] and in the vicinity of London [49]. They have also been observed by other authors on the Equatorial Pacific Ocean [50], the North Atlantic [51], the Mediterranean Sea [24, 52] and even in Alaska [53]. It is agreed that the said particles are composed of ammonium sulfates produced by the neutralisation of sulphuric acid (H_2SO_4) by ammonium (NH_4^+). Charlson and al. [54] emphasises that according to the intensity of this reaction, one observes both mascagnite ($(\text{NH}_4)_2\text{SO}_4$) once the reaction is complete, and ammonium sulfates of varying acidity, such as $(\text{NH}_4)\text{HSO}_4$ and $(\text{NH}_4)_3(\text{HSO}_4)_2$. Since the particles observed here are isolated, according to Mamane and Dzubay [48], they are probably mascagnite. The absence of the nitrogen peak on the analysis spectra is due to the rapid deterioration of the particles under the electronic beam and to the weak intensity of the X-rays emitted by the light elements [46, 50, 51]. No localised source of ammonium appears to exist in Tours, although according to Buijsman and al. [55], in Europe, 95% of anthropogenic emissions of ammoniac originate from agricultural activities, mainly animal excrements and, to a lesser extent, fertilizers.

The other categories of anthropogenic particles are, in order of decreasing abundance, carbonaceous particles, metallic residues and smooth microspherules.

Carbonaceous particles are encountered in groups or clusters composed of a large number of microspherules of diameter ranging from 0.02 to 0.05 μm and are stable under the electronic beam. These agglomerations of microspherules can reach a size of a dozen or so μm (Figure 20, ci-contre). Their

global chemical analysis indicates the presence of an important carbonate matrix associated at times with S, at times with Cl accompanied by traces of Na and S. Such particles are microsoot emitted by petrol-based fossil fuel combustion [56]. They have previously been observed in the atmosphere of Tours [13] and are responsible for the measured levels of BC. Microsoot are the privileged site for the heterogeneous oxidation of SO_2 and its conversion into sulphate [38]. Both terrigenous and biogenic particles may play the same role [57-60] and their amount proportion can assume great importance (filter TA17N).

Metallic residues are exclusively ferriferous and of any shape. They are probably emitted by metal-working industries [57], although no such source has been localised in Tours.

Spherical particles (mean diameter: 5 μm) always have a smooth surface, but their chemical composition may vary. Some are aluminosilicates and contain significant concentrations of K, Ti and Fe. Others are ferriferous (Figure 21, p. 122), sometimes presenting traces of Al, Si, Ca, S ou Ti. These two types of spherules have previously been observed in the air and rain of Tours [13, 14] and are fly-ash emitted by coal [45, 48, 61-64].

Conclusion

The study of the particulate content in the atmosphere of Tours was based on the data obtained during two air sampling campaigns (winter and summer) and required the use of aethalometry to measure the BC, X-Ray Fluorescence for the global chemical analysis of particles and ASEM/ATEM for the individual characterisation of particles.

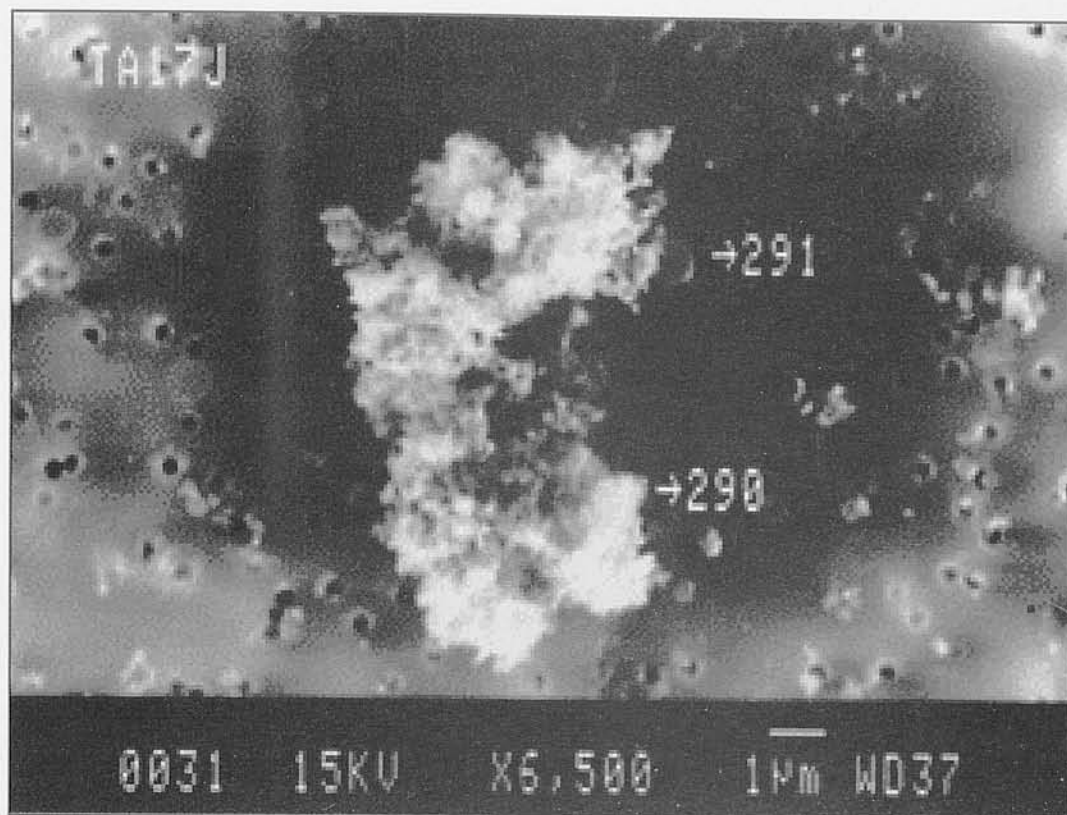


Figure 20.

Agglomeration of sulphated microsoot observed by ASEM.

Photo: M. Derbez (LISA).

Amas de microsuies carbonées et soufrées observé par MEAB.

Photo : M. Derbez (LISA).

From the results of the study it is possible to affirm that the city of Tours is influenced by two main sources of particle emissions: a marine source marked by the considerable concentrations of Na, Mg, Cl and S_{marine} and an anthropic source characterised by the high levels of S_{excess} and BC measured on the site. It follows that the particulate content of the atmosphere varies as a function of the contribution of one or the other of the said sources. It is equally clear how meteorological conditions play an important role: with a depression in the south-west sector, air masses that have stayed over the Atlantic Ocean arrive at Tours, causing an increase in the amount of marine particles in the air (halite or polyhalite crystals, either isolated or in agglomerates). Conversely, in the absence of wind, with strong atmospheric stability, in winter, and only in strongly anticyclonic conditions, the amount of anthropic particles increases. The latter are composed essentially of small isolated particles of ammonium sulphates (principally mascagnite), clusters of sulphated carbonaceous microsoot emitted by automobiles, which are responsible for the measured levels of BC, and finally, a few fly-ash. Sulphate is also

associated with terrigenous or biogenic particles.

Thus, the importance of the amount of sulphate particles in relation to other types of particles, as well as their dual origin, must be taken into consideration in order to determine the mechanism of formation of the gypsum cement of the black crusts encountered on the tuffeau and stained glass windows of the Saint-Gatien Cathedral in Tours. However, the constant and significative decrease of the amount of atmospheric sulphur during the last decades leads probably to a subsequent decrease of sulphate particulates and consequently to a decrease of the development of gypseous black crusts.

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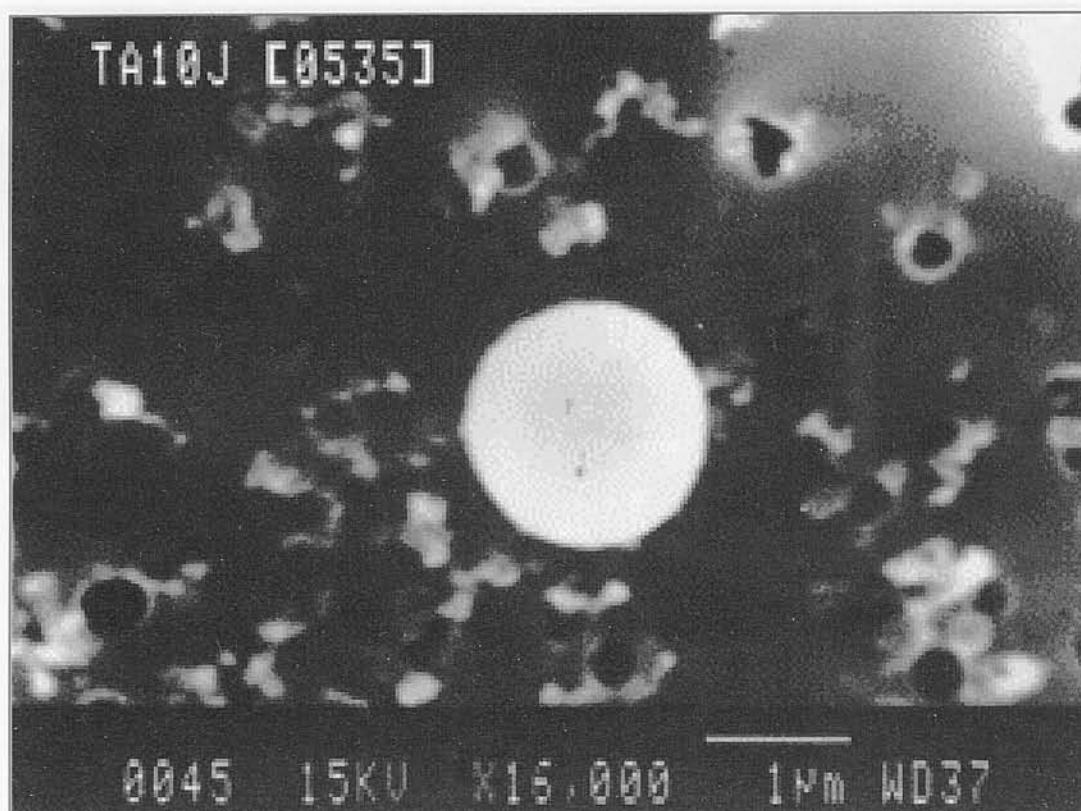


Figure 21.

Smooth hyper-ferriferous fly ash observed by ASEM.

Photo: M. Derbez (LISA).

Cendre volante lisse hyperferrifère observée par MEAB.

Photo : M. Derbez (LISA).

Keywords

Urban atmospheric particles. Ammonium sulphates. Polyhalite. Microsoot. X-ray fluorescence. Aethalometry. Analytical Scanning Electron Microscopy.

Mots clés

Particules atmosphériques urbaines. Sulfates d'ammonium. Polyhalite. Microsuie. Spectrométrie de fluorescence X. Aethalométrie. Microscopie électronique analytique en balayage.

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Introduction

Depuis 1984 et à la demande du ministre de la Santé, l'Institut Pasteur de Lille crée un réseau de quatre stations de prélèvement des métaux lourds sur l'agglomération lilloise. En 1988, un partenariat est créé avec l'ARENA Lille Métropole pour exploiter les dépouilles de pick-upement des métaux dans des stations fixes de réseaux automatisés de mesure. Cette surveillance est destinée pour le futur à

la mise en œuvre d'un réseau de suivi continu et de suivi de l'état de l'air à d'importantes études épidémiologiques [1].

En effet, le développement de réseaux automatisés de mesure de l'air est devenu un enjeu majeur à nos côtés, aux implications pour la santé publique et la recherche sur le cancer [2].

Pour répondre à ces enjeux, des réseaux automatisés de mesure de l'air sont créés, composés de stations de mesure de particules de diamètre aérodynamique $< 10 \mu\text{m}$, les plus fines d'origine humaine, capables de mesurer et de prévoir la concentration en particules (PM_{10}). Ces réseaux sont, en outre, un réseau de mesure de l'air ambiant.

* ARENA LM - Association pour le suivi de l'air de la région lilloise, de mesure et d'alerte sur contamination de l'air métropolitain.

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