

Characterization of Airborne Particles by Element Composition and Size Segregation

1. INTRODUCTION

For more than a decade our research group at the Physics Department in Göteborg has studied the element content of airborne particles in the ambient environment in Sweden (Öblad *et al.*, 1982 ; Larsson and Öblad, 1984 ; Öblad and Selin, 1986 ; Öblad and Selin, 1985). These studies have aimed at identifying element patterns or « fingerprints » from anthropogenic sources relatively close at hand (a few to some ten kilometres) or from large source areas hundreds of kilometres away. Thus at the regional scale element patterns from the incineration of refuse, car exhaust and oil combustion have been investigated (Larsson and Öblad, 1984 ; Öblad and Selin, 1985 ; Djupström *et al.*, 1989), whereas long distance transported (LDT) aerosols have been studied in a virtually unpolluted site close to the west coast of Sweden (Öblad and Selin, 1986). In the present paper we intend to emphasize the kind of information that is obtained by using a combination of dichotomous impactors for sampling the aerosol and a multielement analyzing technique for element analysis. We also intend to present some trends for the levels of particulate S, Zn and Pb in the background aerosols from 1981 to 1988.

2. SAMPLING WITH DICHOTOMOUS IMPACTORS

Atmospheric aerosol size distributions are often bimodal in mass (Whitby and Willeke, 1975) (Fig. 1). The two fractions have largely different origins and a different pH. The fine particles, usually smaller than a few microns in diameter, are acid and mostly of anthropogenic origin. They are created in combustion processes, for example, the coarse mode particles, between a few and twenty microns, have a substantial contribution of

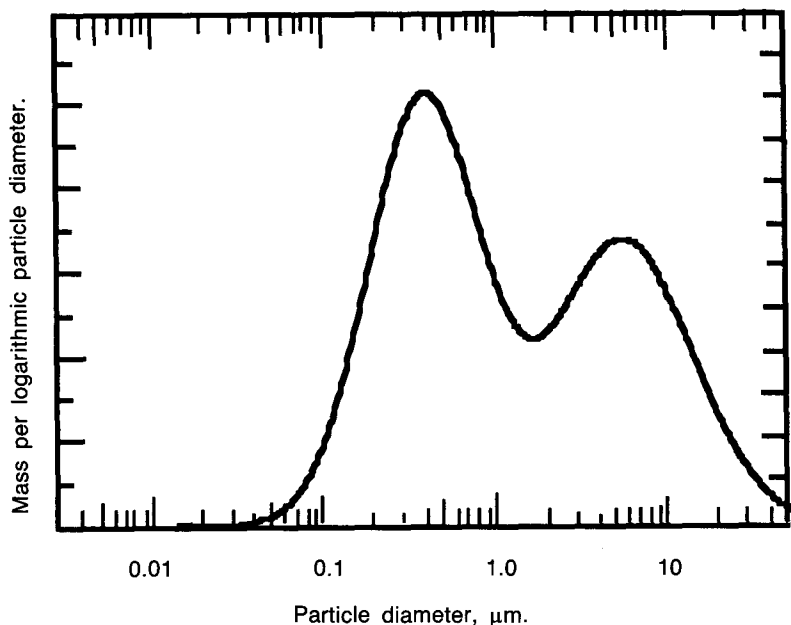


Fig. 1. The mass of the particles in an ambient aerosol often have a bimodal distribution when plotted as a function of the logarithm of the aerodynamic diameter. Elements which are typical of combustion processes, e.g. S, Pb and Zn are usually more abundant in the peak to the left, whereas naturally occurring elements, e.g. Ca and Cl are more abundant in the peak to the right.

natural particles which have been created as a result of mechanical processes, such as soil erosion and sea-spray. They usually have a higher pH than the fine particles. There is almost no mass transfer between the two size fractions (Whitby and Willeke, 1975) and hence relatively little mixing occurs between the two fractions during transportation and dispersion of the aerosol.

The instruments used for sampling in our studies are dichotomous virtual impactors (Sierra Instruments Model 244), which fractionate the particles into one fine particle mode (aerodynamic diameter < 3.5 microns) and one coarse particle mode (aerodynamic diameter between 3.5 and 18 microns). The flow rate at the inlet is $1 \text{ m}^3 \text{ h}^{-1}$.

The aerosol is collected onto two membrane teflon filters with a pore size of 2 microns (Membrana Inc), which have been shown to have a collection efficiency of 99.99 % (Liu *et al.*, 1981). The homogenous deposition of particles onto the filters, which is characteristic for the virtual impactor, is particularly well suited to multielement analysis by the X-ray Fluorescence (XRF) technique (Dzubay *et al.*, 1977).

3. ELEMENT ANALYSIS

The filters containing fine and coarse particles are analysed directly without any preparation in the Energy Dispersive X-ray Fluorescence spectrometer of the Physics Department in Göteborg. All elements heavier than phosphorous can be accurately quantified without any special arrangements (vacuum, He-atmosphere etc.). The filters are exposed to an almost monochromatic X-ray beam, which excites characteristic radiation from atoms in the sample. The resulting X-ray spectra are evaluated and the concentrations of the different elements calculated using a fundamental parameter program (Rindby, 1983). The combination of a dichotomous impactor and EDXRF analysis gives detection limits for the different elements, ranging from 0.1 to 5 ngm^{-3} for a sampling period of 24 hours.

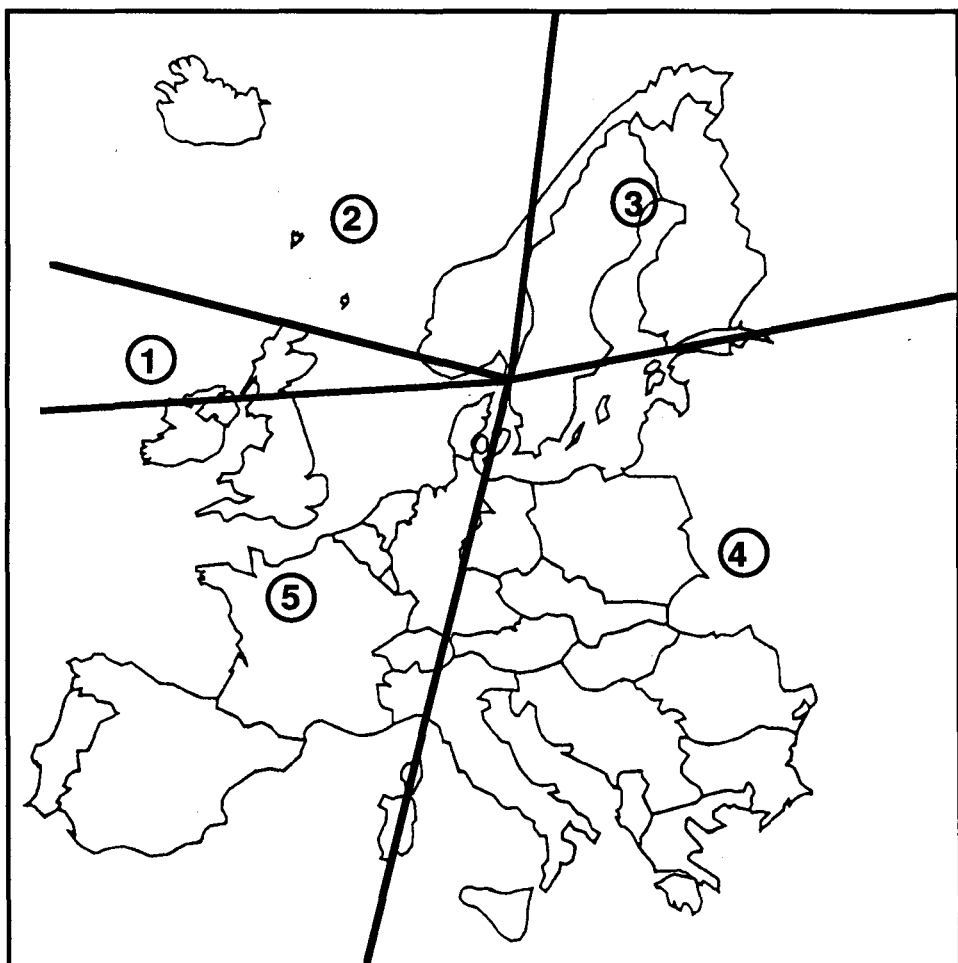


Fig. 2. Map showing the five sectors to which air mass trajectories are ascribed.

4. MEASUREMENTS OF BACKGROUND AEROSOLS

The measurement of background aerosols is of great importance for the study of transboundary pollution as well as for studies of the environmental impact of localized sources. In the latter case it is always necessary to know the background aerosol before the correct apportionments to individual sources can be made. Accordingly, in our measurements, we have always used one impactor at a background site, remote from strong local sources of pollution. The background site is located close to the sea some sixty kilometers from the city of Göteborg. The background aerosol is sampled on the fine and coarse particle filters for approximately 24 hours on a number of consecutive days during which the origin of the air masses

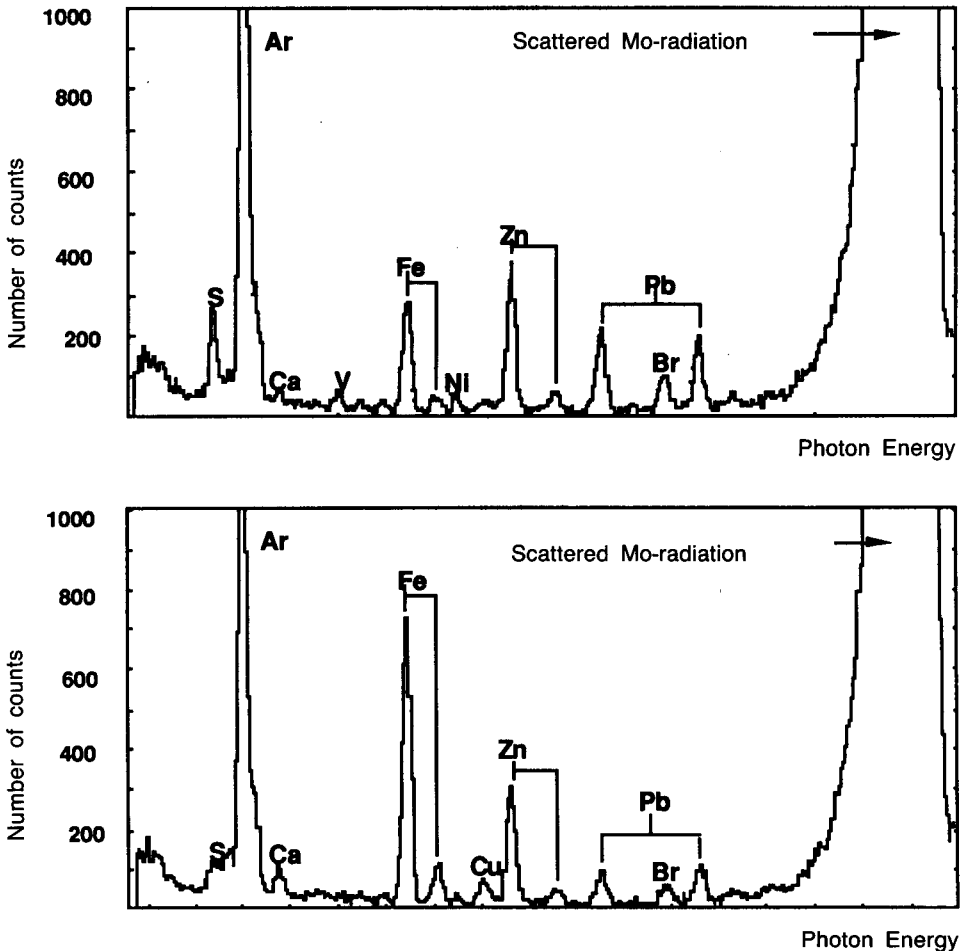


Fig. 3. X-ray spectra of the fine and coarse particles (upper and lower spectrum respectively) from a background aerosol. Note the differences in the concentrations of S, Zn and Pb, characteristic of human activity, and Fe and Ca which are mainly of natural origin.

changes. For each day meteorological data such as wind direction and velocity, precipitation, humidity and barometric pressure are registered. Air mass trajectories at 850 mbar for the measurement periods have kindly been supplied to us by the Norwegian Institute for Air Research (NILU), which obtains the data from the Meteorological Department of Oslo University. In order to facilitate the discussion of air mass history we have assigned each trajectory to one of five sectors as shown in Figure 2 (Lannefors *et al.*, 1983).

5. RESULTS

Median concentrations of S, Zn, Pb, V and Zn for six studies

Figure 3 shows a representative example of X-ray spectra from the fine and coarse particles collected from the background aerosol.

The general behaviour of the fine particle concentrations of Zn, Pb and S measured daily over a long period is illustrated in figure 4, in which the sector assigned to the air mass arriving at the measuring site (see Fig. 2) is also shown. The concentrations have a dramatic sector dependence. For lead the variation in concentration is seen to vary more than seventy times as the air mass history changes from sector five to the clean sector two. It is also interesting to note that the chlorine concentration in the coarse particles is at its highest during those periods when the anthropogenic element concentrations are very low. This typical behaviour shown in Figure 4 is

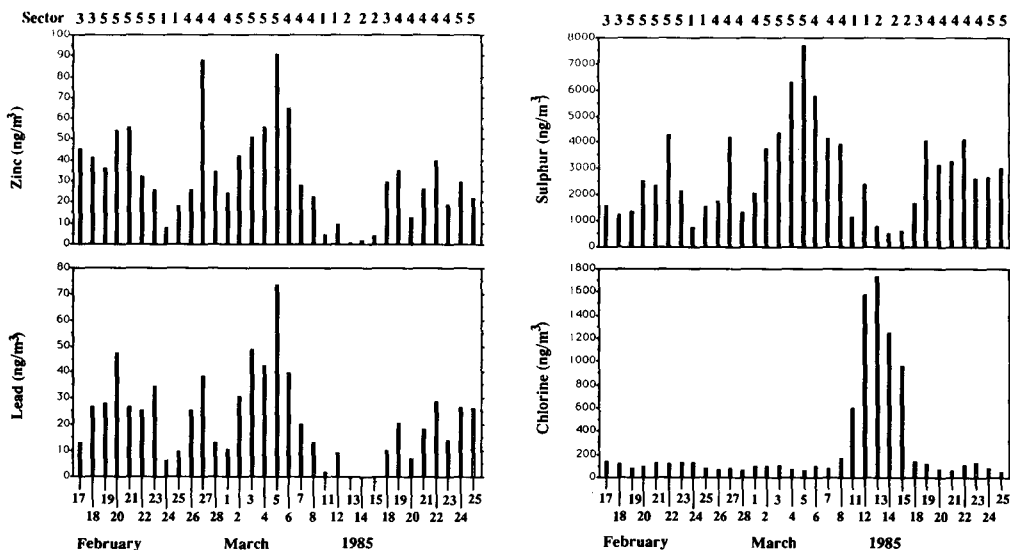


Fig. 4. Concentrations of Zn, Pb and S in fine particles and Cl in coarse particles as measured for 33 days in the winter of 1985. The sectors through which the air masses have been transported are noted in the upper part of the figure.

found in all our measurements. The great variation in element concentrations necessitates making field observations over long periods during which the air mass trajectories change. Table 1 shows the median concentrations for S, V, Ni, Zn and Pb as observed by us in six separate investigations over a number of years. The reason for choosing these elements is that V and Ni are considered to be typical of oil refineries and oil combustion (Djupström *et al.*, 1989), Pb is the most typical fingerprint for automobile exhaust and S and Zn are generally connected to many anthropogenic activities.

TABLE 1. — CONCENTRATIONS OF SOME IMPORTANT ANTHROPOGENIC ELEMENTS IN THE LDT-AEROSOL REACHING THE WEST COAST OF SWEDEN

Median values, in ng/m³

Year	Sulphur		Lead		Zinc		Vanadium		Nickel	
	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse
1981 summer	980	140	5.4	2.4	3.4	1.4	<1.2	<1.2	0.7	0.4
1983 summer	880	140	8.1	3.7	5.7	1.6	6.0	1.2	2.0	0.4
1984 summer	1195	310	2.8	<0.5	4.5	1.4	3.1	<1.2	1.2	<0.4
1984 winter	2800	300	22	1.1	37	4.8	13	<1.2	3.8	0.5
1985 winter	2820	270	21	0.5	30	3.2	7.5	<1.2	2.6	0.6
1988 winter	583	325	3.2	0.6	6.5	1.4	3.5	<1.2	0.7	<0.4

The concentrations in Table 1 indicate, as expected, that the situation is worse in the winter than in the summer. The winter measurements of 1988, however, which include measurements for 18 consecutive days, show very low levels in the fine particle fraction. A closer look at the air mass history during the measurement period shows that there was a clear dominance of air masses passing through sector 2. The sampling period was, therefore not at all typical for the winter but rather exceptional. Instead, the median values from the winters of 1984 and 1985 agree very well. For those measurement periods the air mass history showed a larger variation as illustrated by the sector assignments of Figure 4.

Ratios between coarse and fine particles as indicators for LDT-transport

As seen from the previous sections it is possible to measure the concentrations of different elements in LDT transported aerosols and assign the transport to the measuring site to different air mass trajectories or

Sector 3 3 5 5 5 5 5 1 1 4 4 4 4 5 5 5 5 4 4 4 1 1 2 2 2 3 4 4 4 4 5 5

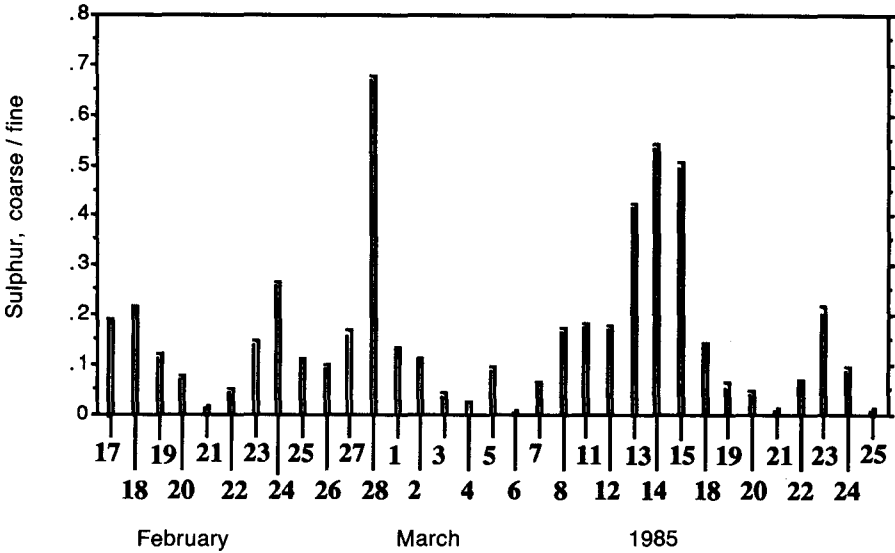


Fig. 5. The ratios between coarse and fine particle concentrations of sulphur vary considerably during a measurement period. Note the relatively low fraction of coarse particles for transport from sector five and the high fraction from sector two.

sectors. This provides knowledge about the *direction* from which the pollutants have come but not about the *distance* from the emitting sources or source regions. For the actual measurement site, situated on the west coast of Sweden, very close to the sea, the identification of pollutants from the western and southwestern parts of Europe is relatively straightforward, since there are no large emitting sources of fine particulate lead, zinc etc. out at sea. Pollutants arriving from the south or southeast are more difficult to assign to a certain country or source region due to the fact that the air masses pass over many sources on their way to the measurement site. It is well known, however, that coarse particles have shorter residence times in the atmosphere than fine particles ; they sediment faster and have a much larger probability of being removed by rain and washout than the fine particles. Accordingly we expect the aerosol to contain a relatively larger fraction of fine particles if the emitting source is far away than if it is situated closer at hand. Figure 5 illustrates the large differences in the ratio between the coarse and fine particles for sulphur.

Changes in the Pb/Zn ratio

The measurements discussed in this paper were performed during the period 1981 to 1988. The main source of lead is automobil exhaust, and

during the period from 1981 to 1988 regulations aimed at lowering the lead concentration in petrol were implemented in many European countries. It is, therefore, of interest to study the changes in the relative contribution of lead to the anthropogenic aerosol during this period. As seen from Figure 4 the variations in Zn and Pb concentrations in the fine particles bear a close resemblance. Figure 6 shows a correlation diagram between fine particulate Pb and Zn for the same case as illustrated in Figure 4 (winter 1985). The correlation is high ($R = 0.86$) and gives a best fit with a Pb/Zn ratio of 0.64.

Table 2 presents the ratios of the median values of Pb and Zn together with the mean values and medians for the Pb and Zn concentrations. The mean values are given for comparison with the medians and are more suitable for use in calculations of e.g. amounts of deposition. On the other hand they are strongly influenced by unusual circumstances — e.g. very high values for a few days — which is why we consider the medians as more appropriate for describing the average concentrations in the atmosphere.

TABLE 2. — Pb/Zn RATIOS, TOGETHER WITH MEAN AND MEDIAN VALUES FOR THE LEAD AND ZINC CONCENTRATIONS IN FINE PARTICLES DURING SIX STUDIES 1981 TO 1988

Year	Zinc (ng/m ³)		Lead (ng/m ³)		(Pb/Zn) Medians
	Mean (std error)	Median	Mean (std error)	Median	
1981 summer	6.0 ± 1.2	3.4	8.7 ± 1.8	5.4	1.59
1983 summer	11.0 ± 5.6	5.7	14.1 ± 4.0	8.1	1.42
1984 summer	4.9 ± 0.9	4.5	3.6 ± 1.1	2.8	0.63
1984 winter	38.1 ± 4.5	37	21.4 ± 2.2	22	0.59
1985 winter	32.6 ± 3.9	30	22.2 ± 2.9	21	0.70
1988 winter	9.5 ± 2.2	6.5	6.1 ± 2.0	3.2	0.50

It is evident from Table 2 that a big change in the Pb/Zn ratio occurred between -81 and -88. In principle the change could be due either to decreased amounts of lead or to increased amounts of zinc. Since there are no obvious reasons why the zinc levels should have increased by a factor of two during this period we conclude that the change in the Pb/Zn ratio

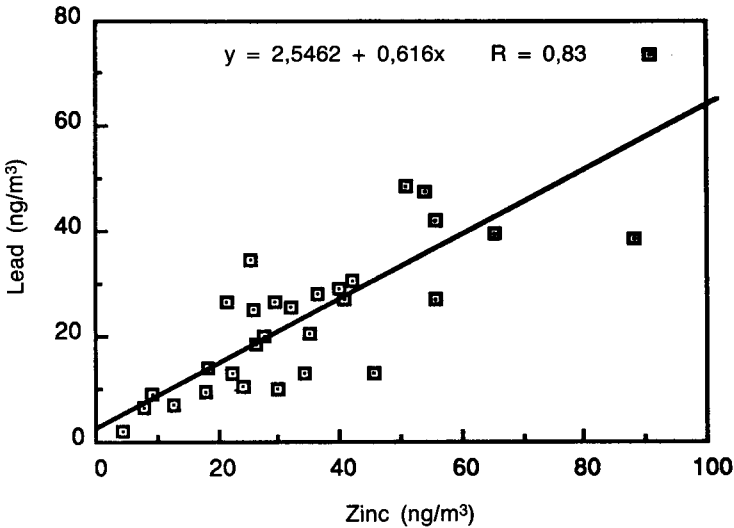


Fig. 6. Correlation between Pb and Zn in the fine particles of the background aerosol arriving at the west coast of Sweden in winter-85.

is due mainly to the increased use of unleaded or lowleaded petrol. As pointed out before, there are large variations in the concentration of the two elements during any normal measurement period, and one would have to make long term studies to measure « true » medians for a whole year. However, the correlations between the Pb and Zn concentrations are high and do not take the absolute values into account. If more data were collected and the assignments of air masses to different regions were taken properly into account one could find a typical Pb/Zn ratio or « fingerprint » for each region or country. Changes in this ratio could then be followed over a number of years. In a similar manner one can study relative changes for any combination of anthropogenic or « natural » elements.

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