

A Field Study of the Relationship between Deposition Rates and Particle Size

INTRODUCTION

Trace elements in airborne particulates are often used as indicators of sources of atmospheric pollutants. These sources can, in a crude manner, be divided into anthropogenic and natural sources. High temperature industrial processes and gas-to-partide transformation usually give rise to small particles with diameters of the order of a few micrometers or less, whereas the particles of natural origin, e.g. sea spray, sand, soil etc generally have a larger aerodynamic diameter. A typical anthropogenic source like car exhaust is characterized by the elements bromine and lead, often in a specific ratio (Öblad and Selin, 1985). For oil-fired plants and refineries sulphur, vanadium and nickel have served as indicators for a long time (Djupström *et al*, 1989). A natural source like sea spray is characterised by sodium and chlorine and soil by calcium, titanium, manganese and iron, although the latter elements are also involved in many high temperature, industrial processes. To sum up : The different elements in aerosol particles are characteristic for the origin of the particles and are thus connected with a certain average particle size (Davidson and Wu, 1989). The deposition of airborne particles plays an important role in the acidification of soils and waters and is the most important mechanism for polluting distant clean areas. The aim of the present work was to study the dry and wet deposition as well as the concentration of aerosol particles in two size intervals. The idea of the study was to use the trace elements in the particles as indicators of particle size.

EXPERIMENTAL DETAILS

Time and place of measurement

The samplers for measuring particle concentration and dry and wet deposition were placed in the central part of the city of Göteborg about 20 metres above street level. The measurements took place on seventeen

successive days in November-December 1990. Because of the low concentrations of some trace elements on the dry deposition filters (see below) sampling was made for two to five days in succession. The total sampling time was thus divided into six periods. During each period the dry and wet deposition instrument was run in parallel with the instrument used for measuring the concentration of fine and coarse particles as described below.

Dry and wet deposition

Dry deposition of atmospheric particles occurs by several physical processes of which the most important are sedimentation, impaction, interception and diffusion. The particle size has a great influence on the importance of the respective processes. As an example, it can be mentioned that the theoretical ratio between deposition from diffusion and sedimentation is of the order of 400 for a $0.01\ \mu\text{m}$ particle but only $5 \cdot 10^{-5}$ for a particle of $10\ \mu\text{m}$ (Hinds, 1982). The particle size also has a great influence on the residence time in the atmosphere. The larger particles have relatively short residence times in the troposphere and are expected to be deposited in the vicinity of the source, whereas the small particles with long residence times will be likely to travel considerable distances.

Wet deposition is another important pathway for removing particles from the air. Small particles often act as condensation nuclei to stimulate the condensation of water in a supersaturated atmosphere. If the particles contain water soluble salts their ability to nucleate is enhanced. For many reasons it is expected that large particles are more efficiently scavenged than small ones.

In the present experiment the dry and wet deposition was measured by using an Andersen acid precipitation sampler. In this instrument the fractions of dry and wet deposition are collected in different vessels (buckets). A sensor reacts to the presence of rain in the air and protects one of the collection vessels with a special lid; if the weather is dry the wet deposition vessel is protected and the dry deposition vessel is exposed to precipitation. If the weather is wet the procedure is the opposite, e.g. the protective lid is placed above the dry deposition vessel and the wet precipitation is collected. In the present experiment filters of the same kind as used in the dichotomous sampler (see following) were placed in a horizontal position in the dry deposition vessel. The different elements in the dry deposition filters were later analysed by Energy Dispersive X-Ray Fluorescence (EDXRF) in the same manner as the filters of the dichotomous sampler (see following). This method gives good detection limits for elements heavier than aluminum. The volume of the wet deposition fraction was measured and the trace elements analysed with EDXRF as the analytical method.

Aerosol sampling

Aerosol sampling was made with a dichotomous impactor, which fractionates the particles into two size fractions: « fine » particles (aerodynamic diameter $< 3.5 \mu\text{m}$) and « coarse » particles ($3.5 \mu\text{m}$ aerodynamic diameter $< 18 \mu\text{m}$), respectively. The air flow through the impactor was 1 m^3 per hour. Usually the dichotomous impactor is used for measurement periods of a few weeks with a change of filters every 24 hours. In the present experiment the concentrations in the air of particles carrying specific trace elements were related to the amount of particles carrying the same trace elements deposited in the dry deposition vessel. By using these data the dry deposition velocity for the different particles could be calculated.

Thin teflon filters (Membrana Inc.) with a pore size of $2 \mu\text{m}$ were used for collecting particles in the dichotomous impactor as well as in the dry deposition vessel. These filters have been shown to have a collection efficiency of 99.99 % (Liu *et al.*, 1981) and are known to have very low concentrations of contaminating elements.

Element analysis

The element concentrations in the fine and coarse particle filters and in the filters in the deposition meter were measured with EDXRF spectrometry. The XRF-spectrometer at Chalmers University of Technology is described by Öblad *et al.* (1982). Detection limits for the different elements in teflon filters are given by Öblad and Selin (1986) and are in the order of ng per cm^2 . This corresponds to ng per m^3 air when daily collection by the dichotomous sampler has taken place.

RESULTS

Calculation of dry deposition velocity

The dry deposition velocity for airborne particles is defined as

$$v = F/C \quad (1)$$

where F is the mass of particles deposited per cm^2 per second and C is the mass-concentration of particles in the air. If the volume is measured in cubic centimeters v will be given in units of cm/s . Most measured data give dry deposition velocities of the order of $0.1\text{-}10 \text{ cm/s}$ for particles of the order of 0.5 to $10 \mu\text{m}$ mass median aerodynamic diameter (Davidson and Wu, 1989).

In the present experiment the mass concentrations of the different trace elements were measured from the dry deposition filter. The respective trace element concentration in the air was obtained by adding together the

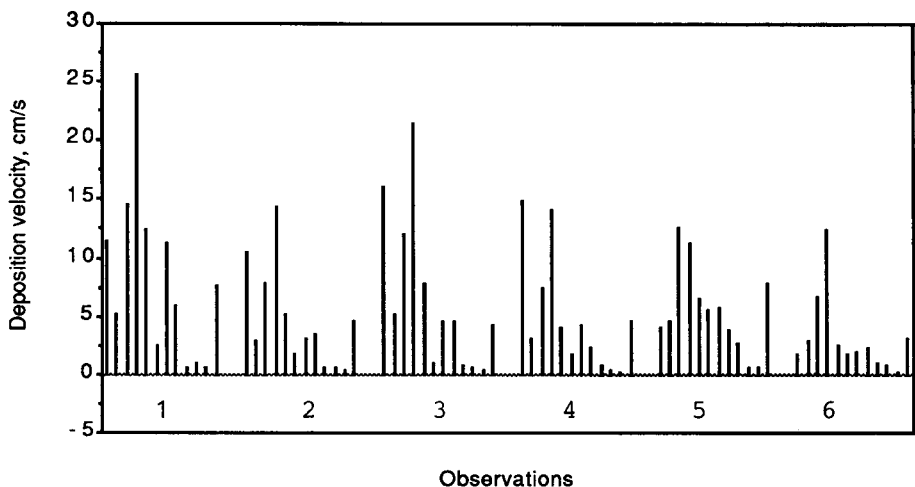


Fig. 1. Dry deposition velocities in cm/s for particles which contain in succession CL, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb and S are shown for each of the six measurement periods.

concentrations of the fine and coarse particle fractions. This procedure may introduce an error because only particles of aerodynamic diameter less than $18\ \mu\text{m}$ are taken into account in the concentration value (C), whereas no such limit is imposed for the particles deposited by dry deposition. The possible errors in the dry deposition rates which may be introduced by the $18\ \mu\text{m}$ cut-off will increase the dry deposition velocity relative the «true» value. This effect will be more likely to occur for the coarse particle elements whereas it is less likely to influence the fine particle deposition rates.

Measurements of dry deposition and coarse/fine particle ratios

The dry deposition velocities for particles characterized by twelve different elements are shown for each of the six measurement periods in Figure 1. During the first, third and fifth period wet deposition also occurred. Note, the similarity in the deposition patterns during the first four periods during which chlorine, titanium and chromium have very high deposition velocities whereas zinc, bromine and lead have low values. During the last two periods the pattern is somewhat different, mainly due to a relatively lower velocity of the chlorine containing particles.

To obtain a real appreciation of the dependence of deposition velocity on aerodynamic diameter a multi-stage impactor would have to be used. In the present experiment only a two stage impactor was used, which fractionated the particles into two size intervals, smaller than or larger than 3.5 microns. Figure 2 shows how the mass ratio between coarse and fine

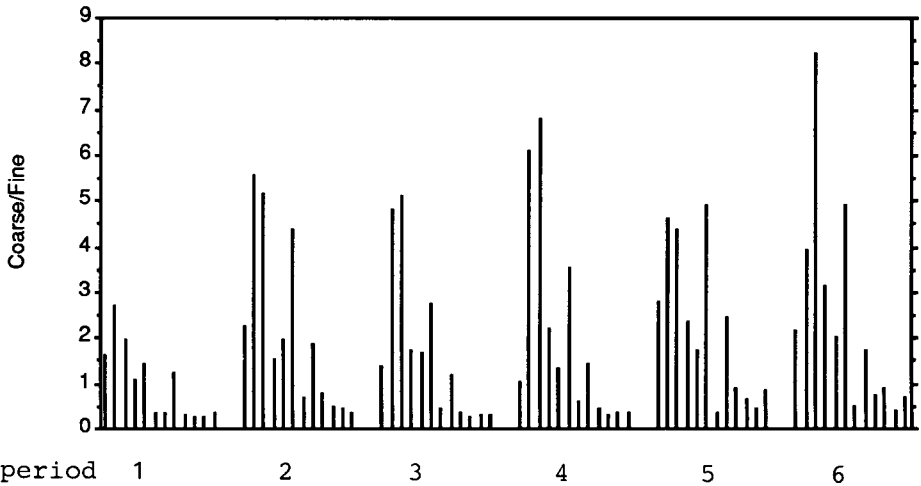


Fig. 2. The ratio between the coarse and fine particle concentrations of different elements for the six measurement periods given in the same order as in Figure 1, namely Cl, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, and S.

particles characterized by different elements varies during the six measurement periods. The same order between elements as given in Figure 1 is used in Figure 2. Note, that although the absolute values of the ratios differ the coarse/fine pattern is fairly similar during the six periods. Typical coarse particle elements are Ca, Ti and Fe. Typical fine particle elements are Zn, Br, Pb and S. By comparing Figs. 1 and 2 one can observe some characteristic features, namely that most of the elements with a high proportion of coarse particles — and thus a large average mass mean diameter — have high deposition velocities whereas the elements with a higher proportion of fine particles have lower dry deposition velocities. Interesting exceptions from the latter are nickel and sulphur. The latter is in the form of sulphate in the particles and has been formed by gas-to-particle conversion. Both nickel and sulphur are emitted by oil refineries and oil combustion. Table 1 shows the arithmetic means and standard deviations for the dry deposition velocities and the coarse/fine concentration ratios for particles characterized by the different elements.

In Table 1 the means and medians are calculated for the six measurement periods. The reason for giving the means as well as the medians and standard deviations is so that the reader can form an opinion of how much the values differ from each other from one period to the next. For lead and nickel for example the coarse/fine means and medians are very close and the agreement is also reflected in the small standard deviations. Since the meteorological conditions change from one period to the next

(three measuring periods had wet as well as dry deposition) the closeness in the values for lead and nickel means that the particle size for these elements is not very sensitive to the weather conditions.

TABLE 1. — COARSE/FINE PARTICLE RATIOS AND DRY DEPOSITION VELOCITIES FOR PARTICLES CHARACTERIZED BY TWELVE ELEMENTS

Element	Coarse/Fine ratio			Deposition velocity cm/s		
	mean	S.D.	median	mean	S.D.	median
Cl	1.87	0.65	1.89	9.73	5.75	10.9
Ca	4.62	1.20	4.72	3.96	1.13	3.80
Ti	5.27	2.15	5.14	10.2	3.25	9.94
Cr	2.01	0.72	1.96	16.5	5.65	14.2
Mn	1.69	0.28	1.70	6.35	3.52	5.77
Fe	3.47	1.74	3.96	2.36	1.61	1.75
Ni	0.47	0.13	0.46	5.09	3.29	4.31
Cu	1.65	0.49	1.57	3.70	1.40	3.65
Zn	0.59	0.25	0.59	1.03	0.77	0.71
Br	0.47	0.25	0.39	0.64	0.18	0.63
Pb	0.36	0.09	0.37	0.36	0.14	0.37
S	0.80	0.74	0.53	5.31	1.95	4.63

A close look at the correlation between the dry deposition velocities and the coarse/fine ratios for the different elements does not show any significant features apart from the general tendencies mentioned earlier. In fact, if all the individual values for the different particles and periods are plotted in a scatter diagram such as Figure 3, the correlation between particle size and deposition velocity that one might expect is completely obscured. Possible reasons for the lack of correlation in this general picture are the different chemistry of the different elements, the effects of meteorological parameters on some of the elements and, above all, the lack of knowledge of the size distribution of the different particles. It is obvious that the division into two size fractions is too crude, and that further segregation is necessary. If, on the other hand, the mean values of Table 1 for dry deposition velocities are plotted against the means of the coarse/fine ratio for only a few of the anthropogenic elements e.g. Pb, Br, Zn and Cu there is a close correlation ($r^2 = 0.999$). This indicates that the elements should be studied in groups with regard to their origin and also, perhaps, their chemistry.

Measurements of wet deposition

The trace element content in the wet deposition was measured as mentioned above. In total 20 mm rain was collected during the three measurement periods when precipitation occurred. By adding internal stan-

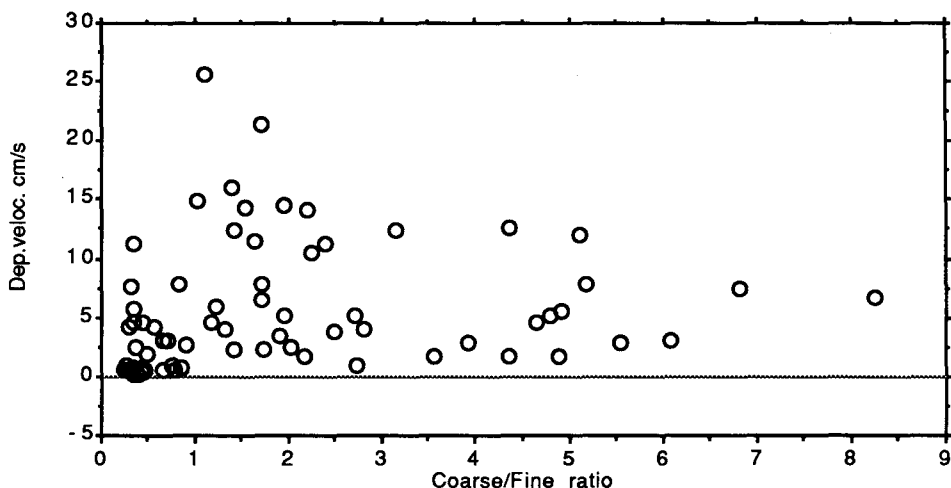


Fig. 3. Deposition velocity versus the ratio between coarse and fine particle concentrations as defined in the text for all the individual measurements.

dards to the rain water the concentration of the different trace elements was calculated. Table 2 presents the amounts of dry and wet deposition for the different elements during the seventeen days that the measurements took place.

TABLE 2. — DRY, WET AND TOTAL DEPOSITION OF ELEMENTS ($\mu\text{g}/\text{cm}^2$) in airborne particles during 17 days in the city-centre of Göteborg

Element	Dry deposition	Wet deposition	Total amount*
Cl	6.23	6.05	12.3
Ca	0.91	2.13	3.04
Ti	0.25	0.42	< 0.66
Cr	0.06	0.04	< 0.10
Mn	0.05	0.02	< 0.07
Fe	0.71	0.08	0.79
Ni	0.01	0.03	< 0.03
Cu	0.03	0.04	0.06
Zn	0.03	0.14	0.17
Br	0.01	0.01	< 0.02
Pb	0.01	0.10	0.11
S	4.39	13.6	18.0

* For the total amount the correct values with three decimals have been added. If the value of either dry or wet deposition is close to the detection limit the sign < has been used.

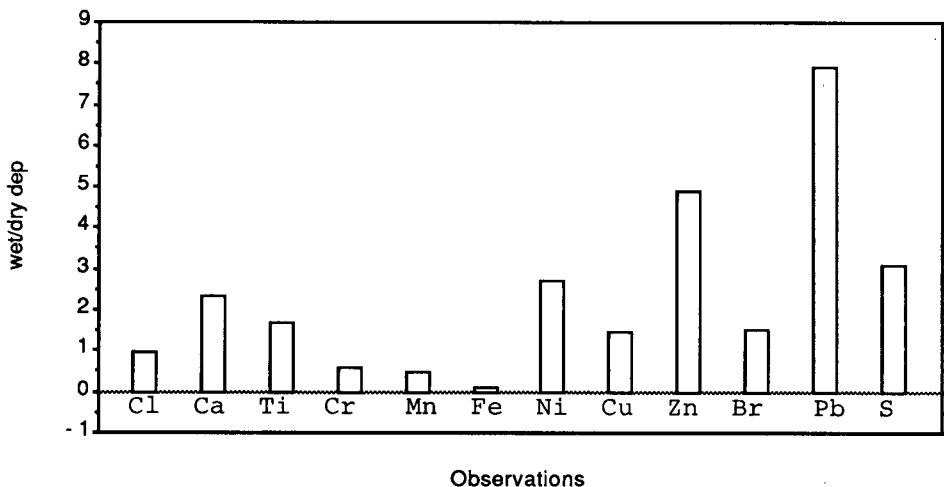


Fig. 4. The ratio between wet and dry deposition of particles characterised by the elements in succession Cl, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, and S for the whole measurement period.

From Table 2 it is evident that S, Cl, Ca and Fe dominate the deposition. The deposition of sulphur alone corresponds to about twice the amount given as average for the whole year for this part of Sweden. This is reasonable since the emissions of sulphur in a city during winter are expected to exceed the average value. It is also interesting to note the difference in the ratio between wet and dry deposition for particles characterized by the different elements as shown in Figure 4.

Wet deposition or precipitation scavenging is generally considered to be greater for large particles than for fine ones due to the deposition mechanisms of impaction, condensation and kinematic coagulation. It is, therefore, interesting to observe that on the contrary it is the fine particle elements: Zn, Pb and S which have the largest wet/dry deposition ratios. A similar observation was also made by Schumann (1989) who found that particles with radii less than one micron were ten to one hundred times more efficiently removed than was predicted by theory.

DISCUSSION

It is highly relevant to ask whether the data quoted above are consistent with previously reported values. To elucidate this point we have compared our data with the report of Davidson and Wu (1989). This comparison is shown in Table 3 for the elements common to the present work and that of Davidson and Wu.

TABLE 3. — DRY DEPOSITION VELOCITIES, v , FOR PARTICLES CHARACTERIZED BY NINE ELEMENTS ACCORDING TO THE PRESENT WORK AND THAT OF DAVIDSON AND WU (1989). N=NUMBER OF MEASUREMENTS

Element	v in cm/s (present work)			v in cm/s (ref work)		N
	mean	S.D.	median	mean	range	
Ca	3.96	1.13	3.80	2.60	0.23-7	14
Ti	10.2	3.25	9.94	3.05	0.5-5.6	2
Cr	16.5	5.65	14.2	1.2	1.0-1.5	2
Mn	6.35	3.52	5.77	1.21	0.27-6.4	13
Fe	2.36	1.61	1.75	2.08	0.5-7.5	13
Ni	5.09	3.29	4.31	1.0		1
Cu	3.70	1.40	3.65	0.81	0.08-1.6	8
Zn	1.03	0.77	0.71	0.34	0.05-0.66	9
Pb	0.36	0.14	0.37	0.32	0.005-1.3	22

The deposition velocities measured in the present work are generally larger than the reference values. This is not surprising in view of the fact that the present measurements were made in the city-centre of Göteborg where the presence of large particles emitted by sources in the city is significant. The relatively large aerodynamic diameter for many of the particles is illustrated in the ratios between the coarse and fine particle concentrations as discussed earlier. Many of the reference values have been obtained in rural areas and are thus not strictly relevant to the present situation. As seen from Table 3 the range of measured dry deposition velocities for particles characterized by the different elements in the previous measurements is rather wide, at least of the order of one magnitude. The number of measurements (N) is often quite small, which adds a further uncertainty to the values quoted. Nevertheless the comparison supports the statement made earlier that the method used in the present experiment for the determination of deposition velocities is useful but will have to be complemented with measurements of aerodynamic diameters for the particles.

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