

EDXRF and TXRF analysis of elemental size distributions and environmental mobility of airborne particles in the city of Riga, Latvia[†]

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Airborne particles were investigated in the central part of Riga during October 2000. Mass, black carbon and elemental concentrations of airborne particles were measured on Teflon filters from a dichotomous impactor, which samples fine (<2.5 µm) and coarse (2.5–10 µm) fractions of particles. In order to obtain more detailed information on the size distributions of different elements, a seven-stage Batelle cascade impactor was used, in which quartz plates treated with silicone grease were utilized as backing for the different stages. Total reflection x-ray fluorescence (TXRF) and energy-dispersive x-ray fluorescence (EDXRF) spectrometry were used for elemental analysis on the quartz plates and Teflon filters. The environmentally mobile part of the fine particle elements in the aerosol was determined by subtraction of x-ray spectra measured before and after sequential leaching of the aerosol filters. The results of the different measurements show that naturally generated street dust and soil particles are dominant in coarse particles, whereas particles generated by human activities are dominant in the size fraction <0.5 µm. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

Increasing attention is being paid to particulate matter with aerodynamic diameters of ≤ 10 µm owing to their hostile effects on human health.¹ Legislation in the USA and Western Europe puts recommended limits on concentrations of inhalable particles.² Since the 1980s, the concept of PM₁₀ (particulate matter with diameters <10 µm) has been popular, and several instruments have been developed for measuring the concentrations and chemical composition of these particles. In the last decade, however, the concept of 'high-risk' respirable particles of smaller size, PM_{2.5}, or even 'ultrafine' particles, PM_{0.1}, has been discussed.^{2–5}

Small aerosol particles in the ambient atmosphere are not only a health hazard but are also known to have an effect on the radiation balance of the Earth,⁶ because they scatter and absorb solar radiation. Black particles are most effective in absorbing solar radiation. Recent studies suggest that black carbon may be the second most important component of global warming.⁷ We will denote black particles 'black carbon' (BC), because carbonaceous particles are considered to be dominant with respect to light absorption.

The increasing recognition of the importance of small aerosol particles has resulted in an increase in monitoring

of PM₁₀ mass concentration in many industrialized countries.^{8–11} The monitoring is, however, concentrated mainly in urban areas. In Latvia, monitoring of air pollution has mainly been focused on gaseous pollutants such as sulfur dioxide, nitrogen oxides, ozone, benzene, toluene, formaldehyde and *p*-xylene.¹² The levels of these pollutants are measured with DOAS-type air monitoring instruments. Measurements of airborne particulate matter and its size distribution are not routinely done for air quality control in Latvia.

It is well documented that environmental effects of aerosol particles depend on their size and chemical composition. Hence there is need to study the chemical composition and other properties, e.g. the black carbon contents and the solubility in water. During mixing of an aerosol with aqueous solutions, the metals of anthropogenic origin are preferentially released, and these have potentially the most harmful impact on the biological community.¹³

The concentrations of metals in fine particle aerosols are dependent on their sources. High-temperature processes are generally known to generate smaller particles whereas mechanical processes generate larger particles.

One of the major tasks in studies of airborne particles is to make a source assignment of the sampled aerosol and thus evaluate the contribution to pollution levels from distant and local sources. The characterization and quantitative determination of elemental or ionic contents in airborne particles have played important roles in identifying sources, properties and processes which involve air pollutants.^{14–20} X-ray methods (ED-EPMA, TXRF, EDXRF and PIXE) have proved especially useful because they are simple to handle

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and can often be used in a non-destructive manner and thus also be subjected to other kinds of analysis before or after x-ray analysis. Furthermore, they allow for detailed studies of individual particles down to the sub-micrometre region.^{16,18} Since recent advances also include low-Z elements, it is possible to obtain a quantification of the main classes of particles present in the aerosol (e.g. the main species of carbonates, sulfates, nitrates, silicates, chlorides, etc.). However, at present there are still limitations on the analysis of particles below 0.5 μm in size at the individual level.¹⁸ For the very smallest particles bulk analysis of sampled aerosol is still a very useful tool, especially in combination with other methods as described in this paper.

The aim of the present work was to study some important properties (elemental size distribution, environmental mobility and black carbon content) of airborne particles in the city of Riga, Latvia, by use of EDXRF and TXRF techniques for elemental analysis of filters, quartz carriers and/or leachates in order to contribute to the identification of sources of particle pollution in this city.

EXPERIMENTAL

Sampling

Location and time of sampling

Airborne particles were sampled in the central part of Riga for 30 days in October 2000. Riga has a population of approximately one million. The sampling instruments were placed on the first lower roof of the Hydrometeorological Agency (15 m above ground level). The meteorological conditions during this period were fairly stable with some rainy days at the end of sampling period. Most of days were sunny with wind speeds around 3–4 m s^{-1} (mainly from the southern direction) and with a mean air temperature of 9.7 °C.

Since the sampling location was near the city centre, there are different possible pollution sources, namely railway (~200 m), tram park (~50 m), River Daugava (~200 m) with estuary in the Baltic Sea (~1 km), heavy traffic (~200 m), streets and an area of private houses with individual heating systems.

Sampling with the dichotomous impactor

Aerosol sampling was performed by use of a dichotomous impactor. An impactor is a device which by use of impaction techniques segregates the airborne particles into fine and coarse size fractions with respect to their equivalent aerodynamic diameter, d_a . Dichotomous impactors have been widely used for some decades, often in combination with thin, high-purity filters that are suitable for analysis by EDXRF.²¹ The impactor in the present work has a flow-rate of 1 $\text{m}^3 \text{h}^{-1}$. At this flow-rate, the two size ranges into which the impactor segregates particles are $d_a = 2.5$ –10 and $<2.5 \mu\text{m}$. The two size ranges are referred to as coarse (c) and fine (f) particles, respectively. The coarse and fine particles are collected on thin Teflon filters of 29 mm diameter and with a pore size of 2.0 μm (SA240PR100). These filters have a high particle retention efficiency.²² Each filter was analysed using EDXRF and weighed with a microbalance

($\pm 1 \mu\text{g}$) before sampling. It was found that the filters had insignificant background levels of the trace elements to be determined. After sampling, the filters were again analysed by EDXRF and weighed, in order to obtain the element and mass concentrations. The Teflon filters were changed manually every 24 h during the entire sampling period.

Sampling with the cascade impactor

The Batelle Cascade impactor used in this work is also based on the principle of inertial impaction. However, in the case of the cascade impactor there is a series of real impaction surfaces. The impactor stages are arranged in order of decreasing cut-point sizes.^{18,19} To achieve different cut-points, the nozzle size is decreased at each stage, which results in an increase in the flow-rate through the nozzle.

A seven-stage PIXE International Model I-1 Inertial Impactor was used. For collection of particles on the impaction stages, quartz plates of diameter 20 mm and thickness 2 mm were used. The impactor was operated with a pump drawing air at a flow-rate of 1 l min^{-1} . At this flow-rate the lower cut-off diameters are 16, 8, 4, 2, 1, 0.5 and 0.25 μm for stages 7, 6, 5, 4, 3, 2 and 1, respectively. Particles with diameter $<0.25 \mu\text{m}$ are collected on a back-up filter. However, the elemental content of the back-up filter was not analysed in this work.

The quartz plates for aerosol collection in the cascade impactor were cleaned with nitric acid and tested for cleanliness by TXRF. Since there is a possibility of particle bounce-off of dry particles,¹⁹ 40 μl of silicone grease in tetrahydrofuran was deposited on the quartz disks. After this pretreatment procedure, the greased quartz plates were again analysed by TXRF and stored in a laboratory-made container. For the cascade impactor, 14 sets of samples were collected in the first half of October 2000. The sampling time for each set of seven quartz plates was about 24 h.

Analytical techniques

The EDXRF spectrometer

The EDXRF spectrometer at the Department of Environmental Physics of Göteborg University and Chalmers University of Technology was used.²³ The instrument is a three-axial energy-dispersive spectrometer, with a conventional silver x-ray tube and a molybdenum secondary target arrangement. This geometry has been shown to have the best peak-to-background conditions. The design was arranged in such a way that the sample is positioned in the horizontal plane. The radiation from the sample was detected by an Si(Li) detector (active area 80 mm^2 , FWHM at 5.9 keV of 173 eV). The x-ray tube was operated at a voltage of 55 kV and a current of 25 mA. The live time of each spectrum was 1000 s. With this instrument, elements from Si and heavier can be detected and quantified.

In order to calculate the concentrations of the different elements in the filters, the spectrometer was calibrated using reference material from NIST (Standard Reference Material 1833) with known concentrations of Si, K, Ti, Fe, Zn and Pb. The x-ray fluorescence spectra were quantitatively analysed by the use of a QXAS (quantitative x-ray analysis system) package.²⁴ Errors in absolute or relative element

Table 1. Minimum detection limits for quantification of some selected elements in airborne particles collected on Teflon filter and analysed by EDXRF

Element	Detection limit (ng cm ⁻²) ^a	Minimum airborne concentration (ng m ⁻³) ^b
Si	1400	360
S	92	23
Cl	40	11
K	14	3.8
Ca	7.8	2.1
Ti	5.1	1.3
V	2.8	0.69
Cr	2.1	0.55
Mn	2.5	0.65
Fe	1.3	0.33
Ni	1.2	0.31
Cu	0.92	0.23
Zn	0.92	0.23
Br	0.62	0.16
Rb	0.54	0.14
Sr	0.63	0.16
Pb	0.92	0.23

^a Detection limits are calculated using three times the square root of the background (3σ). The time of spectrum acquisition considered is 1000 s.

^b The minimum airborne elemental concentrations are calculated with respect to the 24 m³ sampling volume used in this study.

concentrations are generally <10%. The detection limits of the spectrometer are presented in Table 1.

The TXRF spectrometer

In the TXRF technique, a Siemens 18 kW rotating Mo anode system was used as x-ray source. The operating conditions were tube voltage 45 kV, tube current 200 mA and livetime 700 s.

Prior to quantification of elemental concentrations on the cascade impactor stages, the quartz plates were analysed by TXRF to obtain relative element concentrations. For standard addition the procedure described by Spanke *et al.*²⁵ was used. In the present experiment 3 µl of Ga standard solution (from Referensmaterial, Ulricehamn, Sweden) was pipetted directly on to the centre of the sample carrier. The solution droplet was then dried for about 30 min and analysed by TXRF. It was found that the relative concentrations of the elements in the samples had not changed owing to addition of the Ga standard. The detection limits for the TXRF spectrometer are generally in the picogram region,²⁶ but may vary by several orders of magnitude with sample composition.

The black carbon reflectometer

The operating principle of a reflectometer is known as the 'black smoke method'. A light source shines its light on an aerosol filter, and the reflected light is measured by photodiodes located in a black housing. The reflectometer used in the present work (Reflectometer (Black Carbon Detector) for the Particulate Monitor, FH 62 I-R, Environmental

Monitoring ESM Andersen Instruments) was developed by Gagel.^{27,28} The light source is a high-performance LED with maximum emission at 650 nm. The output voltage is converted to a measure of blackness, the 'black smoke number', which is uniquely determined from the three output voltages obtained from the aerosol filter to be evaluated, one filter which is totally black and one filter which is totally white. Provided that thin layers of aerosol particles are collected on the filter (a single dust layer), there is a simple relationship between the concentration of black particles collected on the filter and the three output voltages. The 'black smoke number' can be related to the concentration of black aerosol by use of the Lambert–Beer law.²⁷ The instrument used in the present work was calibrated by the manufacturer. Alternatively, it can be calibrated with some other method for measuring black carbon.

Average element concentrations in fine and coarse particles

Table 2 presents the mean element concentrations for coarse and fine particles in central Riga. In the table, the element concentrations of the fine and coarse particles have been corrected for the fact that a small fraction (about 10%) of the fine particle aerosol is collected on the coarse particle filter. It should be noted that the SDs in Table 2 are not true statistical standard deviations, since they also include meteorological variations and thus true differences in pollution levels. As noted before, the analytical errors are generally below 10%, but day-to-day variations in concentrations are influenced by instrumental errors plus the variations in pollution levels which depend on differences in source strength, in location of strong sources in relation to wind direction, rainfall, humidity, wind speed and other meteorological factors. A general observation from Table 2 is that the mean concentrations are similar to those of other locations in this region,^{20,29,30} but that the level of fine particle sulfur is comparatively low, whereas the levels of fine particle zinc and lead are high.

Mass and black carbon concentrations in fine and coarse particles

In order to characterize the particles in an aerosol, it is important to register as many parameters as possible in a specific measurement campaign. Hence the mass concentrations of the fine and coarse particles were measured with gravimetric methods on the same filters that were subjected to EDXRF analysis. These filters were also subjected to black carbon (BC) analysis by reflectometry. In a previous study²⁰ we have shown that BC determination on the Teflon filters used in the impactor gives the same results as do the glass-fibre filters originally intended for this instrument.^{27,28} The results from mass and BC analysis on the Riga aerosol are given in Table 3, together with the percentage of black carbon in the aerosol mass. When comparing the data in Table 3 with corresponding data from other cities, it can be noted that the fine particle mass concentration is relatively high, in fact a factor of 2–3 larger than those of Göteborg in Sweden and Helsinki in Finland.^{20,31} The percentage of BC in the fine particle mass is, however, very similar to the levels

Table 2. Mean values of element concentrations in Riga aerosol particles obtained by EDXRF analysis ($N = 30$; coarse particles, $2.5 < d_a < 10 \mu\text{m}$; fine particles, $d_a < 2.5 \mu\text{m}$)

Element	Coarse particles		Fine particles	
	Mean concentration (ng m^{-3})	SD (ng m^{-3}) ^a	Mean concentration (ng m^{-3})	SD (ng m^{-3}) ^a
S	32	33	484	294
Cl	56	72	158	157
K	87	49	198	90
Ca	504	358	46	28
Ti	18	9.1	3.6	2.1
V	1.9	0.7	2.8	1.2
Cr	0.7	0.3	3.1	2.4
Mn	7.0	4.7	5.4	3.0
Fe	279	178	68	37
Ni	0.5	0.2	1.5	1.3
Cu	4.5	3.7	6.7	6.7
Zn	8.1	4.0	56	36
Se	0.6	1.1	4.7	21
Br	0.2	0.2	2.9	1.4
Rb	0.5	0.2	0.5	0.3
Sr	1.4	0.66	0.4	0.1
Pb	3.1	1.9	20	9

^a SD = standard deviation (a combination of instrumental SD and meteorological changes).

Table 3. Mass (M) concentrations (μg), and black carbon (BC) concentrations ($\mu\text{g m}^{-3}$) in ambient air in Riga during October 2000 ($N = 30$; c = coarse particles, $2.5 < d_a < 10 \mu\text{m}$; f = fine particles, $d_a < 2.5 \mu\text{m}$)

Property	Mean	Median	SD ^a
Mass (c)	8.2	8.7	5.9
Mass (f)	17.8	14.3	10.2
BC(c)	0.11	0.13	0.15
BC(f)	2.4	2.3	0.99
%BC/M(c) ^b	1.44	1.41	0.65
%BC/M(f) ^b	16.7	16.0	6.4

^a SD = standard deviation (a combination of instrumental SD and meteorological changes).

^b The percentage of BC in the mass concentration is also given.

in Göteborg and Helsinki, which were measured as 13 and 19%, respectively.^{20,31}

Leaching of fine particles into the environment

An important aspect of the hazards of particle pollution is the ability of the particles to dissolve in water and thus be environmentally mobile. The results of sequential leaching indicate the mobility of an element once the aerosol particles are suspended in natural waters.³² In a previous study,³³ we showed how subtraction of an XRF spectrum from the original spectrum after leaching of an aerosol filter in a weak acid can be used to identify the elements which are signatures of environmentally mobile aerosol

particles. Sequential extraction procedures have commonly been used in soil analysis to isolate metals associated with the water/acid-soluble, exchangeable, reducible/oxidizable and residual fractions of elements.^{34,35} In the previous work it was shown that the coarse particles in aerosols from Botswana had a very poor leachability in weak acid and that elements characteristic of anthropogenic fine particle aerosol had a high ability to leach in a weak acid (ammonium acetate).³³ In the present work, the fine particle filters from Riga were leached in both a weak acid (ammonium acetate) and in deionized water. The percentage of leached elements was calculated on the basis of subtraction of x-ray spectra. Figure 1 shows a flow chart of the procedure that was used. Note that the filters were leached in water first and subsequently in ammonium acetate.

Quantitative results for the leachability of elements in the fine particle Riga aerosol are given in Table 4. It is worth noting that the additional leaching in ammonium acetate above that of pure water is within the standard

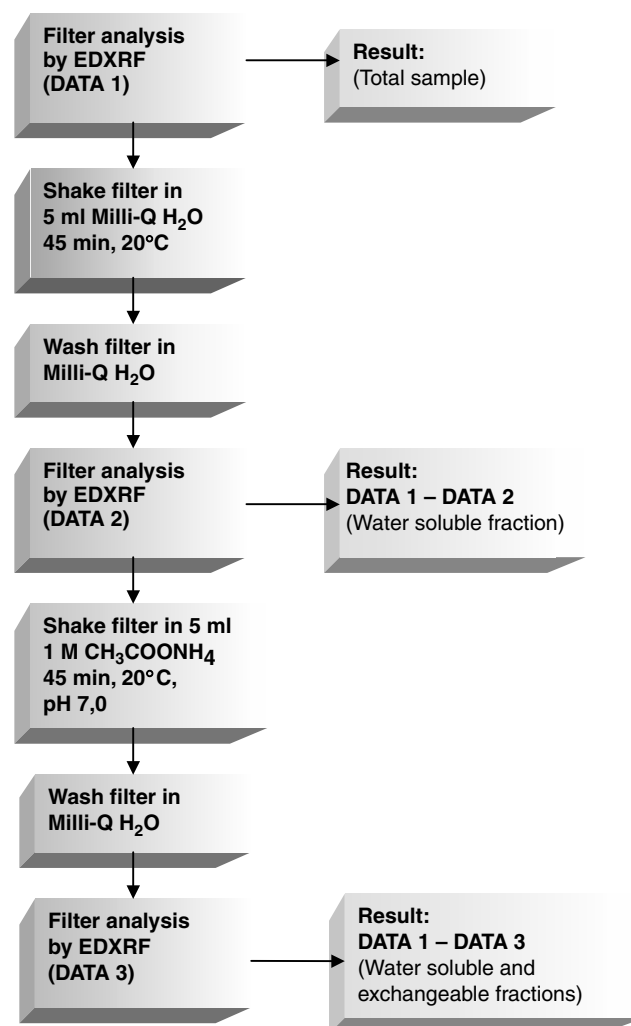


Figure 1. Schematic representation of the different analytical steps in the sequential leaching procedure of aerosol particles, $<2.5 \mu\text{m}$, collected on a Teflon filter. Two fractions, the water-soluble fraction and the exchangeable fraction in 1 M ammonium acetate, are obtained. In the EDXRF analysis the remaining filter after each leaching step is analysed.

Table 4. EDXRF results of mass percentage (*w*) and standard deviation (SD) of the fine fraction of airborne particles soluble in water and 1 M ammonium acetate, respectively

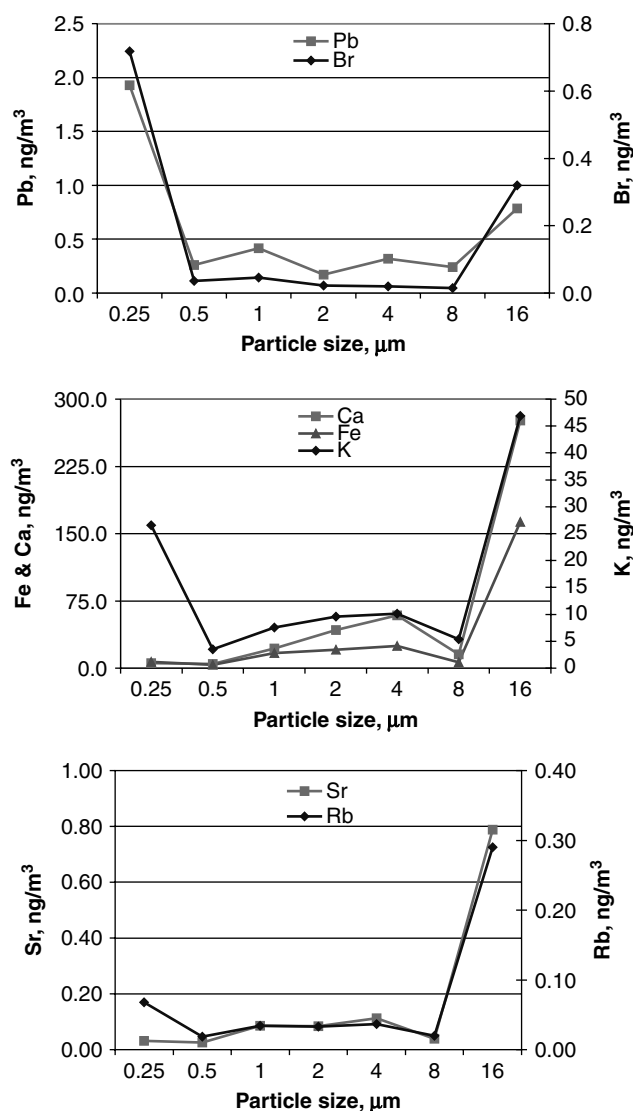
Element	Water		1 M ammonium acetate	
	<i>w</i> (%)	SD	<i>w</i> (%)	SD
Cl	53.1	13.9	56.5	18.5
K	81.8	3.3	84.6	4.4
Ca	82.3	3.8	84.2	5.0
Ti	13.7	13.4	14.4	14.1
Mn	57.3	5.7	56.6	6.9
Fe	14.5	3.5	17.9	4.2
Ni	39.4	14.5	48.3	9.3
Cu	29.6	8.8	37.8	8.0
Zn	77.0	3.3	78.6	5.3
Br	67.3	6.1	72.4	5.0
Pb	44.1	4.5	71.3	4.5

deviations for most elements, but that lead is an exception. The results in Table 4 are in harmony with those of previous leaching experiments in ammonium acetate on fine particles sampled in Gaborone and Selibe-Phikwe in Botswana.³³ In both locations, high levels of K, Ca, Mn, Zn, Br and Pb compounds were found in the environmentally mobile fraction, whereas Ti and Fe were found to have low mobility.

Size segregation of aerosol particles

Information on size-segregated aerosol particles was mainly obtained from the dichotomous impactor, which segregates the particles into two size fractions with a cut-point of 2.5 μm (see Table 2). It is possible, however, to obtain more details on size segregation by making use of the previously described Batelle impactor. This instrument concentrates the particles in small millimetre-sized spots at the respective impactor stages. As described earlier, the analysis of these small spots was most conveniently made in the TXRF spectrometer. The additional information obtained from the combination of quartz plates in the Batelle impactor and TXRF analysis gives more detailed information on the size distribution of the different elements. Typical size distributions are shown in Fig. 2. An observation made from the size distributions is that for some elements, e.g. K, Rb, Pb, Br and also Zn, there seem to be at least two different sources, one of coarse particles and one of fine particles, whereas for Ca, Sr, Ti and Fe there are very low concentrations of particles with diameters $<1\ \mu\text{m}$. For S there was essentially only a fine particle profile in the Riga aerosol.

The trends in Fig. 2 for K, Rb, Pb and Br are very similar to observations made by Ro *et al.*¹⁸ on the size distribution of carbon-rich and organic species sampled in Seoul, Korea. In a previous study K, Rb, Br and Zn in fine particles were found to be typical of biomass burning in Botswana and fine particle K, Pb, and Zn of vehicle emissions in Sweden.²⁰ Hence the size distributions of these elements support their character as 'fingerprints' for the anthropogenic carbon-rich and organic species studied by Ro *et al.*¹⁸

**Figure 2.** Some typical size distributions of different elements of airborne particles sampled by the cascade impactor.

Correlations and factor analysis

Although correlation and principal component analysis can give additional information on sources of airborne particles, one must also be aware of their limitations in source assignments. The main problem arises from the difficulty in evaluating the influence of the meteorological and geographical variables. For example, during certain periods (e.g. low-level inversions), there is a large probability of high pollution levels, and therefore many elements in the fine particle aerosol have positive correlation coefficients with each other. Likewise, if there are strong winds from a certain direction, many aerosols from different sources in this direction will be mixed, and the factor analysis may not be able to resolve the influence of different sources. Therefore, it is important to note that many of the variables are not independent; on the contrary, they have a high degree of positive correlation if originating from the same location or source, particularly if the source is strong.

It can be useful, however, to include element concentrations in both coarse and fine particles in the database and

treat them as separate variables. Other information can be added to this, e.g. black carbon and mass concentrations. In the factor analysis in the present work several runs were made with different sets of variables included. It was found that essentially the same factors appeared in the analysis, even if some variables were omitted. From the combined information from correlation and principal component analysis, a factor representing street dust could be identified. It is represented by the soil-derived elements in coarse particles, namely Ti(c), Fe(c), Ca(c), Sr(c) and Mn(c), but also by some deposits from vehicles, e.g. Pb(c) and Zn(c). The elements connected to the blackest particles are mainly found in the fine particle region. They are represented by K(f), Rb(f), Cu(f), Br(f), Zn(f) and Pb(f), and are most probably due to atmospheric vehicle emissions. In fact, in the previous analysis of aerosol sources in Göteborg the only significant positive correlation coefficients with the blackness component were found for these fine particle elements.³³

DISCUSSION AND CONCLUSIONS

EDXRF is an interesting technique for the determination of elemental contents in aerosol particles sampled on filters, because it is non-destructive and has reasonably low detection limits for many elements which are relevant from an environmental point of view. A major advantage of the technique is that the filters can also be used for other kinds of analysis. In the present work this is illustrated by measurements of mass, black carbon contents and environmental mobility. The simultaneous measurement of many elements on the same sample makes the data obtained suitable for correlation and principal component analyses.

TXRF is a technique which is complementary to PIXE when measuring millimetre-sized small spots of deposited particles in a multistage cascade impactor. This technique gives more detailed information on particle size distributions of different elements, which can be used in support of source identification.

Concentrations of different elements in Riga have large similarities with the corresponding concentrations of the same species in Göteborg. The mass concentration of fine particles is, however, significantly larger in Riga than in Göteborg or Helsinki.^{20,31} This may be due to the fact that restrictions on emissions from vehicles and industry in Latvia have not been implemented as strictly as in Sweden or Finland. However, the percentage of black carbon in relation to mass is essentially the same in the three cities (13–19%).

The coarse particle fraction contains only a weak black contribution in the Riga aerosol. This is similar to what has been observed in measurements in other locations^{20,36} A very large part of the black carbon is found in the PM_{2.5} fraction. This is because the major sources of black carbon are due to combustion processes, e.g. vehicle exhaust and incineration, which give rise to the formation of fine particle aerosols.

Correlation and factor analysis show that in Riga, a dominant factor is street dust, which is a mixture of soil-derived elements, and deposits from human activities. For the fine particles a factor containing K, Rb, Cu, Br, Zn and Pb and identified as atmospheric vehicle emissions was strongly correlated with black carbon.

Combining the information obtained from the results of EDXRF and TXRF analysis with the different kinds of analysis made in the present work and in other publications^{14,18,20,33} gives strong evidence that the smallest particles containing K, Rb, Br, Zn and Pb are black and have high solubility in water. In different studies they turn up as 'fingerprints' of vehicle exhaust and/or of biomass burning. Although rather satisfactory source assignments can be obtained from principal component analysis, it is important to establish complementary methods to separate the two sources in environments where both sources are present. In the work by Hedberg *et al.*,¹⁴ in which emissions from a birch wood combustion wood stove were studied, it was found that the K/Ca ratio was 64 in the wood emissions compared with 1–4 in background air. The Cu/Zn ratio was of the order of 1% in the wood emissions whereas it is about 10% in background air. Hence a more detailed study of elemental ratios at locations with well-known contributions from different sources (in particular vehicle emissions and biomass burning) might be useful for developing techniques for even more reliable source assignments in the future. X-ray methods are ideal for obtaining elemental ratios because they are inherently multielemental.

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