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Elemental content of PM$_{2.5}$ aerosol particles collected in Göteborg during the Göte-2005 campaign in February 2005

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Abstract. The Göte–2005 measurement campaign aimed at studying the influence of the winter thermal inversions on urban air pollution. Elemental speciation of PM$_{2.5}$ aerosol particles, collected on Teflon filters at three urban sites and one rural site in the Göteborg region, was a major part of the study. Trace element analysis was done by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry and the concentrations of S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br and Pb were determined. The elemental content of the particles, local wind speed and direction, and backward trajectories were used to investigate possible sources for the pollutants. We concluded that S, V, Ni, Br, and Pb had their main sources outside the central Göteborg area, since elevated concentrations of these elements were not observed during an inversion episode. Sea traffic and harbour activities were identified, primarily by the S and V content of the particles. This study showed that the elemental analysis by EDXRF presents valuable information for tracing the origin of air masses arriving at a measurement site.

1 Introduction

Air pollution in urban environments is a major problem to human health. This has forced governments to invoke regulations controlling pollution in an effort to protect their citizens. The control is achieved through the provision and implementation of air quality standards that address the concentr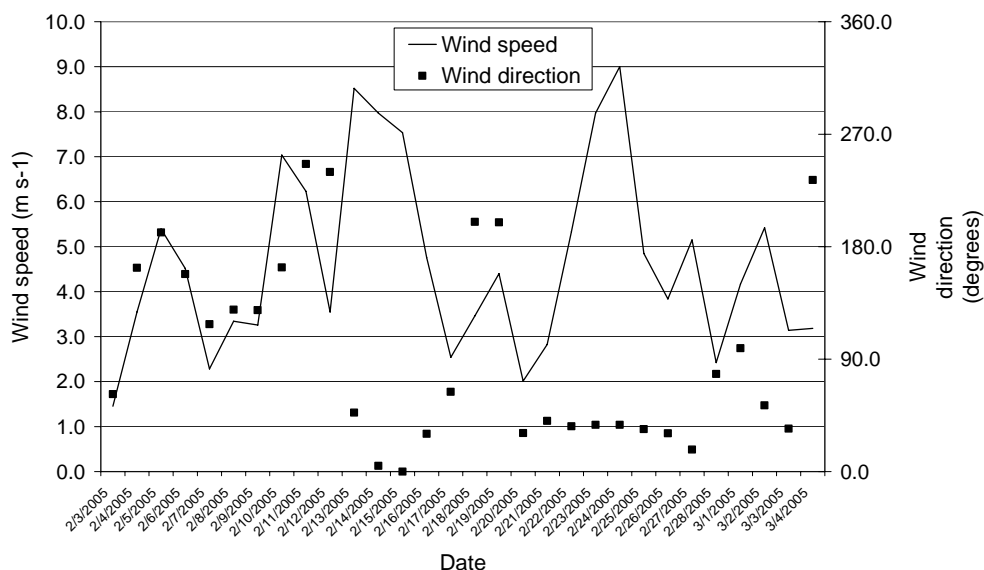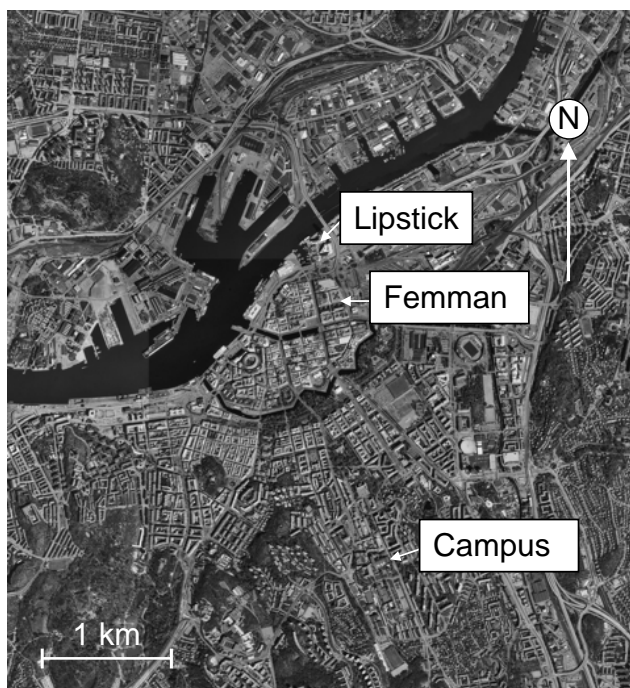ations of the criteria pollutants above which harm to human health may occur. Particulate matter is one of these criteria pollutants which attract increasing global attention. The environmental quality standards for particulate matter that are stipulated for the European Union (European Union, 1999) are hard to follow in many large cities (Baldasano et al., 2003). This is the case for Göteborg, Sweden, where the measurement campaign presented here was carried out in February 2005. The air quality standard, derived from the regulations in chapter 5 of the Swedish environmental code is based on the EU directive 1996/62/EC and its daughter directives. It stipulates the average annual concentration of PM$_{10}$ to be below $40\,\mu\mathrm{g\,m^{-3}}$ with a 24 h limit value of $50\,\mu\mathrm{g\,m^{-3}}$. This annual threshold is expected to be reduced to $20\,\mu\mathrm{g\,m^{-3}}$ by the year 2010. The continued use of PM$_{10}$, an integrative measure of particle mass concentration, as a criteria pollutant is under discussion since new norms based on particles of aerodynamic diameter smaller than $2.5\,\mu\mathrm{m}$ (PM$_{2.5}$) are impending (European Union, 1999). The shift in concern is motivated by the higher anthropogenic input to PM$_{2.5}$ mass concentration compared to the input from natural sources and their ability to be transported over long distances thus influencing a larger part of the population. The capability of atmospheric wind systems to transport PM$_{2.5}$ aerosol particles over long distances not only affects the exposure, but also the analysis of the air mass trajectories which together with the analyzed elemental content of the particles assist in source apportionment studies. There are several examples of poor health that are associated with particulate matter even at levels close to the background concentrations found in most parts of the United States and Europe (Dockery et al., 1993; Pope and Dockery, 2006; Schlesinger et al., 2006). The reason for the health impact might be related to the content of the particles. The integrated particulate mass

Fig. 1. The average wind speed (m s^{-1}) and wind direction (degrees) for the measurement period calculated from noon each day. The day indicated in the figure the date as when the filters were collected. 0 (and 360) degrees represents wind coming from north, 90 degrees is east, 180 degrees south and 270 degrees is westerly winds.

Fig. 2. Map showing the location of the urban measurement sites in Göteborg, Sweden.

parameter, PM$_{10}$ or PM$_{2.5}$, is not easy to use for source apportionment. Consequently, a more detailed knowledge of the constituents of the particles is of great value (Ariola et al., 2006; Artinano et al., 2004; Chow and Watson, 2002;

Molnár et al., 2006). The measurements of the current study were part of a four week winter air pollution measurement campaign, Göte–2005, conducted in Göteborg, Sweden. The focus of these measurements was to describe the trace element content of PM$_{2.5}$ particles in Göteborg, the influence of temperature inversions on particle mass concentration and composition, and possible sources of the trace elements in the particles.

2   Site description and experimental details

The measurements were conducted in Göteborg (57.69° N; 11.98° E), where a population of about 500 000 inhabitants live, on the Swedish west coast in February 2005 as part of the air pollution measurement campaign, Göte–2005. The main aim of the Göte–2005 campaign was to study the influence of wintertime temperature inversions on the air pollution situation in Göteborg. The central parts of Göteborg are located in a valley along the Göta River with the sea to the west. Despite its close location to the sea, Göteborg is frequently affected by elevated air pollution levels due to night time temperature inversions, especially during the winter months. Normally the yearly air quality standard limits of the regulated air pollutants are not exceeded. Consequently, Göteborg is classified as a city with good air quality. During 2005 the main problem was connected to NO$_2$ exceeding the 24 h air quality standard limit while the concentration of PM$_{10}$ never exceeded the limit at the central urban background air quality monitoring station in Göteborg. The prevailing wind direction is south west throughout most of

the year and precipitation is frequent but not heavy. February is normally a cold winter month in Göteborg and in 2005 the temperature varied between $-9.1°C$ and $+7.3°C$ with an average temperature of $-0.6°C$. Part of the measurement period was windy as several low pressure systems passed Göteborg. The wind was north-easterly or north-north-easterly (Fig. 1) for 40% of the campaign period. The average wind speed and wind direction for the measurement period were calculated from noon each day to match the filter changing time of the PM$_{2.5}$ samples. The indicated date in the figure is the date when sample/fresh filters were collected/loaded. PM$_{2.5}$ particles were collected at three sites, Femman, Campus and Lipstick (Fig. 2), representing different urban conditions, and at one rural site, Råö. All these sampling sites were located in places without point sources in the near vicinity.

The Femman site was placed on the roof of a commercial complex located in the busy centre of Göteborg. The site is the main monitoring station for air quality in the city and it is maintained by the local environmental office in Göteborg since 1965. It was chosen as an urban background site. The sampler was positioned approximately 30 meters above ground. Aerosol samples were collected between 4 February and 3 March 2005 at this site. The Chalmers Campus area is situated 2 km south of the city centre. The area represents a less busy area which is traversed by a yearly average of 8000 vehicles per day. The Campus sampling site was located approximately 10 m above ground level, 50 m above sea level and 20 m from the street. Aerosol sampling took place between 7 and 28 February 2005 at this site. The Lipstick building is located on sea level 500 m north-north east of the Femman site, in the docklands in the central parts of Göteborg. The sampling site was located 88 m above ground level. This site was selected with the expectation that it would be above low level inversions. Aerosol samples were collected between 17 and 26 February 2005 at this site. The rural sampling site was at Råö (57.41° N; 11.93° E) which is located 35 km south of Göteborg. It was close to the sea a few meters above sea level. The sampler had its inlet approximately 1.5 m above ground and aerosol samples were collected between 11 and 26 February.

Particle collection was done on 25 mm diameter Teflon filters with a pore size of 3μm (PALL Teflo^{TM} R2PI025) using plastic cyclones (Casella Ltd, UK). The flow through the cyclone was kept constant by a critical orifice to maintain a particle cut off diameter of 2.5μm. Samples were changed at noon on a daily basis, except at Råö where samples were changed at an interval of four to seven days due to the expected low particle concentrations at the site. The meteorological information during the measurement campaign period was obtained from the local environmental office in Göteborg.

All obtained samples were analyzed for their elemental content by Energy Dispersive X-Ray Fluorescence (EDXRF) spectrometry (Van Grieken and Markowicz, 1993). The

Table 1. Detection limits (DL) in ng m^{-3} for the analysed elements.

| Element	DL
S	40
Cl	15
K	3.8
Ca	2.3
Ti	1.3
V	1.0
Mn	0.56
Fe	0.44
Ni	0.43
Cu	0.38
Zn	0.33
Br	0.23
Pb	0.29

spectrometer is based on three-axial geometry with a Mo secondary target that facilitates a good signal to background ratio giving low detection limits, Table 1. The spectrometer was operated at 55 kV and 25 mA and the samples were analyzed for 1000 s (Boman et al., 2005; Gatari et al., 2006). For calibration of the spectrometer, thin film standards with specified uncertainty of 5% in the elemental concentration were used (Micromatter Inc., Seattle, WA, USA). By repeatedly (five times) analysing two aerosol filter samples the mean analytical precision of the spectrometer was determined to be 5% (Molnár et al., 2006). Spectral evaluation was done with the AXIL software program (Bernasconi et al., 2000). A Dionex Ion Chromatograph was used to analyse the SO$_4^{2-}$ content in the samples collected at the three urban sites between 17 and 26 February (Janhäll et al., 2003). The analysis was done using IONPAC A59-S as analytical column with a 1.8 mM Na$_2$CO$_3$/1.7 mM NaHCO$_3$ eluent at a flow of 2 ml m^{-1} for conductivity detection. The determination of particle mass on the filters was done by a Mettler Toledo MT5 micro balance.

3 Results and discussion

The average concentrations and uncertainties of S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Br and Pb in all samples from the four measurement sites were evaluated and are shown in Table 2. Among the detected elements S, Cl, K, Ca and Fe dominated in the sampled atmospheric aerosol particles. The uncertainty in Table 2 includes

Table 2. Full campaign concentration averages with standard deviations (St. Dev.) in ng m^{-3} for the analysed elements and the PM$_{2.5}$ mass concentrations at the four sites. Sampling period at Femman was between 4 February and 3 March 2005, at Campus between 7 to 28 February, at the Lipstick site between 17 to 26 February and at Råö between 11 and 26 February. PM$_{2.5}$ concentration is given in μg m^{-3}. Concentrations below detection limit (DL) have been replaced by DL/2 in the statistical calculations. N=Number of filter samples collected.

| | Femman | | | Campus | | | Lipstick | | | Råö | | |
| | N=29 | | | N=26 | | | N=17 | | | N=4 | | |
	Average		St. Dev.	Average		St. Dev.	Average		St. Dev.	Average		St. Dev.
S	1400	±	1100	1300	±	920	630	±	380	1200	±	690
Cl	580	±	620	520	±	560	430	±	290	120	±	180
K	150	±	94	120	±	72	82	±	36	120	±	100
Ca	46	±	30	47	±	32	49	±	35	50	±	44
Ti	3.1	±	3.5	3.9	±	6.8	2.2	±	3.3	3.1	±	2.6
V	2.5	±	3	1.5	±	2.1	0.72	±	0.71	3.5	±	4.1
Mn	2.9	±	2	2.3	±	2.2	1.6	±	1.6	2.1	±	1.5
Fe	100	±	77	82	±	61	82	±	56	60	±	46
Ni	5.6	±	8.9	3.1	±	3.5	3	±	2.6	2.7	±	3.2
Cu	3.6	±	2.6	2.9	±	1.7	3.1	±	1.9	3.6	±	4.5
Zn	31	±	26	27	±	29	16	±	7.9	24	±	19
Br	2.8	±	2.2	2.2	±	1.7	3.3	±	1	3.6	±	4.9
Pb	6.2	±	9.5	5.3	±	7.8	2.6	±	3.9	5.7	±	5.5
PM$_{2.5}$	14	±	12	12	±	9	6.5	±	3	6.9	±	3.5
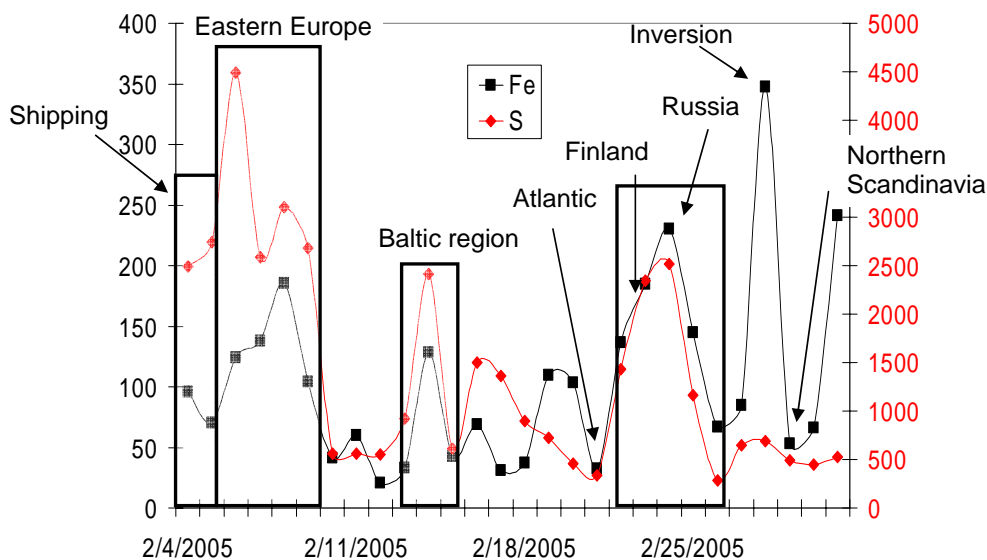
Fig. 3. The S and Fe concentration at the Femman measurement site given on a daily basis together with indications of the possible origin of the air masses. The inversion period between 27 and 28 February is indicated in the figure.

Table 3. Simultaneous sampling period 17–26 February concentration averages with standard deviations (St. Dev.) in ng m^{-3} for the analysed elements, SO$_4^{2-}$ and the PM$_{2.5}$ mass concentrations at the three city sites. SO$_4^{2-}$ and PM$_{2.5}$ mass concentration is given in μg m^{-3}. Concentrations below detection limit (DL) have been replaced by DL/2 in the statistical calculations.

	Femman			Campus			Lipstick		
	Average		St. Dev.	Average		St. Dev.	Average		St. Dev.
S	1200	±	790	1200	±	920	630	±	380
Cl	500	±	410	390	±	180	430	±	290
K	120	±	41	83	±	55	82	±	36
Ca	46	±	30	48	±	43	49	±	35
Ti	3.8	±	4.2	5.9	±	10	2.2	±	3.3
V	1.9	±	2	0.93	±	1.4	0.72	±	0.71
Mn	2.7	±	2.2	2.2	±	2.7	1.6	±	1.6
Fe	110	±	68	83	±	71	82	±	56
Ni	5.5	±	6.2	3.8	±	3.7	3	±	2.6
Cu	3	±	1.6	3	±	1.8	3.1	±	1.9
Zn	25	±	19	22	±	21	16	±	7.9
Br	1.7	±	0.9	2	±	2.1	3.3	±	1
Pb	5.4	±	8.3	4.4	±	7.3	2.6	±	3.9
SO$_4^{2-}$	4.4	±	3.4	3.6	±	2.5	2.1	±	2.3
PM$_{2.5}$	9.2	±	5.1	8	±	4.3	6.5	±	3

variations induced by meteorological conditions, sampling variations and analytical uncertainties in the EDXRF evaluation of the elements. PM$_{2.5}$ mass concentrations in μg m^{-3} are also included in Table 2. The concentrations for most elements were above the detection limit (DL) in a majority of the samples. In the cases where concentrations were below DL the elemental concentration was represented by DL/2 in the statistical calculations (Hornung and Reed, 1990). The entry <DL in the tables indicates that more than half of the samples had concentrations below DL. Table 3 shows concentrations from samples collected over the period 17 to 26 February 2005. The samples were collected simultaneously at the three measurement sites in the city and are presented to facilitate comparison between them. The Teflon filters used in the measurement campaign were the optimum choice for EDXRF analysis but not ideal for ion chromatography, thus the SO$_4^{2-}$ determinations have higher uncertainties, assessed to be 15%.

For most of the elements in Table 2 the difference between average concentrations from the four sampling sites was small and within a factor of two. However, the daily concentrations of different elements were highly variable and this was mainly due to different weather conditions, as indi-

cated by the high standard deviations in Tables 2 and 3 and the varying concentrations of sulphur at the Femman measurement site. This is illustrated in Fig. 3.

An example of the influence of polluted long distance transported air masses was seen in the elemental composition of the analyzed aerosol particles in the period 6 to 9 February. The concentrations of S and Pb were found to be distinctly high in these samples. The S concentration was more than two times higher (3200±880 ng m^{-3} and 2600±880 ng m^{-3} at the Femman and Campus sites, respectively), than the average concentration in Table 2, suggesting an influence originating from combustion of S rich coal in Eastern Europe for energy production. This origin was confirmed by the calculated 72 h back trajectories (Draxler and Rolph, 2003). These trajectories show that the air masses arriving in Göteborg during that period had passed over the more polluted areas of Eastern Europe. The Pb concentrations were more than three times higher (23±8 ng m^{-3} and 17±9 ng m^{-3} at the Femman and Campus sites, respectively) than the average concentration in Table 2, probably originating from the use of leaded gasoline, phased out only recently in that part of Europe (UNEP, 2006). Janhäll et al. (2003) did measurements at different heights on the Gustavii Cathedral in the centre

Table 4. The three main components of the Principal Component Analysis of the elemental concentrations at the three city sites during 17–26 February. The results are Varimax rotated with Kaiser normalization. Elemental component contributions higher than 0.7 are indicated in bold. % Var. is the percentage explained by the component.

	Femman			Campus			Lipstick		
	Comp.1	Comp.2	Comp.3	Comp.1	Comp.2	Comp.3	Comp.1	Comp.2	Comp.3
S	**0.95**	0.16	0.04	**0.81**	0.49	−0.21	0.11	**0.90**	−0.19
Cl	−0.36	**0.71**	−0.37	−0.18	−0.13	**0.96**	**0.75**	−0.46	0.06
K	**0.89**	0.27	0.23	**0.71**	0.58	−0.18	0.57	0.45	0.26
Ca	**0.88**	0.42	−0.05	**0.87**	0.37	0.00	0.30	0.26	**0.72**
Ti	**0.94**	−0.01	0.21	**0.97**	−0.08	−0.11	**0.98**	0.12	0.06
V	0.53	0.59	−0.54	0.27	**0.90**	−0.03	−0.20	0.46	−0.22
Mn	0.64	0.57	0.35	**0.78**	0.47	−0.07	**0.74**	0.24	0.54
Fe	**0.83**	0.01	0.53	**0.85**	0.44	-0.20	**0.96**	0.25	−0.03
Ni	**0.84**	0.09	0.32	0.17	**0.92**	−0.19	-0.07	0.03	-0.07
Cu	0.27	0.10	**0.93**	**0.74**	0.39	0.40	**0.78**	−0.02	0.39
Zn	**0.95**	0.00	0.28	**0.83**	0.52	−0.13	0.38	**0.91**	0.06
Br	0.21	**0.84**	0.30	0.37	**0.92**	0.06	0.00	−0.22	**-0.85**
Rb	**0.97**	−0.01	−0.02	**0.94**	0.21	−0.11	0.01	**0.93**	−0.17
% Var.	58	17	16	51	32	10	32	26	14

of Göteborg in 1999 to investigate the vertical distribution of different air pollutants. Although Total Suspended Particles (TSP) were measured the concentrations of S and Pb were only slightly higher than the ones measured in this study. This reinforces their conclusion that S and Pb are mainly in PM$_{2.5}$ and thus can be transported over long distances.

Implications of emissions from sea traffic and harbour activities were found on 4 and 5 February. These days the S concentrations were high, reaching 2600 ng m^{-3} and 1900 ng m^{-3} at Femman and Campus, respectively. The back trajectories indicated that the air masses passed over the North Sea, UK, and Denmark before reaching Göteborg. The high S concentration might have originated from ship emissions, both in the vicinity of Göteborg and on the North Sea. Göteborg hosts the largest port within the Nordic countries and the international sea traffic is allowed to use fuels with high S content. The V and Ni concentrations were also high, 8.9 and 6.8 ng m^{-3} for V and 3.8 and 2.4 ng m^{-3} for Ni at Femman and Campus, respectively, implicating the ship emissions as suggested in previous studies (Isakson et al., 2001; Molnár et al., 2006). With air arriving from south west, thus passing the harbour area, not only the human activities can be considered. There is also an input of sea salt particles containing sulphate compounds as well as Cl (Janenicke and Schutz, 1988). Although the majority of the sample mass

from sea salt particles is found in the larger fraction of the particle range, above PM$_{2.5}$, an influence on PM$_{2.5}$ can also be seen. Pérez et al. (2008) estimated that in Barcelona, also a sea side city, on an average 2% of the PM$_{2.5}$ mass was made up of particles from sea spray, compared to 5% in PM$_{10}$. Negral et al. (2008) estimated the ratio between marine and non-marine SO$_4^{2-}$ to approximately 1:100 in PM$_{2.5}$ aerosol particles collected in the coastal city of Cartagena, Spain. If a similar ratio is assumed for Göteborg the largest part of the measured S did not come from sea salt but from other sources, most likely ships passing outside Göteborg or manoeuvring in the harbour.

The concentrations of most elements had a different variation pattern at the high Lipstick site compared to the Femman and Campus sites. Principal component analysis (PCA) on concentrations obtained over the period 17 to 26 February, when samples where collected simultaneously at the three city sites, confirmed the different variation patterns. The first and most influencing component of the PCA, explaining more than 50% of the variation, exhibited similar elemental loadings for data from Femman and Campus sites, but the same variance dependency could not be seen at the Lipstick site, Table 4. These differences revealed dissimilarities in sources influencing the three city locations. The elements can be representative of several sources, pointing at a mixed

Table 5. Two days urban sampling comparison of average concentrations in ng m^{-3} for the analysed elements. <DL means below detection limit. PM$_{2.5}$ and PM$_{10}$ mass concentrations are given in μg m^{-3}. PM$_{10}$ mass concentrations are from the local environmental office (Brandberg, 2005).

	Femman		Campus		Lipstick	
	20–21/2	23–24/2	20–21/2	23–24/2	20–21/2	23–24/2
S	390	2400	770	2700	820	970
Cl	310	290	290	300	280	280
K	75	180	88	170	82	110
Ca	16	92	31	120	39	53
Ti	<DL	10	<DL	23	<DL	6.2
V	<DL	4.1	<DL	4.8	<DL	<DL
Mn	<DL	5.1	<DL	6.5	1.4	4.1
Fe	68	210	62	210	66	100
Ni	2.7	15	5.8	7.5	2.1	3.4
Cu	4.1	3.8	1.7	5.5	2.4	3.4
Zn	13	57	14	59	16	23
As	<DL	8.9	2.7	7.9	<DL	6.8
Br	0.69	2.1	1.4	4.8	2.7	3.1
Pb	<DL	20	<DL	17	7.5	9.6
PM$_{2.5}$	3.1	17	5.8	14	6.1	9.7
PM$_{10}$	11	26	11	26	11	26

aerosol of mainly crustal origin. The second component at Femman contained Cl and Br, and could represent the influence of sea spray, while the component represented by Cu, having the only high elemental load, could be a signature of non tailpipe emissions from traffic (Molnár et al., 2007). It was surprising to find high loading of V and Ni in the second component at Campus site, since V and Ni are tracers of heavy fuel oil combustion and thus could be assumed to influence the down town Femman site as well. Since Cl, that is known to be a signature element of sea salt, is in a component of its own at the Campus site, the high loadings of V, Ni and Br in component two might instead indicate the influence of combustion of heavy fossil fuels, from both sea traffic and Eastern Europe region. The wind direction during this period was dominated by north easterly winds, with westerly winds at the beginning of the period. At Femman a high loading of Ni was found in the first component while a moderately high loading of V was attributed to the second compound, indicating a more mixed aerosol at Femman. Factor analysis of PM$_{2.5}$ aerosol particles collected at the Campus area by Moloi et al. (2002) showed that most of the collected PM$_{2.5}$ aerosol particles at that time came from sea spray and indus-

trial activities in the harbour area. That was characterised by Cl, Ni, and Br. The influence of vehicle emissions was also identified by the content of K, Cu, Zn and Pb in the same study.

While the elemental concentrations at Femman and Campus were more than doubled on the 23 and 24 February compared to those on 20 and 21 February, the concentration at the Lipstick site did not change to the same extent, Table 5. Twenty-third and 24 February were characterized by high wind speeds, between 6 and 11 m s^{-1}, compared to 1–6 m s^{-1} for the rest of the period, 17 to 26 February. Although the local wind direction was more or less stable with north-easterly winds between 20 and 26 February, 72 h back trajectories showed that the air masses were coming from different areas on different days, suggesting different source regions as illustrated in Fig. 3. The air masses arriving to Göteborg during 20 and 21 February were coming from the northern part of the Atlantic Ocean, the North Sea and Scandinavia. The following day there was a rapid change in direction and air masses were now arriving from southern and middle Finland. On the 23 and 24 February the air masses were coming from the central Russia region. As the wind

speed thereafter decreased more of the air originated from the Baltic countries before coming from the northern part of Norway and Sweden on 26 February. The trace element data showed a general increase of many of the elemental concentrations on 23 and 24 February compared to 20 and 21 February as depicted by Fe and S in Fig. 3.

Despite the fact that the airborne particles were being collected over several days, the same trend of increasing elemental concentrations was seen in the data from Råö when samples collected between 14 and 21 February and the ones for 21 to 25 February were compared. An explanation is that there are more coarse particles in the air during the windy period and as a result more of them join the PM$_{2.5}$ fraction. This phenomenon was shown in an investigation on effects of wind speed on the relation between particles of different sizes by Kim et al. (2005). If the elements Ca, Ti and Fe are used as indicators for particles with crustal origin, a high influence of crustal particles is seen during the windy days. The influence of crustal particles in the PM$_{2.5}$ particle range was also seen by Pérez et al. (2008) in Barcelona, Spain. In comparison to the monthly average concentration of $20.5\,\mu g\,m^{-3}$ recorded by the local environmental office, relatively high PM$_{10}$ concentrations that ranged between 21.5 and $33.6\,\mu g\,m^{-3}$ were reported on the same days in February. The higher concentrations of S, V, and Ni on 23 and 24 February were likely to originate from combustion processes in the eastern part of Europe where the air masses passed before reaching Göteborg. These elements are normally found in the fine particle fraction and can thus be transported long distances before the settling of the particles. The good correlation between the S concentrations obtained from the EDXRF analysis with the sulphate concentrations from the IC analysis (r^2=0.96) implied that most of the measured particulate S was in the form of sulphate.

The higher Pb concentration during the windy days was likely due to particles originating from Eastern Europe. Although unleaded gasoline is used in all countries in the region (UNEP, 2006) lead is still dispersed in particles that are resuspended by strong winds and traffic. Pb is also dispersed from the tail pipe systems of cars that previously used leaded fuel. Cl was the only element with stable concentration during the period 20 to 24 February, Table 5, indicating little influence from sea salt and this agreed well with the wind direction over the period.

The night between the 27 and 28 February had a strong night inversion that was identified by Brandberg (2005) with a vertical temperature difference of $+ 0.2°C\,m^{-1}$. The positive vertical temperature difference was sustained for almost 12 h. Despite the 24 h sampling period, covering more than the inversion episode, the increase in concentration for most elements was approximately a factor of two when compared to the median concentration for the whole measurement campaign period, with the exception of Cl and Fe. The highest recorded Fe concentrations over the whole measurement campaign period were $350\,ng\,m^{-3}$ at Femman and

$230\,ng\,m^{-3}$ at the Campus site, respectively. Similarly Cl concentrations were the second highest at $2400\,ng\,m^{-3}$ and $1500\,ng\,m^{-3}$ at both sites respectively. The local environmental office had their highest PM$_{10}$ mass concentration at the same time with an hourly maximum of $177\,\mu g\,m^{-3}$ on 27 February at 11:00 p.m., an eightfold increase compared to the monthly average of $20.5\,\mu g\,m^{-3}$. This type of night and early morning inversion episodes is known to lead to higher concentrations of traffic related elements in Göteborg like K, Cu, Zn and Pb (Janhäll et al., 2006). However this was not evident from these 24 h measurements, probably because the inversion layer was broken before morning rush hours.

The highest Cl concentrations were recorded on 10 February when the wind was coming from the North Sea area in the south west direction from Göteborg with a speed of approximately $6\,m\,s^{-1}$. The Cl concentration indicated the influence of sea salt particles. Comparing the ratio between S and Cl in sea salt (S/Cl=0.05) (Jaenicke and Schutz, 1988) with the ratio in the samples from 10 February (S/Cl=0.2 at the Femman and Campus sites) a relative excess of S was revealed and that could indicate emissions from sea traffic.

A comparison of elemental concentrations between the Campus and Råö sites, Table 2, showed only slightly higher ($<$50%) levels at the Campus site, or no difference at all, for elements normally connected to urban activities like traffic and industries (V, Fe, Ni, Cu, Zn, Pb). This, together with the fact that Pb concentrations were below the annual national environmental quality standard limit value of $0.5\,\mu g\,m^{-3}$ for Pb in ambient air in all samples indicated that the urban air in Göteborg is comparatively clean when trace elements are considered.

The current study confirms earlier source apportionments in Göteborg. A measurement made by Moloi et al. (2002) in March 2000 on the same campus area as in this campaign showed the same range of concentrations for most trace elements. The averages of S concentrations differed by almost 50% between the two Campus measurements with the highest S concentration in the current study. Pb was measured in 2000 but it was below the detection limit in this study, indicating a general decrease of Pb in the particles due to the use of unleaded gasoline. In a European Community Respiratory Health Survey (ECRHS) Götschi et al. (2005) measured the elemental content of PM$_{2.5}$ for one year including March 2000 in 21 locations in Europe, including Göteborg city. The reported concentrations were very similar to those measured in Stockholm and Uppsala in the same study, the ones obtained by Moloi et al. (2002) and in this study. Götschi et al. (2005) observed a difference of up to 80 times for some elements between the locations used in their study. The results included large seasonal and daily variations in elemental concentrations rendering difficulties in the epidemiological assessment of the fine particle influence on human health. A relatively high daily variation was also seen in the present study which is a phenomenon entrenched in the weather system variations.

4 Summary and conclusions

During the measurement campaign one night-time temperature inversion was recognised as well as some days with exceptionally high elemental concentrations. Since the concentrations of S, V, Ni, Br, and Pb did not increase during the inversion their major sources had to be seen as of non local origin. Back trajectory studies pointed to Eastern Europe as a major source area for S, Fe, Zn, and Pb. In this detailed study the main parameters influencing the elemental content of the PM$_{2.5}$ particles were found to be wind speed and wind direction. These parameters were matched by back trajectory studies, since the areas over which the air masses had been passing played a major role in the composition of the PM$_{2.5}$ particles. The detailed analysis of differences in elemental composition and interpretation of the results provides an improved understanding of the influences of possible sources on the elemental concentrations in urban aerosol particles. Pinpointing more explicit sources is not possible since the air is mixed during long distance transport and long measurement times leading to the conclusion that shorter measurement periods are needed as well as better knowledge of emission from different sources. From the analysis of the elemental composition it can be concluded that S is a suitable tracer for air masses coming from both Eastern Europe and ship emissions. High concentrations of V and Ni indicated influence from sea traffic and the harbour area as well as Eastern Europe. A comparison between the elemental ratios of sea salt elements and the same elements in the analysed particles makes it possible to estimate that three quarters of the measured S does not come from the sea salt, but from other sources. These sources are most likely sea traffic in the same sea. The inversion period helped us conclude that Pb and S are not emitted in the Göteborg area despite the influence from sea traffic that was noted on the other days. It can be concluded that trace element analysis is an effective tool for estimation of air mass origin, which could be confirmed by trajectory analysis.

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