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Trace element analysis of airport related aerosols using SR-TXRF

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Abstract—Air quality issues of international airports are becoming more and more important due to the dynamic growth of air traffic. Fine particulate matter (PM_{2.5}) originating from emissions of aircrafts, ground handling vehicles, passenger related cars, and point sources is the most critical pollutant in airport areas. The sources have large temporal and spatial variation. In order to correlate the elemental composition of fine particulate matter in different size fractions to airport related sources, special instrumentation and analytical technique need to be used. A novel combination of cascade impactor sampling and total reflection X-ray fluorescence (TXRF) analysis employing synchrotron radiation is presented in this paper. The method allows quantitative determination of ultra-trace amounts (pg m⁻³) of most elements from samples collected for less than 20 min, while retaining the full size resolution of the impactor. Size-fractionated aerosol samples were collected on silicon wafers using a 7-stage May cascade impactor, close to the runway and next to the aircraft stands at Budapest Ferihegy Airport. The comparison of the size distribution of the elemental concentrations for different locations could allow us to differentiate between end-of-pipe and other emission sources. Typical elements coming from combustion processes (Zn, Pb), aircraft related emissions (Cu), as well as road salting processes (Cl) could be determined. Elements connected to crustal erosion and resuspension (Fe, Ti, Ca) had maximum concentration in the micrometer size fractions (1–4 µm). The combination of May impactor sampling and TXRF analysis described in this paper has a potential to be used in industrial/traffic processes where the time scale of the event is similar to the typical sampling durations, even using laboratory scale equipments.

Key-words: airport, air quality, fine particulate matter, trace elements, TXRF, synchrotron radiation

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1. Introduction

Airport air pollution is coming to be more and more remarkable, since it shows one of the most dynamic growth in the transport sector. Large international airports operate monitoring systems (*Farias and ApSimon, 2006; Unal et al., 2005; Schürmann et al., 2007*) for continuous controlling of classical air pollutants (CO, NO_x, SO₂, O₃, PM₁₀, and PM_{2.5}). The statistical analyses of these long time series show that the most important pollutants which have the largest contribution to urban air quality are the nitrogen-oxides, since limiting value exceedence occurs only in NO_x concentration values (*Farias and ApSimon, 2006*). Whereas, measurement campaigns performed at Budapest Ferihegy International Airport during the year of 2006 show that limiting value exceedence can be detected only in particulate matter (PM₁₀) concentrations, and the only component which show higher values than downtown and suburban areas at Budapest is the fine fraction of particulate matter (PM_{2.5} – particles with aerodynamic diameter smaller than 2.5 µm) (*Groma et al., 2007*). Additionally, recent publications show that PM_{2.5} causes more severe health effects than coarse particles (*Kampa and Castanas, 2008*).

PM_{2.5} monitoring measurements were carried out using a Tapered Element Oscillating Microbalance System (TEOM) (http://www.thermo.com/eThermo/CMA/PDFs/Product/productPDF_2006.pdf) next to the runway (see *Fig. 1*), where the main particle emission sources are the starting, landing, and taxiing aircrafts, in addition to the background, since other traffic sources are far from the measurement site. Since we could determine correlation between aircrafts and PM_{2.5} concentration values, it is obvious that aerosol originating from emissions of aircraft is detectable (*Bozó et al., 2006*).

Airport related particles originate from aircraft end-of-pipe emission and erosion (brake, concrete, and tire). Moreover, not only aircrafts but also emissions of ground supporting vehicles, point sources, and passenger related cars have to be taken into account. Also, resuspension of crustal particles is a significant source. Since the most polluted sites were found to be the handling and terminal areas (apron) – where human activity is the most remarkable –, measurements capable of source apportionment are needed. Multi-element chemical analysis is one of the most adequate tools for deriving fingerprints of different sources of fine particulate matter. Also, the opportunity of short sampling time is needed, because the duration of an aircraft landing and taxiing nearby parking places is approximately 1 to 3 minutes, while touch down takes a few seconds. For this reason, development of a multielemental analytical technique for aerosol samples allowing very high temporal resolution is required, since compounds in gas phase can be measured with time resolution as low as 1 minute. This would allow a time-resolved correlation between pollutant gases and the composition of primary and secondary aerosols.

Methods allowing the analysis of individual aerosol particles on-line or from samples collected during very short time are useful for source apportionment studies. The recently developed aerosol mass spectrometers (AMS) now have the opportunity to be able to measure the size and the chemical composition of individual particles with a very high time resolution (*Takegawa et al.*, 2006), and can also be used as a monitoring instrument. The combination of time-resolved aerosol collector and computer-controlled electron probe microanalysis (CC-EPMA) of a few thousand individual particles can allow a 10 min time resolution (*Laskin et al.*, 2003). Using the AMS or CC-EPMA methods only the major chemical composition can be specified, from which the different particle types (mineral dust, sulfate, nitrate, organic) can be differentiated. Although this kind of information can be very attractive for studies of airport-related aerosols, the minor or trace elemental composition of aerosols in different size fractions is an important fingerprint of the airport related sources. The latter can be addressed by bulk trace elemental analysis of size-resolved aerosol samples collected for very short time. The aimed high size resolution as well as time resolution results in sample masses less than a microgram, which requires a very sensitive analytical method.

Total reflection X-ray fluorescence spectrometry using high flux synchrotron radiation (SR-TXRF) provides several great advantages for aerosol characterization. Because of the natural collimation of the incident beam, the high intensity of the fluorescence radiation and the low spectral background, SR-TXRF allows a non-destructive detection of trace and ultra-trace atmospheric concentrations (ng m^{-3} , pg m^{-3}) of most elements in size fractionated aerosol. Quantification and standardization of the TXRF technique is straightforward compared to EPMA or AMS.

Recent investigations present many studies about aerosol measurement methods which have high time resolution and low detection limits. These developments are usually based on size fractionated aerosol sampling combined with TXRF analyses. Results show that they are capable for determination of specific elements, source identification, and fingerprint analysis based on samples collected within hours (*Dudzinska-Huczuk and Bolalek*, 2007; *Lammel et al.*, 2007). Whereas, a great disadvantage of these methods lies in the necessity of a pretreatment of the sample carriers used in TXRF analysis in some cases (*John et al.*, 2001). Moreover, higher time and size resolution is needed to study atmospheric processes having characteristic times in the range of hours (*Lammel et al.*, 2007). Since our aim was to study even shorter environmental processes, we needed to develop a method which has better time resolution characteristics. Since the risk of contamination is higher at lower amounts (ng) of samples, the applied technique should be devoid of this problem. Sampling with May impactor combined with SR-TXRF seemed to be a good alternative, since this technique does not need any pretreatment of

samples, and also non-destructive, which allows one to perform further analysis on the collected aerosols.

The aim of this study is (i) to introduce an aerosol analysis method which has potential to use in industrial/traffic processes where the time scale of the event is similar to the typical sampling duration, and (ii) to present its suitability for trace element analysis of airport related aerosols.

2. Materials and methods

2.1. Sampling

Aerosol samples were collected in the inside area of Budapest Ferihegy Airport. The airport is located 15 km south-east from the city center of Budapest. A highway with approximately 50,000 cars day⁻¹ traffic is located 2 km far from the airport area. The potential measurement sites inside the airport were limited, because movements at the airport area were strictly regulated. Hence, it was not possible to go closer to the runway than 150 meters. To overcome the security problems and reduce influence of road transfer, measurements were performed near the runway and next to terminal buildings (apron) (see Fig. 1).

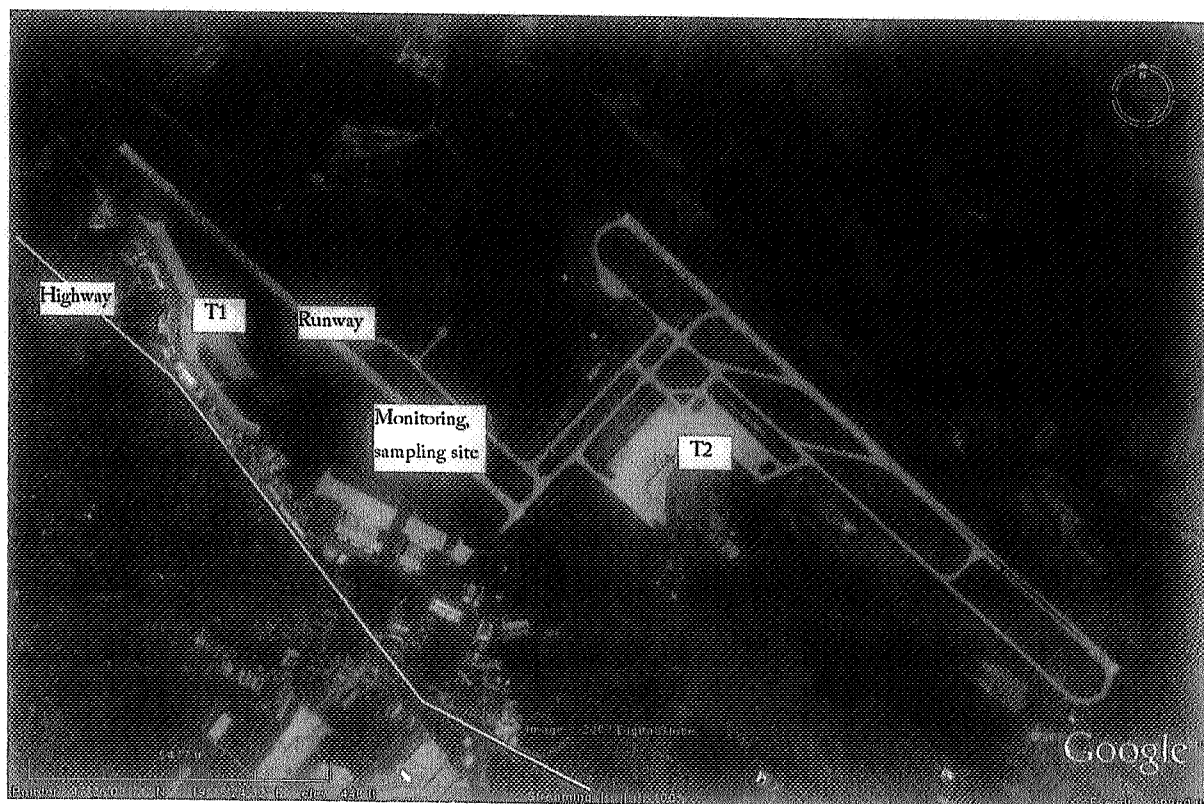


Fig. 1. Measurement sites at Budapest Ferihegy Airport.

First, samples were collected on $20 \times 20 \text{ mm}^2$ silicon wafers using a 7-stage May cascade impactor (May, 1975). The May impactor has aerodynamic cut-off diameters of 16, 8, 4, 2, 1, 0.5, $0.25 \text{ }\mu\text{m}$ for stages 1–7, respectively, at 20 l min^{-1} sampling flow rate. The sampling duration took 1 (for stage 7), 5 (for stage 6), 10 (for stage 5), and 20 minutes (for stage 4) to obtain the best loading of particles on the impacted strips. Since in this study we aim to investigate the fine aerosol fraction only, aerosol collection was performed only for the above specified four stages (4 to 7). The May impactor has an impacting slit at each stage, and thus the aerosols collected on a silicon substrate show a pattern of a thin line with approximate dimensions of $20 \text{ mm} \times 0.3 \text{ mm}$. To be able to calculate concentration values for each trace element, an internal standard, a Cr strip with a known mass was placed on the Si wafers exactly at the same position as particles from the air sample, prior to collection of particulate matter on the Si carriers. Two sample sets were collected on January 12, 2006 at the runway and Terminal 2 (high traffic: 8 aircraft movements during sampling time), and one at Terminal 1 (low traffic: 1 aircraft movement during sampling time) on January 15, 2006 (hereafter, T2 and T1, respectively). The last sampling day was a Sunday with much lower traffic in the city of Budapest.

Ionic compounds were measured in order to obtain daytime and nighttime averages of sulfate concentrations in $\text{PM}_{2.5}$, samples were collected on $1 \text{ }\mu\text{m}$ pore-size Teflon filters for 12 h at the terraces of terminal buildings. The cyclone used for the fine aerosol sampling had a cut-off diameter of $2.5 \text{ }\mu\text{m}$ at 10 l min^{-1} flow rate. The total sampled air volume was approximately 7 m^3 for all samples. The 12-hour average concentrations of sulfate were measured using ion chromatography (IC), after leaching the filter samples in water.

2.2. Multielemental analysis

Measurements were performed at HASYLAB Beamline L using a total-reflection X-ray fluorescence vacuum chamber (Streli *et al.*, 2005). An automatic sample loader (Meirer *et al.*, 2006) was installed to establish the opportunity to measure 8 samples consecutively without the necessity to close the beam shutter and open the vacuum chamber, resulting significant time saving during the beam time. A special sample holder was used to mount the $20 \times 20 \text{ mm}^2$ Si wafer pieces with the aerosol samples collected in strip form. The synchrotron radiation energy was adjusted to 18.4 keV by means of the NiC multilayer monochromator. The SR beam had a vertical dimension of 1.4 mm and a horizontal dimension of 0.2 mm .

A Vortex Radiant Silicon Drift Detector (SDD) in use was equipped with a special collimator with a 1.5 mm wide slit made of Mo, in order to fit to the geometry of the impacted aerosol samples. As X-ray photons emerging from the total 20 mm length of the aerosol strip could not be detected using the SDD applied, the homogeneity of the aerosol deposition was tested. For the test scans,

the sample strip and the collimator slit was perpendicular to the X-ray beam, therefore, only 1.4 mm section of the sample strip was excited. The vertical scans were performed by moving the sample–detector system relative to the position of the beam using a stepping motor. The step size was set to 1 mm, and the individual spectra were collected for 3 s. Measurements with the new collimator resulted in excellent reproducibility of the individual scan steps. The interpretation is clearly a shielding of the off-lier contaminants as the slit prevented their detection and the geometry of the detector collimator fit to the sample. The measurements aiming the determination of the elemental concentrations were carried out applying the SR beam parallel to the sample strip. The position of the sample strip was determined using vertical scans with 0.2 mm step size. Individual spectra were collected at the strip positions for 100 s. The net characteristic X-ray intensities of the elements were calculated by evaluating the spectra by non-linear least-squares fitting using the AXIL program (*Vekemans et al.*, 1994). In order to calculate the relative sensitivity curve of the setup, 30 nl of a multielement standard solution (11355 Multi Element Standard IV, Merck) containing 1 ng of each element was pipetted onto a Si wafer and measured by SR-TXRF.

3. Results and discussion

3.1. Sample homogeneity

Samples were collected directly on Si wafers containing 5.75 ng Cr in a 300 μm wide strip in the middle centerline of the wafers. As the geometry of the Cr strip was chosen to be similar to that of the deposited aerosol particles, Cr could be efficiently used as internal standard for the SR-TXRF measurements. The standards were provided by the Research Institute for Technical Physics and Materials Science (Budapest, Hungary) (*Watjen et al.*, 2000). The important issue is to make sure that the measured 6 mm sections of the aerosol strip are representative for the total length and thus for the calculation of the total mass deposited here. Only if this is proven, the extrapolation from the mass calculated for 6 mm to the total mass deposition is permitted. The total mass deposited represents the aerosol concentration (ng m^{-3}) in the collected air volume. For this purpose 18 mm of the existing 20 mm strips were measured successively by scanning 3×6 mm along the strip. Results shown in *Fig. 2* demonstrate that the Fe intensities normalized to ring current vary within 10% relative standard deviation during the three scans, supporting the proposed extrapolation.

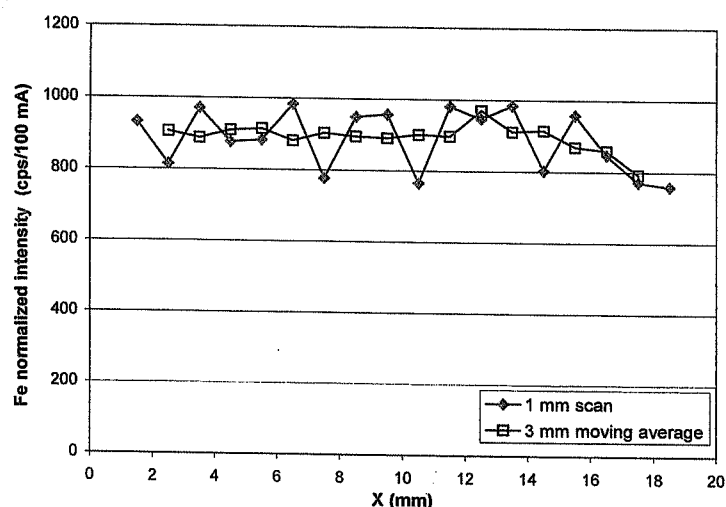


Fig. 2. Results of homogeneity test of impacted aerosol strip.

3.2. Elemental analyses

Long term measurement data showed slight differences between PM_{10} and $PM_{2.5}$ concentrations (Groma *et al.*, 2007). For this reason size fractionated aerosol analyses were only done on the smaller sized particles ($0.25\text{--}4\text{ }\mu\text{m}$ aerodynamic diameter). Also, larger particles occur in smaller number concentration (particles m^{-3}) naturally, requiring longer sampling time, which does not make any sense on the time-scale of aircraft movements. May impactor sample collection combined with SR-TXRF analysis has the opportunity to calculate elemental concentrations from extremely small sampling volumes. Detection limits achieved for 20-minute sampling time are ranging from ng m^{-3} for the light elements (Al, Si) to pg m^{-3} for the medium Z elements like Rb and Sr in the present matrix (see Table 1). The detection limits were calculated for 100 s measuring live time and 100 mA ring current.

Table 1. Detection limits for each element detected in aerosol particles collected at airport sites

Element	Detection limit (pg m^{-3})
S	451.3
Cl	282.8
K	107.9
Ca	68.3
Ti	39.9
Cr	23.4
Fe	13.3
Cu	4.6
Zn	3.4
Se	2.4
Br	2.3
Sr	3.6
Pb	5.8

The concentrations of the elements in the samples were calculated based on SR-TXRF spectra collected for 100 s, using the Cr strip as internal standard. A typical spectrum is presented in *Fig. 3*.

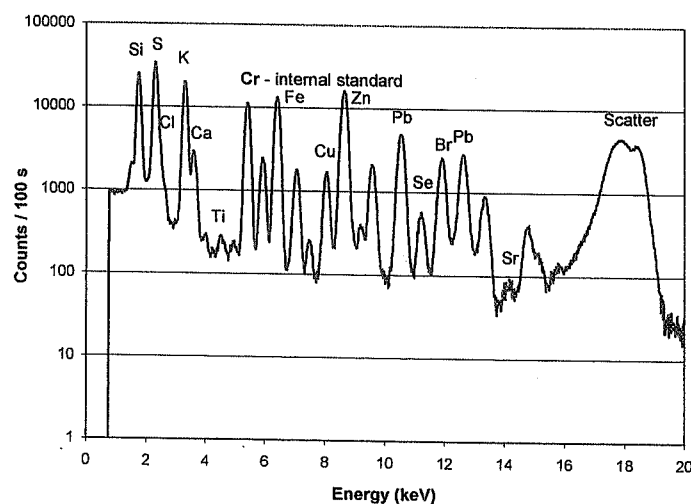


Fig. 3. Typical SR-TXRF spectrum of an aerosol sample collected at the airport, 0.5–1 μm size fraction.

The SR-TXRF measurement results of airport related aerosols sampled by May impactor are presented in *Fig. 4*. Since aerosols were collected in 4 different size fractions at 3 different sites, measurement results for 12 samples are presented here. Each diagram is relevant for one of the elements studied (S, Cl, K, Ca, Ti, Fe, Cu, Zn, Se, Br, Sr, Pb). Each column is relevant for a measurement site: runway, T2 – high traffic (85%) and T1 – low traffic (15%), respectively. Size distribution of concentrations for a specific element is presented within the columns. Diagrams are scaled to the maximum values of the different elements. Measurement results shown in *Fig. 4a–l* confirm facts which were previously expected for typical suburban areas, besides results which show specialties of airport related aerosols. Aerosols originate from long range transport, city plume, and local sources. Local sources show large variability in the airport, since aircrafts, ground supporting vehicles, and also passenger cars have to be taken into account. The emission characteristics are all different, some of them are well known, but some – especially aircraft related – particulates chemical composition is still unknown.

Onsite measurements were recently performed by NASA to improve air quality emission inventories (*Aviation Particle Emissions Workshop*, 2004). These results are very well detailed, but the instrumentation requirement is huge, and no trace element composition analysis can be performed. It follows that the combination of impactor sampling and SR-TXRF analysis presented in this paper provides complementary information.

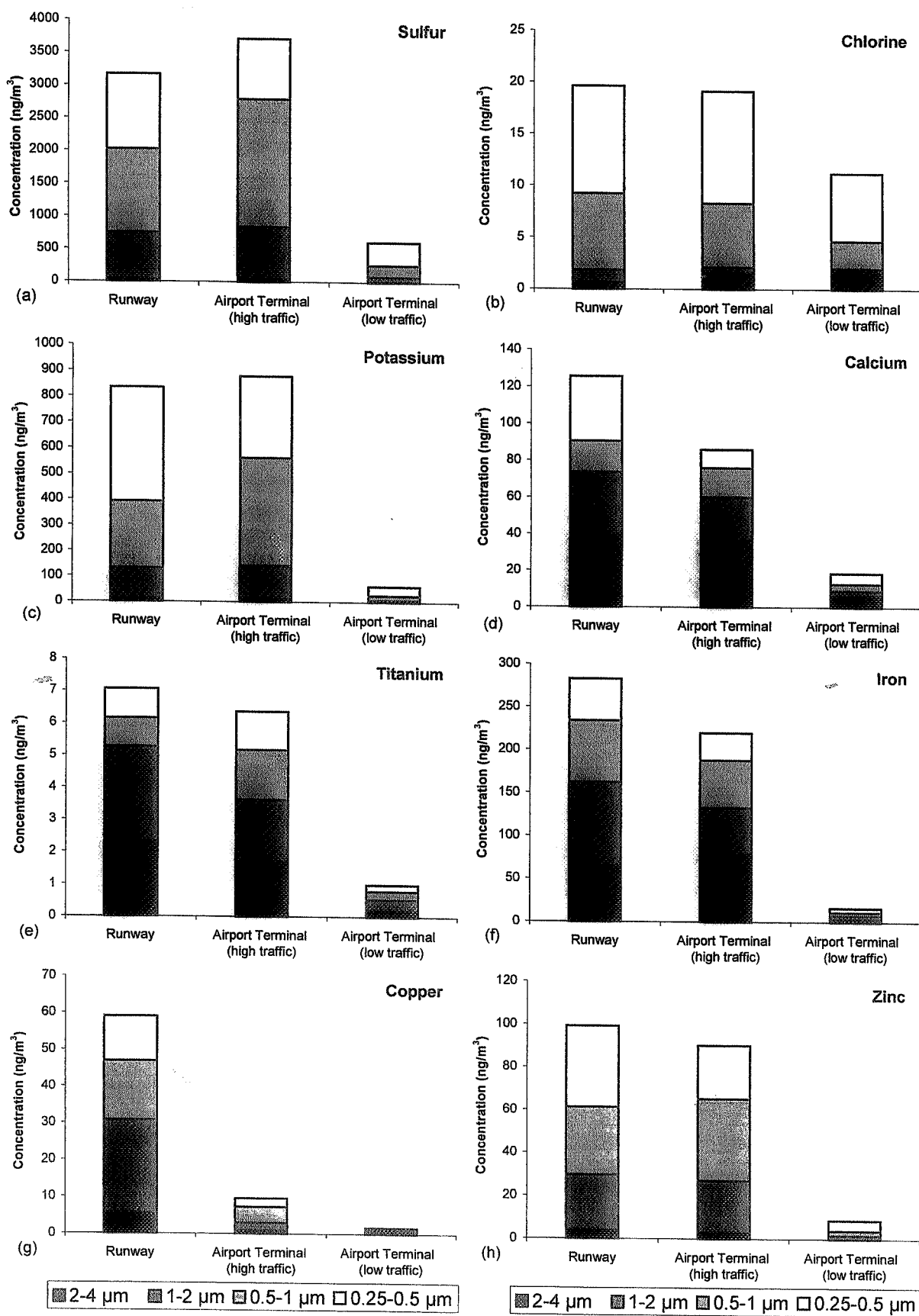


Fig. 4. Size distribution of elemental concentrations at different sites.

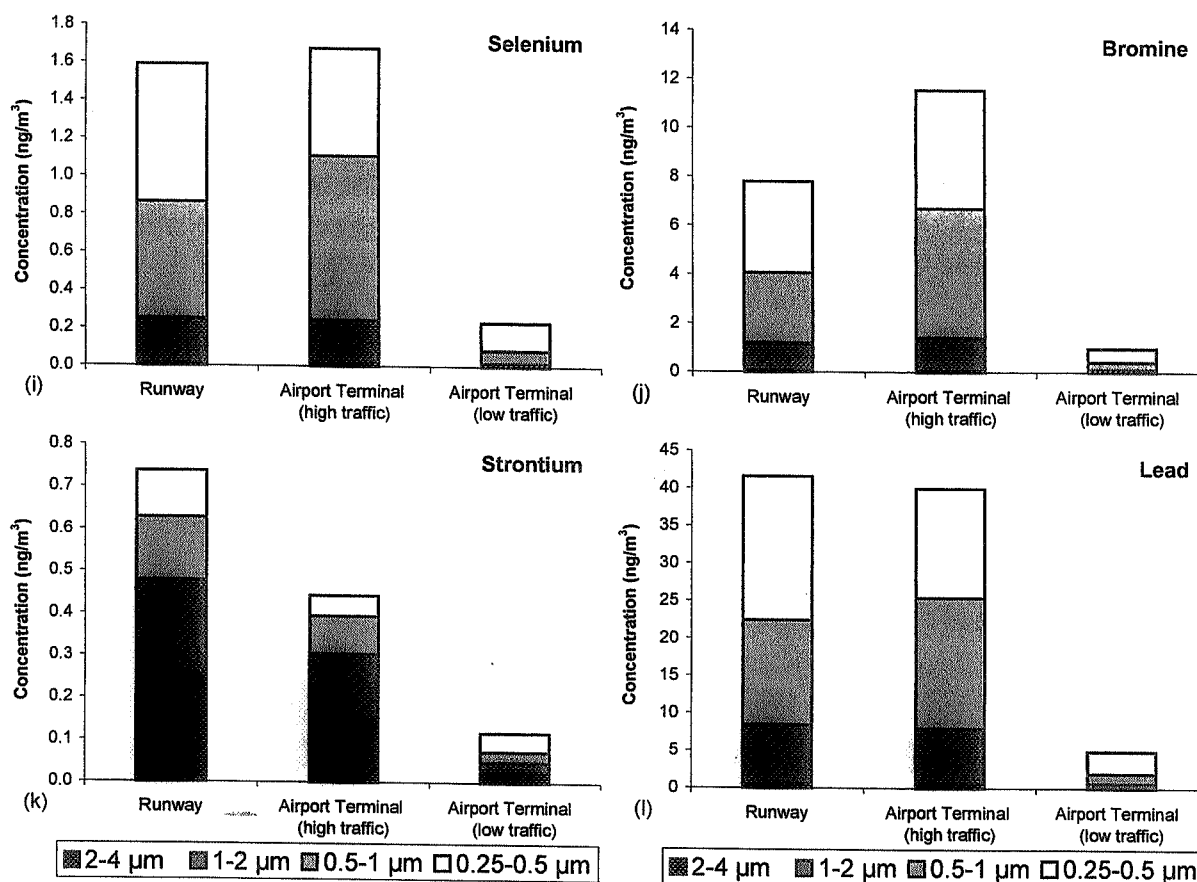


Fig. 4 (continued). Size distribution of elemental concentrations at different sites.

Not only combustion processes, but also resuspension, erosion, and formation of secondary aerosols (which can be classified in typical size fractions) contribute to the ambient particulate concentration. Therefore, measurement results can be discussed in 3 different aspects: (i) size distribution, (ii) magnitude of concentration values at different sites, and (iii) typical elements at different sites. It is obvious to see that concentrations of all elements measured at runway and terminal building with larger traffic (T2) are much higher than values at the other terminal with lower traffic (T1). This is due to the different number of air as well as ground vehicle movements around the sampling sites. Sample collections at the runway and T2 (just after each other) were done during one of the largest aircraft traffic peaks (around 1 p.m.), while sampling at T1 was performed during really small number of vehicle movements. Airport traffic does not only mean the movements of aircrafts, but also ground supporting and passenger cars which both show correlation with aircraft movements. To be able to determine the origin of the aerosol, samples collected at different sites need to be compared. Since the source properties at terminal buildings are complex (large temporal and spatial variation), it is not possible to determine the origin of particles from their chemical composition.

Results from terminal building compared to results from the runway allow one to differentiate between the sources.

It is well-known that sulfate is dominant in smaller size fractions. According to *Kerminen et al.* (2004), the size distribution of sulfate shows a maximum at around 0.3 μm for rural and around 0.7 μm for urban aerosols, based on measurements at several European sites. Previous studies of Hungarian background aerosol have even revealed that the preferred modal diameter of sulfate compounds is smaller in the summer than in the winter (*Mészáros et al.*, 1997). As it can be seen in Fig. 4a, the shape of the size distribution is similar to that observed by impactor sampling and IC measurements reported in the literature (*Kerminen et al.*, 2004; *Mészáros et al.*, 1997). The highest sulfur concentration obtained by SR-TXRF is in the 0.5–1 μm fraction at the runway and at T2, and in the 0.25–0.5 μm fraction at T1. It means that the size distribution of sulfur has a more rural characteristic for low traffic conditions, and more urban at sites influenced by high traffic.

Significant amount of Cl was found to be present in the largest size fraction studied (2–4 μm). Besides long-range transport of sea salt, chlorine also originates from the salt used for preventing ice formation on roads during winter time. The SR-TXRF results are in accordance with this, since the decrease of the traffic intensity at the airport has less influence on the concentrations of Cl than other elements (see Fig. 4b).

Ca, Fe, and Ti show similar size distribution at the three locations (see Figs. 4d, 4e, 4f). Also, the total concentration values of these elements have similar ratio among the three sites. This means that the source of particles containing these elements must be the same. Since these elements dominate in larger particulates, one can say that they probably originate from resuspension (by movements of vehicles and the blowing effect of the aircraft engine).

Zinc and lead (see Figs. 4h, 4i) are usually connected to combustion processes in the engine (*Tesseraux*, 2004). Traffic related particles containing these elements usually occur in fine aerosols, which is in good agreement with our results. Because concentration values of these elements show similar magnitudes: high at high traffic periods and low at the time of low traffic, but no significant difference could be seen at the runway and T2, one can say that particulates containing these elements should originate from the airport related ground supporting vehicles as well as from the city traffic, transported to airport area.

Significant differences between apron and runway areas are in copper concentration values (see Fig. 4g). Copper rich particles probably originate from aircraft brake pad erosion. No other studies have been done connected to the erosion during aircraft landing, which means further investigations are needed to be done on this subject.

High concentration values of potassium usually occur near wood-burning emission sources which cannot be found inside, but probably somewhere

outside, near the airport area. This is confirmed by the fact that sulfur has a really similar size distribution to potassium (see *Figs. 4a, 4c*), which is also connected to wood-burning processes in previous studies (*Osán et al.*, 2002).

Since strontium is chemical substituting element for calcium, the size distribution and Sr/Ca ratio at different sampling sites should be the same. Although Sr was found to be present at sub-ng m⁻³ concentration levels (see *Figs. 4k* and *4d*), the present measurement results confirm these assumptions. This very good correlation between Sr and Ca concentrations in all size ranges clearly shows the suitability of SR-TXRF for trace element analysis of aerosol samples.

Selenium and bromine rich particles were found to be dominant in the submicrometer size fractions (see *Figs. 4i, 4j*), therefore, these trace elements can be connected to the combusted fuels used either in air or in ground traffic. The detection of this small quantity in these small size-fractions confirms the fact that this method opens up new opportunities in aerosol analysis research.

3.3. Comparison of IC and SR-TXRF measurements

Since the sulfate content of the PM_{2.5} aerosol at the airport could be measured by IC from 12-hour filter sampling on the same day, it is worth to compare the results obtained by the two techniques. SR-TXRF sulfate concentrations were calculated from stoichiometry based on the sum of the sulfur concentrations for the size fractions in the 0.25–2 µm range.

PM_{2.5} sampling on Teflon filters was done on T2 terminal building during both days, when aerosol collection was performed with the May impactor. Since a large air volume is needed for the IC analyses, the samples were collected for 12 hours. Because the meteorological and traffic conditions are not stationary, it is not trivial to compare the results of these samples with those from SR-TXRF analyses, which are samples collected for much shorter time. *Table 2* shows the results of sulfate concentrations obtained by ion chromatography and SR-TXRF.

Comparing IC and SR-TXRF measurement results for samples originating from the same site during a larger airport traffic volume period shows similar values (less than 20% difference). Also, SR-TXRF results at the runway are in the same magnitude of the ones mentioned above. However, sulfate concentration of aerosol particles collected for 12 hours and analyzed by IC is higher than those measured by SR-TXRF, which should be explained by the fact that a significant sulfate mass can be present in ultrafine particles smaller than 0.25 µm. Also, the short time May impactor sample collection was not performed during the highest traffic period (inside and outside the airport). This also confirms the fact, that long range transport is one of the most important sources of aerosols containing sulfate, besides the local emission and formation effects. To study the contribution of these processes further measurements are needed.

The use of the recently developed ambient ion monitor (<http://www.urgcorp.com/systems/pdf/9000.pdf>) that allows IC measurements of ionic compounds in PM_{2.5} at a time resolution of 15 minutes would lead to a more accurate comparison between IC and SR-TXRF results. However, this new IC system is still not capable for providing size-fractionated information.

Table 2. Differences in sulfate concentrations analyzed by IC and SR-TXRF

Sampling site, method	Runway SR-TXRF	T2, SR-TXRF	T2, IC
Concentration (ng m ⁻³)	9,500	11,100	13,500

4. Summary and conclusion

Aerosol collection with May impactor combined with the SR-TXRF analytical method could be efficiently used to study atmospheric processes on the time scale of minutes. The sampling and trace element analysis were performed at airport sites near sources which show high spatial and temporal variability. Measurements and trace element analysis at airport sites with such high size resolution have never been done before. We could determine typical aircraft originated particles from these extremely small sampling volumes.

Since the concentration of PM_{2.5} found to be the most critical at airport sites, the aim of our measurements was to determine the airport related aerosol particles. Typical elements of combustion processes like zinc and lead could be determined as well as special, aircraft related particles, namely high copper concentrations were detected near the runway, which is due to aircraft brake erosion. Size fractioned sampling allowed us to sort out particles from not airport related combustion processes, since, for example, due to resuspension, typical aerosols in larger size fractions (Ca, Fe, Ti) can be shown. Also, from the comparison of concentration magnitudes at different sites, we could identify elements originating from wood burning processes like potassium and sulfur, which are connected to atmospheric transport.

Low detection limits (in the range of pg m⁻³) could be achieved from 20 minutes sampling time thanks to the excellent properties of synchrotron radiation. This short time collection allows to study temporal variation of elemental concentrations in size-fractioned aerosols. SR-TXRF measurements have proven the fact that the most important elements occur in concentrations above detection limits. By choosing the most adequate size and time resolution to that samples, the method prospects to use laboratory TXRF instrumentation also. The aim of our further developments is to establish an instrumentation using the above performed methods which can be used in monitoring measurements.

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