

Impact of mineral components and selected trace metals on ambient PM10 concentrations

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ABSTRACT

PM10 levels of the mineral components Si, Al, Fe, Ca, Mg and some trace metals were measured at three different sites in the urban area of Vienna (Austria). Observed trace metal concentrations varied between less than 0.1 ng m^{-3} (Cd) and approximately 200 ng m^{-3} (Zn), mineral components showed enhanced concentrations ranging from $0.01 \text{ } \mu\text{g m}^{-3}$ (Ca) to $16.3 \text{ } \mu\text{g m}^{-3}$ (Si). The contribution of the respective mineral oxides to PM10 mass concentrations accounted on average for $26.4 \pm 16\%$ ($n = 1090$) of the PM10 mass, with enhanced rates in spring and autumn (monthly averages of up to 40%) and decreased contributions in the cold season (monthly averages below 10%). The atmospheric occurrence of Al, Ti and Sr could be assigned to crustal sources, whereas for the elements Ba, Ca, Fe, Mg, Mn and V an increased contribution of non-crustal origin was observed. PM10 levels of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Sn and Zn were predominantly derived from man-made emissions. Intersite comparison indicated that urban PM10 mass concentrations and PM10 levels of As, Pb and Zn were predominantly influenced from the transport of aerosols from outside into the city, whereas for the elements Ba, Mg, Ca, Cu and Fe a distinctly increased impact of local emissions was observed. The contribution of these urban emissions to total PM10 concentrations was estimated by calculating the so-called "urban impact", which was found to be $32.7 \pm 18\%$ ($n = 392$) in the case of PM10 mass concentrations. The investigated elements accounted on average for $31.3 \pm 19\%$ ($n = 392$) of the observed PM10 mass increase. The mean values for the "urban impacts" of individual elements varied between 25.5% (As) and 77.0% (Ba).

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1. Introduction

The short-term standard for particulate matter PM10 is violated in many European cities (e.g. Querol et al., 2004; Van Dingenen et al., 2004), therefore the current air-quality status of PM10 is under investigation in many countries, in particular to understand the source terms of the particulate matter and to propose a catalogue of measures to avoid further exceeding of the limiting value. For a targeted reduction of PM10 levels, detailed knowledge of sources and their respective contribution to the PM levels is required. Balancing total PM10 mass by chemical species or groups of compounds and multiple approaches including receptor sites outside the regulated area have been proposed to reduce the uncertainties specified above (e.g. Schauer and Cass, 2000; Maenhaut et al., 2002; Van Dingenen et al., 2004).

Not much attention was given until now to the mineral fraction of PM10 in European studies. This was due to the fact that the major crustal element Si was not analyzed in most studies since the

common filter material used for high-volume filter samples is glass or quartz fiber. Nevertheless some groups report data for Si in airborne particulate matter; in these studies Si was only indirectly determined from the contents of Al on the basis of experimental equations (e.g. Querol et al. 2001 used the equation $\text{SiO}_2 = 2 \times \text{Al}_2\text{O}_3$). For the direct measurement of Si the use of an organic filter substrate such as cellulose nitrate (e.g. Okuda et al., 2004), polycarbonate (e.g. Almeida et al., 2006) or Teflon (e.g. Furujsjö et al., 2007) is required. The results published so far demonstrate clearly that Si is an important contributor to ambient particulate matter concentrations. For example, Salma et al. (2002) derived from measurements of the elemental composition of PM10 samples at different sites in Budapest (Hungary) that the mean contribution of Si to the PM10 mass varied between 1.3 and 10.6%. Comparable results were derived by Vecchi et al. (2007) from a study performed in the urban area of Milan (Italy). However, for assessment of the whole mineral fraction in PM10 not only Si but also the remaining crustal elements Al, Ca, Fe and Mg have to be considered. Handler et al. (2008) reported for a site in Vienna (Austria) that these five mineral components accounted together for $20.5 \pm 4.4\%$ of the PM10 mass. Appropriate measures for reduction of ambient PM10 levels should therefore consider these crustal elements. For this

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purpose more detailed knowledge about occurrence (spatial and seasonal patterns) and sources of mineral components in airborne particulate matter is required.

The present article aims at covering new and additional information on the contribution of the mineral components Si, Al, Fe, Ca, Mg and the trace metals As, Ba, Cd, Cr, Co, Cu, Mn, Ni, Pb, Sb, Sn, Sr, Ti, V and Zn to urban PM₁₀ samples. Based on the analysis of three complete annual cycles of PM₁₀ samples, which were collected in 2004 at three air-quality-monitoring sites in Vienna (Austria), the seasonal variation of the elemental composition has been determined, information about the contribution of geogenic and anthropogenic emission sources has been deduced, and finally the impact of urban emissions on local PM₁₀ mass and individual element concentrations has been estimated.

2. Experimental

2.1. Sample collection

PM₁₀ aerosol samples were collected from January 1, 2004 to December 31, 2004 on a daily basis at three different sites within the city of Vienna. All investigated sites were part of the Viennese air-pollution-monitoring net operated throughout the whole sampling period by the Viennese Environmental Protection Office. Two sites were situated inside the city and thus influenced by local emissions as well as by long-range transport, whereas the third location was at the border of Vienna. The first inner-city site, Rinnböckstraße (160 m above sea level [a.s.l.]), is strongly influenced by traffic emissions from the nearby A23, the busiest highway in Austria. Kandlerstraße situated next to a small crossing in the west part of Vienna at 230 m a.s.l. represented the second city sampling site. The air quality at this site is additionally influenced by a nearby housed waste collection place and a parking lot for liquefied gas-powered public transit buses. This sampling location is therefore representative of urban suburbs with moderate traffic. The third site (Schafberg) was located on a hill (320 m a.s.l.) at the west border of Vienna. Sample collection was performed in a park next to a public swimming bath with several pools, which is surrounded by family houses and allotments. In case westerly wind flows this site represents the background air-pollution level of Vienna.

Aerosol collection was performed at all three sites in accordance to PM₁₀ sampling procedures standardized in EN 12341. PM₁₀ samples were collected simultaneously with automated Leckel Low Volume samplers (Sven Leckel GmbH, Berlin, Germany) at a flow rate of 2.3 m³ h⁻¹ and Digital High Volume samplers (Digital Elektronik AG, Hegnau, Switzerland) at 30.5 m³ h⁻¹. High-volume samples were collected on Quartz fiber filters (Pallflex, Tissuquarz 2500QAT-UP Ø 150 mm) and used for gravimetric analysis of the aerosol mass and quantification of carbonaceous species (not presented in this manuscript). Low-volume samplers were operated with cellulose ester filters (Pall, Gelman, GN-4 Metrical, Ø 47 mm), used for measurements of mineral components and selected trace metals. Air volumes collected within 24 h (from 0 am to 12 pm) varied between 54 and 56 Nm³ (at 273 K, 1013 hPa) for low-volume samples, for high-volume samples they ranged from 700 to 750 Nm³ (273 K, 1013 hPa). For transport between sampling sites and the EPO laboratory filter holders with the loaded filters were stored in stainless steel transport magazines (Leckel GmbH). After balancing, the filters were stored in polystyrene Petri dishes sealed with parafilm until analysis.

2.2. Analysis

Gravimetric analysis of the quartz fiber filters was performed by the Viennese Environmental Protection Office in accordance to EN

12341 after 48 h equilibration at 20 ± 1 °C and 50 ± 5% relative humidity. Sample filters were weighed before and after sampling, and the determined mass difference was equal to the amount of collected particulate matter.

Metal analysis was performed on the sampled cellulose ester filters with X-ray fluorescence spectroscopy (XRF), inductively coupled plasma atomic emission spectroscopy (ICP-AES) and electro-thermal atomic absorption spectroscopy (ET-AAS). Measurement of Si and Al has been conducted using a Philips X'Unique II (model 1480) wavelength-dispersive X-ray fluorescence spectrometer. For further analysis, samples were completely mineralized using a microwave procedure, hydrofluoric acid and *aqua regia*, followed by an open vessel treatment of the digested samples with perchloric acid for quantitative removal of elemental carbon. The prepared sample solutions have been investigated for selected trace metals and mineral components using ICP-AES (Ba, Ca, Cd, Cr, Co, Cu, Fe, Mg, Mn, Ni, Sn, Sr, Ti, V, Zn) and ETAAS (As, Pb and Sb). A more detailed description of the digestion procedure and the applied analytical methods has been presented recently (Handler et al., 2008).

Instrumental detection limits of the applied methods were calculated as three times the standard deviation of field blanks, which showed only marginally increased signals compared to procedural blanks, indicating that impurities of used reagents and filter substrates were negligible. The obtained instrumental detection limits varied from less than 100 ng L⁻¹ (Sr) to 20 µg L⁻¹ (Sn), which corresponds to method detection limits of 0.02 (Sr) to 4 (Sn) ng m⁻³ for the collected aerosol samples. The accuracy and applicability of the mentioned procedures have been evaluated by analysis of the certified reference materials NIST SRM 2709 (San Joaquin Soil) and NIST SRM 1646a (Estuarine Sediment). The concentrations determined for individual crustal elements and trace metals agreed well with the certified contents. Measurement uncertainties were calculated from the standard deviations of replicate analyses of these certified reference materials, derived results varied between less than 1% for major sample constituents (e.g. Ca, Fe, Si, etc.) and approximately 10% for elements with concentration levels close to the respective method detection limits (e.g. Cd and Co).

3. Results and discussion

3.1. PM₁₀ concentrations

Lowest particle mass concentrations were observed at the urban background site Schafberg, increased values were determined for Kandlerstraße, and highest PM levels were obtained for Rinnböckstraße, the site next to the inner-city highway. For all three sites the observed mean concentrations (Table 1) were within the typical range reported for urban samples (e.g. Stedman, 2002; Van Dingenen et al., 2004; Hueglin et al., 2005). Querol et al. (2004) presented a detailed compilation of PM₁₀ concentrations in airborne particulate matter for different European Urban areas indicating that Bern and London showed results comparable to the present study, whereas remarkably higher PM₁₀ levels were found for Berlin. Mean annual concentrations of the crustal elements Al, Ca, Fe, Mg and Si varied between 0.1 (Mg) and 2.1 (Si) µg m⁻³, and trace metals showed concentrations ranging from 0.3 (Cd) to 48 (Zn) ng m⁻³ (Table 1). The derived results were in good agreement with the findings reported in the literature for European cities (Artinano et al., 2003; Querol et al., 2004; Puxbaum et al., 2004; Götschi et al., 2005; Moreno et al., 2006; Dongarra et al., 2007).

The concentrations of the investigated main and trace components varied during the entire sampling period at all three sites, as can be deduced from the relatively large standard deviations and the concentration ranges presented in Table 1. Changes in the

Table 1
Concentrations for particle mass and individual elements in PM10.

	Kendlerstraße		Rinnböckstraße		Schafberg	
	Annual Mean	Range	Annual Mean	Range	Annual Mean	Range
Particle mass and mineral components in [$\mu\text{g m}^{-3}$]						
PM	27.7 ± 17.2	6.1 – 125	32.5 ± 18.0	7.8 – 124	20.4 ± 13.4	4.4 – 94.6
Si	1.84 ± 1.82	0.06 – 14.3	2.08 ± 1.92	0.18 – 16.3	1.90 ± 1.21	0.03 – 12.3
Al	0.52 ± 0.49	0.04 – 4.54	0.57 ± 0.53	0.06 – 4.86	0.34 ± 0.39	0.02 – 4.37
Mg	0.26 ± 0.34	0.04 – 2.81	0.25 ± 0.23	0.04 – 2.16	0.10 ± 0.08	0.03 – 0.75
Ca	1.31 ± 1.88	0.06 – 16.2	1.23 ± 1.36	0.10 – 13.0	0.43 ± 0.61	0.01 – 5.96
Fe	0.78 ± 0.36	0.05 – 2.99	0.74 ± 0.44	0.19 – 3.97	0.25 ± 0.25	0.04 – 2.86
Trace metals in [ng m^{-3}]						
Zn	40 ± 19	7.8 – 110	48 ± 26	11.5 – 196	27 ± 16	3.5 – 98
Cu	21 ± 15	5.2 – 120	20 ± 10	1.9 – 78	7.2 ± 7.1	0.8 – 110
Mn	13 ± 6.8	3.0 – 65	14 ± 8.3	3.8 – 72	6.3 ± 4.5	1.4 – 43
Ba	12 ± 6.8	2.9 – 57	12 ± 6.2	3.6 – 51	3.5 ± 2.5	0.3 – 17
Ti	15 ± 16	0.4 – 140	20 ± 21	0.5 – 181	9.8 ± 9.9	0.1 – 109
Pb	11 ± 7.7	1.1 – 53	11 ± 10	1.6 – 77	8.9 ± 7.1	0.1 – 41
Sr	2.7 ± 2.6	0.4 – 23	2.7 ± 2.2	0.1 – 19	1.2 ± 1.0	0.2 – 11
V	1.4 ± 1.0	0.1 – 5.5	2.1 ± 1.2	0.1 – 7.7	1.3 ± 0.8	0.2 – 4.2
Cr	5.5 ± 6.8	0.1 – 59	5.0 ± 3.2	0.3 – 13	3.8 ± 5.3	0.2 – 2.5
Cd	0.5 ± 0.4	0.1 – 2.8	0.5 ± 0.3	0.1 – 1.5	0.4 ± 0.3	0.1 – 2.4
Sn	2.0 ± 1.7	0.1 – 12	1.7 ± 1.5	0.1 – 8.2	1.5 ± 1.6	0.1 – 6.5
Ni	5.7 ± 5.7	0.2 – 36	9.9 ± 6.4	0.2 – 51	7.0 ± 13	0.1 – 98
Co	1.8 ± 1.1	0.1 – 4.7	0.9 ± 0.6	0.1 – 3.5	1.4 ± 1.6	0.1 – 11
As	0.9 ± 1.1	0.2 – 9.7	1.2 ± 1.7	0.2 – 16	0.7 ± 0.6	0.2 – 3.2
Sb	2.5 ± 2.3	0.9 – 19	3.3 ± 1.9	0.7 – 13	1.5 ± 1.6	0.7 – 19

meteorological conditions as well as changes in the source emission and transformation rates of the investigated species were responsible for the observed alterations with time. Thus co-variations in the time series of single element concentrations at a respective site, even at different concentration levels, are indicative of a common source. Accordingly, similar sources could be expected for the mineral components Si and Al, in particular geogenic sources and the resuspension of road dust, since an excellent correlation between these elements was observed at all three sites ($r^2 = 0.99$). Similar results were found for Ca, Mg and Sr with correlations in the order of $r^2 > 0.95$ between the examined elements at Kendlerstraße and Rinnböckstraße. A fairly high correlation ($r^2 > 0.85$) was observed between Fe, Mn and Ti at both inner-city sites, which showed also a relatively good correlation to the elements Ca, Mg and Sr ($r^2 > 0.8$), whereas compared to Si and Al only reduced correlations were found ($r^2 \sim 0.6$). These results indicate that Fe, Mn and Ti concentrations were rather determined by Ca and Mg sources than by Si and Al sources. The decreased correlations found between these elements at the site Schafberg ($r^2 > 0.7$) point to a reduced influence of Ca, Fe, Mg, Mn, Sr and Ti emitting sources at the background site. The trace elements Ba and Cu exhibited correlations of $r^2 > 0.8$ at all investigated sites, pointing to motor vehicle emissions as the primary source for ambient Ba and Cu levels in PM10. Between the concentration cycles of As, Cd, Co, Cr, Ni, Pb, Sb, Sn, V and Zn, only poor correlations were found, indicating that the atmospheric occurrence of these elements is influenced by different sources.

3.2. Seasonal pattern

Based on the results derived for individual samples, monthly concentration averages were calculated, which were used for construction of annual concentration cycles (Fig. 1). Interpreting the derived results, distinct differences were observed for the individual components. The PM10 mass (Fig. 1a) for example showed a seasonal distribution pattern with low summer and higher winter concentrations, which was expected for PM10 due to enhanced combustion activities of the civil population in the cold season. Interestingly, the elements Pb and Zn exhibited comparable

results, although no significant correlation was observed between the time series of the daily samples. Distinctly different annual concentration profiles were observed for the elements Al, Ca, Fe, Mg, Mn, Si, Sr and Ti, which revealed enhanced concentrations in spring and autumn and reduced values in summer and winter. Although the concentration curves of all mentioned analytes showed a bimodal behavior, clear differences between the individual elements were observed. In particular the elements Al, Fe, Mn, Si and Ti exhibited a profile with two comparable concentration maxima in March and September (Figure 1b presents the monthly average concentration profiles for Si as a representative example for this group of elements), whereas Ca, Mg and Sr showed a dominant maximum in the first four months and only slightly elevated concentrations in autumn (for illustration, the time series of Ca are depicted in Fig. 1c). The absolute concentration maxima obtained for Ca, Mg and Sr in March were caused by a high concentration episode in week 12 (March 15 – March 21). Within this period for all three sites the highest PM10 concentrations of the year had to be reported, which were along with an over-proportional increase in crustal element concentrations (the contribution of the mineral components Si, Al, Fe, Ca and Mg in this period yielded up to 35.6% of the PM10 mass). The source for this high-concentration episode was the street cleaning performed to remove the gritting material dispersed on the road surface as de-icing agent in winter. In contrast to the previously mentioned components Ba, Cu, and Sb revealed no distinct seasonal profile, and their concentrations vary slightly around the annual mean throughout the whole sampling period (Fig. 1d), a result which hints to omnipresent sources emitting continuously independent from seasonal or meteorological variations such as brake abrasion of motor vehicles (Sternbeck et al., 2002; Lough et al., 2005; Handler et al., 2008). This assumption explains the elevated Ba, Cu and Sb concentration levels at the inner-city sites, since traffic intensities at Kendlerstraße and Rinnböckstraße are distinctly higher than at Schafberg. For the remaining elements Cd, Co, Cr, Ni, Sn and V, no interpretable concentration patterns were derived, since most samples showed values in the order or below the respective detection limits, disabling the calculation of representative monthly averages.

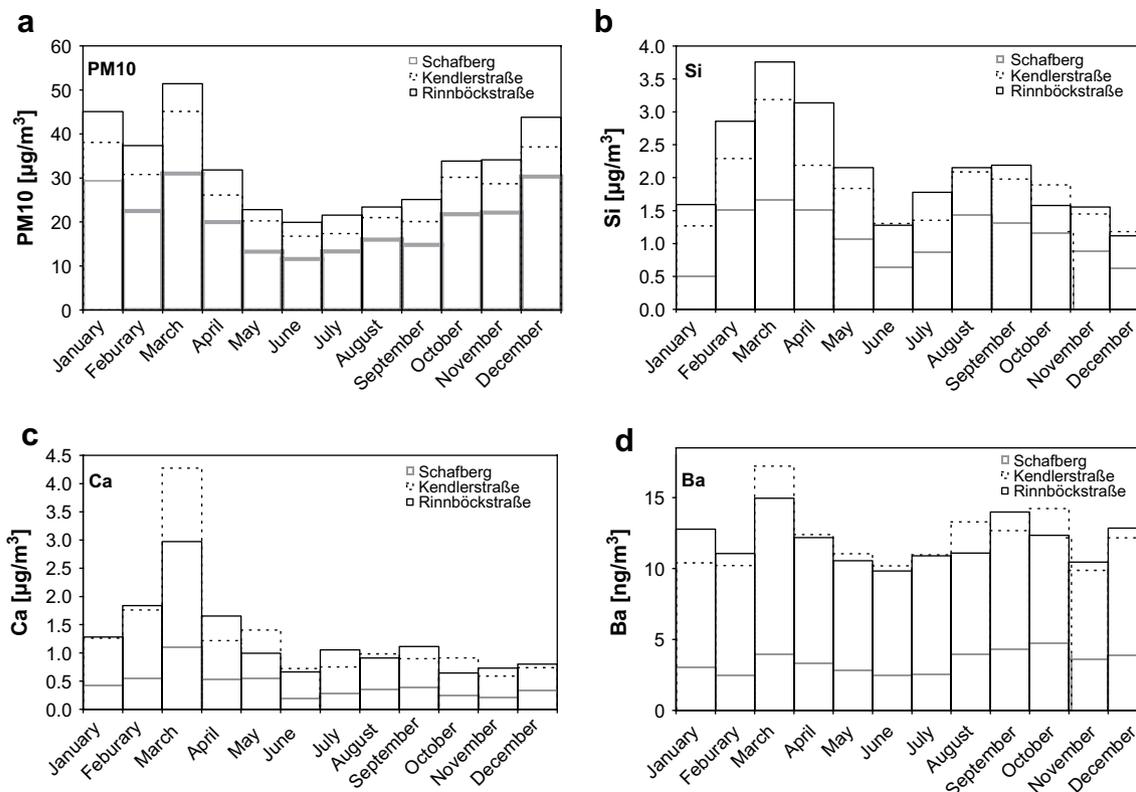


Fig. 1. Monthly averaged concentration profiles for particle mass (a), Si (b), Ca (c) and Ba (d) in PM10.

3.3. Contribution of mineral components and trace metals to PM10

The sum of the investigated crustal elements yielded on average $10.8 \pm 7.2\%$ (Schafberg), $15.5 \pm 8.9\%$ (Rinnböckstraße) and $17.5 \pm 9.0\%$ (Kendlerstraße) of total PM10 mass concentrations, whereas trace elements contributed not more than 1% to PM10 mass. These results are in good agreement with findings of Salma et al. (2002), Furusjö et al. (2007) and Vecchi et al. (2007) who reported mean contributions in the order of 3 to 32% of total PM10 mass concentrations for different sites in Europe. However, since the mineral components Si, Ca, Fe, Al and Mg were assumed to be present rather in the form of oxides than in elemental form, it is recommended to convert the measured element concentrations into the respective mass concentrations of the most common oxides for PM10 mass balances (Kleeman et al., 2000). Using this approach mean contributions of $31.7 \pm 16\%$ (Kendlerstraße), $27.8 \pm 14\%$ (Rinnböckstraße) and $22.3 \pm 17\%$ (Schafberg) were obtained for the mineral fraction (considering the oxides SiO_2 , Al_2O_3 , CaO , MgO and Fe_2O_3).

In view of the fact that the PM10 mass and the investigated elements showed differences in their annual concentration cycles, a varying contribution of mineral components and trace metals to the PM10 mass could be expected. Verification of this assumption was performed by calculating the concentration pattern for the mineral fraction and the remaining trace metals and subsequent comparison with the corresponding PM10 levels. Figure 2a presents the monthly averaged concentrations derived for the mineral fraction, indicating for all three sites a similar seasonal variation, with decreased concentrations in winter and distinctly enhanced values in spring and autumn. Monthly averages for cumulated trace metal concentrations yielded annual profiles with minor differences between the summer and winter months (Fig. 2b), excepting March for which increased results were observed at all three sites. In a next step the relative contributions of these two fractions to total PM10 mass concentrations were calculated, resulting in a

seasonal pattern with distinct variations throughout the whole year for both fractions. In the case of the trace metals, the relative contribution of this fraction to PM10 increased from winter to summer at all investigated sites (Fig. 2d), a result which was expected since the PM10 mass showed in summer a more pronounced concentration minima (Fig. 1a) compared to the cumulated trace metals (Fig. 2b). For the mineral fraction a more complicated behavior was observed, which results from the divergent seasonal variation of PM10 and individual mineral components. As depicted in Fig. 2c, the relative contribution of the mineral fraction to PM10 showed a bimodal distribution at all sites with maxima in spring and autumn and minima in the winter months. At the site Rinnböckstraße for example, the mineral fraction in April accounted for approximately 40% of the PM10 mass concentration, whereas for December a decreased relative contribution of only 13% was obtained (Fig. 2c). This result hints at reduced emissions of mineral components in winter, which might be explained with the coverage of natural and anthropogenic Si, Al, Fe, Ca and Mg emitting areas such as mountains, rocks, farmland, streets and buildings with snow, leading to a decrease in the source strength of these important emission sources. Additionally, enhanced combustion activities of the civil population in the cold season must be considered, which cause an increase of the PM10 concentration due to the emission of elemental carbon and organic species, resulting in a reduced impact of the mineral fraction.

3.4. Contribution of crustal and non-crustal sources to ambient PM10 levels

The presence of mineral components and individual trace metals in airborne particulate matter can be attributed to both natural and anthropogenic processes. Important geogenic sources are volcanic eruptions, dust storms, rock weathering and forest fires, and anthropogenic emissions are caused from the combustion

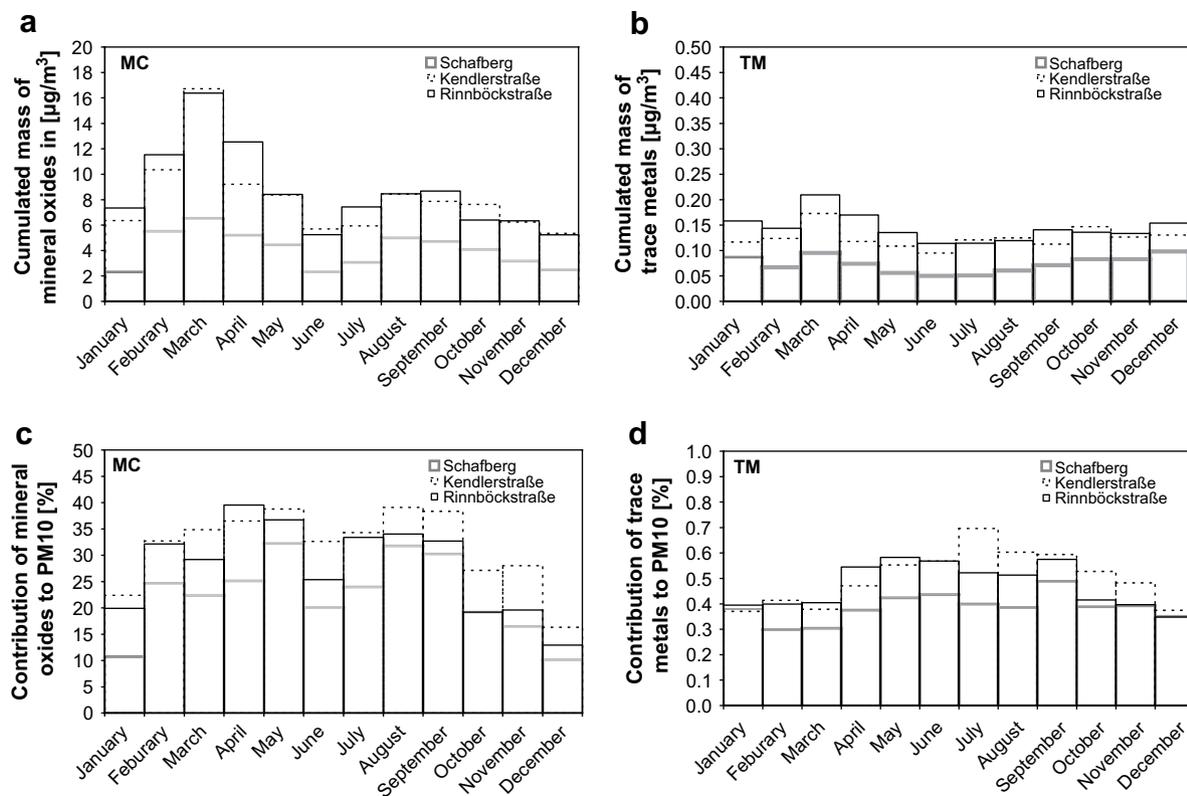


Fig. 2. Monthly averaged profiles for cumulated mineral oxides and trace metal concentrations (a,b), and their contribution to urban PM10 levels (c,d).

of fossil hydrocarbons (Pacyna and Pacyna, 2001), from metallurgical industries (Alastuey et al., 2006) and traffic (Sternbeck et al., 2002; Lough et al., 2005; Handler et al., 2008). A common approach for evaluation of anthropogenic influences on ambient trace metal concentrations is the use of enrichment factors (Zoller et al., 1974). However, application of this concept for differentiation between natural and anthropogenic sources of individual elements in airborne particulate matter is difficult, since anthropogenic processes such as resuspension of rock-forming mineral dust by traffic will be considered as a natural contribution although a purely anthropogenic phenomenon (Moreno et al., 2006). Thus, enrichment factors cannot be used as rigorous, objective or sensitive tools to detect or prove anthropogenic impact on the environment (Reimann and de Caritat, 2005).

Therefore, we used an advanced approach to provide information about the degree of human interference at the investigated sampling sites. In a first step we calculated the concentration ratios between the individual elements and the most important crustal component silicon for all sampling events. The derived results showed for most elements significant variations throughout the investigated sampling period, indicating additional and/or varying emission sources for these elements. In a second step annual cycles for each element were created, which were based on the monthly averages calculated from the individual sampling events. Comparison of the derived results with the composition of the "upper earth crust" (Wedepohl, 1995) indicated for Al, Ti and Sr only marginally increased element-to-silicon concentration ratios whereas all other elements revealed distinctly enhanced ratios (Fig. 3). The increase observed in the element-to-silicon ratios of Mg, Ca, Fe and all other investigated elements could be explained with the impact of non-crustal emission sources. Based on the assumption that the compositions of possible anthropogenic Si emissions (e.g. resuspension of road dust) are similar to that of natural emissions

(conservation of crustal element ratios), a differentiation between crustal and non-crustal emissions is possible.

The PM10 fraction which could be attributed to crustal origin has been estimated for each element using the determined Si concentrations and the results reported for the composition of the upper earth crust (Wedepohl, 1995). Information about the non-crustal origin of the investigated elements, which is indicative of anthropogenic influences since the results derived for this fraction represent a lower limit for the contribution of man-made emissions to the observed PM10 levels, has been derived from the differences between measured PM10 concentrations and the approximated crustal fraction (Table 2). As can be deduced from the presented results, the predominant part of the observed Al concentrations was of crustal origin, an expected outcome since Al as well as Si was derived from pavement wear and the resuspension of soil and road dust. A moderate increase in the contribution of non-crustal sources was obtained for Ti and Sr. Nevertheless, approximately 2/3 of the determined PM10 concentrations could be assigned to crustal emissions. The results obtained for Ba, Ca, Fe, Mg, Mn and V indicate that anthropogenic emissions are more important contributors to ambient concentrations levels in PM10 than sources which are related with the emission of Si (natural or man-made). Potential anthropogenic sources for Ba, Fe, Ca and Mg are traffic-derived emissions such as brake abrasion and resuspension of road dust (Lough et al., 2005; Handler et al., 2008), whereas oil combustion has been reported as an important source of Mn and V (Samara and Voutsas, 2005). The remaining elements As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Sn and Zn exhibited results greater than 90% for the contribution of non-crustal emissions to total PM10 concentrations, indicating that anthropogenic sources were predominantly responsible for ambient PM10 levels. Important man-made emission sources for these elements are combustion processes and construction activities (Pacyna and Pacyna, 2001; Querol et al., 2002; Puxbaum et al.

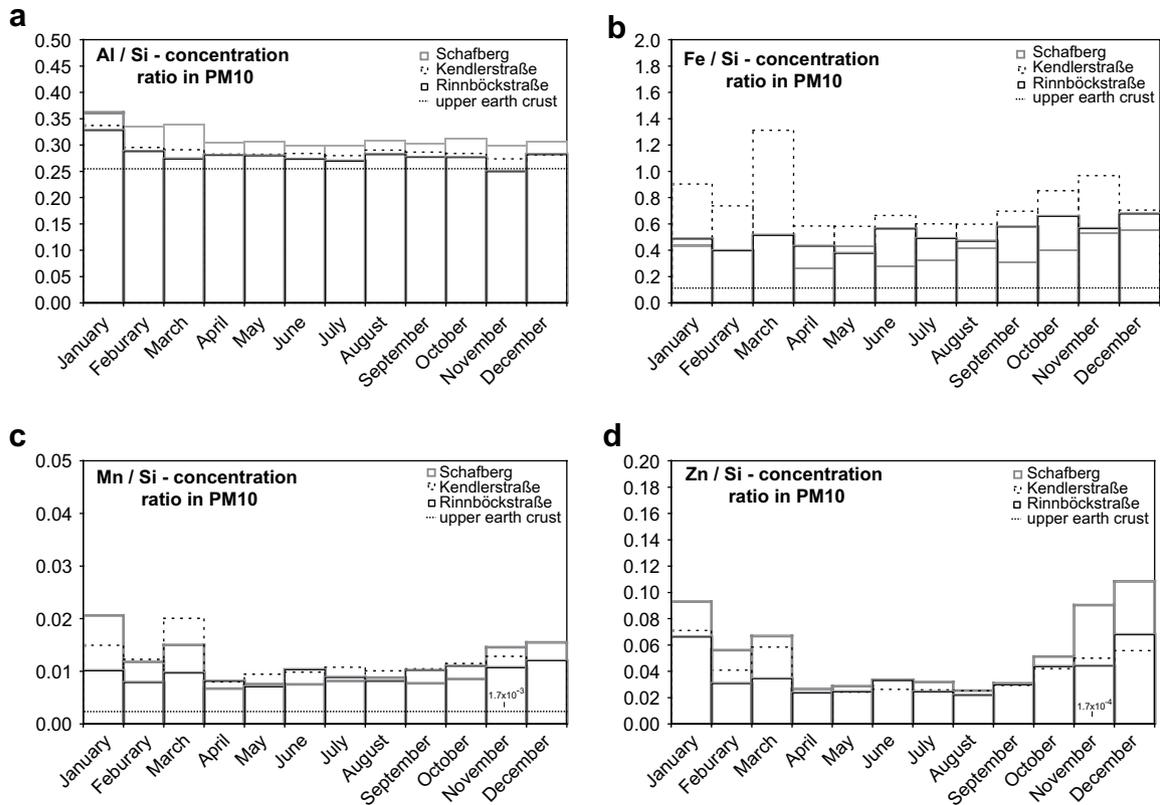


Fig. 3. Monthly averaged profiles for individual element to Si concentration ratios: Al (a), Fe (b), Mn (c) and Zn (d).

2004) as well as traffic emissions (Sternbeck et al., 2002, Lough et al., 2005, Handler et al. 2008). Comparison between the results of individual sampling sites revealed similar findings for most elements (Table 2). Only the elements Ba, Ca, Fe, Mg and Mn showed an enhanced crustal origin at the site Schafberg, a result which points to the presence of additional or even more effective sources for these elements at the inner-city sites.

3.5. Intersite comparison—coefficient of divergence (COD)

The great number of investigated components (21), together with the wide variation in chemical component concentrations

Table 2

Contribution of non-crustal emission sources to overall PM₁₀ concentrations, mean values (*n* varied between 156 and 357) and corresponding standard deviations were calculated using the entire data set for daily concentrations.

	Kendlerstraße [%]	Rinnböckstraße [%]	Schafberg [%]
Al	9.3 ± 12	7.2 ± 11	16.7 ± 12
Mg	62.9 ± 21	61.9 ± 18	56.7 ± 27
Ca	81.9 ± 13	81.0 ± 11	69.5 ± 23
Fe	76.8 ± 16	72.5 ± 15	58.0 ± 15
Zn	99.2 ± 0.7	99.2 ± 0.7	99.1 ± 1.2
Cu	99.6 ± 0.4	99.5 ± 0.5	99.1 ± 1.1
Mn	75.5 ± 16	75.5 ± 13	72.1 ± 19
Ba	67.6 ± 20	62.9 ± 22	44.2 ± 31
Ti	26.4 ± 30	16.1 ± 24	37.2 ± 34
Pb	98.8 ± 1.2	98.6 ± 1.7	98.8 ± 2.9
Sr	38.7 ± 29	30.4 ± 27	39.9 ± 31
V	70.8 ± 24	81.9 ± 12	81.4 ± 17
Cr	92.8 ± 8.0	92.3 ± 8.4	89.0 ± 18
Cd	99.8 ± 0.3	99.5 ± 0.3	99.8 ± 0.2
Sn	98.2 ± 3.3	96.7 ± 5.2	98.6 ± 2.2
Ni	94.5 ± 10	98.5 ± 3.5	96.4 ± 6.7
Co	93.2 ± 11	86.3 ± 13	92.2 ± 13
As	97.9 ± 1.9	98.2 ± 1.7	98.7 ± 1.3
Sb	99.9 ± 0.1	99.9 ± 0.1	99.9 ± 0.1

achieved during this study, hamper the evaluation of results. Particularly it is difficult to derive site-specific information about local or regional influences of main emission sources. For identification of similarities or differences in the temporal concentration patterns of the three sampling sites, the calculation of coefficients of divergence is recommended (Wilson et al., 2005), which are defined as follows:

$$\text{COD} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (1)$$

where x_{ij} represents the concentration of the investigated analyte on sampling event i at site j , x_{ik} is the concentration of this component for the same event i at site k , and n is the number of total sampling events. The coefficient of divergence (COD) is self-normalizing and can be calculated from short-term measurements as well as from long-term averages (Wongphatarakul et al., 1998). A COD value close to zero indicates similarity of the two investigated sampling sites, whereas COD values of divergent sites converge to one. Application of this procedure to the data set yielded the results presented in Table 3. In the case of Cd, Co, Cr and Sn, no COD values were presented, since for these elements a lot of samples showed concentrations below the respective detection limits, disabling the calculation of representative COD values (due to the limited number of appropriate data pairs).

The relatively low COD values obtained for the PM₁₀ mass (< 0.30) revealed that throughout the whole year the PM₁₀ levels of all three sites were mostly influenced by similar sources (e.g. regional emissions or long-range transport) and only to a minor extent by site-specific local emissions, which were assumed to be responsible for the differences between the individual sites. Comparable COD values were observed for Zn, Pb and As, indicating that emission sources are either spatially uniformly distributed or

Table 3

COD values between individual pairs of sampling sites calculated separately for each analyte using the entire data set for daily concentrations.

	Rinnböckstraße - Kendlerstraße	Kendlerstraße - Schafberg	Rinnböckstraße - Schafberg
Ba	0.17	0.58	0.59
Fe	0.18	0.59	0.55
Ni	0.54	0.52	0.56
Cu	0.21	0.54	0.55
Ca	0.29	0.54	0.54
Ti	0.35	0.45	0.54
Sb	0.39	0.32	0.49
Si	0.26	0.38	0.44
Mn	0.17	0.39	0.43
Mg	0.24	0.40	0.42
V	0.42	0.38	0.35
Sr	0.24	0.39	0.41
Al	0.26	0.35	0.41
As	0.33	0.23	0.34
Zn	0.17	0.26	0.33
Pb	0.22	0.30	0.28
PM10	0.13	0.19	0.27

there are no important local emission sources and the ambient concentration of these elements might be dominated by long-range transport. Different results were achieved for the investigated mineral components and remaining trace metals. Basically, for all elements a better uniformity was derived between Rinnböckstraße and Kendlerstraße, whereas an increased diversity was found between Schafberg and the two inner-city sites (Table 3). The good agreement between the COD levels of the inner-city sites implies that these sites are more similar to each other than to the background site. A result which indicates that either the background site or both inner-city sites were influenced by additional or at least more effective sources. Taking into account the divergent characteristics of the sampling locations, the observed differences could be attributed to supplementary emissions inside the city which cause an improved similarity between Kendlerstraße and Rinnböckstraße. The differences observed in the COD values of Al, Mg, Mn, Sb, Si, Sr and Ti for example (increased from about 0.25 to approximately 0.40) could be explained with an enhanced resuspension of road dust, weathering of facades and construction activities inside Vienna. For Ca an increased divergence between the inner-city sites and Schafberg was observed (COD values of 0.54), which results from the use of Ca-containing de-icing agents inside the city. Greatest differences were derived for COD levels of Ba, Cu and Fe, which showed CODs of approximately 0.2 between Rinnböckstraße and Kendlerstraße and enhanced values in the range of 0.54 to 0.59 between city sites and urban background. This outcome points to a distinct impact of local Ba, Cu and Fe emissions inside the city such as brake abrasion of motor vehicles (Lough et al., 2005; Handler et al., 2008), causing an improved similarity between Rinnböckstraße and Kendlerstraße and a rather poor uniformity between Schafberg and the mentioned inner-city sites.

3.6. Urban impact

The results presented so far demonstrated that most analytes exhibited enhanced PM10 concentrations at both inner-city sites when compared to the findings of the background site. The observed differences could be attributed to supplementary emissions inside the city, which cause an increase in the respective PM10 concentrations. In this context construction of buildings, road work, weathering of facades, traffic and small-scale industry as well as combustion activities of the civil population must be considered. The contribution of these urban emissions to total PM10 concentrations could be estimated by calculating the so-called “urban impact”, which is defined as the difference between observations at

the inner-city sites and the urban background site related to the results of the respective inner-city sites (Lenschow et al., 2001). However, when calculating the urban impact for the sites Kendlerstraße and Rinnböckstraße it has to be considered that the background site Schafberg was located at the west border of Vienna, and therefore only results from sampling events with more frequent westerly winds were used (which was the case in 196 days of 366 days in the year 2004). PM10 levels derived from days with prevailing easterly, northerly or southerly wind flows were neglected. Another prerequisite of this approach are positive concentration differences between the results of the two inner-city sites and the urban background site. Therefore, all events with a higher background than inner-city concentration were eliminated from the data set and not included in the calculation of the urban impact. Application of this concept yielded between 170 and 193 suitable sampling events for the PM10 mass and the investigated crustal elements at both sites, and reduced numbers of 120 to 150 samples were observed for most trace metals. Averaged results and the ranges observed for the urban impact of individual analytes are summarized in Table 4. In the case of Cd, Co, Cr, Sn and V, no mean values were presented, since less than 33% of the possible sample events fulfilled the mentioned requirements, disabling the calculation of representative impact factors.

The urban impact achieved for the PM10 mass at Kendlerstraße ($28.4 \pm 4.0\%$, $n = 193$) and Rinnböckstraße ($43.4 \pm 13.6\%$, $n = 193$) indicates that airborne particulate matter concentrations at these inner-city locations were mostly affected by regional emissions and long-range transport, and local emissions from the urban area contributed only to a minor extent to ambient PM10 levels. This result is in good agreement with recently published data of Puxbaum et al. (2004), who reported that up to 2/3 of ambient PM10 levels in Vienna originate from transport of polluted air masses from outside into the city. The chemical composition of the difference between PM10 mass levels of inner-city sites and the background sites, however, is considered to reflect the impact of the urban sources on the city aerosol. Harrison et al. (2004) reported that the aerosol forming the “urban increment” of roadside PM10 particles consists mainly of elemental carbon, organic material and mineral dust. In fact contributions of the mineral components and

Table 4

Urban impact (%) calculated separately for the two inner-city sites using only results from sampling events fulfilling the requirements mentioned in the text.

	Kendlerstraße		Rinnböckstraße	
	Annual Mean	Range	Annual Mean	Range
PM	28.4 ± 14.0	2.3 – 73.1	43.4 ± 13.6	4.3 – 76.9
Si	50.3 ± 22.0	2.3 – 93.0	58.5 ± 22.6	7.9 – 93.9
Al	44.9 ± 23.1	2.8 – 90.0	52.8 ± 24.1	4.4 – 93.6
Mg	52.3 ± 19.8	8.0 – 93.9	57.9 ± 15.6	9.1 – 86.5
Ca	68.6 ± 17.8	2.1 – 94.7	69.5 ± 18.6	12.3 – 95.9
Fe	76.4 ± 11.3	31.0 – 93.8	73.3 ± 12.7	27.7 – 91.7
Zn	37.9 ± 16.3	0.2 – 89.1	48.2 ± 17.1	3.4 – 87.6
Cu	71.5 ± 11.8	14.4 – 93.3	74.0 ± 14.1	11.4 – 96.8
Mn	57.2 ± 12.7	11.2 – 89.4	60.9 ± 13.9	12.8 – 84.7
Ba	76.1 ± 9.2	50.5 – 93.3	77.0 ± 11.9	17.5 – 94.0
Ti	61.1 ± 19.9	1.0 – 99.4	66.8 ± 22.8	13.5 – 97.5
Pb	37.4 ± 21.5	0.9 – 97.9	36.3 ± 23.4	1.6 – 97.0
Sr	53.3 ± 16.0	7.8 – 88.4	55.6 ± 19.2	6.5 – 87.7
V	*	1.0 – 71.5	49.7 ± 19.5	1.0 – 88.6
Cr	*	7.2 – 95.2	*	10.7 – 95.2
Cd	47.1 ± 25.7	1.9 – 92.2	*	2.1 – 94.1
Sn	*	58.3 – 89.4	*	41.6 – 92.3
Ni	60.0 ± 19.9	21.0 – 96.0	68.8 ± 22.7	11.9 – 98.7
Co	*	5.7 – 97.9	*	15.6 – 90.5
As	25.5 ± 27.9	0.1 – 80.8	29.8 ± 28.7	0.1 – 88.5
Sb	39.0 ± 29.2	0.1 – 87.0	56.3 ± 30.9	0.1 – 92.3

* Calculation of representative averages not possible (less than 65 valid sample pairs available).

trace metals investigated in this study were $23.5 \pm 12.6\%$ (Rinnböckstraße) and $40.7 \pm 22.1\%$ (Kendlerstraße) of the observed additional PM₁₀ pollution (urban impact), and the remaining part could be attributed to species which were not analyzed such as carbonaceous compounds or soluble ions like ammonium, nitrate and sulfate.

Interpreting the results derived for individual elements distinct differences were observed (Table 4). Whereas the elements As and Pb revealed similar results for the urban impact as observed for the particle mass, the mineral components Ca, Fe and Ti and the trace metals Ba, Cu and Ni showed distinctly increased relative contributions (60 to 80%) of local emissions to ambient concentration levels. These results confirm that local concentrations of As and Pb were predominantly caused by regional sources and long range transport (see previous chapter), while concentrations of Ba, Ca, Cu, Fe, Ni and Ti were largely affected by local emissions. The increased concentration levels of Ba and Cu could be linked to the enhanced influence of traffic emissions inside the town, whereas the “urban impact” observed for the crustal elements Ca, Fe and Ti appears to originate from the various dust-generating processes inside the city. Calcium for example is a normal constituent of soils and is used for construction materials and as a filler in road surfacing materials. Additionally, the use of Ca-containing de-icing agents inside the city has to be considered. Iron is emitted from geogenic sources such as soil and dust, and additionally anthropogenic sources such as traffic and steel production have been reported (Lough et al., 2005). For the elements Al, Mg, Mn, Si, Sr and Zn significant contributions of urban emissions to local pollution levels were found (with mean “urban impacts” in the order of 40 to 60%, see Table 4), but less pronounced than observed for Ba, Ca, Cu, Fe, Ni and Ti. Further interpretation of the derived data set revealed a good agreement between the findings observed for the two inner-city sites, a result which might be explained with the fact that both sampling sites were mainly influenced from traffic emissions. The relatively large intervals derived for the “urban impact” of individual elements at both sampling sites were also notable (Table 4), indicating that the effect of additional urban emissions on local pollution levels is quite variable (e.g. at the site Kendlerstraße the contribution of local emissions to ambient Cu concentrations ranged between 14.4 and 92.9%).

4. Conclusions

Levels of the mineral components Si, Al, Fe, Ca, Mg and selected trace elements in PM₁₀ were determined at 2 inner-city sites and one suburban site in Vienna (Austria) throughout the year 2004. The seasonal variation of particle mass and single element concentrations in PM₁₀ revealed distinct differences for individual components but only minor variations between the investigated sampling sites. Elements with common emission sources exhibited similar annual concentration profiles, for example the elements Al, Ca, Mg, Mn, Si, Sr and Ti showed bimodal concentration profiles with maxima in March and September. For Ba, Cu and Sb, no distinct profile was observed, which hints to omnipresent sources for these elements emitting continuously independent from seasonal or meteorological variations such as brake abrasion of motor vehicles.

The investigated mineral components were found to be major constituents of airborne particulate matter, a result which confirms recently reported observations. The contribution of the respective mineral oxides to PM₁₀ mass concentrations ranged on a daily basis between 0.1 and 70.8%, and monthly averages varied between 9.1% (December at the site Schafberg) and 39.7% (April at the site Rinnböckstraße). On average ($n = 1090$) the cumulated mass of SiO₂, Al₂O₃, CaO, MgO and Fe₂O₃ accounted for $26.4 \pm 16\%$ of the PM₁₀ mass.

Based on the determined silicon concentrations the fractions of PM₁₀ which could be assigned to crustal and non-crustal origin have been estimated. The derived results indicated that ambient PM₁₀ levels of Al, Ti and Sr were dominated from crustal sources, whereas for Ba, Ca, Fe, Mg, Mn and V, a considerable contribution of non-crustal (anthropogenic) emissions was observed. Highest man-made contributions were achieved for the elements As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Sn and Zn, suggesting that anthropogenic emissions such as traffic as well as industrial and combustion processes are the primary sources for these elements in PM₁₀.

PM₁₀ concentrations of the investigated elements appeared to be fairly similar at all sampling sites, which suggests that despite the long-range transport, the local emissions of these components were relatively evenly distributed in Vienna. Exceptions were the elements Ba, Fe, Ca, Mg and Cu for which distinctly increased concentrations were observed at the inner-city sites pointing to additional or at least more effective sources at these sites.

Estimation of the urban impact revealed that urban emissions contributed only for approximately 1/3 of local PM₁₀ mass concentrations, indicating that PM₁₀ levels of urban sampling sites were predominantly influenced by the transport of aerosols from outside into the city. Contrary to the results observed for PM₁₀ mass and elements such as As, Pb, V and Zn showed the mineral components Ca and Fe as well as the traffic-derived elements Ba and Cu and a distinctly increased influence of local emissions on ambient concentration levels, pointing to a decreased contribution of regional sources and long-range transport.

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