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VERTICAL DISTRIBUTION OF METAL DEPOSITION RATES NEXT TO A MAJOR URBAN ROAD IN BUDAPEST, HUNGARY

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Abstract: Dust and metal deposition are of important significance as an indicator of local air quality. However, their vertical deposition characteristics at greater heights are not well known. Settling dust samples were collected at four heights and at both sides of a 40 meters high building next to a busy urban road in Budapest, Hungary. In this study, concentrations and monthly deposition rates of nine elements are (Ba, Ca, Cr, Cu, Fe, Mn, Pb, Sr, Zn) evaluated. The study site can be characterized by average settling dust load showing a slight seasonal variation. Highest contamination was found for Cu, Pb and Zn. The sources of these metals could be the traffic and the weathering of materials of the built environment. The enrichment of these metals is generally the highest at the road-side of the building and at lower sampling heights, but Pb and Zn may show strong enrichment even at 33 m and at the low-traffic side of the building. This is generally the highest in the dry and windy periods suggesting the dominance of the re-suspension of urban soil and road dust in the metal deposition. The vertical dust and metal deposition patterns mostly correspond to the supposed air-flow model but just in case of highest chance of re-suspension a special model is needed to clearly describe the deposition patterns. This is probably due to the simultaneous effect of weather conditions and the morphology of natural and built environment.

Key words: settling dust, trace metals, geoaccumulation index, traffic pollution, urban geochemistry

1. INTRODUCTION

Airborne dust particles have been widely associated with health disorders as presented by numerous studies. In the past, their estimates have tended to be of total suspended particles, while recent attention has focused on the study of their PM10 and PM2.5 fractions which may penetrate to the innermost regions of the lung easily (Samet et al., 2000). However, particles with a diameter of up to 100 μm can be inhaled or ingested, and those below 32 μm may reach the bronchial tubes causing health damage by diseases or due to their mobile toxic components (WHO and UNEP, 1992).

Airborne dust particles can be divided into two groups: the settling dust sediment and the suspended particles (Remeteiová et al., 2007). The settling dust sediment is created by particles with great sedimentation power and their delay time in the atmosphere is very short. The major mass of this material consist of natural mineral phases, but anthropogenic particles are also widely detectable there (Farkas & Weiszburg, 2006). The particles, after their sedimentation, can also contaminate soils, groundwater (and even the food chain) by their mobile toxic components. Pollutants which are carried by settling dust cause generally near-source pollution. Therefore, dust deposition and that of the dust components have important significance as an indicator of local air quality (Vento & Dachs, 2007).

In urban environments, and especially in those areas where population and traffic density are relatively high, human exposure to hazardous substances is expected to be significantly increased (Popescu & Dumitrescu, 2000a). This is often the case near busy traffic axis in city centers, where urban topography and microclimate may contribute to the creation of poor air dispersion conditions giving rise to contamination hotspots (Vardoulakis et al., 2003). In such areas, airborne particulate matter is expected to show unique sedimentation characteristics.

Studies on sources, compositions, and distribution of settling dust are necessary for the risk assessment of dust to atmospheric quality, ecology, and human health. This is especially true for the urban environment, where the horizontal distribution characteristics of airborne particulate matter (and that of its toxic components) have been widely studied in the last few decades (Laidlaw & Filippelli, 2008). It has been also shown that people breathing at different heights are subjected to different concentrations of airborne particulate matter in the urban environment from the pavement up to 3 meters height (Micallef et al., 1998). However, there are no data on the sedimentation characteristics of dust and its components at greater heights. In this study, we aimed to study the changes in vertical deposition rates of metals (up to 33 meters at a building overtowering its environment) both from anthropogenic and natural sources at different sides of a tower building next to a busy urban road in Budapest, Hungary.

2. MATERIALS AND METHODS

Settled dust samples were collected according to the Hungarian standard (MSZ 21454/1-83) using glass pots of 2000 mL containing 500 mL distilled water and 0.500 ± 0.001 g of algaecide (analytical grade methyl 4-hydroxybenzoate) with continuous supply of the water. Altogether 8 sampling pots were placed on the front and the back sides, respectively of a building at a busy road at heights of 2, 9, 21 and 33 meters (Fig. 1). The number of overpassing vehicles and trains are over 50,000 and 250 per day there (Budaörsi Street, Budapest, Hungary), respectively (MK Zrt, 2011). The prevailing wind direction is towards the road (NW), which is strengthened by the dolomite hills behind and the plains in the front of the building. The building towers above its surroundings by 15-20 m so it may significantly influence the wind flow structures around itself. The 100-year-average seasonal precipitation amounts in Budapest are as follows: 134 mm in spring, 157 mm in summer, 132 mm in autumn and 109 mm in winter (Hungarian Meteorological Service, www.met.hu).

The continuous seasonal sampling started on the 1st of December, 2008 and finished on the 30th of November, 2010 (64 samples altogether). The sampling pots were drained at the first day of each season. The dust and water were separated by vacuum filtering using a Millipore filter with pores of 2 μm. Our magnetic measurements (data are not shown here) of the dust samples and the filtered liquid showed that there are no particles present in the water phase which could give magnetic sign (even superparamagnetic ones either). Additionally, there were no detectable dust amounts found in the liquid phase after centrifuging the liquid at 6000 rpm for 15 minutes.

After the weight measurements of the air dried samples the dust was separated in ultrasonic bath from the filters. The recovery of the dust was always above 98%. Concentrations of Ba, Ca, Cr, Cu, Fe, Mn, Pb, Sr, and Zn in the samples were analyzed by a Thermo Niton XL3 type X-ray fluorescence spectrometer pressed in alumina sample holders. Relative standard deviations of the parallel analyses are as follows: 13% for Ba, 9% for Ca, 19% for Cr, 7% for Cu, 4% for Fe, 13% for Mn, 7% for Pb, 6% for Sr, and 5% for Zn. Due to the separation of liquid phase, water-dissolved metal amounts are not presented here.

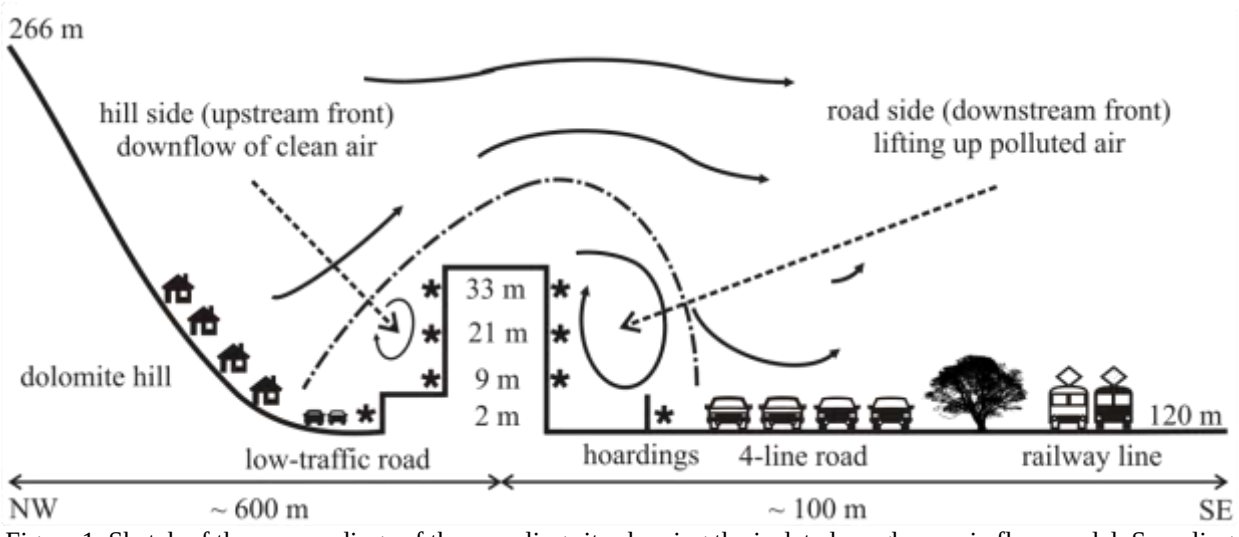

Figure 1. Sketch of the surroundings of the sampling site showing the isolated roughness air-flow model. Sampling locations are shown by the stars (✶), supposed air-flow directions by continuous arrows.

Monthly (30 days) deposition rate (De in mg/m2) for an element were calculated using the formula De=Ce*M/A/T*30, where Ce is the concentration of a given element (mg/g), M is the weight of the settled dust (g), A is the area of the sampling pot (m2) and T is the time of sampling (days). Threshold limit values are also given in monthly deposition rates in Hungary. Geoaccumulation indexes were also calculated after Ji et al. (2008) using the formula Igeo=ln(Ce/1.5Be), where Ce is the concentration of metal in the sample (mg/kg) and Be is the geochemical background value (mg/kg) of the same element. The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences. The geoaccumulation index consists of the following classes: <0 practically uncontaminated, 0-3 moderately contaminated, 3-6 heavily contaminated, >6 extremely contaminated. Regional background values were chosen using the geochemical map of Hungary (Ódor et al., 1997).

3. RESULTS AND DISCUSSION

3.1. Dust deposition rates

The average monthly dust deposition rate is 6.9 g/m^2, but it shows large variation between 0.5 and 20.9 g/m^2. These values are in similar ranges as reported for other urban environments (Krolak 2000; Inomata et al., 2009; Zhao et al., 2010; Muntean et al., 2012), but our data show a bit higher average values. The threshold limit value for the dust deposition is 16 g/m^2 for urban areas in Hungary (Bartófi, 2000). This value is exceeded only in 5 samples out of 64, exclusively in the summer season and at the front side of the building. The dust deposition has reached the 90% of the threshold limit value in further 5 cases. These samples were also collected in the summer season and at the front side of the building, as well as in the spring season at 2 meters at the front. However, there is no still significant difference between the front and back side of the building either in averages or in ranges of deposited dust amounts.

Autumn and winter samples are generally characterized by low quantities and nearly uniform vertical distribution (on average 3.0-3.4 and around 3.8 g/m^2 monthly, respectively) with highest values at 2 meters at front. For the latter we do not have a complete record for 2009, due to freezing and breaking of sampling pots. In spring samples the dust amounts are sharply decreasing upwards at the front side of the building, while a nearly uniform vertical distribution was found at the back side, with much higher values in 2010 (on average 9.4 g/m^2) than in 2009 (on average 6.7 g/m^2). The average quantities of settling dust are largest in the summer samples (10.4-11.2 g/m^2). This was also observed by Krolak (2000) in similar weather conditions. In the summer, the vertical distribution peak is observed at 9 m both at the front and the back sides of the building. That and the lowest deposition rates at 2 m back (prevented site by local morphology) are why generally higher average dust depositions were found at 9 m than at 2 m.

According to Zhao et al., (2010) strong wind and dry climate conditions enhance the dust deposition. Re-suspension of roadside soil and street dust may compose the major part of the settling dust. Up to 50-70% of the airborne dust may originate from this kind of re-suspension (Hunt et al., 1993; Young et al., 2002). This contribution to the airborne dust is much higher in dry seasons especially when it is coincide with the time of strong wind conditions. As this is the case at the end of spring and at the most part of summer in Budapest, Hungary, the highest dust deposition can be explained primarily by the weather conditions. Contrarily, wet surface inhibits this process resulting in low dust deposition in autumn and winter. Unfortunately, the excess growth of algae in the sampling pots during summer may have also influenced the final weight of our samples despite of the algaecide used. We think, however, that they do not influence the dust deposition pattern significantly and do not have any effect on the metal amounts deposited.

According to the isolated roughness air-flow model, high buildings may affect wind flow structures in two ways (Oke, 1988): first, creating downflow close to the upstream front elevation (the back side in our case) which transports clean air to pedestrian levels, and second, developing a separation bubble over the downstream front elevation (the front side) which lifts up the polluted air from the pedestrian level (see Fig. 1). The seasonal dust deposition patterns found generally correspond to this model except in summer, when the maximum in dust deposition at 9 meters claims an explanation by a specific air-flow model. This special case, however, may be related to the co-influence of local morphology and weather conditions.

3.2. Enrichment of metals in the settling dust

The average concentrations and their ranges in the settled dust samples are shown in Table 1 for the 9 studied metals. The concentrations are in the similar range as found in Central European towns (Krolak, 2000; Popescu & Dumitrescu, 2000b). As background values for settling dusts are not available, geoaccumulation indexes for the settling dust samples were calculated to compare their metal concentrations

to that of surface geological formations representing the regional geochemical background. Table 1. Metal concentration and deposition in the settling dust.

	Average concentrations and their ranges		Average depositions and their ranges	
	(mg/kg)		(mg/m^2/30days)	
Ba	479	235-780	3.8	0.2-12.9
Ca	28,511	6301-62,978	237	4.4-1084
Cr	143	90-215	0.8	0.1-2.3
Cu	291	152-627	1.8	0.2-8.3
Fe	21,959	8726-31,848	154	4.2-580
Mn	512	284-1035	3.5	0.3-11.1
Pb	774	50-6011	8.1	0.1-126
Sr	102	12-179	0.8	0.1-3.0
Zn	1379	374-3342	10.3	0.3-50.0

Based on this index, two main groups of the studied metals were found which could be also subdivided (Fig. 2). The first group is that of Ca, Fe, Mn and Sr showing no significant enrichment in the settling dust. In this group Ca and Sr show moderate enrichment in some cases. These metals are considered to be the marker of construction dust in urban areas on the one hand (Ji et al., 2008), while their slight enrichment can be also due to the presence of dolomite hill behind the building, on the other. In the particulate matter of Meknes, Morocco, Tahri et al., (2012) also found that these elements originate mainly from anthropogenic sources, but the potential of their contamination from anthropogenic sources cannot be ruled out in the case of Ca and Mn, while Cr, Cu, Pb and Zn were attributed mainly to anthropogenic sources.

The other studied metals all show moderate enrichment in the settling dust samples. However, as Ba and Cr show only a weak enrichment in all of the studied samples, Pb, Zn and Cu show heavy contamination in several samples. Copper and Zn can be characterized by heavy contamination primarily at the front side and at lower heights, while Pb at the back side too. Highest geoaccumulation index values were found primarily in the summer and some of the spring samples. With a detailed study of 15 Chinese cities, Ji et al., (2008) found that the coarse dust fraction is occasionally slightly contaminated with Ca, Cr, Ni and Cu, while the fine dust fractions are mostly heavily contaminated with Cr, Co, Cu, Pb and Zn. According to the detailed mineralogical and magnetic analyses of the same samples as presented here (Márton et al., 2011), the main source of heavy metal pollution supposed to be the traffic in our case. Metals showing contamination can originate from traffic sources (Sutherland, 2000): Ba is used in lubricating oil additives and fuel synthesis, Cu in bearing and brushing wear, moving engine parts and brake-lining wear, Pb in tire wear, lubricating oil and grease, bearing wear and brake linings, and Zn in vulcanization of tire wear, motor oil, grease, under coating and brake linings. Additionally, some of these metals (Cu, Pb and Zn) are common components of the built environment (concrete and asphalt) too.

3.3. Metal deposition rates

The average monthly metal deposition rates and their ranges in the settled dust samples are much higher than metal deposition in rural environments (Kvietkus et al., 2011). Also lower values were found for Cu, Pb and Zn in several urban areas, e.g. Tokyo, Japan (Sakata & Marumoto, 2004) and Chicago, USA (Yi et al., 2001). However, similar values were found in Clermont, USA (Shahin et al., 2000) and in numerous Polish towns (Krolak, 2000) and much higher values in Izmir, Turkey (Odabasi et al., 2002).

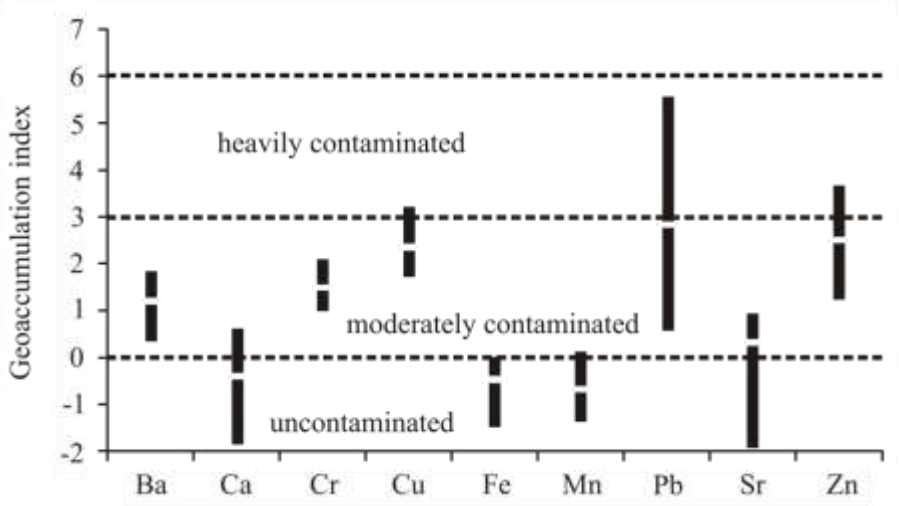

Figure 2. Averages (white lines) and ranges (black columns) of geoaccumulation indexes for the studied metals.

Threshold limit value is only given for Pb in Hungary which is 1.2mg/m^2 (Bartófi, 2000). This value is exceeded in most of the studied samples.

Monthly metal deposition values were in similar range for the different seasons for a given element. The only conspicuous change in deposition values were found in the summer samples at 9 meters and also at the back side of building, where 2-5 times higher values were found for each studied metal compared to all other sampling date and place. As this phenomenon was observed for each studied metal, it could not be explained by the changes in metal sources. Available data do not allow drawing clear conclusions but summer weather conditions and air flow characteristics could be the primary reason for this special deposition characteristic in our case. Other studies did not find significant seasonal variation in monthly metal deposition in urban areas (Odabasi et al., 2002) or they have found slightly higher values in the heating seasons (Krolak, 2000). In our case however, the contribution of soil/dust re-suspension could be so significant (mainly in the summer season) that it may overwrite the effect of certain anthropogenic activities.

Hierarchical cluster analysis based on the linear correlation between the metal deposition rates at the different sampling sites showed that there are three major metal groups showing similar characteristics in their spatiotemporal deposition pattern (Fig. 3). These groups are as follows: 1) Ba, Pb; 2) Ca, Fe, Mn, Sr, Zn; and 3) Cu, Cr. These latter two metals show unique deposition pattern which do not show any similarity to that of other metals. Additionally, metals in the first two groups show much more similarity to each other in their vertical deposition patterns that Cu or Cr do. Such differences in deposition patterns suggest differences in host phases for the studied elements.

Generally, there are no differences in their order of magnitude of the metal depositions when different sampling levels are compared (Fig. 4). The only sampling level, where consistently low values were found is at 2 meters and at the back side of the building. This sampling site is at a protected place due to the morphology of natural and built environment. Slightly higher differences within the different sampling levels were found at the front than at the back side. The dominant metal deposition pattern is the decrease of metal deposition upwards at the front side, except summer when there was found a maximum at 9 meters. This pattern was the most conspicuous for Ba and Pb. Most of the metals showed much more uniformed pattern with lowest values at the highest sampling site. Highest values were found for Cu and Cr at the lowest sampling point in each case. Contrarily, the highest metal deposition was found often at the highest sampling level at the back side of the building with no preference for any metal or season. However, metal deposition patterns show much more similarity than at the front side.

Similarly to the dust deposition characteristics, higher metal depositions at lower levels at the front side and at the higher levels at the back side of the building correspond to the isolated roughness air flow model. However, summer weather conditions (dry and strong winds) may significantly modify this deposition pattern in our case.

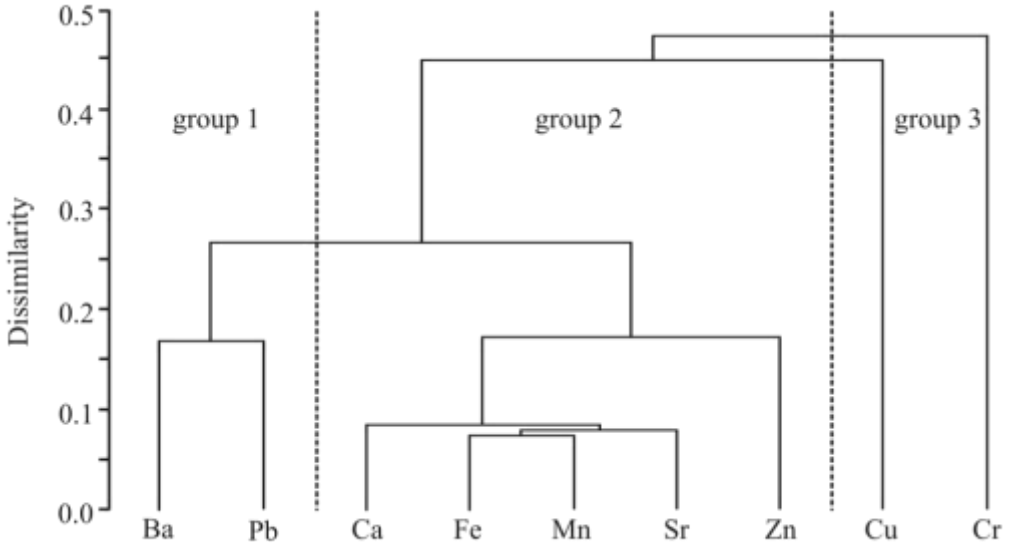

Figure 3. Results of the hierarchical cluster analysis of the metal deposition rates. The higher the similarity, the more similar the vertical deposition pattern.

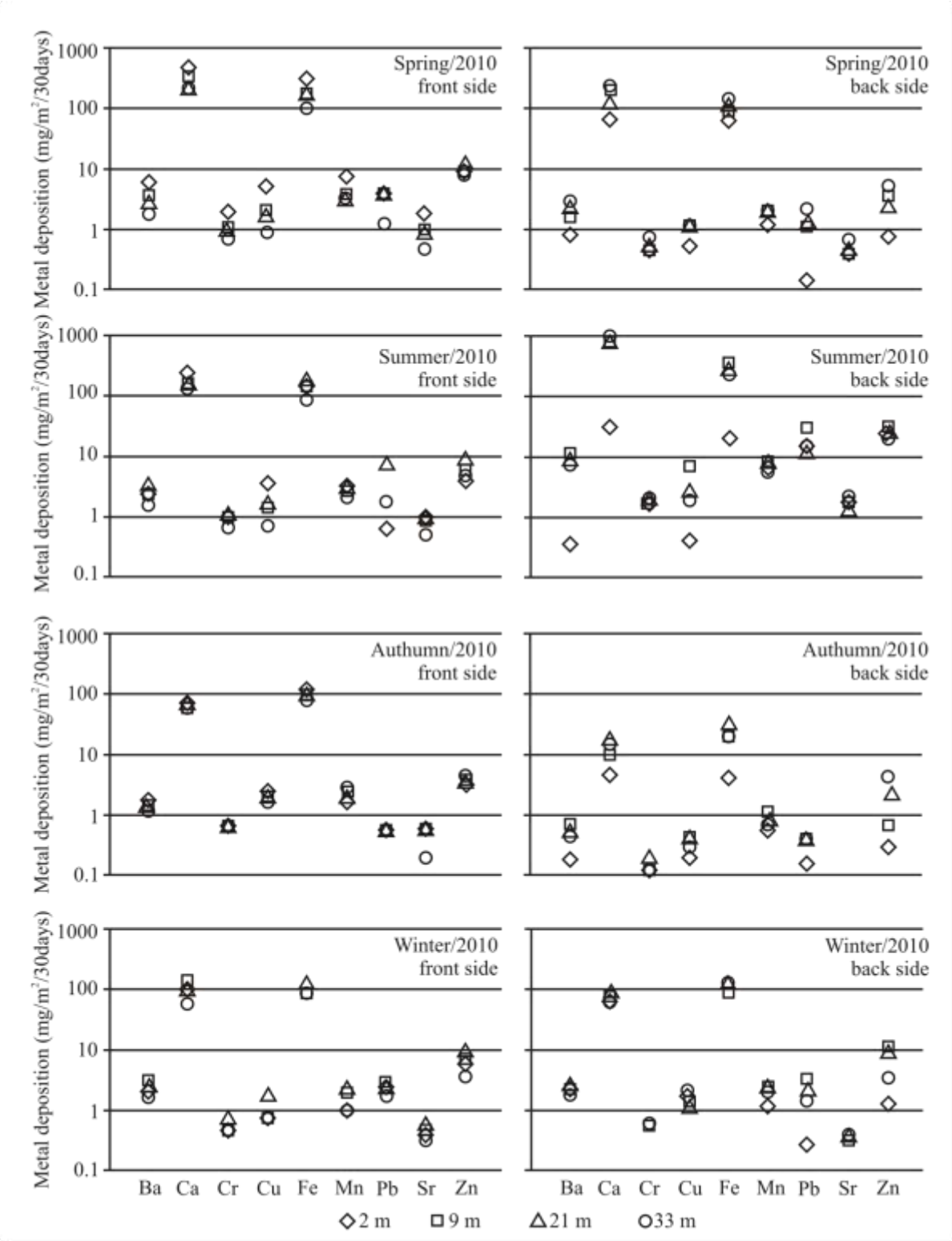

Figure 4. Vertical metal deposition patterns for the period between 1/03/2010 and 28/02/2011.

4. CONCLUSIONS

The study site can be characterized by average settling dust load with deposition values below the threshold limit value. The vertical deposition pattern show slight seasonal variation. Highest dust loads were found in summer which is primarily due to weather characteristics.

Calcium, Fe, Mn and Sr do not show significant contamination in the samples, but the occasionally high concentrations of Ca and Sr were related to their presence of construction materials and the potential effect of local geology. Contrarily, the samples were moderately contaminated by Ba,

Cr, Cu, Pb and Zn. These latter two metals often showed heavy contamination, too. The enrichment of these metals is generally the highest at the road-side of the building and at lower sampling heights, but Pb and Zn may show strong enrichment even at 33 m and the former metal at the low-traffic side of the building. Their enrichment is generally the highest in the dry and windy periods suggesting the dominance of the re-suspension of urban soil and road dust in the metal deposition.

This process dominates the seasonal deposition pattern not only of these metals but also that of the dust. The similar vertical deposition pattern of both dust and metals also support this dominance. The vertical dust (and metal) deposition pattern mostly corresponds to the supposed air-flow model but just in case of highest chance of re-suspension a special model is needed to clearly describe the deposition patterns. This is probably due to the simultaneous effect of weather conditions and the morphology of natural and built environment.

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