Atmospheric Pollution Research

Characterization of trace elements in PM$_{2.5}$ aerosols in the vicinity of highways in northeast New Jersey in the U.S. east coast

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ABSTRACT

To characterize the spatial and temporal variations of atmospheric concentrations of trace elements in particulate matter with diameter less than 2.5 µm (PM$_{2.5}$) derived from vehicle emissions, aerosol sampling was conducted near the heavily trafficked New Jersey Turnpike (NJTPK) at East Rutherford, New Jersey in the U.S. east coast from September 2007 to September 2008. Aerosol samples were collected by Partisol–FRM Model 2000 air samplers at three sites within 150 m away from the NJTPK and analyzed by inductively coupled plasma mass spectrometry (ICP–MS). Concentrations of 13 trace elements (i.e., aluminum, cadmium, cobalt, chromium, copper, iron, lead, manganese, nickel, antimony, scandium, vanadium and zinc) varied as a function of distance away from NJTPK within 150 m. The concentrations of Al, Cd, Cr, Cu, Fe and Pb along the three sites decreased significantly away from the highway. In contrast, the concentrations of Mn, Sb, and Sc showed significantly positive correlations with distance. There were not clear concentration trends for Co, Ni, V and Zn with distance. Most trace elements showed slightly higher concentrations in spring and summer, except for Ni that was more enriched in the fall and winter. All measured trace elements showed higher concentrations on weekdays than on weekends, indicating high impact of traffic emissions on air pollution. In both summer and winter, most trace elements were enriched in daytime aerosols, and this trend was stronger in the winter. Meteorological conditions, mainly wind speed and wind direction, were found to affect the spatial and temporal concentration variations of trace elements in the ambient air at this location.

1. Introduction

Fine aerosol particles in the ambient air, particularly particles with diameters less than 2.5 micrometer, have a strong impact on human health by inducing illnesses such as inflammation on the epithelial surfaces in the lungs (e.g. Dockery et al., 1989; Harrison and Yin, 2000; Poschl, 2005). In addition, fine particles from traffic related emissions are often enriched in potentially toxic trace elements (Hlavay et al., 1992; Fernandez Espinosa et al., 2002), such as Cr from fuel combustion, Sb and Cu from brake–lining materials (Huang et al., 1994), and Zn from tire tread (Adachi and Tainosho, 2004). When the concentrations of trace elements in aerosols exceed critical thresholds, they may pose potential toxic effects on human health and ecosystem (Berggren et al., 1990; Carter et al., 1997; Spurny, 1998). Therefore, it is important to quantify trace element concentrations in PM$_{2.5}$ aerosols near the highways, significant sources of air pollutant emissions.

Concentration gradients of air pollutants from vehicle emissions on highways have been studied in several urban regions such as California in the U.S. (Dzubay et al., 1979; Kim et al., 2002; Zhu et al., 2002a; Zhu et al., 2002b) and in other countries, such as the Netherlands (Brunekreef et al., 1997; van Vliet et al., 1997; Roorda–Knape et al., 1998) and Australia (Morawska et al., 1999; Hitchins et al., 2000). Zhu et al. (2002b; 2004) found that the concentrations of black carbon decreased away from highways within a distance of 150 m in Los Angeles, and aerosol mass concentrations were also found to be decreasing away from highways in Australia (Hitchins et al., 2000) and in the Netherlands (Janssen et al., 1997). However, some studies found no obvious

concentration variations near highways, neither in total PM mass nor in fine particulate mass (Morawska et al., 1999). On the other hand, temporal concentration variations of air pollutants were also observed. Kim et al. (2002) and Zhu et al. (2004) reported higher concentrations of ultrafine particles and black carbon in summer during the daytime, while temporal variations of trace element concentrations were also found to be a function of the prevailing meteorological conditions including their upwind sources (Singh et al., 2002).

The most of the recent studies on vehicle emissions have primarily focused on the concentrations of gaseous pollutants, black carbon, the total mass and the number concentrations of particles; few measurements have been made for traffic–generated trace elements in PM$_{2.5}$. Besides, there is little information on temporal concentration variations of trace elements on the seasonal, weekday/weekend, and diurnal basis near highways, which is important to assess the short–term air quality and its potential relationships with episodes of un–healthy events. This research focuses on the characteristics of selected trace elements which may pose toxic effects on human health in PM$_{2.5}$ particulate matter, heavily impacted by traffic emissions. We collected one–year time series of PM$_{2.5}$ samples from three sites within a 150 m distance from the New Jersey Turnpike (NJTPK), a major highway in the state of New Jersey, to quantify the temporal and spatial variability of these elements. Results from this work can provide useful information on chemical composition of fine particulate matter derived from traffic. The results can also be used to support further studies on the impacts of traffic–generated pollutants on human health.

2. Methods

2.1. Sampling

To characterize the concentration variations of selected trace elements associated with $PM_{2.5}$ impacted by highway traffic emissions, three sampling sites were set up at 50 m (platform A), 100 m (platform B) and 150 m (platform C) from the median strip of the NJTPK (48.84°N, 74.10°W), located at East Rutherford (Figure 1) in northeastern New Jersey. The NJTPK is a major high-way with a traffic volume of more than 80 000 vehicles per day most of the time. During snowy weather events, snow plowing and salting services are usually used. This sampling area, next to the NJTPK, is an open field covered by bushes, wetlands, and dirt roads. Three sampling platforms were constructed along a flat plain perpendicular to the NJTPK at a height between ~2 to 5 meters above the ground. Aerosol samples were collected by three identical R&P Partisol®–FRM Model 2000 air samplers with $PM_{2.5}$ inlets (Rupprecht&Patashnick Co., Inc, NY) that operate with a flow rate of 16.7 L min^{-1} at each site. Teflon membrane filters were used as the sampling media (VWR, 1.0 μm pore size, 47 mm diameter). For a time–series study, samples were collected every sixth day at 24 hour intervals (8:00 am to 8:00 am the following day) from 09/21/2007 to 09/21/2008 at three sites simultaneously (Table 1). Fewer samples were collected from platform B, due to sampler operation failure. In addition, two 2–week periods of intensive sampling were conducted in winter (01/2007 and 03/2007) and summer (07/2008), with samples being collected twice a day (7:00–19:00 and 19:00–the next 7:00) to further explore seasonal and diurnal variations in trace element concentrations. During each intensive period, 12 samples were collected at each platform except for platform B, due to sampler failure. After each sampling, filters were stored immediately in a refrigerator until chemical analysis.

Table 1. Sampling information

Sampling Type	Sampling period	Number of Samples		
		Platform A	Platform B	Platform C
Time series	09/21/07 - 09/21/08	59	47	58
Winter Intensive	01/29/08 - 01/31/08	6	2	6
	03/07/08 - 03/09/08	6	6	6
Summer Intensive	07/17/08 - 07/29/08	10	10	10
	09/04/08	2	2	2

2.2. Chemical analyses

The concentrations of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sc, V and Zn were determined by inductively coupled plasma mass spectrometry (ICP–MS) (Finnigan™ ELEMENT2, Thermo Scientific) at the Institute of Marine and Coastal Science at Rutgers University. The detection limit of the instrument for each tested trace element is less than 1 ppq and the precision is ~2%. All sample filters were first digested with concentrated HNO_3 (Optima A460–500, Fisher Scientific) and HF (Optima A463–250, Fisher Scientific) using a Microwave Accelerated Reaction System (MARS, CEM Corporation) (EPA method 3052). There were three digestion steps: (1) heating to 170 ± 5 °C in 5.5 minutes, (2) holding at 170 ± 5 °C for 30 minutes, and (3) cooling down to room temperature. Di-gested solutions were then diluted by Milli–Q water (18 MΩ cm^{-1}) (Milli–Q Academic System, Millipore Corporation) to reach solution acidity with ~4% of HNO_3 before injection into the ICP–MS system.

The digestion recovery was quantified by Standard Reference Material 2783 (National Institute of Standards and Technology),

using the same digestion procedures for samples. The recovery for Al, Cu, Fe, Pb, V, Zn, Co and Cr ranged from 91.3 to 103%, except for Ni which was 46.4%, based on which the concentrations of this element in samples were adjusted.
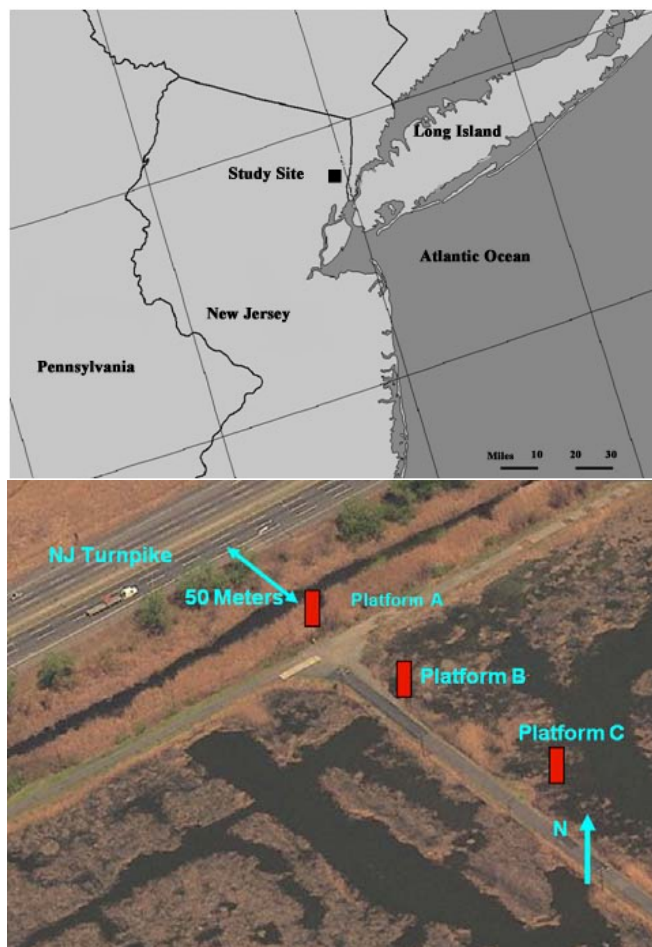
Figure 1. Maps of the study region (upper panel) and sampling sites (lower panel, modified based on the original project proposal).

3. Results and Discussions

3.1. Annual concentrations of trace elements

Table 2 shows the mean concentrations and ranges of the 13 trace elements from one–year time–series samples. The average concentration of Cu, a typical element from brake–lining materials, was 39 ng m^{-3} at platform A, with a range from 1.47 ng m^{-3} to 266 ng m^{-3}. This average value of Cu was significantly higher than those observed at sites with less traffic impacts in this region, such as at Rutgers Garden in New Brunswick in central New Jersey (7.7 ng m^{-3}) and at Sandy Hook on the New Jersey coast (4.7 ng m^{-3}) in New Jersey (Gao et al., 2002). This suggests that traffic emissions could be a significant contributor to atmospheric Cu at this location. A strong correlation was found between Cu and Sb at platform A ($R^2 = 0.562$); as Sb and Cu could be co–products in brake processes (Stechmann and Dannecker, 1990; Pakkanen et al., 2001; Weckwerth, 2001), high concentrations of Cu observed at this location could be an indicator of the extensive use of brakes in the vehicles. Additional source for atmospheric Cu over this area could be a copper mine in nearby Watchung Mountain, Bound Brook, New Jersey. The concentrations of atmospheric Ni ranged from 0.105 ng m^{-3} to 29.0 ng m^{-3} with an average of 7.79 ng m^{-3} at platform A, which was significantly higher than the average Ni concentrations at two less–traffic–impacted sites in New Jersey (Gao et al., 2002) and one rural site in New York (Yang et al., 2002), and almost tripled the concentrations at road sites in Spain and

England (Fernandez Espinosa et al., 2001; Harrison et al., 2003). The average concentration of Sb at platform A was approximately 1.39 ng m^{-3}, lower than at less–traffic–impacted sites in New Jersey (Gao et al., 2002) and New York (Yang et al., 2002) but consistent with those observed in England and India (Kumar et al., 2001; Harrison et al., 2003). However, Pb and Zn had average concentrations 3.26 ng m^{-3} and 14.7 ng m^{-3} respectively, and they were less than the concentrations observed near highways in Cincinnati (Martuzevicius et al., 2004). V had a mean concentration of 2.84 ng m^{-3} at platform A, two times less than the other roadsides in the Netherlands and Japan (Janssen et al., 1997; Furuta et al., 2005). These results clearly indicate that vehicles as pollution emission sources contribute differently to different trace elements in the ambient air, and there are also regional differences with respect to the strength of pollutant emissions.

To roughly separate trace elements from crustal and non–crustal sources, crustal enrichment factors (EFs) were applied to the results. The equation for the calculation of EFs is shown below:

$$EF_{Al}(X_i) = \frac{(X_i/Al)_{PM2.5}}{(X_i/Al)_{Crust}} \qquad (1)$$

where $(X_i/Al)_{Crust}$ is the average ratio of each trace element to Al in the crust (Taylor and McLennan, 1985), and $(X_i/Al)_{PM2.5}$ is the ratio in PM$_{2.5}$ samples, with Al being used as a crustal representative element. By convention, an arbitrary average EF value of <10 indicates that a trace element in an aerosol has a significant crustal source, and in contrast, an EF value of >10 is considered as a significant proportion of an element with a non–crustal source (Chester et al., 1999).

The sequence of trace element EFs at each of the three platforms with respect to the levels of the crustal enrichment was the same as indicated in Figure 2: Sc, Fe, and Mn are crustal elements (EFs≤10) and the others are non–crustal elements (EFs>10). Since Al, Sc, Fe and Mn are typical crustal elements. Their occurrence near the highway may suggest that re–suspension of soil particles from the ground contribute to their abundance in aerosols at the sampling sites.
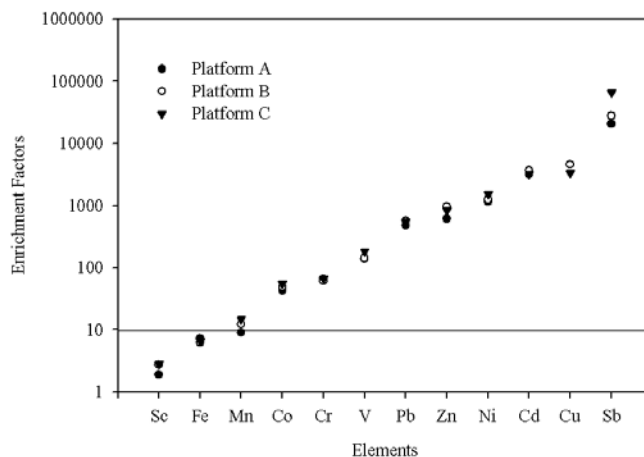

Figure 2. *Enrichment factors of trace elements in PM$_{2.5}$ samples at three platforms. The solid line indicates EFs = 10, which is used as a separation between crustal and non-crustal elements.*

Table 2. *Concentrations of trace metals at three platforms from time series sampling (ng m^{-3})*

| Elements	Platform A [a]Ave., Med. (Range)	[b]N	Platform B [a]Ave., Med. (Range)	[b]N	Platform C [a]Ave., Med. (Range)	[b]N	Gradients ng m^{-3} per 50 m	R^2
Al	27.3, 23.3 (2.06-107)	59	21.9, 15.9 (3.67-79.4)	42	21.5, 16.1 (2.09-74.8)	58	-3.60	0.895
Cd	0.107, 0.0858 (0.0122-0.379)	59	0.0966, 0.0772 (0.0029-0.679)	45	0.0829, 0.0478 (0.0018-0.729)	58	-0.0190	0.997
Cu	39.0, 20.1 (1.47-266)	59	30.2, 23.4 (0.0157-139)	45	22.3, 13.8 (0.214-95.5)	58	-3.18	0.999
Pb	3.26, 2.83 (0.599-16.7)	59	3.01, 2.69 (0.309-14.8)	44	2.95, 2.19 (0.195-15.6)	58	-0.320	0.943
Cr	0.786, 0.600 (0.137-3.15)	59	0.567, 0.501 (0.0413-2.09)	45	0.622, 0.475 (0.113-2.38)	58	-0.0625	0.719
Fe	86.6, 68.6 (20.1-826)	59	58.2, 53.9 (0.722-160)	45	62.3, 48.1 (3.60-180)	57	-10.2	0.792
Co	0.146, 0.0802 (0.0096-1.07)	59	0.129, 0.0812 (0.0039-0.562)	45	0.150, 0.0995 (nd-0.876)	57	0.009	0.179
Mn	1.83, 1.41 (0.586-6.93)	38	1.95, 1.75 (0.568-5.17)	30	2.37, 1.80 (0.0600-8.22)	37	0.195	0.952
Ni	7.79, 6.77 (0.105-29.0)	54	6.61, 5.77 (0.161-17.9)	42	8.09, 6.91 (0.0032-27.5)	54	0.0700	0.192
Sb	1.39, 0.976 (0.212-5.36)	59	1.47, 0.989 (0.153-7.21)	44	3.49, 1.42 (0.170-37.9)	57	0.222	0.882
Sc	0.0071, 0.0054 (0.0007-0.038)	59	0.0078, 0.0070 (0.0010-0.024)	45	0.0085, 0.0078 (0.0003-0.074)	58	0.0001	0.999
V	2.84, 1.88 (0.0411-23.5)	59	2.30, 1.84 (0.0034-9.86)	45	2.93, 1.99 (0.0101-18.5)	58	0.0550	0.132
Zn	14.7, 10.8 (2.75-53.2)	59	18.1, 11.8 (2.24-181)	45	15.6, 12.6 (1.31-59.9)	58	0.900	0.255

[a] *Values are reported in both average (Ave.) and medium (Med.).*
[b] *Number of samples.*

Non–crustal trace elements associated with PM$_{2.5}$ near the highways mostly come from vehicle emissions (Weckwerth, 2001; Sternbeck et al., 2002). The combustion of the fuels is the principal source for Co, Ni, and V, while tire rubber abrasion and brakes are found to be the major contributors to Cd, Pb, Cu, Sb and Zn in the ambient air near high–traffic zones (Pacyna, 1998; Sternbeck et al., 2002; Singh et al., 2002; Adachi and Tainosho, 2004). Sb showed the highest EFs among all trace elements, coincident with previous works at Ho Chi Minh City (Hien et al., 2001) and Tokyo (Iijima et al., 2008). The average concentration of Zn at platform A was 14.7 ng m^{-3}, comparable to those at Sandy Hook (16 ng m^{-3}) and New Brunswick (18 ng m^{-3}) in the same regions (Gao et al., 2001). However, the average concentration of Zn at this location is 2–4 times lower than those in Seville, Spain (Fernandez Espinosa et al., 2002). As zinc could come from multiple sources, such as vehicle emissions, tire tread (Pierson and Brachaczek, 1983; Rogge et al., 1993; Huang et al., 1994; Smolders and Degryse, 2002), diesel soot, oil industries and coal combustion (Nriagu and Pacyna, 1988), the lower concentration of Zn here compared to that in Spain may be indicative of the regional difference in the strength and types of pollutant emissions.

3.2. Concentration gradients of trace elements along three platforms

The ambient concentrations of traffic related trace elements at a specific location could be affected by the distance away from the vehicle emission sources. The decreasing concentration gradients of certain components in aerosols were reported in previous studies, including total particle number and mass concentrations of black carbon (Hitchins et al., 2000; Zhu et al., 2002a), and some studies found that correlation between particle number concentrations and distance was non–linear (Zhu et al., 2002a). Table 2 shows two groups of elements: one with de-creasing concentration gradients (Al, Cd, Cu, Pb, Cr and Fe) and the other with increasing concentration gradients (Co, Mn, Ni, Sb, Sc, V and Zn). The concentrations of Al, Cd, Cu and Pb continuously decreased from platform A to platform C, while Cr and Fe showed discrete decreasing. A strong linear relationship between the concentrations and the distance away from the highway was found for Cd, Cu and Fe (Figures 3a, 3b, and 3c). The decreasing concentration gradient of Fe is the steepest, followed by that of Cu, and the gradient of Cd is the least. This difference could be attributed to the differences in aerosol size distributions. Cd is
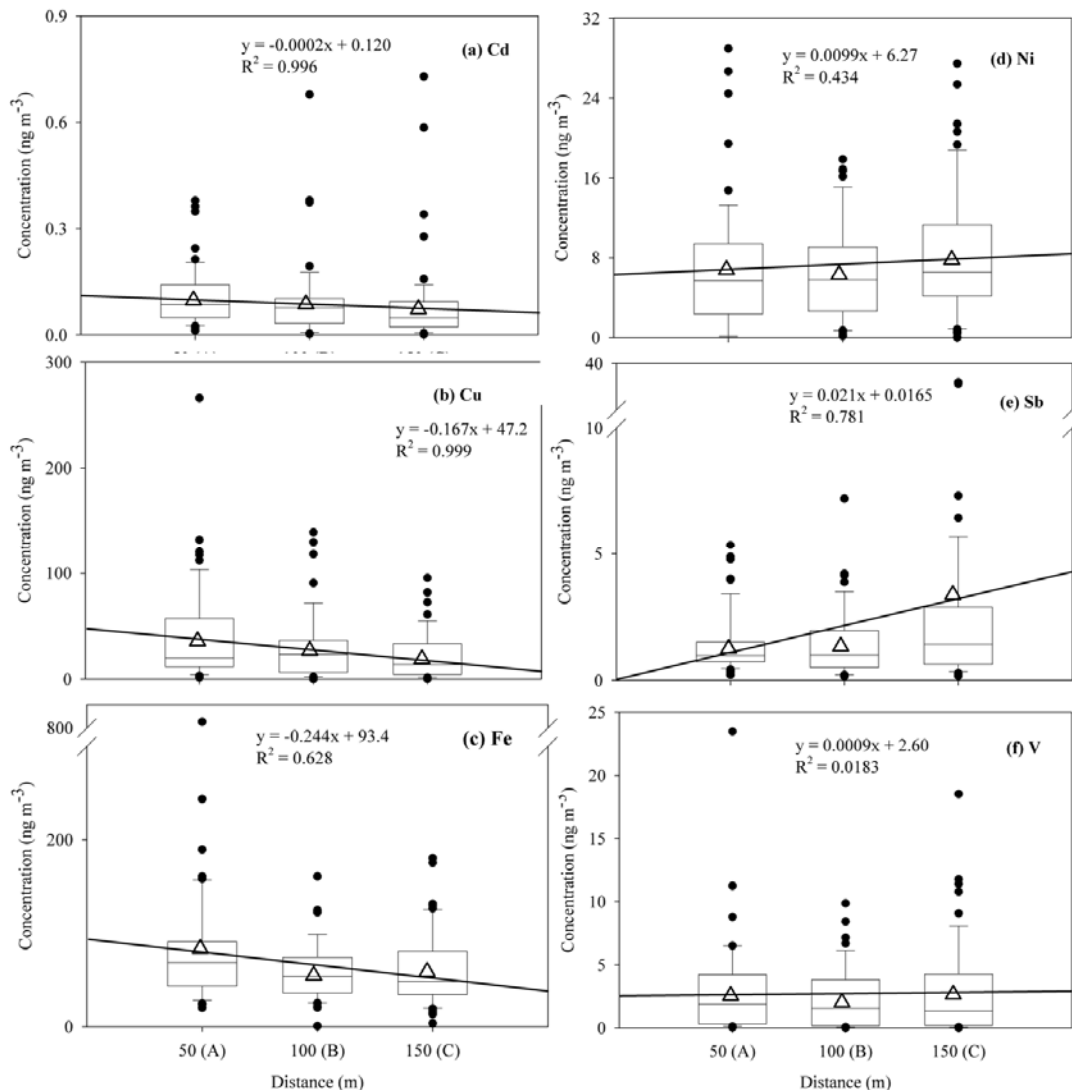
Figure 3. *Annual concentration distributions (•) and annual mean concentrations (Δ) of trace metals at three platforms: (a) Cd, (b) Cu and (c) Fe present trace elements with decreasing concentration gradients and (d) Ni, (e) Sb and (f) V present trace elements with increasing concentration gradients.*

more enriched in particulates less than 1 µm, while Fe and Cu are more associated with particles larger than 1 µm and would have a larger deposition velocity. Therefore, more Fe and Cu attached particles could deposit within 150 meters away from the highway.

The concentrations of Co, Mn, Ni, Sb, Sc, V and Zn showed increasing gradients (Table 2). The steepest gradient of Sb was caused by three extremely high values at platform C on July 11th, 23th, and August 4th (37.8, 19.3 and 37.9 ng m^{-3}), which are almost 20–30 times higher than results from other roadsides (Hien et al., 2001). In Figure 3e, the concentration of Sb (with three extreme values) is proportional with distance, while the correlation is even higher ($R^2 = 0.867$) without the extremely values. In general, increasing concentration gradients were related to the enrichment of trace elements in ultrafine particles. In this study, Co, Ni, Sb, V and Zn all showed concentration peaks around particles with diameter 0.078 µm or less (Gao, unpublished data). As finer particles have relatively longer residence times in the air, and are deposited more slowly, they can be transported over longer distances (Allen et al., 2001). It is more likely that they would deposit at platform C than at platform A. In addition, fine particles may undergo certain processes in the air such as coagulation; these processes may also result in the concentration increases of these ele

ments with distance. However, Mn and Sc were enriched in coarse particles. Since they are crustal elements, their increasing trends may result from different effects on different sampling locations. Higher concentrations of Mn and Sc at platform C may reflect the influence of soil particle re–suspension near that platform.

In both concentration gradients as a function of distance shown in Table 2, there were not significant concentration variations of these trace elements in PM$_{2.5}$ aerosols along the three platforms within 150 m distance from the highway. This suggests that these trace elements in PM$_{2.5}$ may have long residence times in the air and can be transported to the downwind regions. Therefore, highway–derived PM$_{2.5}$ pollutants may affect larger areas far from the immediate high–traffic emission zones.

3.3. Temporal concentration variations of trace elements

Seasonal concentration variations. To investigate the temporal patterns of trace elements in PM$_{2.5}$ at this location, the concentrations of 13 elements at three platforms were averaged and presented in seasonal, weekday–weekend and diurnal time periods. In this study, the seasonal patterns are shown for spring (March – May), summer (June – August), fall (September –
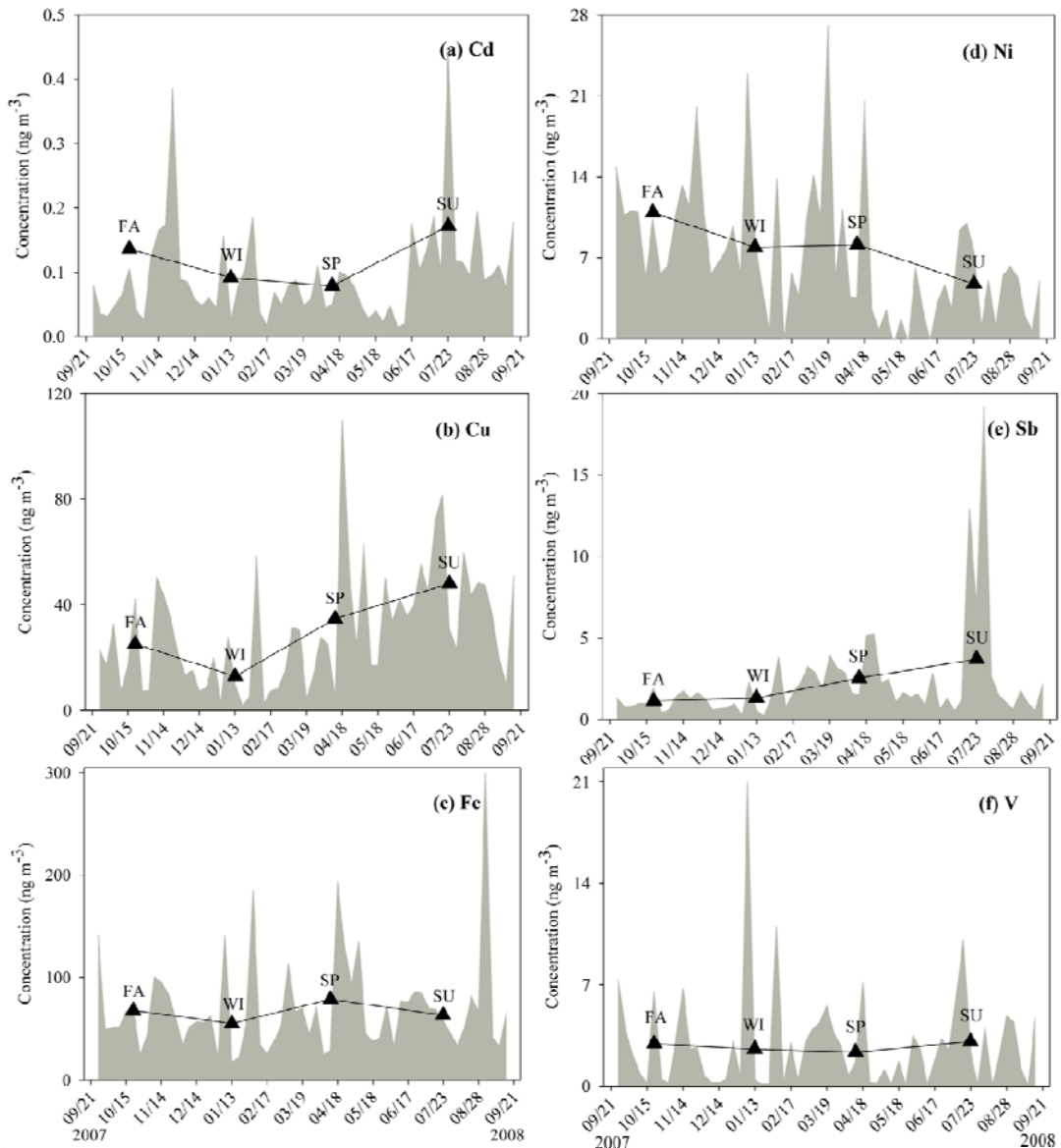

Figure 4. Time series of average concentrations of trace metals at three platforms.

November) and winter (December – February). Although the concentrations of these trace elements varied seasonally (Figure 4), there were not clear patterns, consistent with previous studies (Gao et al., 2002; Heal et al., 2005). Most of the trace elements (except Ni) displayed higher concentrations in spring and summer. Concentrations of some elements (Cd, V, Mn and Co) slightly increased in warm seasons, while for others, the concentrations increased more significantly. For example, the average concentration of Fe in spring and summer was 70.9 ng m^{-3}, higher than its average value of 61.4 ng m^{-3} in the fall and winter (Figure 4c). The concentration of Cu in warm seasons almost doubled its value in cold seasons (Figure 4b). This result is consistent with previous studies on trace elements in aerosols. Pike and Moran (2001) and Azimi et al. (2005) reported higher concentrations of several trace elements in bulk samples in spring and summer, such as Al. Heal et al. (2005) found that most water soluble trace elements in PM$_{2.5}$ had slightly higher concentrations in the summer, although Ni showed higher concentrations in fall and winter in this study (Figure 4d), similar to results reported by Pike and Moran (2001). Several studies also reported certain parameters showing higher values in winter than in summer, including total mass and number concentrations of aerosols, mass concentration of particles less than 2 μm as well as concentrations of certain trace elements (Bilos et al., 2001; Hussein et al., 2004; Furuta et al., 2005; Hussein et al., 2006). As reported in a previous study (Peltier et al., 2008), higher concentrations of Ni in winter may be the result of enhanced residential combustion.

Seasonal variations of trace elements in the atmosphere could be affected by traffic flows and meteorological conditions, such as wind speed and direction (Charron and Harrison, 2005). Since certain trace elements in PM$_{2.5}$ aerosols originate primarily from vehicle emissions, traffic volumes may control their concentrations. Figure 5 shows that total traffic flow on the NJTPK was slightly higher in spring and summer, consistent with seasonal concentration variations of most trace elements. However, the correlations between concentrations of Cu and Co, two typical elements from vehicle emissions, at platform A and total traffic volume were not significant, with R^2 ranging from 0.0298 (Co) to 0.285 (Cu). The patterns of Cu concentration variation at platform A and total traffic volume were similar at certain periods (Figure 5a). For example, the highest concentration of Cu on April 18th may be the result of higher traffic flow on that day. In addition, concentrations of all trace elements showed negative correlation with wind speed, similar to the correlations between aerosol number concentrations and wind speed (Charron and Harrison, 2003; Hussein et al., 2004; Hussein et al., 2006). At platform A, the concentrations of Cd had the highest negative correlation with wind speed (R^2 = 0.279) (Figure 5b). Clearly the lower the wind speed was, the higher the number concentrations were, resulting in the reduction in particle transport and accumulation of particles in the ambient air. Wind direction was also considered an important meteorological factor influencing pollutant concentrations (Hitchins et al., 2000). In this work, we categorized the wind directions into two types: upwind which blew from sampling sites to the highway and downwind from the opposite direction, with the latter resulting in more traffic pollutants to the sampling sites. In general, spring and summer were dominated by downwind (25/44 days were downwind), whereas fall and winter were mainly influenced by upwind (21/39 days). Therefore, prevailing downwind in warm seasons could be a partial reason for seasonal concentration variations of trace elements at this location.

Weekly concentration variations of trace elements. The average concentrations of all trace elements showed higher concentrations on weekdays than on weekends at the three platforms (Figure 6). The average concentration of Fe on weekdays was 80.1 ng m^{-3}, which almost doubled the concentration on weekends. Other trace elements also showed concentrations that were 19.7–42.4% higher on weekdays than on weekends; except Cd and Cu, for which there was no significant concentration difference. The weekday–

weekend concentration variations of trace elements may be related to the number concentration variation of aerosol particles, which showed significant correlations with traffic activities (Hussein et al., 2004), especially with diesel combustion. This comparison clearly demonstrates that the extent of highway pollutant emissions is directly associated with traffic volume.
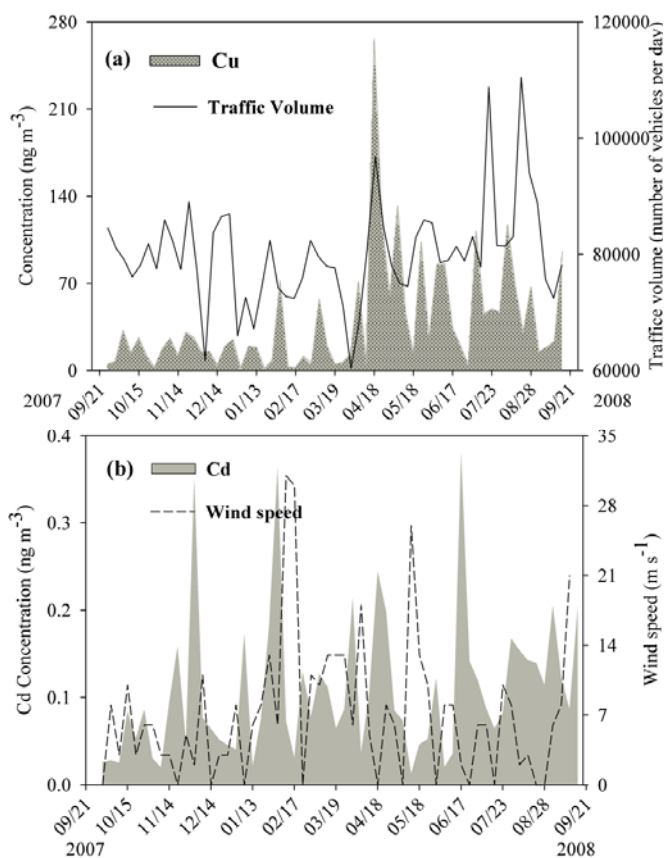
Figure 5. (a) *Time series of the concentrations of Cu at platform A and total traffic volume on NJTPK; **(b)** Time series of the concentrations of Cd at platform A and wind speed.*
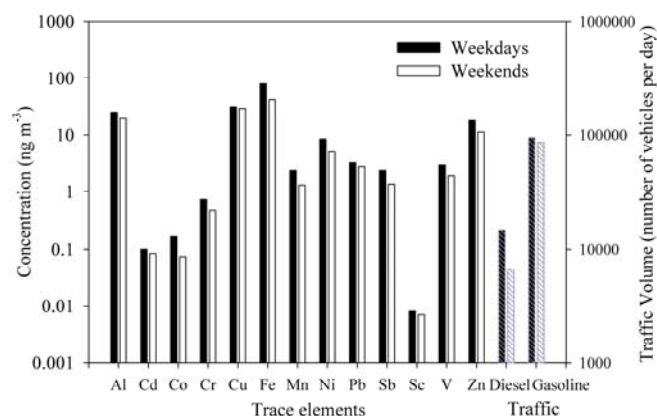
Figure 6. *Comparison between weekday and weekend concentrations of trace metals and comparison between weekday and weekend traffic volumes.*

Diurnal concentration variations of trace elements. Figure 7 shows diurnal concentration variations of trace elements based on two intensive sampling episodes in winter and summer. Most trace elements, including Al, Cd, Co, Fe, Mn, Ni, Pb, Sc, V and Zn, showed higher averaged concentrations (combining data from three platforms) during the day, consistent with previous work (Bilos et al., 2001), because traffic flow was higher during the daytime than that during the nighttime. The diurnal variation may follow the

behavior of total suspended particles, observed with increased concentrations during the daytime (Colombo et al., 1999; Kim et al., 2002; Singh et al., 2002). However, other trace elements, Cu, Cr and Sb, showed higher average concentrations during the night. This pattern may result from steady input of these trace elements from some pollutant sources, and it may also be due to smaller particles enriched with these elements, having longer resident time in the air. The diurnal and seasonal variations showed in Figure 7 also were highly related to wind speed. Similar to one–year time–series samples, the concentrations of all trace elements had negative correlations with wind speed. In addition, partial "U–shape" between concentration and wind speed has been observed in five elements (Al, Cd, Cr, Cu and Fe). For example, in Figure 8, Cd and Fe both showed inverse correlations with wind speed, and such correlations were stronger during the day.

3.4. Temporal concentration gradients of trace elements along three platforms

Results from three platforms showed similar seasonal variations. In general, higher concentrations at platform A corresponded to higher concentrations at platforms B and C and vice versa, although there were several exceptions. On September 3, 2008 for example, Fe concentration at platform A was 826 ng m^{-3}, an extremely high value compared to its time–series concentrations. At platforms B and C, Fe concentrations were only 57.2 ng m^{-3} and 13.4 ng m^{-3}, even lower than the annual average.

A similar situation occurred for Sb with three unusually high values at platform C on July 11, 23 and August 4, 2008. Since there were no significant changes in traffic density and weather conditions on those days, it was hard to explain whether those exceptions were facts or results of contamination.

Time–series samples at the three platforms provided more information regarding concentration gradients (Table 3 and Figure 9). In the fall, all trace elements showed increasing concentration gradients. From platform A to platform C, the concentration increases ranged from 21.7% (Fe) to 119% (Cu). The concentration of Cu increased by 10.5 ng m^{-3} per 50 meter. However, in winter, spring and summer, most trace element concentrations showed a decreasing trend; for example, the decay rate of Cu was 1.36 ng m^{-3} per 50 meters in winter, 23.9 ng m^{-3} per 50 meters in spring and 14.5 ng m^{-3} per 50 meters in summer. Generally, the concentration decay rates of most trace elements were lower as a function of distance from NJTPK in winter than in summer, except for two elements, Mn and Sb, which showed increasing concentration gradient in all seasons (Table 3). The concentration gradients in different seasons may be caused by the seasonal variation of wind speed and wind direction, so called "dilution effect" (Zhu et al., 2002a, Zhu et al., 2002b; Zhu et al., 2004). In summer, wind is stronger and more frequently blowing from NJTPK to sampling sites, while in winter wind speed is lower and downwind is dominant. Therefore, warm season showed higher concentration decay rates.
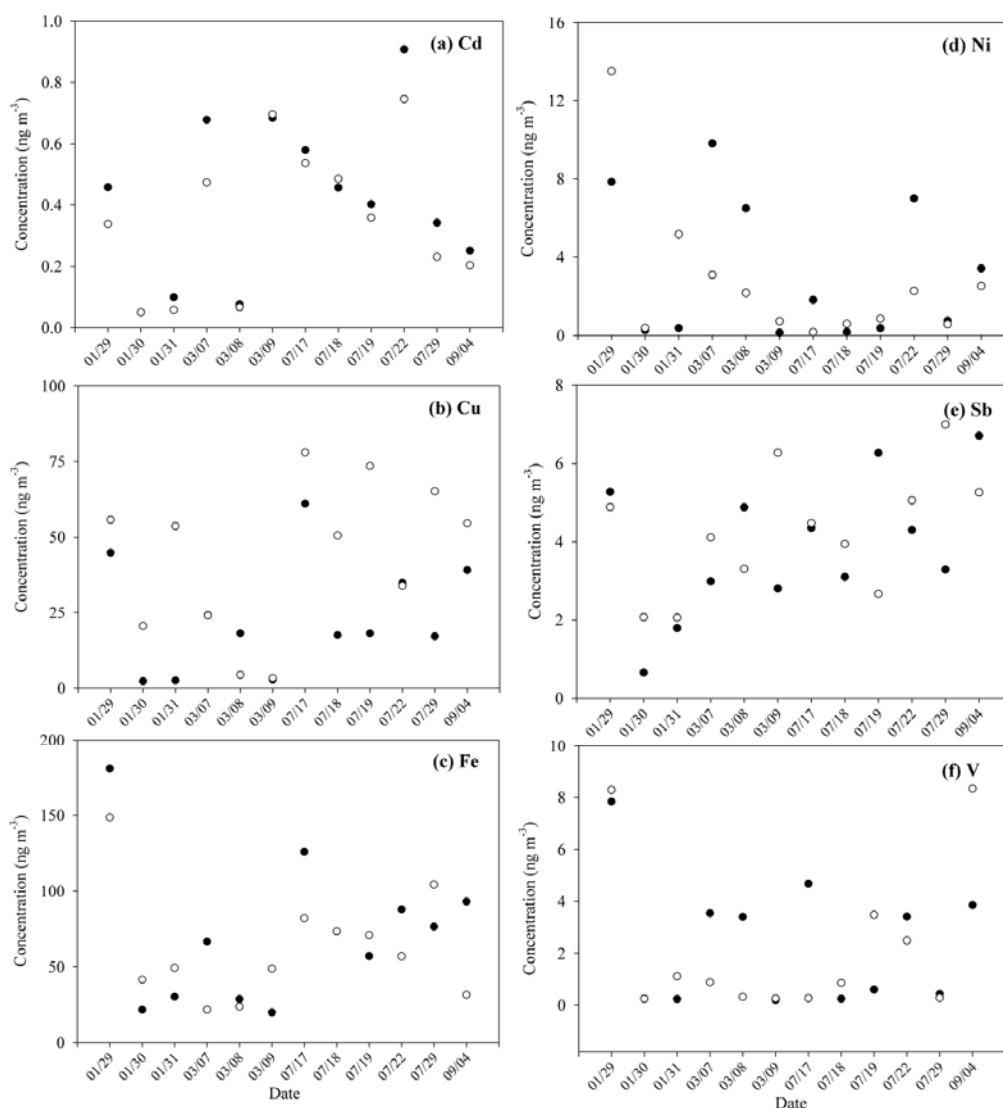

Figure 7. *Diurnal concentration variations of **(a)** Cd, **(b)** Cu, **(c)** Fe, **(d)** Ni, **(e)** Sb and **(f)** V. Black dots represent day time and circles present night time.*
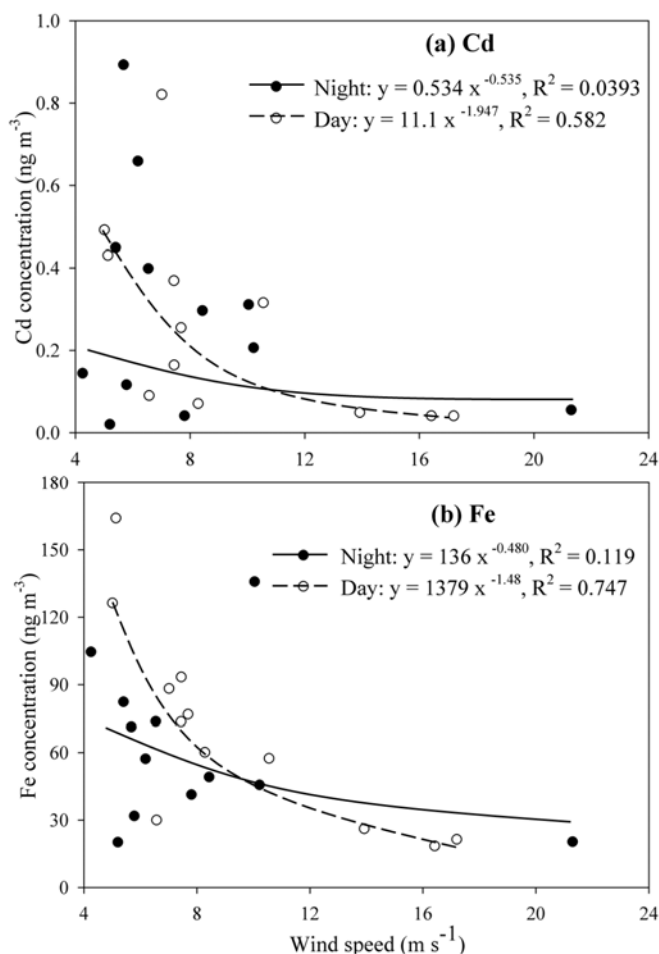
Figure 8. (a) *Correlations between concentrations of Cd and wind speeds during day and night time;* **(b)** *correlations between concentrations of Fe and wind speeds during day and night time.*

In addition, three platforms showed different seasonal concentration standard deviations. In general, trace elements with decreasing gradients showed larger standard deviations at platform A, while those with an increase gradient showed higher values at platform C (Table 3). For example, the standard deviation of annual Cu concentrations at platform A was two times larger than that at platform C. This coincidence could be the result of different size distributions and the consequent aerosol deposition

locations. Trace elements associated with coarse and fine particles may precipitate more at platforms A and B. On the other hand, trace elements attached to ultrafine particles could be transported over a longer distance to reach platform C and could lead to stronger seasonal variations at this point.

These concentration gradients also existed in two sets of intensive samples in the day and night (Table 4). Eight trace elements (Co, Cr, Fe, Mn, Ni, Pb, Sb and Zn) showed increasing concentration gradients at night in winter, whereas during daytime, decreases in concentration gradients occurred more often. In the summer intensive sampling, except for Mn and Sb, air concentrations of other trace elements showed a negative correlation with distance both in the day and night.

4. Conclusion

Results from this study on the spatial and temporal variations of trace element concentrations carried out from 09/2007 to 09/2008 led to the following conclusions:

Within 150 m distance from the NJTPK, the annual mean concentrations of Al, Cr, Co, Cu, Fe, and Pb decreased with distance from the highway, while the concentration gradients of Co, Mn, Ni, Sb, Sc, V and Zn displayed an opposite direction. In winter, spring and summer, most of the trace elements exhibited decreasing concentration gradients, while in the fall, the increasing concentration gradients were the major patterns. However, there were not significant differences in the concentrations of these elements in PM$_{2.5}$ within the target distance, suggesting that they could be transported beyond the highway zones and have an impact on larger areas. Most trace elements showed higher concentrations in spring and summer at platforms A and B, but several trace elements displayed higher values in the fall and winter at platform C. All trace element concentrations were higher on weekdays than those on weekends, indicating the impact of higher traffic volumes during daytime on the extent of air pollution. Most trace elements (Al, Cd, Co, Fe, Mn, Ni, Pb, Sc, V and Zn) showed higher concentrations in the day time, while others (Cr, Cu and Sb) had higher concentrations dominated at night. The trace element concentration variations at this location were likely affected by both the traffic volume and wind speeds and directions. Heavier traffic and downwind from the highway probably could lead to the higher concentrations of certain trace elements in highways–dominated regions.

Table 3. *Seasonal concentration gradients of trace metals and standard deviations at three platforms*

Elements	Concentration Gradients (ng m^{-3} per 50 m)				Seasonal Concentration Standard Deviation		
	Fall	**Winter**	**Spring**	**Summer**	**Platform A**	**Platform B**	**Platform C**
Al	3.34	1.37	-4.84	-8.67	14.8	8.44	4.56
Cd	0.0323	-0.0284	-0.0384	0.0028	0.0179	0.0421	0.0609
Co	0.0424	-0.0034	-0.0231	-0.004	0.0741	0.0484	0.0698
Cr	0.118	-0.0845	-0.0222	-0.319	0.237	0.185	0.187
Cu	10.5	-1.36	-23.9	-14.5	25.8	20.0	12.4
Fe	7.42	-5.33	-10.3	-11.5	12.7	12.5	14.9
Mn	-	0.582	0.159	0.548	0.232	0.754	0.244
Ni	1.57	0.214	-0.595	-0.406	1.98	2.38	3.451
Pb	0.695	-0.196	-0.300	-0.365	0.716	0.742	0.489
Sb	0.238	0.437	0.399	3.72	0.446	1.06	3.48
Sc	0.0009	0.0042	-0.0012	-0.0014	0.0023	0.0017	0.0033
V	1.12	-0.185	-0.213	-0.189	0.505	0.604	0.891
Zn	4.69	-0.0810	-1.33	-0.237	4.20	5.32	5.14

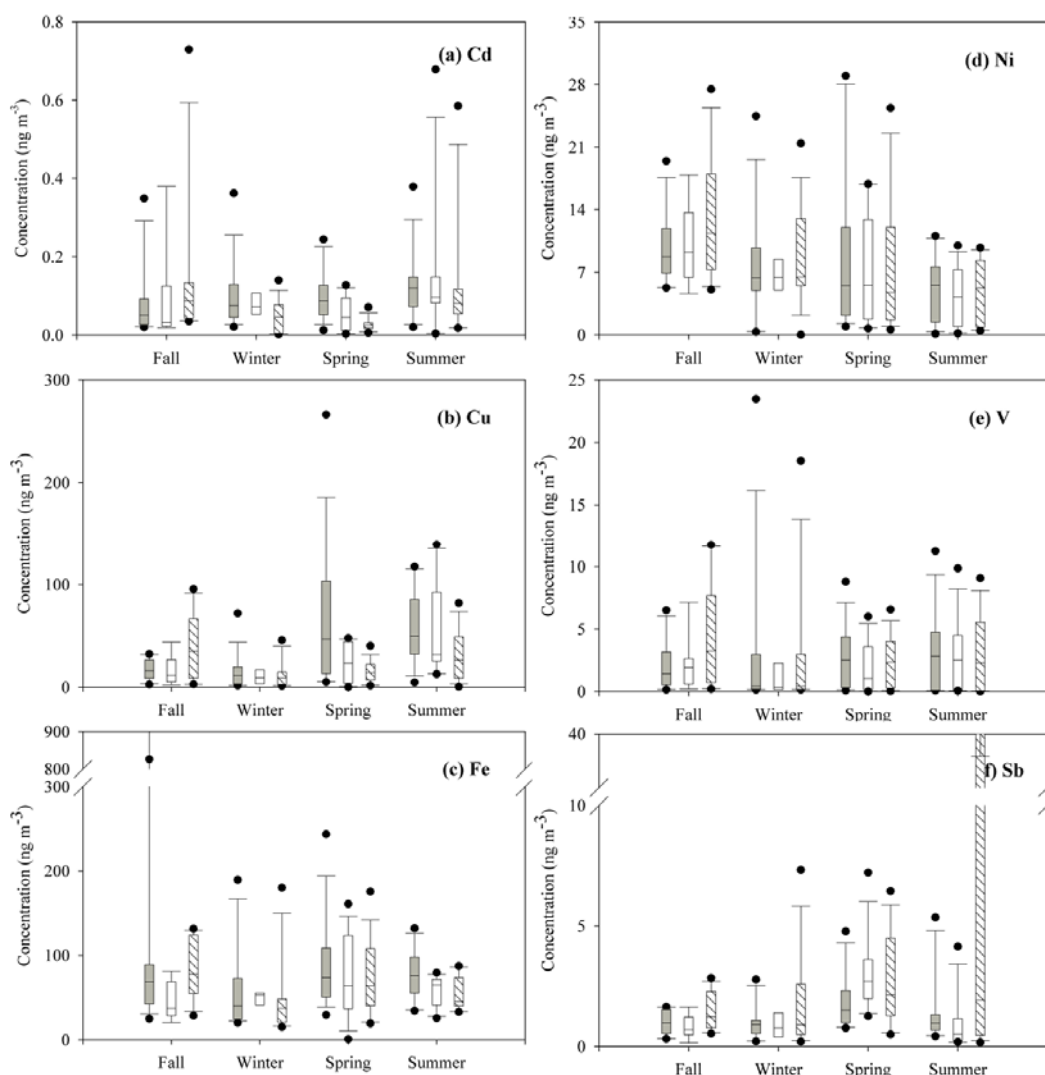*- Mn was not measured at the first run of ICP-MS.*

Figure 9. Seasonal concentration variations of trace metals at three platforms: �☐ are samples at platform A☐ are samples at platform B; and ▨▨ are samples at platform C.

Table 4. Diurnal concentration variations of trace metals at three platforms from intensive sampling (ng m⁻³)

Elements	Winter Day Platform			Winter Night Platform			Summer Day Platform			Summer Night Platform		
	A	B	C	A	B	C	A	B	C	A	B	C
Al	53.7	20.9	26.9	36.3	35.8	34.6	75.7	54.4	42.3	55.8	39.8	38.5
Cd	0.156	0.150	0.048	0.095	0.220	0.053	0.254	0.193	0.300	0.181	0.133	0.138
Co	0.213	0.358	0.187	0.234	0.249	0.260	0.174	0.167	0.164	0.066	0.058	0.050
Cr	0.586	1.13	0.530	0.596	1.04	0.870	1.25	0.546	0.696	0.843	1.04	2.37
Cu	27.4	15.9	9.53	69.0	8.70	8.02	30.1	36.4	19.5	58.7	74.5	33.6
Fe	70.2	76.0	59.6	66.2	56.9	71.8	107.3	69.3	67.2	75.8	57.3	61.1
Mn	2.14	3.23	3.80	1.81	2.00	8.29	2.76	2.12	2.12	2.09	1.15	1.19
Ni	6.03	11.3	6.56	5.95	6.58	9.38	6.19	6.16	6.95	3.50	3.89	3.16
Pb	3.29	4.44	2.72	2.72	3.53	3.05	5.13	5.13	3.64	4.75	5.34	2.93
Sb	2.66	5.64	3.84	3.05	5.89	6.29	1.97	0.373	2.04	5.80	1.56	1.51
Sc	0.008	0.008	0.008	0.008	0.005	0.006	0.016	0.015	0.013	0.010	0.011	0.008
V	2.41	3.88	2.21	1.81	2.22	1.75	2.06	2.08	1.96	3.05	3.11	1.09
Zn	22.5	33.8	36.6	17.2	22.2	42.7	15.6	16.5	14.2	12.9	12.2	10.9

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References

Adachi, K., Tainosho, Y., 2004. Characterization of heavy metal particles embedded in tire dust. *Environment International* 30, 1009-1017.

Allen, A.G., Nemitz, E., Shi, J.P., Harrison, R.M., Greenwood, J.C., 2001. Size distributions of trace metals in atmospheric aerosols in the United Kingdom. *Atmospheric Environment* 35, 4581-4591.

Azimi, S., Rocher, V., Muller, M., Moilleron, R., Thevenot, D.R., 2005. Sources, distribution and variability of hydrocarbons and metals in atmospheric deposition in an urban area (Paris, France). *Science of the Total Environment* 337, 223-239.

Berggren, D., Bergkvist, B., Falkengren-Grerup, U., Folkeson, L., Tyler, F., 1990. Metal solubility and pathways in acidified forest ecosystems of south Sweden. *Science of the Total Environment* 96, 103-114.

Bilos, C., Colombo, J.C., Skorupka, C.N., Rodriguez Presa, M.J., 2001. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. *Environmental Pollution* 111, 149-158.

Brunekreef, B., Janssen, N.A., de Hartog, J., Harssema, H., Knape, M., von Vliet, P.V., 1997. Air pollution from truck traffic and lung function in children living near motorways. *Epidemiology* 8, 298-303.

Carter, J.D., Ghio, A.J., Samet, J.M., Devlin, R.B., 1997. Cytokine production by human airway epithelial cells after exposure to an air pollution particle is metal-dependent. *Toxicology and Applied Pharmacology* 146, 180-188.

Charron, A., Harrison, R.M., 2005. Fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) particulate matter on a heavily trafficked London highway: sources and processes. *Environmental Science and Technology* 39, 7768-7776.

Charron, A., Harrison, R.M., 2003. Primary particle formation from vehicle emission during exhaust dilution in the roadside atmosphere. *Atmospheric Environment* 37, 4109-4119.

Chester, R., Nimmo, M., Preston, M.R., 1999. The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: a coastal site in the Western Mediterranean. *Marine Chemistry* 68, 15-30.

Colombo, J.C., Landoni, P., Bilos, C., 1999. Sources, distribution and variability of airborne particles and hydrocarbons in La Plata area, Argentina. *Environmental Pollution* 104, 305-314.

Dockery, D.W., Speizer, F.E., Stram, D.O., Ware, J.H., Spengler, J.D., Ferris, B.G.J., 1989. Effects of inhalable particles on respiratory health of children. *The American Review of Respiratory Disease* 139, 587-594.

Dzubay, T.G., Stevens, R.K., Richards, L.W., 1979. Composition of aerosols over Los Angeles freeways. *Atmospheric Environment* 13, 653-659.

Fernandez Espinosa, A.J., Ternero Rodriguez, M., Barragan de la Rosa, F.J., Jimenez Sanchez, J.C., 2002. A chemical speciation of trace metals for fine urban particles. *Atmospheric Environment* 36, 773-780.

Fernandez Espinosa, A.J., Ternero Rodriguez, M., Barragan de la Rosa, F.J., Jimenez Sanchez, J.C., 2001. Size distribution of metals in urban aerosols in Seville (Spain). *Atmospheric Environment* 35, 2595-2601.

Furuta, N., Iijima, A., Kambe, A., Sakai, K., Sato, K., 2005. Concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from 1995 to 2004. *Journal of Environmental Monitoring* 7, 1155-1161.

Gao, Y., Nelson, E.D., Field, M.P., Ding, Q., Li, H., Sherrell, R.M., Gigliotti, C.L., Van Ry, D.A., Glenn, T.R., Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on $PM_{2.5}$ particulate matter over the New York-New Jersey harbor estuary. *Atmospheric Environment* 36, 1077-1086.

Harrison, R.M., Tilling, R., Callen Romero, M.S., Harrad, S., Jarvis, K., 2003. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. *Atmospheric Environment* 37, 2391-2402.

Harrison, R.M., Yin, J., 2000. Particulate matter in the atmosphere: which particle properties are important for its effects on health? *The Science of the Total Environment* 249, 85-101.

Heal, M.R., Hibbs, L.R., Agius, R.M., Beverland, I.J., 2005. Total and water-soluble trace metal content of urban background PM_{10}, $PM_{2.5}$ and black smoke in Edinburgh, UK. *Atmospheric Environment* 39, 1417-1430.

Hien, P.D., Binh, N.T., Truong, Y., Ngo, N.T., Sieu, L.N., 2001. Comparative receptor modelling study of TSP, PM_2 and PM_{2-10} in Ho Chi Minh City. *Atmospheric Environment* 35, 2669-2678.

Hitchins, J., Morawska, L., Wolff, R., Gilbert, D., 2000. Concentrations of submicrometre particles from vehicle emissions near a major road. *Atmospheric Environment* 34, 51-59.

Hlavay, J., Polyak, K., Wesemann, G., 1992. Particle size distribution of minerals phases and metals in dusts collected at different work-places. *Fresenius Journal of Analytical Chemistry* 344, 319-321.

Huang, X., Olmez, I., Aras, N.K., Gordon, G.E., 1994. Emissions of trace elements from motor vehicles: potential marker elements and source composition profile. *Atmospheric Environment* 28, 1385-1391.

Hussein, T., Karppinen, A., Kukkonen, J., Harkonen, J., Aalto, P.P., Hameri, K., Kerminen V-M., Kulmala, M., 2006. Meteorological dependence of size-fractionated number concentrations of urban aerosol particles. *Atmospheric Environment* 40, 1427-1440.

Hussein, T., Puustinen, A., Aalto, P.P., Makela, J.M., Hameri, K., Kulmala, M., 2004. Urban aerosol number size distributions. *Atmospheric Chemistry and Physics* 4, 391-411.

Iijima, A., Sato, K., Yano, K., Kato, M., Kozawa, K., Furuta, N., 2008. Emission factor for antimony in brake abrasion dusts as one of the major atmospheric antimony sources. *Environmental Science and Technology* 42, 2937-2942.

Janssen, N.A.H., Van Mansom, D.F.M., Van Der Jagt, K., Harssema, H., Hoek, G., 1997. Mass concentration and elemental composition of airborne particulate matter at street and background locations. *Atmospheric Environment* 31, 1185-1193.

Kim, S., Shen, S., Sioutas, C., Zhu, Y.F., Hinds, W.C., 2002. Size distribution and diurnal and seasonal trends of ultrafine particles in source and receptor sites of the Los Angeles basin. *Journal of the Air and Waste Management Association* 52, 297-307.

Kumar, A.V., Patil, R.S., Nambi, K.S.V., 2001. Source apportionment of suspended particulate matter at two traffic junctions in Mumbai, India. *Atmospheric Environment* 35, 4245-4251.

Martuzevicius, D., Grinshpun, S.A., Reponen, T., Gorny, R.L., Shukla, R., Lockey, J., Hu, S., McDonald, R., Biswas, P., Kliucininkas, L., LeMasters, G., 2004. Spatial and temporal variations of $PM_{2.5}$ concentration and composition throughout an urban area with high freeway density-the Greater Cincinnati study. *Atmospheric Environment* 38, 1091-1105.

Morawska, L., Thomas, S., Gilbert, D., Greenaway, C., Rijnders, E., 1999. A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road. *Atmospheric Environment* 33, 1261-1274.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134-199.

Pacyna, J.M., 1998. Source Inventories for Atmospheric Trace Metals. In: Harrison, R.M., van Grieken, R.E. (Eds.), Atmospheric Particles, IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, Vol. 5. Wiley, Chichester, UK, pp. 385-423.

Pakkanen, T.A., Loukkola, K., Korhonen, C.H., Aurela, M., Makela, T., Hillamo, R.E., Aarnio, P., Koskentalo, T., Kousa, A., Maenhaut, W., 2001. Sources and chemical composition of atmospheric fine and coarse particles in the Helsinki area. *Atmospheric Environment* 35, 5381-5391.

Peltier, R.E., Hsu, S.I., Lall, R., Lippmann, M., 2009. Residual oil combustion: a major source of airborne nickel in New York City. *Journal of Exposure Science and Environmental Epidemiology* 19, 603-612.

Pierson, W.R., Brachaczek, W.W., 1983. Particulate matter associated with vehicles on the road. II. *Aerosol Science and Technology* 2, 1-40.

Pike, S.M., Moran, S.B., 2001. Trace elements in aerosol and precipitation at New Castle, NH, USA. *Atmospheric Environment* 35, 3361-3366.

Poschl, U., 2005. Atmospheric aerosols: composition, transformation, climate and health effects. *Argewandte Chemie-International Edition* 44, 7520-7540.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosols: 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environmental Science and Technology* 27, 1892-1904.

Roorda-Knape, M.C., Janssen, N.A.H., De Hartog, J.J., Van Vliet, P.H.N., Harssema, H., Brunekreef, B., 1998. Air pollution from traffic in city districts near major motorways. *Atmospheric Environment* 32, 1921-1930.

Singh, M., Jaques, P.A., Sioutas, C., 2002. Size distribution and diurnal characteristics of particle-bound metals in source and receptor sites of the Los Angeles Basin. *Atmospheric Environment* 36, 1675-1689.

Smolders, E., Degryse, F., 2002. Fate and effect of zinc from tire debris in soil. *Environmental Science and Technology* 36, 3706-3710.

Spurny, K.R., 1998. One the physics, chemistry and toxicology of ultrafine anthropogenic, atmospheric aerosols (UAAA): new advances. *Toxicology Letters* 96-97, 253-261.

Stechmann, H., Dannecker, W., 1990. Characterization and source analysis of vehicle-generated aerosols. *Journal of Aerosol Science* 21, S287-S290.

Sternbeck, J., Sjodin, A.A., Andreasson, K., 2002. Metal emissions from road traffic and the influence of resuspension-results from two tunnel studies. *Atmospheric Environment* 36, 4735-4744.

Taylor, S.R., McLennan, S.M., 1985. The continental crust: its composition and evolution. Blackwell Scientific Publications, Oxford, Boston, Palo Alto, Victoria.

van Vliet, P., Knape, M., de Hartog, J., Janssen, N., Harssema, H., Brunekreef, B., 1997. Motor vehicle exhaust and chronic respiratory symptoms in children living near freeways. *Environmental Research* 74, 122-132.

Weckwerth, G., 2001. Verification of traffic emitted aerosol components in the ambient air of Cologne (Germany). *Atmospheric Environment* 35, 5525-5536.

Yang, K.X., Swami, K., Husain, L., 2002. Determination of trace metals in atmospheric aerosols with a heavy matrix of cellulose by microwave digestion-inductively coupled plasma mass spectroscopy. *Spectrochimica Acta Part B-Atomic Spectroscopy* 57, 73-84.

Zhu, Y., Hinds, W.C., Shen, S., Sioutas, C., 2004. Seasonal trends of concentration and size distribution of ultrafine particles near major highways in Los Angeles. *Aerosol Science and Technology* 38, 5-13.

Zhu, Y., Hinds, W.C., Kim, S., Shen, S., Sioutas, C., 2002a. Study of ultrafine particles near a major highway with heavy-duty diesel traffic. *Atmospheric Environment* 36, 4323-4335.

Zhu, Y., Hinds, W.C., Kim, S., Sioutas, C., 2002b. Concentration and size distribution of ultrafine particles near a major highway. *Journal of the Air and Waste Management Association* 52, 1032-1042.