Characterization of atmospheric trace elements on PM$_{2.5}$ particulate matter over the New York–New Jersey harbor estuary

Y. Gao[a],*, E.D. Nelson[b], M.P. Field[a], Q. Ding[a], H. Li[a], R.M. Sherrell[a], C.L. Gigliotti[b], D.A. Van Ry[b], T.R. Glenn[b], S.J. Eisenreich[b]

[a] *Institute of Marine and Coastal Sciences, Rutgers University, New Brunswick, NJ 08901, USA*
[b] *Department of Environmental Sciences, Rutgers University, New Brunswick, NJ 08901, USA*

Abstract

The purpose of this work is to characterize trace elements associated with atmospheric particulate matter of 2.5 μm and smaller in size (PM$_{2.5}$) over the New York–New Jersey (NY–NJ) Harbor Bight. Using low-volume PM$_{2.5}$ samplers, aerosol particulate samples were simultaneously collected for the first time at three locations in the region, Sandy Hook in the coast, New Brunswick and Liberty Science Center (Jersey City) in nearby urban areas, during January 1998–January 1999. Sample analysis for trace elements was accomplished by inductively coupled plasma mass spectrometry. Many elements in ambient air exhibit strong spatial gradients from urban centers to the coast, and the concentrations of most elements at Liberty Science Center are significantly higher than at the other two locations. Seasonal patterns are not apparent for most elements at all locations, suggesting continuous contributions from their sources. The elements Pb, Cd, Zn, Cu, Ni, V, Sb, are enriched by factors of 200 to 20,000 relative to their natural abundance in crustal soil. Major sources that contribute to the atmospheric loading of these elements include fossil fuel combustion, oil combustion, metal processing industry, and waste incineration. Atmospheric dry deposition of these trace elements associated with PM$_{2.5}$ to the coastal waters of the NY–NJ estuary may account for a significant portion of the total dry deposition fluxes for these elements. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: New York–New Jersey harbor atmosphere; PM2.5 particulate matter; Trace elements; Aerosol characteristics

1. Introduction

The coastal marine atmosphere adjacent to large urban and industrial centers can be strongly impacted by pollution emissions, resulting in high loading of pollutants in the ambient air (Baker et al., 1997; Chester et al., 1994; Eisenreich et al., 1997; Gao et al., 1996; Holsen et al., 1997; Ondov et al., 1997; Scudlark et al.,

1994). Among airborne pollutants are trace elements such as Cd, Pb, Sb, Zn, etc. associated with suspended particulate matter from a variety of pollution emission sources. High concentrations of certain trace elements in aerosol particles in coastal air could not only result in enhanced air-to-sea deposition fluxes of the elements to coastal waters, consequently affecting the coastal ecosystem (Church et al., 1984; Wu et al., 1994; Yang et al., 1996), but they could also be transported over the open ocean, affecting the composition of the remote marine atmosphere (Kim et al., 1999; Arimoto et al., 1992; Ellis et al., 1993). Thus it is critical to obtain detailed information on the levels and chemical

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*Corresponding author at: Program in Atmospheric and Oceanic Sciences, Princeton University, Princeton, NJ 08544-0710, USA.

E-mail address: yuangao@splash.princeton.edu (Y. Gao).

composition of airborne particulate matter containing trace elements in the source regions in order to quantitatively estimate the magnitude of their air-to-sea deposition and their effects on the remote marine atmosphere. On the other hand, high concentrations of airborne trace elements may seriously affect air quality, posing direct influences on human health (Chapman et al., 1997; Ghio et al., 1999). As pollution-derived elements are often concentrated on fine particles, they could remain suspended in air with relatively long residence times and could efficiently penetrate human lungs. Thus, trace metals associated with fine aerosol particles may contribute to particulate toxicity (Prahalad et al., 1999). However, understanding the mechanisms linking particulate air pollution and adverse health consequences remains a challenge, due in part to the lack of information on elemental composition of fine particles. In particular, detailed determination of toxic element concentrations on fine aerosol particles over the coastal regions directly downwind of intense pollution emission sources, such as the New York–New Jersey (NY–NJ) Metro area, are largely unknown.

The NY–NJ Harbor Bight is of special importance because it is surrounded by industrial sectors in New Jersey and the metropolitan complex of New York City, as well as many highways across the area, which act as continuous sources of many trace elements in fine particulate matter to the ambient air. On the other hand, air circulation along the coastline may dilute air pollution loading to some extent. Until recently, these issues have not been addressed in detail for this region. To investigate characteristics of airborne pollution-derived trace elements over the NY–NJ Harbor/Bight, we first focused on selected trace elements associated with particulate matter equal to and smaller than 2.5 μm diameter in size, known as $PM_{2.5}$, a size class that is more important than larger particles with respect to human health problems. The target elements in this study are Cd, Cr, Cu, Ni, Pb, Sb, V and Zn. For the purposes of data interpretation, elements Al and Fe were also included. We used a simultaneous and identical sampling approach to collect $PM_{2.5}$ particulate samples at three locations to determine the spatial and seasonal variations of these elements. We also applied enrichment factor and multivariate analyses to explore the sources and inter-element relationships. Data from this study should be useful to the evaluation of elemental composition of fine particulate matter over the NY–NJ Metro-coastal region. These results could further be used to study the linkage between particulate toxicity and health problems and to evaluate the atmospheric input of trace elements to the coastal waters. The results should be applicable to other coastal atmospheric environments that are strongly altered by human activities.

2. Methodology

2.1. Sampling

Sampling of trace elements associated with $PM_{2.5}$ particulate matter was conducted at three sites around the NY–NJ Harbor-Bight during January 1998–January 1999 period (Fig. 1). These sites were chosen to represent different environmental characteristics: (1) Sandy Hook (SH, 40.46°N, 74.00°W), a coastal site located on a peninsula between Raritan Bay and the off-shore NY Bight; (2) New Brunswick (NB, 40.48°N, 74.43°W), an inland suburban site located in an agricultural/botanical area near several local highways; (3) the Liberty Science Center (LSC, Jersey City, 40.71°N, 74.05°W), located in the middle of the metropolitan New York and New Jersey industrial sectors. The SH site is considered to be the primary site in this study, with a complete 12-month sampling; the NB and LSC sites are considered as supporting sites mainly for the purpose of comparison. Considering all three sites located within the "source region", however, the elemental characteristics at these three sites were expected to show similarity.

Sample device was a modified Cal Tech type $PM_{2.5}$ low-volume aerosol sampler (anodized aluminum). During sampling, particles $\leqslant 2.5$ μm entered a mixing chamber in the sampler where they were split into two channels, with each having the same flowrate of $\sim 9 \, 1 \, min^{-1}$. One channel collects particulate matter for elemental/organic carbon analysis and the other collects particulate matter for trace element analysis. The mean volume filtered at the three sites ranged 9.6–12 (SD = 1.0–2.5) m³. Sample collections at the three sites took place every six days, with a sampling duration of ~ 24 h (Table 1). The sampling media for trace elements was Millipore HA mixed cellulose filters (47 mm diameter, 0.45 μm pore size; Millipore Corp., Bedford,
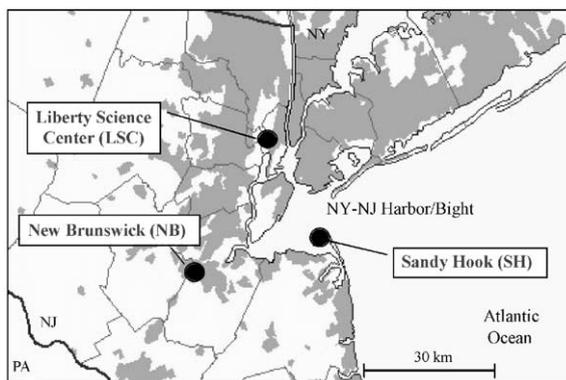

Fig. 1. Map of the New York (NY)–New Jersey (NJ) Harbor Bight and the sampling sites, modified from The National Atlas, USGS.

Table 1
Sampling information at three locations

Sites	Sampling period[a]	# of samples	Location features
Sandy Hook	January 1998–July 1999	59	Coastal
Liberty Science Center	October 1998–January 2000	45	Urban
New Brunswick	January 1998–December 1999	62	Urban

[a] Sample collection was not continued for certain periods of time due to power failure.

MA) that were pre-cleaned with successive hydrofluoric and hydrochloric acids (Maring et al., 1989). Sample loading on and unloading from polycarbonate filter folders was exclusively restricted to clean-room procedures. All samples were kept refrigerated until analyses except for the period of shipment between sampling sites and the laboratory at Rutgers University.

2.2. Chemical analysis

The concentrations of Al, Cd, Cr, Cu, Fe, Ni, Pb, Sb, V and Zn associated with $PM_{2.5}$ particulate matter were determined on a magnetic sector inductively coupled plasma mass spectrometer (ELEMENT, Finnigan MAT, Bremen, Germany) at the Institute of Marine and Coastal Sciences, Rutgers University. Samples analyzed in the solution phase were digested using strong mineral acids. One quarter of each sample filter (total area of $4.3\,cm^2$) was placed in a 15 ml Teflon screw-cap vial (Savillex Corp., MN) and a mixture of optima grade HNO_3/HF (Seastar Chemicals, Inc., British Columbia, Canada) was added to each vial. Complete dissolution of samples was achieved after a period of leach at room temperature and 4 h digestion on a hot plate at $140°C$ followed with evaporation to near dryness in a Class 100 HEPA flow bench. Samples were then redissolved for analysis with $20\,\mu L$ optima HNO_3 and diluted with deionized/distilled water to a final acid strength of $\sim 2\%$ HNO_3.

The ELEMENT has three resolution ($R = M$ $(\Delta M)^{-1}$ at 10% peak height) settings: low resolution (LR where $R = 300$), medium resolution (MR where $R = 4300$), and high resolution (HR where $R = 9300$). For this application, which was similar to the analysis of digested filtered marine particulate samples, low- and medium-resolution settings were selected (Cullen et al., 2001). To calculate the concentrations of the target elements in unknown samples, before each analytical run, external calibration curves were constructed from serial dilutions of a multi-element standard (High Purity Standards, Charleston, SC). Raw intensities were normalized to the initial sensitivity for In in each resolution and corrected for instrument blank. Slopes (correlation coefficients of $r > 0.999$) for the external standard curve were computed for all elements

$(cps\,ppb^{-1})$ and used to calculate the concentration in unknown samples. The final concentrations were corrected with combined reagent and filter blanks. To evaluate potential matrix effects 10 samples were spiked with a known concentration of the analytes of interest. Recovery of spiked elements ranged from $94–109$ ($\pm 6–14$)%. The accuracy of the analytical procedure was further assessed using Urban Particulate Matter #1648, a Standard Reference Material of National Institute of Standards and Technology (NIST, Gaithersburg, MD). The recovery of the target elements ranged between 93–106%, and the average precision determined from sample splits and duplicate digest aliquots averaged from 1.3–2.9% for all target elements. The overall average uncertainty associated with elemental air concentrations was $\leqslant 7\%$.

3. Results and discussions

3.1. Spatial variations

The ambient concentrations of pollution-derived trace elements at a specific location are largely dependent upon the distance from their sources, in general, reflecting the impacts of point-source emissions and the removal processes. However, it is not clear if such a spatial pattern holds for sites that are close to each other and are all located within the "source region". Fig. 2 presents the comparisons of the average concentrations of selected trace elements associated with $PM_{2.5}$ aerosol particles at Sandy Hook, New Brunswick, and Liberty Science Center. Obvious spatial variations were observed in the ambient levels of trace elements, with higher concentrations at the Liberty Science Center site than at the other two sites, and the concentrations of trace elements at Sandy Hook in general appeared to be the lowest. For example, the average ambient concentrations (standard deviation in parentheses) of Pb were 7.9 (5.4) $ng\,m^{-3}$ at the Liberty Science Center, 6.6 (6.5) $ng\,m^{-3}$ at New Brunswick, and 4.9 (3.6) $ng\,m^{-3}$ at Sandy Hook. In the case of Cu, the average concentrations were 17 (16) $ng\,m^{-3}$ at the Liberty Science Center, 7.3 (4.0) $ng\,m^{-3}$ at New Brunswick, and 4.7 (5.4) $ng\,m^{-3}$ at Sandy Hook. A further analysis using Student–
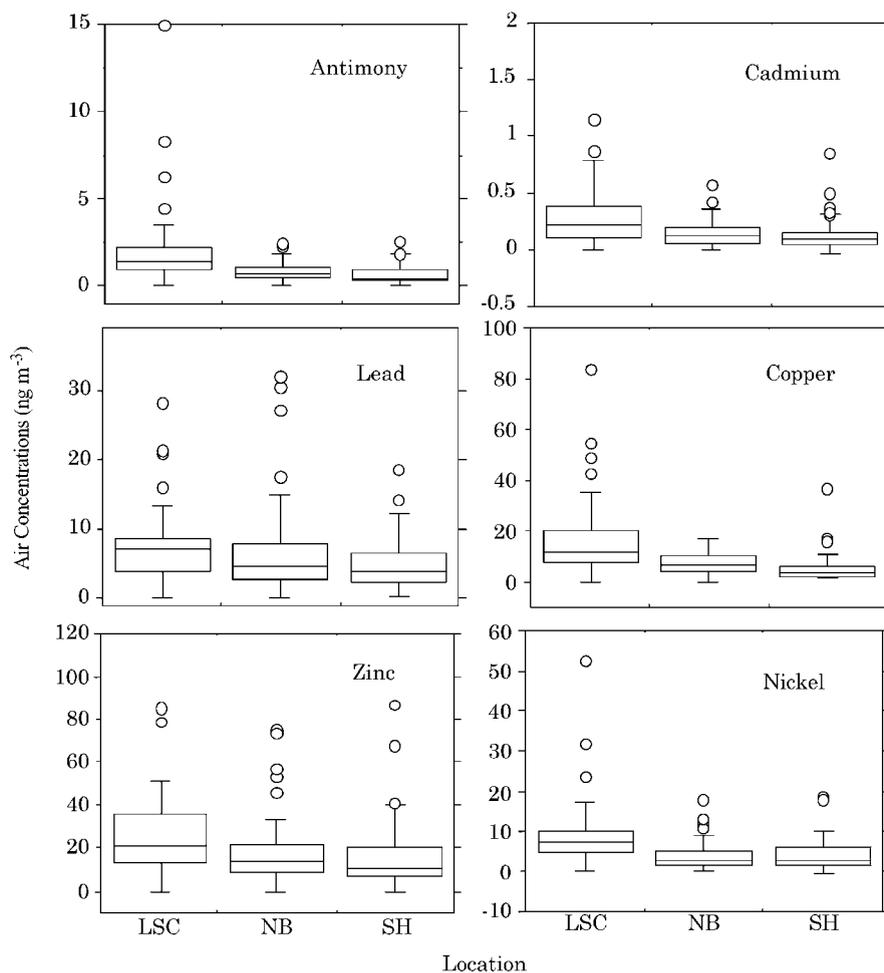
Fig. 2. Ambient concentrations of trace elements at three locations: (1) the Liberty Science Center (LSC), (2) New Brunswick (NB), and (3) Sandy Hook (SH). Number of samples analyzed for each location: LSC = 42; NB = 59; SH = 58. The results are presented by box plots. Each box encloses the 10th, 25th, 50th (median), 75th, and 90th percentiles of the concentrations. The values above the 90th and below the 10th percentiles are plotted as outlying open circles.

Newman–Keuls (SNK) test on three datasets reveals that the concentrations of most elements at Liberty Science Center are significantly higher than those at other two sites (Table 2), suggesting that the LSC site is more influenced by pollution emissions.

This spatial concentration gradient with a decrease toward the coast could be largely due to the dilution of the urban air with the clean marine. Using radionuclide tracers, Kim and colleagues found that the intrusion of pristine marine air could contribute to relatively low concentrations of ^{210}Pb and stable Pb relative to ^{7}Be as observed on the upper eastern shore of Chesapeake Bay (2000a). In addition, dry deposition of aerosol particles along the path of air masses moving away from point sources could also be an important mechanism for the removal of trace elements (Chester et al., 1994), which

could contribute to the observed spatial concentration gradient.

Similar spatial patterns for aerosols were also found from other studies in coastal regions. Wu et al. (1994) measured the concentrations of trace elements in aerosols at two locations, the Wye site in northern Chesapeake Bay, and the Elms site in central Chesapeake Bay. They found that concentrations of most elements are more often significantly elevated at Wye than at Elms, attributed to the Wye site receiving greater influence of pollutant sources in Baltimore. This spatial concentration pattern may have direct effects on atmospheric deposition, resulting in a similar deposition gradient. Scudlark et al. (1994) compared the results from precipitation measurements at the two sites and concluded that wet deposition fluxes of Al, As, Cd, Cr,

Table 2
Differences in trace element concentrations associated with PM2.5 among three sites by Student–Newman–Keuls test

Element	Site	N	Mean (SD) (ng m^{-3})	SNK grouping[a]	P-value
Al	LSC	45	39 (28)	A	0.2967
	NB	61	27 (29)	A	
	SH	59	32 (51)	A	
Cd	LSC	45	0.34 (0.37)	A	0.0001
	NB	60	0.15 (0.11)	B	
	SH	60	0.14 (0.14)	B	
Cr	LSC	45	2.7 (3.7)	A	0.0148
	NB	48	1.4 (2.0)	B	
	SH	44	1.3 (1.3)	B	
Cu	LSC	44	17 (16)	A	0.0001
	NB	62	7.3 (4.0)	B	
	SH	60	4.7 (5.4)	B	
Fe	LSC	41	160 (110)	A	0.0001
	NB	62	83 (49)	B	
	SH	60	55 (47)	C	
Ni	LSC	45	10 (9.0)	A	0.0001
	NB	60	4.0 (3.6)	B	
	SH	55	4.0 (3.8)	B	
Pb	LSC	44	7.9 (5.4)	A	0.0168
	NB	58	6.6 (6.5)	B, A	
	SH	60	4.9 (3.6)	B	
Sb	LSC	45	2.1 (2.5)	A	0.0001
	NB	61	0.88 (0.52)	B	
	SH	60	0.63 (0.52)	B	
V	LSC	45	9.2 (8.9)	A	0.0001
	NB	62	3.6 (3.5)	B	
	SH	60	5.4 (4.2)	B	
Zn	LSC	45	29 (19)	A	0.0003
	NB	62	18 (15)	B	
	SH	60	16 (15)	B	

[a] Means with the same letter are not significantly different.

Cu, Fe, Mn, Ni, Se and Zn are higher at Wye than those at Elms. A recent study conducted in the same region by Kim et al. (2000b) shows that wet deposition fluxes at Stillpond in northern Chesapeake Bay are higher than at Lewes, a remote site on the mid-Atlantic coast. Over the North Sea, the observed average concentrations of Zn, Cu, and Pb in aerosols at a Kiel Bight site are higher than those at several southern sites in the same region, attributed to proximity to urban sources (Chester et al., 1994). These studies suggest that the general phenomenon of decreasing elemental concentrations with distance from a regional point source may be accentuated in coastal areas due to proximity of clean marine air masses. These spatial characteristics of trace elements in the ambient air would have direct impacts on the

magnitudes and distributions of the fluxes of trace elements at different locations.

3.2. Temporal variation

To investigate the temporal patterns of trace elements in PM$_{2.5}$ particulate matter in the area, we present the atmospheric concentrations of six elements (Sb, Ni, Cu, Cd, Pb, and Zn) as a function of time, focusing on samples collected at Sandy Hook, the primary site. The atmospheric concentrations of these elements varied dramatically on a weekly basis as indicated in Fig. 3. The concentrations ranged from 0.85–36 ng m^{-3} for Cu, 0.26–18 ng m^{-3} for Ni, 0.080–2.6 ng m^{-3} for Sb, and 1.4–87 ng m^{-3} for Zn. Among a variety of factors affecting temporal concentration variations for aerosol trace elements at a specific location are wind direction, precipitation frequency which can drive removal fluxes, changes in source emission strength with time, as well as changes in aerosol particle-size distributions that affect their atmospheric residence time.

Despite the dramatic shifts in the weekly concentration levels of trace elements at this location, however, seasonal cycles were not clearly observed. This suggests that the atmospheric concentrations of these elements on
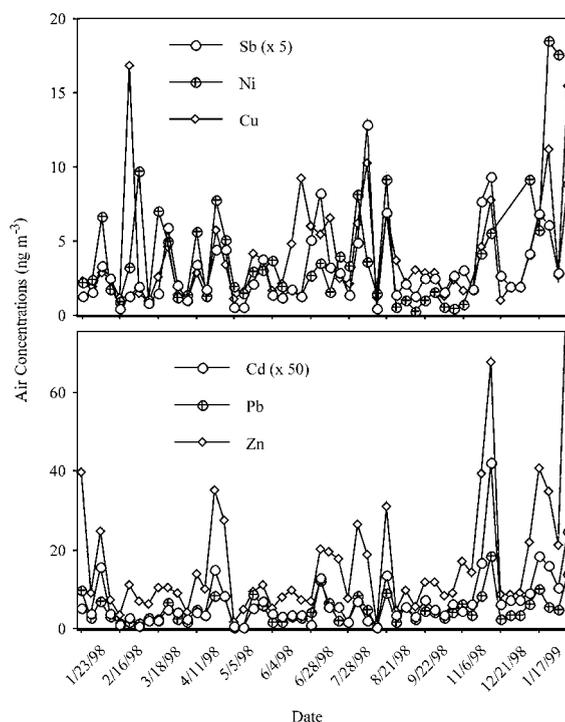

Fig. 3. Seasonal variations of selected trace elements in PM$_{2.5}$ samples at Sandy Hook collected during the period of 1998–1999.

$PM_{2.5}$ particles are not very sensitive to the seasonal variation of ambient conditions such as temperature. A similar result was obtained in the North Sea where trace element concentrations do not change dramatically during different sampling periods (Baeyens and Dedeurwaerder, 1991). However, the dramatic changes in daily concentrations could be affected by variation of emission rates, wind dynamics, precipitation episodes, etc. Over the North Sea, the atmospheric loading of particulate trace metals is affected by different wind sectors (Baeyens and Dedeurwaerder, 1991). Over Chesapeake Bay, precipitation scavenging could exponentially remove atmospheric ^{7}Be, ^{210}Pb, and to a lesser extent stable Pb (Kim et al., 2000a). Due to mixed influences of different processes on the loading of atmospheric trace elements, more intense sampling than the every-six-day sampling approach used in this study would be more appropriate to interpret temporal variation of trace elements with meteorological episodes.

Another feature revealed in Fig. 3 is that the elemental concentrations were strongly covariant throughout the sampling period. For example, the concentration variations of Cd, Pb, and Zn are almost in phase. This co-varying weekly pattern suggests that their levels in the ambient air were controlled more or less by similar processes and certain elements are likely attributed to the same sources.

3.3. Sources of trace elements

3.3.1. Enrichment factor

The crustal enrichment factor method has commonly been used as a first step in attempting to evaluate the strength of the crustal and non-crustal sources (Gao et al., 1992). The enrichment factor for any element X relative to crustal material is defined by

$$EF_{crust,X} = (X/Y)_{air}/(X/Y)_{crust},$$

where $EF_{crust,X}$ is the enrichment factor of X, Y is a reference element for crustal material and $(X/Y)_{air}$ is the concentration ratio of X to Y in the aerosol sample, and $(X/Y)_{crust}$ is the average concentration ratio of X to Y in the crust. If $EF_{crust,X}$ approaches unity, crustal soils are likely the predominant source for element X. Operationally, given local variation in soil composition, if $EF_{crust,X}$ is >5, the element X may have a significant fraction contributed by non-crustal sources.

To determine the strength of crustal and noncrustal sources for trace elements associated with $PM_{2.5}$ particles, the enrichment factor was calculated for each element based on samples collected at three sites and presented in Fig. 4. We use aluminum (Al) as the reference element in this study based on chemical composition of the earth crust (Taylor and McLennan, 1985), assuming minor contributions of pollutant Al. Fig. 4 indicates that the atmospheric concentrations of
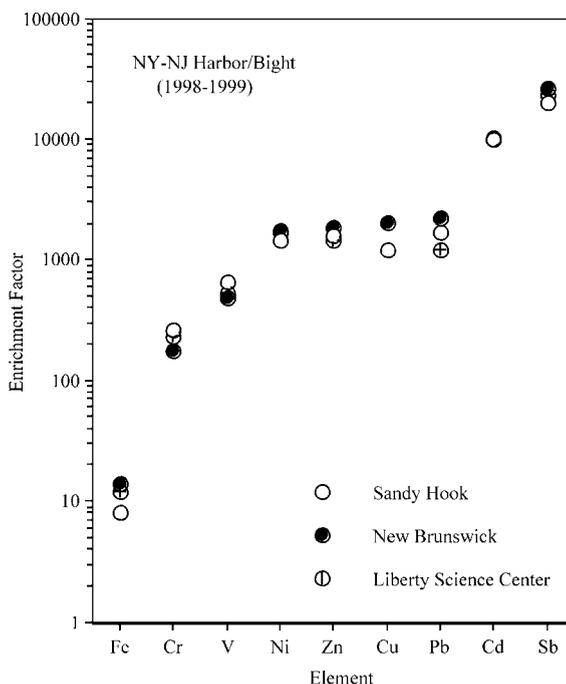

Fig. 4. Enrichment factors of selected trace elements relative to Al for the $PM_{2.5}$ samples collected at three locations during the period of 1998–1999.

Cd, Cr, Cu, Ni, Pb, Sb, V, and Zn in $PM_{2.5}$ fine particles are 200–20 000 times higher than those expected from crustal soil. The high enrichment suggests that the dominant sources for these elements are non-crustal and a variety of pollution emissions may contribute to their loading in the ambient air. With very similar patterns for enrichment factors at all three locations (Fig. 4), pollution emissions clearly impact the entire NY–NJ harbor area. Most of the elements at the Sandy Hook site are relatively less enriched than at the other two sites, except for Cr and V. Non-crustal Cr likely reflects a variety of pollution sources, in particular coal combustion and sewage sludge incineration (Nriagu and Pacyna, 1988). Non-crustal V is primarily from the combustion of heavy fuel oil (Rahn and Lowenthal, 1984. We speculate that there could be more oil industry and waste incineration activities occurring near Sandy Hook. On the other hand, the enrichment factors for Zn and Pb at Liberty Science Center are lower than at the other two locations, although the absolute concentrations of these two elements are higher. Simple calculations of the crustal fraction using the mean concentrations in Table 2 and mean crustal composition (Taylor and McLennan, 1985) indicate that crustal Pb only accounts for ∼0.13% of the total and crustal Zn accounts for ∼0.14% at all three sites. Therefore, we cannot speculate that the crustal source could play

even a minor role on the air loading of Pb and Zn in the area.

3.3.2. Factor analysis

To further identify common sources for pollution-derived trace elements over the NY–NJ Harbor Bight, we applied factor analysis to the combined trace element concentration data obtained at Sandy Hook, Liberty Science Center, and New Brunswick. This analyses was conducted using Varimax rotated principal component analysis, with three factors or components being extracted which describe groups of trace elements with different sources (Table 3). We did not consider this analysis for individual sites because the reliability of the technique is dependent on sample size. The commonalties for individual elements range from 0.86 (for Zn) to over 0.9 for the remaining nine elements considered (Sb, Cd, V, Ni, Pb, Cu, Al, Fe, Cr). This indicates the fact that the three component solutions are quite satisfactory, explaining 94% of the variance. These factors clearly indicate the different source components for trace elements over the region.

The first factor that explains the most of the variance (72%) has high loading of all elements investigated with the exception of Al and Fe. It represents the main types of the pollution sources in the region, most likely waste incinerators (Sb, Cd, Pb, Cr, Zn), oil burning (V, Ni), and pyrometallurgical non-ferrous metal production (Pb) (Nriagu and Pacyna, 1988). These sources could contribute significantly to the loadings of the elements in our study region. Chemical mass balance calculations suggest that over Chesapeake Bay, incinerators are the principal sources of air loadings of Cr ($\sim 80\%$), Cd ($\sim 80\%$), Sb ($\sim 60\%$) and Zn ($\sim 75\%$), oil combustion contributes to $\sim 80\%$ of the total V loading, and atmospheric Pb is primarily derived from incineration as well as motor vehicles (Wu et al., 1994). These sources

not only affect the regional air loadings of the elements, their impacts can reach far over the ocean. Arimoto et al. (1995) reported that non-crustal V observed at Bermuda is primarily attributed to pollution emission from heavy fuel oil. However, the difficulties in separating this complex pollution into individual components are likely related to the timescales of variation in source emissions and underlying physical processes relative to the sampling intervals. For example, source variability and the meteorological processes likely have short characteristic time constants that are averaged over the 24 h sampling intervals.

Interestingly, a high loading is found for Fe in Factor 2 associated with Zn. Atmospheric Fe is commonly considered a crustal element, and its current association with Zn suggests that pollution emissions, in particular incineration and fossil fuel combustion (Nriagu and Pacyna, 1988), may contribute to atmospheric Fe in the region, in addition to crustal soil. Results from the Mediterranean region suggest that atmospheric Fe is enriched relative to its crustal abundance due to the influence of pollution emissions in the region (Kubilay et al., 2000). Over the North Sea, Fe associated with aerosols is found to be moderately enriched relative to the average crustal composition (Baeyens and Dedeur-waerder, 1991). A recent study conducted at a coastal site in China also shows that atmospheric Fe is enriched in fine aerosol particles, attributed to either fly ash from coal combustion or natural origin (Gao and Anderson, 2001). Thus anthropogenic emissions may perturb the natural cycle of certain crustal elements such as Fe. However, it remains a challenge at present to quantitatively separate atmospheric Fe of pollution origin from that of crustal origin.

The third factor is solely related to Al. This is consistent with the lack of correlation found between Al and the rest of the elements in this study. This may suggest that crustal soil is the dominant source for Al in fine suspended particulate matter at this location, either due to episodic presence of crustal substances brought to the area from distant sources or resuspended local soil. This is consistent with the estimate by Wu et al. (1994) that about 80% of the atmospheric Al over Chesapeake Bay are derived from soil.

A correlation matrix for all elements combined from three locations is shown in Table 4. Results show that most elements measured in the fine fraction of the NY–NJ aerosols are highly correlated with each other, suggesting well-mixed components clearly originating from different sources and/or from multiple similar sources.

Table 3
Factor loadings of trace element data combined from three sites (Sandy Hook, Liberty Science Center, New Brunswick)

Element	Factor 1	Factor 2	Factor 3	Commonality
Sb	0.98	0.05	0.11	0.98
Cd	0.99	0.03	0.11	0.98
V	0.95	0.24	0.08	0.97
Pb	0.93	0.30	0.09	0.96
Ni	0.93	0.25	0.01	0.93
Cu	0.92	0.22	0.12	0.92
Zn	0.56	0.74	0.04	0.86
Al	0.14	0.19	0.97	0.99
Fe	0.00	0.93	0.19	0.90
Cr	0.98	0.03	0.10	0.98
% Variance	72.5	14.3	7.91	94.7

3.4. Estimates of dry deposition fluxes

We used a dry deposition model to estimate the atmospheric input of trace elements through particle dry

Table 4
Correlations among trace elements combined from three sites (bold correlations are significant at $p < 0.05$)

Element	Sb	Cd	V	Pb	Ni	Cu	Zn	Al	Fe	Cr
Sb	1.00	1.00	**0.95**	**0.94**	**0.92**	**0.94**	**0.56**	0.24	0.10	**0.99**
Cd		1.00	**0.94**	**0.93**	**0.91**	**0.93**	**0.55**	0.23	0.08	**0.99**
V			1.00	**0.95**	**0.96**	**0.92**	**0.73**	0.25	0.23	**0.94**
Pb				1.00	**0.93**	**0.92**	**0.77**	0.27	0.28	**0.92**
Ni					1.00	**0.90**	**0.70**	0.20	0.23	**0.91**
Cu						1.00	**0.66**	0.28	0.26	**0.92**
Zn							1.00	0.28	**0.58**	**0.56**
Al								1.00	0.33	0.23
Fe									1.00	0.08
Cr										1.00

deposition. In this model, the dry deposition flux was calculated as the product of the measured atmospheric concentration of an element and a dry deposition velocity. We used the annual average atmospheric concentrations obtained at Sandy Hook to estimate the level of the annual dry deposition fluxes of the target elements. Based on considerations of dry deposition velocities used in several coastal regions (Baker et al., 1997; Chester et al., 1994; Church et al., 1984; Gao et al., 1992; Holsen et al., 1997; Yang et al., 1996; Quinn et al., 1992), we chose 0.1 and $0.5\,\mathrm{cm\,s^{-1}}$ as the lower and upper values for dry deposition velocities for pollution-derived elements (Table 5). However, due to the fact that the actual dry deposition velocities may vary dramatically under different meteorological conditions (Chester et al., 1994), the fluxes obtained using this approach should involve substantial uncertainties and could only serve as first approximates.

Results indicate that the magnitudes of the dry deposition fluxes of most elements to this area are comparable to those in nearby coastal regions, such as the Chesapeake Bay (Baker et al., 1997). For example, the dry deposition fluxes for Pb at SH ranged from 0.15 to $0.76\,\mathrm{mg\,m^{-2}\,yr^{-1}}$. In the Chesapeake Bay, the Pb flux averaged $0.69\,\mathrm{mg\,m^{-2}\,yr^{-1}}$. In the case of Cu, the dry deposition fluxes at SH were from 0.15 to $0.73\,\mathrm{mg\,m^{-2}\,yr^{-1}}$, similar to the value of $0.34\,\mathrm{mg\,m^{-2}\,yr^{-1}}$ in the Chesapeake Bay. It is worth mentioning, however, that the results from the Chesapeake Bay were obtained during the period of 1990–1992, approximately 7 yr earlier than this study. In addition, the dry deposition fluxes of trace elements in this work were derived from $PM_{2.5}$ samples only, a portion of the total particulate matter. Therefore, further evaluation of the present levels of the total dry deposition fluxes of trace elements to the NY–NJ harbor estuary should be taken cautiously. Considering pollution-derived elements are primarily associated with submicrometer aerosol particles, dry deposition of trace elements associated with $PM_{2.5}$ from this

Table 5
Atmospheric dry deposition fluxes of pollution-derived trace elements associated with $PM_{2.5}$ to the New York–New Jersey harbor estuary

Element	Mean concentrations (SD) $(\mathrm{ng\,m^{-3}})$	Dry deposition fluxes $(\mathrm{mg\,m^{-2}\,yr^{-1}})$
Cd	0.14 (0.14)	0.0042–0.021
Cr	1.3 (1.3)	0.040–0.20
Cu	4.7 (5.4)	0.15–0.73
Ni	4.0 (3.8)	0.12–0.62
Pb	4.9 (3.6)	0.15–0.76
Sb	0.63 (0.52)	0.020–0.10
V	5.4 (4.2)	0.17–0.84
Zn	16 (15)	0.50–2.5

study may represent a significant portion of the total atmospheric dry deposition to the NY–NJ harbor estuary.

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