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Heavy Metal Contamination of Roadside Dusts: a Case Study for Selected Highways of the Greater Toronto Area, Canada Involving Multivariate Geostatistics

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ABSTRACT

A good understanding of roadside soil contamination and the location of pollution sources is important for addressing many environmental problems. The results are reported here of an analysis of the content of metals in roadside dust samples of four major highways in the Greater Toronto Area (GTA) in Ontario, Canada. The metals analysed are Pb, Zn, Cd, Ni, Cr, Cu, Mn and Fe. Multivariate geostatistical analysis including Correlation Analysis (Ca), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) is used to estimate soil chemical composition variability. The correlation coefficient shows that most of the pairs exhibit positive correlations, the exceptions being Zn-Cd, Mn-Cd, Zn-Cr, Pb-Zn and Ni-Zn. PCA shows that the three eigenvalues are less than one and suggests that the contamination sources are processing industries and traffic. HCA classifies heavy metals in two major groups. The geostatistical analysis allows geological and anthropogenic causes of variations in the contents of roadside dust heavy metals to be separated and common pollution sources to be identified.

Key words: Heavy metals, contamination, multivariate geostatistics, roadside dust, highways, Toronto, Canada

INTRODUCTION

In recent years, much concern has been expressed over the problem of urban soil contamination with heavy metals due to rapid industrialization and urbanization (Sun *et al.*, 2010). The concentrations of heavy metals and toxic elements in roadside soils and dust can provide valuable information about pollution levels in urban and industrial areas since, in most cases, such concentrations reflect the extent of the emissions of these elements from anthropogenic sources (Fergusson, 1990; Harrison *et al.*, 1981). Lead in particular is an ubiquitous environmental pollutant and its presence in soils has been extensively studied and attributed to the use of alkyl-lead compounds such as antiknock additives in petrol (Ward, 1990; Gratani *et al.*, 1992). Many studies have been reported on the contamination of roadside environments with various elements, especially heavy metals such as Cu, Fe, Cr, Zn, Pb and Ni. These elements are released into the roadside environment as a result of combustion, mechanical abrasion and normal wear and tear (Carlosena *et al.*, 1998). Lagerwerff and Specht (1970) attribute the presence of Ni to gasoline and of Cd and Zn to tires and motor oil. Mn like Pb is used as a vehicle fuel additive (Loranger and Zayed, 1994).

A trend for higher concentrations of heavy metals to be present on streets where traffic is more likely to undergo stop-start manoeuvres, such as at traffic lights, has been noted by Akhter and Madany (1993), Ellis and Revitt (1982), Fergusson *et al.* (1980), Dyke *et al.* (1989), Harrison *et al.* (1985), Hamilton *et al.* (1984), Howari and Banat (2001), Abu-Rukah (2001), Wei and Yang (2010), Ghrefat *et al.* (2011), Dao *et al.* (2010) and Morton-Bermea *et al.* (2009). Soils bordering highways often have high contents of heavy metals. Almost all the above mentioned studies reveal that deposition of metals is highest close to the roadside, with the contamination diminishing rapidly with distance from the road.

Webster *et al.* (1994) applied multivariate geostatistics to provide a more objective assessment of the sources of some heavy metals in topsoil, based not only on visual inspection of the concentration maps but also on a quantitative analysis of the spatial variability of the elements and their relationships on different spatial scales. Moreover, they used multivariate methods to compare the results of principal component analyses carried out on the concentration data with the experimental indicator variogram applied to some categorical information, in order to relate the concentration of heavy metals to the geology and land use of the area.

Multivariate geostatistics use information arising from relationships among variables in order to improve estimations for variables and to identify the different causes of variations over different spatial scales (Castrignano *et al.*, 2009). Several factors affecting soil variations are likely to have a short-range influences, whereas others operate over longer distances; soil variables are thus expected to be correlated in a scale-dependent way. Therefore, the scale-dependent correlation structure of some soil variables, assuming it can reflect different sources of variability, becomes important in environmental investigations. However, this requires a particular statistical approach combining classic principal component analysis to describe correlation structure of multivariate data sets, with geostatistics that take into account the co-regionalized nature of the variables (Sollitto *et al.*, 2010).

The present study deals with important and very busy highways in and around the city of Toronto, in the province Ontario, in Canada. Specifically, major 400 series highways (401, 400, 404 and the Don Valley Parkway) within the Greater Toronto Area (GTA) are considered (Fig. 1). The objectives are to assess roadside dust contamination by heavy metals in the GTA. High concentrations of traffic flow are thought to be the main cause of elevated heavy metals concentrations, although the parent material mineralogical and chemical composition in addition to the different types of land use could be the other causes. The multivariate geostatistics approach used here formulates hypotheses regarding the main sources of contamination in the roadside dust and reveals scale-dependent variations of chemical soil properties.

BACKGROUND

Study area: Toronto is located in southern Ontario on the northwestern shore of Lake Ontario (Fig. 1). With over 2.5 million residents, it is the fifth most populous city in North America. Its metropolitan area with over 5 million residents is the seventh largest urban region in North America. Toronto is at the heart of the Greater Toronto Area and is part of a densely populated region in Southern Ontario known as the Golden Horseshoe, which is home to over 8.1 million residents, approximately 25% of Canada's population (Table 1) (Statistics Canada, 2006).

The 400 series of highways make up one of the primary vehicular networks in the south of the province and they connect to numerous border crossings with the U.S, the busiest being the Detroit-Windsor Tunnel and the Ambassador Bridge (via Highway 401) and the Blue Water Bridge

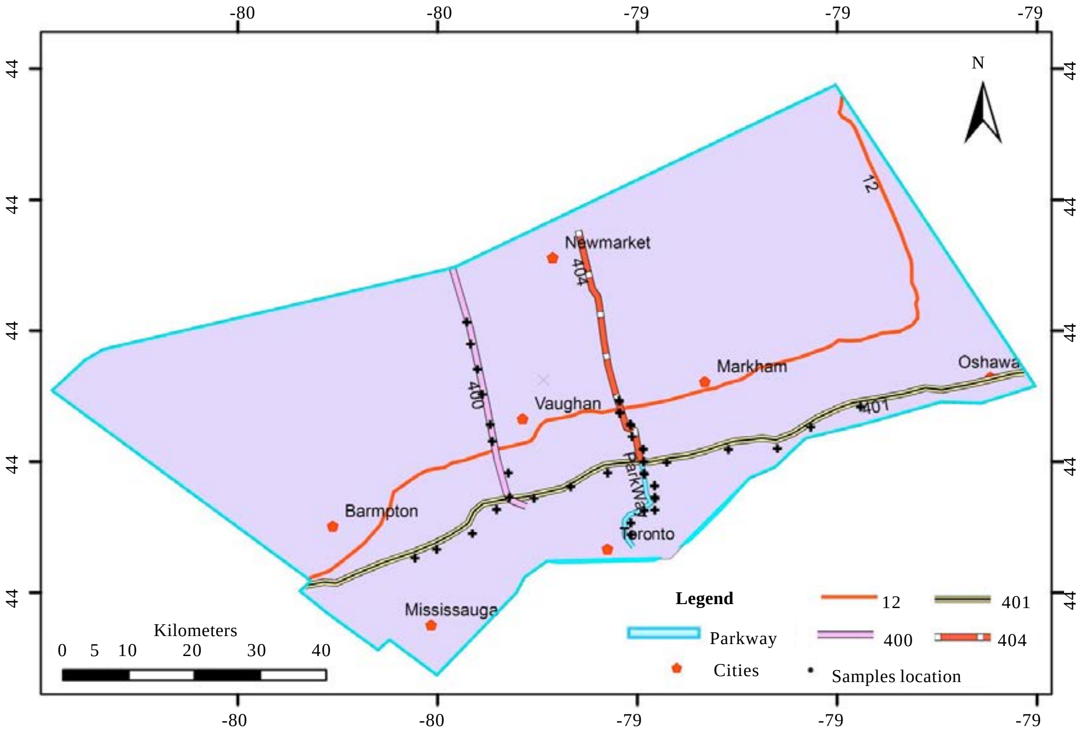

Fig. 1: Map of sampling and study area in the Greater Toronto Area (horizontal axis shows latitudes and vertical axis longtitudes)

(via Highway 402). The primary highway along the southern route is Highway 401 (also called the Highway of Heroes), the busiest highway in North America and the backbone of Ontario's road network, tourism and economy (Thurston, 1991).

Highway 401 extends across southwestern, central and eastern Ontario. It is one of the world's busiest highways; a 2006 report estimated the annual average daily traffic count on Highway 401 in Toronto between Weston Road and Highway 400 at 431,900 and up to 500,000 on some days (University of Toronto, 2010; OECD, 2009).

King's Highway 400, known commonly as Highway 400 and historically as the Toronto-Barrie Highway, is a 400-series highway in Ontario linking the city of Toronto in the urban and agricultural south of the province with the scenic and sparsely populated central and northern regions. Highway 400 is the second longest freeway in the province, the Trans-Ontario Highway 401 being the longest (OECD, 2009).

The Don Valley Parkway (DVP) is a controlled-access six-lane expressway in Toronto connecting the Gardiner Expressway in downtown Toronto with Highway 401. North of Highway 401, the expressway continues as Highway 404 to Newmarket. The Parkway runs through the parklands of the Don River valley, after which it is named. The parkway operates well beyond its intended capacity of 60,000 vehicles per day and is known for its daily traffic jams; some sections carry an average of 100,000 vehicles a day (OECD, 2009).

King' Highway 404, also known as Highway 404, is a 400-series highway in Ontario connecting Highway 401 and the Don Valley Parkway in Toronto with Newmarket. The controlled access freeway also connects with Highway 407 in Richmond Hill.

Table 1: Characteristics of selected highways in the Greater Toronto area

Highway designation	Total length (km)	Year inaugurated	North/east end	South/west end	Description
400	209.0	1952	Bowes Street/Mc Dougall drive in Parry sound (connects to Highway 69)	Maple leaf drive overpass in Toronto	Highway 400 is Toronto's main highway link to York Region, Barrie and Muskoka. It is the second longest highway in the state Highway 400 is expected to be extended to Sudbury by 2017
401	817.9	1952	Quebec border (connects to Autoroute 20)	Highway 3 in Windsor	Highway 401 is the backbone of the 400-Series network taking nearly 30 years to be built and running across the entire length of Southern Ontario. It has traffic volumes of over 500,000 per day in some areas of Toronto, making it one of the busiest highways in the world (4)
Don Valley Parkway	15.0	1961	Highway 401 (continues as Highway 404)	Gardiner expressway -downtown Toronto	The Don Valley Parkway (DVP) is a controlled-access six-lane expressway in Toronto connecting the Gardiner Expressway in downtown Toronto with Highway 401. North of Highway 401, the expressway continues as Highway 404 to Newmarket. The parkway runs through the parklands of the Don River valley, after which it is named. It is patrolled by the Toronto Police Service, and has a maximum speed limit of 90 km/h for its entire length
404	36.8	1977	Herald Road /Green Lane in East Gwillimbury	Highway 401 and Don valley Parkway in Toronto	Highway 404 is the second north-south freeway in York Region and connects the northeastern suburbs and Toronto as the Don Valley Parkway. It is one of two highways (along with Highway 403) with dedicated 24/7 high-occupancy vehicle (HOV) lanes and the only one with a dedicated HOV off-ramp to Highway 401 westbound at the Highway 401/Don Valley Parkway junction

Geology, terrain, soils and land use: The bedrock geology of Ontario is variable in lithology, structure and age, although approximately 61 percent of the province is underlain by Precambrian rock of the Canadian Shield (Thurston, 1991). In the Phanerozoic age, sedimentary rocks developed in marine basins along the northern border of the Shield, forming the Hudson Bay lowlands and in the Great Lakes Basins in the south (Fig. 2). The Shield can be divided into three major geological and physiographic regions, from the oldest in the northwest to the youngest in the southeast. The northwestern region, known as the Superior Province, is more than 2.5 billion years old. This region, which can be described as lying north and west of the present city of Sudbury, is composed mainly of felsic intrusive rocks forming the rocky Severn and Abitibi uplands (Bostock, 1970). The central region, known as the Grenville Province, is 1.0 to 1.6 billion years old. This region lies to the south of Sudbury and is dominated by metasedimentary rocks that form the Laurentian highlands. The Penokean hills, a fold belt and the Cobalt plain, an embayment, constitute the Southern Province, which is a narrow region approximately 1.8 to 2.4 billion years old extending from Sault Ste. Marie in the west approximately to Kirkland Lake in the east.

To the north of the Shield, in the area generally referred to as the Hudson Bay lowlands, the bedrock is composed of carbonate sedimentary formations. These formations date primarily from

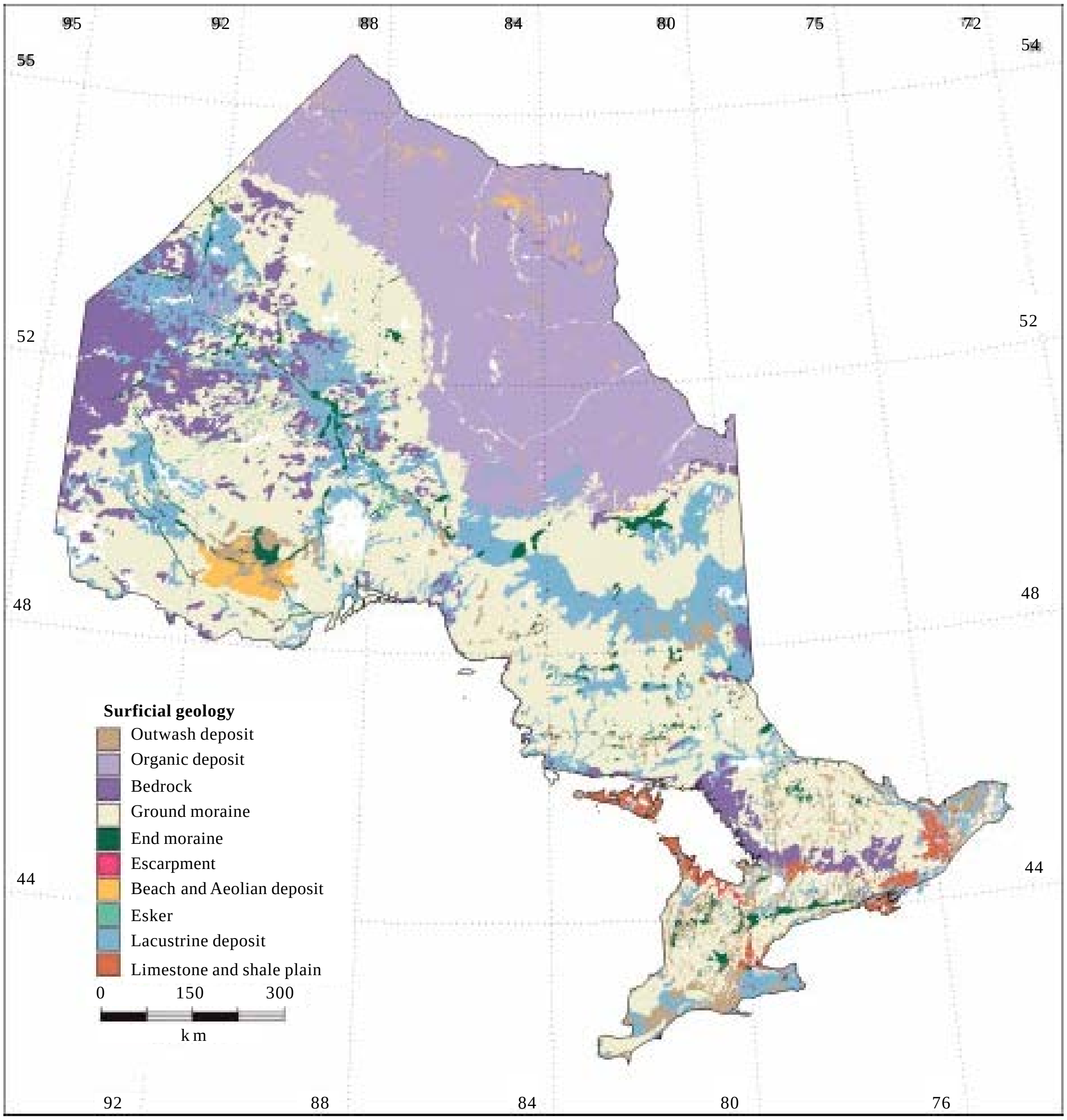

Fig. 2: Surficial geology of Ontario. (FLEP/OMNR, 1996)

the Silurian period, but there are significant areas from the Ordovician and Devonian periods as well. Other sedimentary rocks occur near the city of Ottawa, in an area referred to as the Ottawa embayment, as well as throughout areas north of Lakes Erie and Ontario (Dyke *et al*., 1989). The clastic and marine carbonate bedrock of southern Ontario is interrupted by the Frontenac axis, a southern extension of the Shield, which intersects the St. Lawrence Seaway east of Kingston. The Frontenac axis has different forest cover and land use patterns than areas to either the west or east, due to its uneven terrain and shallow acidic soils, both characteristic of the Canadian Shield (Fig. 2).

The nature of soil development in Ontario depends on local combinations over time of climate, parent material, terrain, vegetation and other organisms. Soils are formed by the physical and chemical weathering of bedrock and glacial parent material and are continually modified and shifted by water, wind and gravity. Where glacial action has scoured away overlying deposits, the soils of Ontario closely reflect the underlying bedrock. Other soils reflect the tills and other morainic and lacustrine materials deposited by advancing and retreating ice sheets and their melt water. The Canadian System of Soil Classification (Agriculture Canada, 1987) is a standard series of orders and component great groups by which soils can be identified and described. Six of the soil orders in this classification are predominant in Ontario. These are the organic and related organic cryosolic soils in northern parts of the province, brunisols in the northwest part of the Shield and south of the Shield, podzols over much of the central and southern Shield, luvisols in the Claybelt and over much of southern Ontario and gleysols in poorly drained areas and in the Claybelt lacustrine deposits. Regosolic soils are dominant only in a thin band along the southwest shore of Hudson’s Bay. Figure 3 illustrates the soil orders and great groups that occur most extensively in Ontario, based on composition within the Soil Landscapes of Canada mapping units (AAFC, 1996).

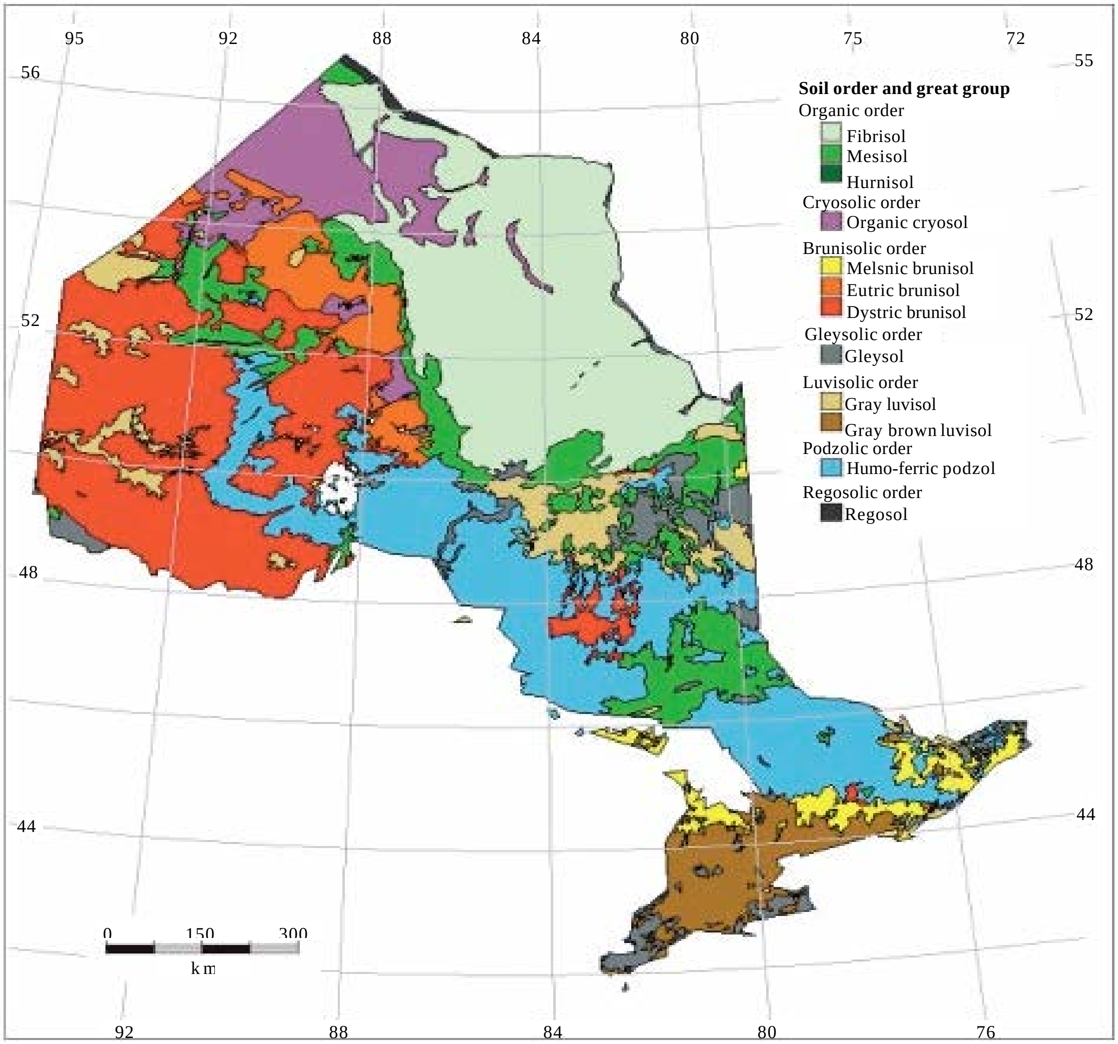

Fig. 3: Dominant soil orders and great groups in Ontario, based on Soil Landscapes of Canada units (AAFC, 1996)

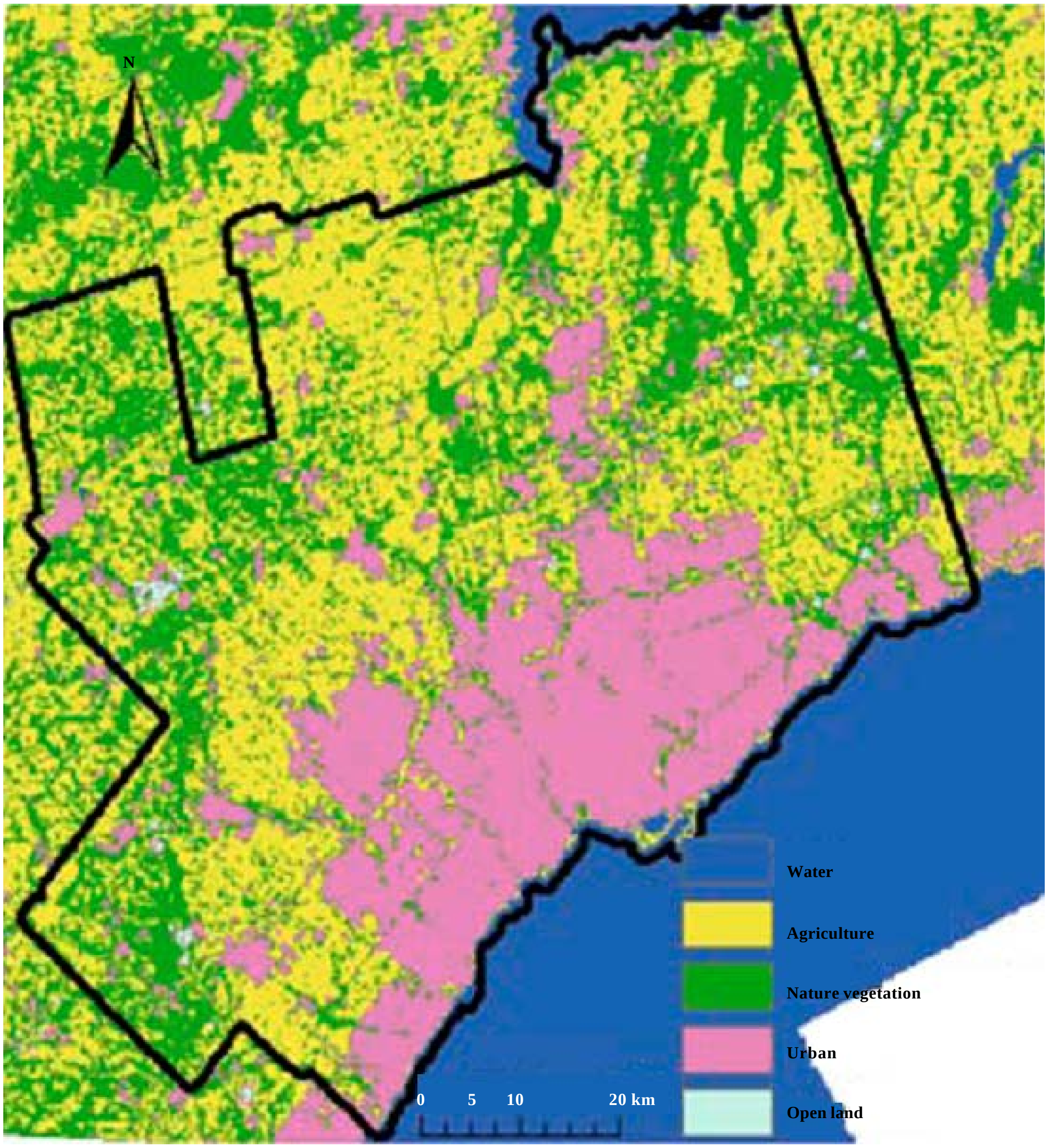

Fig. 4: Land use maps of Greater Toronto Area for the 2000s

From the early 1990s to the early 2000s, the total area of settlement and developed land in the GTA has increased by 513 km^2. Meanwhile, the area of agricultural land and naturally vegetated land has decreased by 114 and 423 km^2, respectively. As evident in Fig. 4, most of the land use/cover changes, similar to population change, have occurred at the urban-rural fringe within the northern portion of the GTA. In this area agricultural lands and naturally vegetated lands had been converted to new settlement or development areas.

MATERIALS AND METHODS

Collection of samples: A total of 42 road dust samples were collected from four highways in the Greater Toronto Area: 401, 400, 404 and Don Valley parkway. The road dust samples were collected from forty two locations perpendicular to the traffic flow on these selected GTA highways (Fig. 1). The highway lengths are 817.9 km for the 401, 209 km for the 400, 36.8 km for the 404 and 15 km for the Don Valley Parkway and they have an estimated average traffic flow of 750,000 vehicles per day, mostly trucks and microbuses. The sampling sites are located at distances of 0 to 3 m from the roadside.

Geochemical analyses: The sediment samples were transported to the laboratory in polyethylene bags and dried in an oven at 60°C for 24 h. Different grain size fractions were selected for the analysis of metals: <2 μm fraction (Statistics Canada, 2006; Morton-Bermea *et al.*, 2009; Abu-Rukah, 2001), <63 μm fraction (Calmano *et al.*, 1982), <150 μm fraction and <2 mm fraction (Wong and Mak, 1997). In the present study, the contamination of sediments with particle size fractions below 2 μm were investigated using the pipette method (Gee and Bauder, 1986), in which a sample is pipetted at different times and various depths of the suspension of the sample in a measuring cylinder. The pipetted suspension is condensed and dried and the mass ratio of the pipetted fraction is determined by weighing. Then, 0.5 g of the pipetted fraction was digested using 4 mL of HNO_3 (65%), 2 mL of HF (40%) and 4 mL of $HClO_4$ (70%). The solution of the digested samples was analyzed with an Atomic Absorption Spectrometer (PYE UNICAM SP9) for lead (Pb), zinc (Zn), cadmium (Cd), nickel (Ni), chromium (Cr), copper (Cu), manganese (Mn) and iron (Fe). For quality control, all sediment samples were analyzed in triplicate and mean values were calculated. Also, analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix to monitor the possibility of sample contamination during digestion and subsequent analysis. The absorption wavelength and detection limits, respectively, were as follows: 228.8 nm and 0.0006 ppm for Cd; 240.7 nm and 0.007 ppm for Co; 324.7 nm and 0.003 ppm for Cu; 248.3 nm and 0.005 ppm for Fe; 279.5 nm and 0.003 ppm for Mn; 232.0 nm and 0.008 ppm for Ni; 217.0 nm and 0.02 ppm for Pb; and 213.9 nm and 0.002 ppm for Zn.

The accuracy of the Atomic Absorption Spectrometer measurements was assessed by analyzing the standard reference material NIST, SRM 1646. The calculation of the different statistical parameters was performed using the SPSS (Statistical Program for the Social Sciences) software package.

RESULTS AND DISCUSSION

Metals concentrations: The mean concentrations (in ppm) of metals in road dust for the selected highways in the present study are as follows: Cd (0.51), Cu (162), Fe (40,052), Cr (197.9), K (9647.6), Mg (577.4), Ca (102,349), Zn (200.3), Mn (1202.2), Pb (182.8) and Ni (58.8). These means are for all sample locations for the four highways considered (400, 401, 404 and Don Valley Parkway).

Minimum and maximum concentrations, the mean values and standard deviations for each of the analyzed metals and the background values, are presented in Table 2. In general, the concentration of the various metals varies widely in the studied highways. The mean concentrations for the road dust samples are higher than their background values, suggesting that the presence of these metals in road dust around the GTA are influenced by heavy traffic as well as the anthropogenic sources around the highways.

Table 2: Statistical summary of heavy metal levels (in ppm) for the collected roadside dusts

Highway	Parameter	Cd	Cr	Cu	Fe	Zn	Mn	Pb	Ni
400	Minimum	0.47	64.8	53.90	1474	39.3	100	118.3	34
	Maximum	0.50	260.2	286.10	67495	1367	2725	205	80
	Range	0.03	195.3	232.10	66021	1328	2625	87	46
	Mean	0.492	148.9	178.60	51784	456	1330	170	53
	Median	0.494	131.0	168.20	59685	252	1226	186	49
	Std. deviation	0.010	73.4	76.95	22881	468.3	991	35.9	17.7
	Variance	0.00	5399.0	5921.00	5.2	219362	983006	1289	315
	Kurtosis	2.70	-0.83	-0.04	5.70	1.83	-1.36	-2.02	-0.94
	Skewness	-1.52	0.82	-0.31	-2.32	1.50	0.289	-0.44	0.82
401	Minimum	0.46	57.3	113.60	30254	81.3	187	32.5	32
	Maximum	0.95	558	392.10	70050	366.8	3125	378.7	327
	Range	0.49	500.6	278.40	39797	285.5	2938	346.2	295
	Mean	0.539	230.2	186.00	52558.5	221.6	1506.4	205.1	80.2
	Median	0.495	181.7	151.90	52770	245.9	1543	177.5	58
	Std. deviation	0.136	137.4	83.40	10240	82.1	761.7	112.9	78.2
	Variance	0.019	18882	6962.00	10008	6746	580331	12751	6119
	Kurtosis	8.762	1.87	2.72	1.21	-0.242	1.62	-1.33	11.47
	Skewness	2.91	1.28	1.78	-0.499	-0.298	0.083	0.206	3.35
404	Minimum	0.48	115.3	76.20	28712	56.8	471	124.7	16
	Maximum	0.56	310.5	230.30	60325	290.9	2450	212.2	62
	Range	0.08	195.1	154.10	31613	234.1	1979	87.5	46
	Mean	0.508	187.8	134.70	44799.6	156.1	1391.9	152.1	39.2
	Median	0.503	173.4	134.20	45840	157	1467	141	36
	Std. deviation	0.022	52.6	47.30	10415	81.5	616.4	26.3	16.2
	Variance	0.00	2770	2246.0	1.1	6646	380017	696	265
	Kurtosis	3.0	2.15	0.05	-1.04	-0.62	-0.78	1.88	-1.53
	Skewness	1.50	1.20	0.53	-0.126	0.60	0.08	1.54	-0.13
Don valley parkway	Minimum	0.48	84.1	106.1	38178	85.3	150	105.2	33
	Maximum	0.54	316.7	249.5	52655	342.7	2188	321.8	110
	Range	0.05	232.6	143.4	14478	257.4	2038	216.6	77
	Mean	0.50	203.3	154.1	44988.5	183.7	1367.1	196	58.7
	Median	0.497	233.1	151.2	44355	145	1651	183	48
	Std. deviation	0.015	80.0	40.8	4446	92	779	60	25
	Variance	0.00	6410	1668	197757	8635	606844	3626	642
	Kurtosis	0.73	-1.4	1.5	-0.72	-0.65	-1.49	0.558	1.23
	Skewness	1.08	-0.36	1.15	0.27	0.94	-0.49	0.796	1.49
Overall	Minimum	0.46	57.3	53.9	1474	39.3	100	32.5	16
	Maximum	0.95	558	392.1	70050	1367.8	3125	378.7	327
	Range	0.49	500.6	338.1	68576	1328.5	3025	346.2	311
	Mean	0.512	197.9	162.2	48234.5	232.8	1407.2	182.8	58.8
	Median	0.497	173.7	151.2	48821	184.8	1519	166.3	52.25
	Std. deviation	0.074	94.88	64.52	12263	220	747	72.31	46.56
	Variance	0.006	90003	4163	1.58	48738	559458	5229	2167
	Kurtosis	30.43	3.74	3.13	4.00	17.68	-0.54	0.912	27.7
	Skewness	5.27	1.40	1.41	-1.24	3.80	-0.053	0.96	4.85

Basic statistics: The statistics calculated for the data sets provide information about the frequency distribution of the concentrations of chemical elements in the roadside dust; the results are

Table 3: Average heavy metal concentration (in ppm) in urban soils from different cities in the world

Element	Bangkok	Hamburg	Madrid	Oslo	Palermo	Central London	Hong Kong
Cr	26.4	95.0	74.7		34.0		
Cu	41.7	146.6	71.7	123	63.0	73	24.8
Ni	24.8	62.5	14.1	41	17.8		
Pb	47.8	168.0	161.0	180	202.0	294	93.4

Table 4: Pearson's correlation coefficients between heavy metals in the road dust samples (n = 42)

	Cd	Cr	Cu	Fe	Zn	Mn	Pb	Ni
Cd	1							
Cr	0.067	1						
Cu	0.038	0.3010	1					
Fe	0.181	0.2750	0.452**	1				
Zn	-0.010	-0.1467	0.114	0.035	1			
Mn	-0.068	0.395**	0.265	0.529**	0.117	1		
Pb	0.220	0.339*	0.214	0.152	-0.019	0.474**	1	
Ni	0.0229	0.357*	0.029	0.020	-0.053	0.051	0.356*	1

**Correlation is significant at the 0.01 level (2-tailed), *Correlation is significant at the 0.05 level (2-tailed)

summarized and compared with some reference values in Table 2. The background concentrations of the elements in the roadside dust mostly exceed the average element concentrations in the upper continental crust (Wedepohl, 1995) and for all are not similar to the worldwide median values in roadside dust (Reimann and de Caritat, 1998).

Most of the heavy metal concentrations for the analyzed samples exceed the maximum permissible concentrations and are higher than the corresponding values in the earth's crust as well as those of average world soils (Table 3).

Correlation coefficient analysis (CA): Pearson's correlation coefficients of heavy metals in roadside dust of the Greater Toronto Area are listed in Table 4. Most of the metal pairs exhibit positive relations (except for Zn-Cd, Mn-Cd, Zn-Cr, Pb-Zn and Ni-Zn) but few of them are significant at 95 and 99% confidence levels. Cd, Cu, Fe, Pb, Mn and Ni are significantly positively correlated with each other, which may suggest a common origin, such as traffic flow or industrial activities. Also, Pb exhibits a very weak positive correlation with Cd, Cu and Fe, while Ni exhibits a very weak positive correlation with Cd, Cu, Fe and Mn. The source for Pb may be heavily traffic activities in the study area.

Principal component analysis (PCA): Principal component analysis is applied to assist in identifying the sources of pollutants. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each of them, are calculated using the software package SPSS 15. The results (Table 5) show that the three eigenvalues less than 1 (0.866, 0.352 and 0.033) account for approximately 93% of the total variance. The third of these eigenvalues (0.033) explains about 2.7% of the total variance, which is a significant contribution towards the explanation of cumulative variance.

Table 5 displays the three components. The first component explains approximately 31% of the total variance and is loaded heavily with Cu, Fe and Mn. This source of this component may be

Table 5: Total variance explained and rotated component matrices for heavy metals

	Component		
Parameter	1	2	3
Cd	0.04	0.06	0.97
Cr	0.39	0.67	-0.04
Cu	0.70	0.02	0.05
Fe	0.79	0.01	0.12
Zn	0.32	-0.39	-0.09
Mn	0.76	0.26	-0.17
Pb	0.34	0.64	0.20
Ni	-0.10	0.80	-0.10
Explained variance	2.50	1.30	1.10
Explained variance (%)	31.10	16.70	13.20
Cumulative % of variance	31.10	47.80	61.00
Eigenvalue	0.90	0.40	0.00

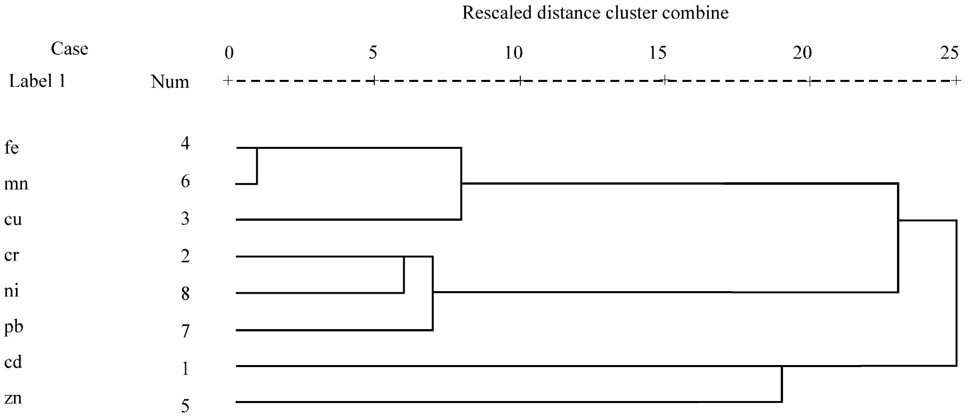

Fig. 5: Cluster analysis results

industrial and traffic. This observation is also evident from the presence of various metal processing industries in the area in addition to the traffic flow. Component 2 is loaded with Cr and Pb and accounts for 16% of the total variance. The source could be the soils in the area with traffic. Component 3 is correlated very strongly with Cd, which has a high loading value (0.79) and explains 13.2% of the total variance. The source of this factor may be contributions mainly from traffic, especially trucks and cars.

Hierarchical cluster analysis (HCA): Before performing a cluster analysis, the variables are standardized by means of z-scores; then Euclidean distances for similarities in the variables are calculated. Finally, hierarchical clustering is determined by applying Ward's method with the standardized data set. The results of the cluster analyses for the variables are shown in Fig. 5 as a dendrogram. The cluster has two larger subgroups: The first contains only the variables Fe, Mn, Cu, Cr, Ni and Pb and the second includes Cd and Zn.

Table 6: Heavy metal comparison in the road dust samples of 400-401 highways using student's t-test

Parameter	Degree of freedom	t-value	p-value
Cd	17	1.19	0.26
Cr	17	1.43	0.17
Cu	17	0.19	0.85
Fe	17	0.10	0.92
Zn	17	-1.73	0.10
Mn	17	0.43	0.66
Pb	17	0.78	0.44
Ni	17	0.89	0.38

Table 7: Heavy metal comparison in the road dust samples of 404-401 highways using student's t-test

Parameter	Degree of freedom	t-value	p-value
Cd	21	0.73	0.470
Cr	21	0.96	0.340
Cu	21	1.78	0.088
Fe	21	1.80	0.086
Zn	21	1.92	0.070
Mn	21	0.39	0.690
Pb	21	1.52	0.140
Ni	21	1.70	0.100

Table 8: Characterizations of canonical functions

Discriminant function	Eigenvalue	Canonical correlation	Variance explained (%)	Cumulative (%)	df	Wilks A
1	0.845^{a}	0.677	91.6	91.6	6	0.503
2	0.770^{a}	0.268	8.4	100.0	2	0.928

Student's t-test analysis: The t-test is used to assess whether the mean heavy metals in Highway 401 are statistically different from those of Highways 400 and 404. The results show that the mean differences in heavy metal levels in these three highways are not statistically different at the 95% confidence interval. In this case, the p-value is greater than 0.05 and the t statistic values are less than those of critical t values (Table 6 and 7).

Discriminant analysis: Once divergent chemical signatures are determined and associated with a contamination event, an objective is to determine the chemical or chemicals responsible for the divergent signature. Simple statistics (mean, min. and max.) for each chemical within each observed signature are relevant diagnostics (Anderson *et al.*, 2009). A plot of observations obtained by discriminate functions (Fig. 6) shows that the analyzed chemicals for the selected highways in the study area exhibit four grouped centroids. Based on the results from Table 6-8, Cu, Fe and Zn are identified as the elements of the highest importance for the discriminations representing the four highways. For these, the lowest p-values are observed (0.07). The next steps in the discriminate analysis are carried out for the elements exhibiting the highest significance in the discrimination process; the results (Table 5) show that Cu, Fe, Cd, Mn and Pb have the highest values (0.70, 0.79, 0.76, 0.97 and 0.67, respectively).

The primary value of discriminate analysis is its ability to determine contaminants of concern among a suite of measured chemicals, along with the most important differences between site-

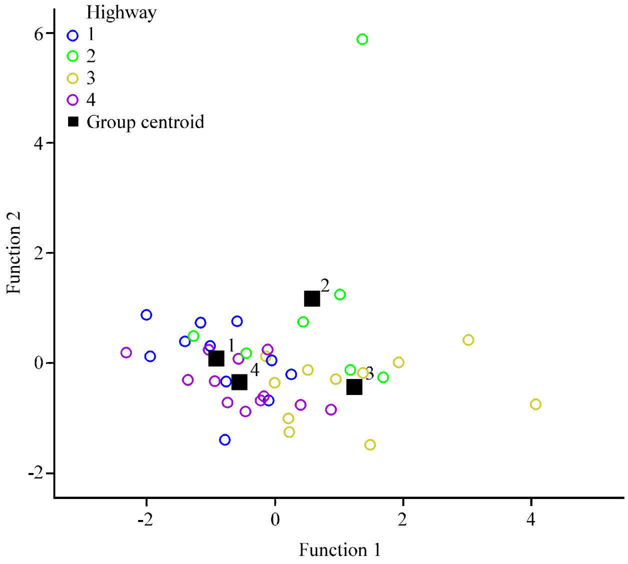

Fig. 6: Plot of observations in the space of discriminate variables

related and reference subsets. From the quantitative and qualitative assessments performed here for chemical contaminants, most of the elements analyzed are demonstrated to be contaminants in the study area.

CONCLUSION

Mean total heavy metal concentrations are found in roadside dust and soils along selected major highways in the Greater Toronto Area. The concentrations are higher than the maximum concentrations of the corresponding elements in the average world soil. The assessment of pollution in the GTA highways reveals some significant environmental situations, where increased heavy metal concentrations result from various processes acting at different spatial scales. The variation in the metal concentrations in the roadside dust and soils have both natural and anthropogenic origins.

The correlation coefficients show positive correlations for most of the heavy metal pairs, exhibit except Zn-Cd, Mn-Cd, Zn-Cr, Pb-Zn and Ni-Zn. Principal component analysis demonstrates that the three eigenvalues are below 1 and suggests that the contamination sources are related to processing industries, traffic and soils in the area. Cluster analysis identifies the presence of two bigger subgroups. The multivariate geostatistical techniques applied support environmental studies by helping to distinguish between geological and anthropogenic causes of pollution and allowing hypotheses to be formulated on the probable sources of pollution.

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