Multivariate statistical analysis of urban soil contamination by heavy metals at selected industrial locations in the Greater Toronto area, Canada

Yousef H. Nazzal[1]*, Nassir S.N. Al-Arifi[3], Muhammad K. Jafri[3], Hossam A. Kishawy[2], Habes Ghrefa[3], Mahmoud M. El-Waheidi[3], Awni Batayneh[3] and Taisser Zumlot[3]

[1] Department of Applied Sciences & Mathematics, College of Arts & Sciences, Abu Dhabi University, P.O. Box 59911, Abu Dhabi, UAE; (*corresponding author: Yousef.Nazal@gmail.com, yousef.nazzal@adu.ac.ae; tel. 00971509620945; fax. 0097125860183)

[2] Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada

[3] Department of Earth and Environmental Sciences, Yarmouk University, Irbid 21163, Jordan

Geologia Croatica

ABSTRACT

A good understanding of urban soils metal contamination and locating their pollution sources due to industrialization and urbanization is important for addressing environmental problems. Urban soil samples near industrial locations in the Greater Toronto Area (GTA), Ontario, Canada were analyzed for metal (Cr, Mn, Fe, Ni, Cu, Zn, and Pb) contamination. Multivariate geo-statistical analysis (correlation matrix, cluster analysis, principal component analysis) was used to estimate the variability of the soil chemical content. The correlation matrix exhibits a negative correlation with Cr. The principal component analysis (PCA) displays two components. The first component explains the major part of the total variance and is loaded heavily with Cr, Mn, Fe, Zn, and Pb, and the sources are industrial activities and traffic flows.

The second component is loaded with Ni, and Cd, and the sources could be lithology and traffic flow. The results of the cluster analysis demonstrate three major clusters: 1) Mn-Zn, 2) Pb-Cd-Cu and Cr, 3) Fe-Ni. The geo-accumulation index (I_{geo}) and the pollution load index (PLI) were determined and show the main I_{geo} values to be in the range of 0-1.67, indicating the studied soil samples are slightly to moderately contaminated with Cr, Fe, Cu, Zn, and Cd, and moderately contaminated with Pb, while Ni, and Mn fall into class "0". Regarding the PLI, the lowest values are observed at stations 6, 7, 9, 10, 11, 12, 25, 27 and 28, while the highest values are recorded for stations 1, 5, 6, 13, 14, 16, 17, 18, 20, 22 and 24, and very high PLI readings are seen for stations 5, 13, 16, 17, 18, 22 and 24. These data confirm that in addition to heavy traffic flows, the chemical and metallurgical type of industries are the major source for soil pollution in the GTA.

Keywords: Heavy metals, multivariate analysis, pollution loading index, Greater Toronto Area

1. 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., 2008).

Many studies indicate that urban soils are contaminated by heavy metals, and this phenomenon has been attributed mainly to modern industries, traffic and mining activities in urban areas (NAZZAL et al., 2012, 2014; XIAOYU LI et al., 2013; DE KIMPE & MORAL, 2000; GALLAGHER et al.,

2008). The concentrations of heavy metals and toxic elements in roadside soils and dust can help inform about pollution levels in urban and industrial areas since such concentrations usually reflect the extent of the emissions of these substances from anthropogenic sources (FERGUSSON, 1990; HARRISON et al., 1981). Lead is a particularly widespread pollutant and its presence in soils has been linked to the use of alkyl-lead compounds such as antiknock additives in gasoline, GRATANI et al. (1992), NAZZAL et al. (2014).

Soils along highways often have high contents of heavy metals. Further, a trend has been noted towards higher concentrations of heavy metals on streets where traffic is more likely to undergo stop-start operations, e.g., at traffic lights (AKHTER & MADANY, 1993; ELLIS & REVITT, 1982; FERGUSSON et al., 1980); DYKE et al., 1989; JOHNSTON et al., 1985; HAMILTON et al., 1984; HOWARI & BANAT, 2001; ABU-RUKAH, 2002; WEI & YANG, 2010; WEI et al., 2009; DAO et al., 2010; MORTON-BERMEA et al., 2009). Most of these studies indicate that metal deposition peaks closest to the roadside and diminishes rapidly with increasing distance from the road.

There are generally two main sources of heavy metals in the soils (LI et al., 2009b) I) natural background, representing heavy metals concentrations derived from parent rocks; and II) anthropogenic, caused by agrochemical activity, organic amendments, animal manure, mineral fertilizer, sewage sludge and industrial waste and dusts. Over the last few decades, the natural input to soils of several heavy metals due to pedogenesis has been surpassed, at local through to regional and global levels, by anthropogenic inputs (FACCHINELLI et al., 2001; NRIAGU & PACYNA, 1988; XIAOYU Li et al., 2013).

Recent studies of pollution along highways in the greater Toronto area (GTA), in Ontario, Canada (NAZZAL et al., 2012, 2014) have identified some significant environmental situations, with increased heavy metal concentrations resulting from various processes acting at different spatial scales. These variations in metal concentrations in the roadside dust and soils have both natural and anthropogenic origins.

The Greater Toronto Area is the third-largest industrial market in North America, and factories and other industrial properties are major contributors to employment and the economy. Manufacturing in the GTA increased at a rate of 4.6% per annum in the fourth quarter of 2013. Toronto is consistently ranked near the top in terms of global competitiveness, innovation and quality of life, and possesses multi-sector strength, depth of talent and a driving economic and financial engine. As the business and financial capital of Canada, the GTA economy contributes $286 billion (approximately half of which comes directly from Toronto) annually to the Canadian economy. The GTA has a wide range of industries and services, supporting a range of business needs. Between 1990 and 2010, the region's economy grew from $140 billion to $240 billion (in 2002 CAD dollars), while Ontario's economy grew from $310 billion to $490 billion.

WEBSTER et al. (1994) have applied multivariate geostatistics to provide a more objective assessment of the sources of some heavy metals in top soils, based on both visual inspection of concentration maps and quantitative analyses over varied spatial scales of the spatial variability of the elements and their relationships. They used multivariate methods to relate concentrations of heavy metals to the local geology and land use, by comparing the results of principal component analyses carried out on concentration data with the experimental indicator variogram for selected categorical information.

Multivariate geostatistics uses information arising from relationships among variables to improve estimations for variables and to identify the different causes of variations over different spatial scales (CASTRIGNANO et al., 2009). Some factors affecting soil variations exhibit short-range effects while others are important over greater distances. Hence, soil variables are anticipated to correlate in a scale-dependent manner, and this correlation structure of some soil variables, providing it reflects different variability sources, is important in environmental studies. Such activities require a statistical approach that combines classic principal component analysis, to describe correlation structure of multivariate data sets, with geostatistics, to account for the coregionalized nature of the variables (SOLLITTO et al., 2010).

Here, we apply this method to the GTA, with the objective of improving understanding of the environmental impacts in that region and their causes. As part of the investigation, the authors undertook field sampling to identify sources, site-specific pollution and profiles of pollutant concentrations in the form of heavy metals and their geochemical associations.

2. MATERIALS AND METHODS

2.1. Study Area

As the third largest industrial area in North America, industrial entities are major contributors to the economy and employment of the GTA. The varied industries are operating in this area impact air, water and soil quality. In addition, the region has dense urban traffic and its major highways (Highways 401, 400 and 404, and the Don Valley Parkway) exhibit daily traffic flows of about 920,000 vehicles (NAZZAL et al., 2012).

Toronto is located in southern Ontario on the north western shore of Lake Ontario (Fig. 1). With over 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 (GTA), and is part of a densely populated region in Southern Ontario known as the Golden Horseshoe, with over 8.1 million residents, representing approximately 25% of Canada's population (POPULATION OF CENSUS METROPOLITAN AREA, 2006).

As table 1 shows the GTA has industries of many types (e.g., agriculture, food, textiles, metallurgical, chemical, electronic, machinery, etc.). These industries release large amounts of solid, liquid and gaseous wastes. To identify possible sources of soil pollution in the study area, dusts and particle
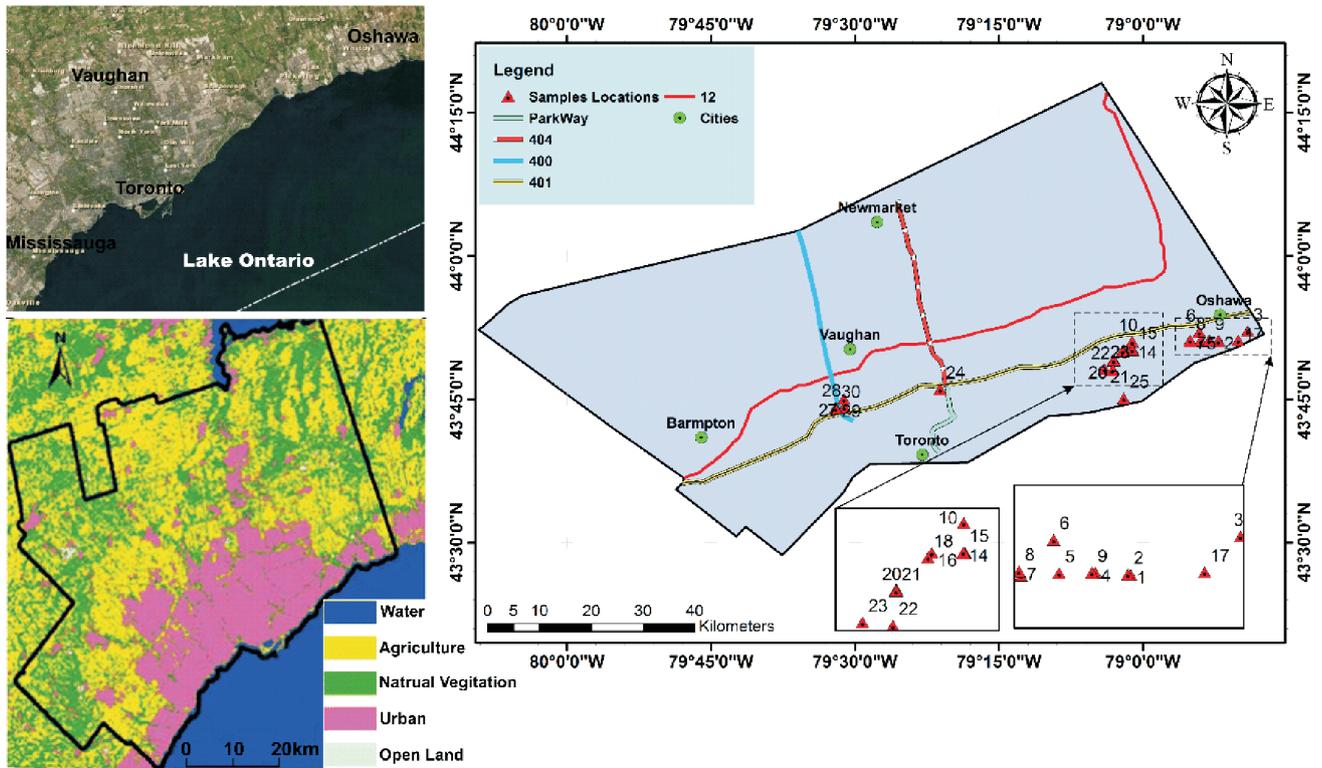
149

Nazzal et al.: Multivariate statistical analysis of urban soil contamination by heavy metals at selected industrial locations in the Greater Toronto area, Canada **Geologia Croatica**

Figure 1: A map of the sampling and study location in the Greater Toronto Area. Values on horizontal axis denote latitude, and on vertical axis denote longitude.

emissions are assessed. This information, with data on the geology, soils, land-use patterns, topographic environment of the area and other physical and technical conditions, allow soil pollution sources in the study area to be investigated.

2.2. 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 rocks of the Canadian Shield (THURSTON, 1991). In the Phanerozoic, 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. The Shield can be divided into three major geological and physiographic regions, with the oldest in the northwest and the youngest in the southeast. The northwestern region, known as the Superior Province and lying north and west of Sudbury, is more than 2.5 billion years old. This region is composed mainly of felsic intrusive rocks forming the rocky Severn and Abitibi uplands (BOSTOCK, 1970). The central region, known as the Grenville Province, at 1.0-1.6 billion years old and lying to the south of Sudbury, is dominated by metasedimentary rocks that form the Laurentian Highlands. The Penokean hills, a fold belt, and the Cobalt plain, an embayment, comprise the Southern Province, which is a narrow region approximately 1.8-2.4 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 Hudson Bay lowlands, the bedrock is composed of carbonate sedimentary formations. These formations date primarily from the Silurian period, but there are also significant parts representign the Ordovician and Devonian periods. Other sedimentary rocks exist near 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 compared to areas to the west or east, due to its uneven terrain and shallow acidic soils, both of which are characteristic of the Canadian Shield.

The Canadian System of Soil Classification AGRICULTURE CANADA (1987) is a standard series of orders and component groups by which soils can be identified and described. Six of the soil orders in this classification predominate in Ontario: 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 (AGRICULTURE AND AGRI-FOOD CANADA, 1996).

Table 1: Industries and manufacturers in the Greater Toronto Area (2014) (Source: http://www.toronto.net/Industries_and_Manufacturers.html).

Type of industry	No. of manufacturers	Type of industry	No. of manufacturers	Type of industry	No. of manufacturers
Agriculture	18	Textile products	10	Safety equipment	48
Brick & Concrete	8	Wood products	41	Aviation industry	11
Computer equipment	37	Casting, molding & machinery	35	Chemical & allied products	39
Electrical products	18	Conveyor systems	8	Drugs	2
Energy	85	Electronic solutions	53	Factory automation	19
Food production	78	Engineering	84	Heating & verification	22
Household furniture	8	Glassware & China ware	22	Industrial equipment	129
Industrial supplies	70	Hydraulic products	11	Leather clothing	7
Lighting products	12	Insulation	21	Mining & exploration	18
Medical & diagnostics	45	Machinery	41	Sanitation	4
Paper products	17	Metal working	122	Telecommunications	159
Stone products	32	Plastic products	47	Waste management	67

From the early 1990s to the early 2000s, the total area of settlement and developed land in the GTA increased by 513 km^2, while the areas of agricultural and naturally vegetated land decreased by 114 and 423 km^2, respectively.

2.3. Collection of Samples

A total of 30 soil samples were collected from industrial locations in the Greater Toronto Area in August 2013. At every field station, samples were collected with a manually operated stainless steel auger, within the surface 10 cm and mainly from grassland. The soil sample raw weight was about 1 kg.

2.4. Geochemical Analyses

The soil samples were transported to the laboratory in polyethylene bags and dried in an oven at 60 °C for 24 h. The time duration between sampling and bringing them to the lab was 24 hours. Different grain size fractions were selected

for the analysis of metals: <2 μm (POPULATION OF CENSUS METROPOLITAN AREAS, 2006; MORTON-BERMEA et al., 2009; ABU-RUKAH, 2002) <63 μm (CALMANO & WELLERHAUS, 1982), <150 μm, and <2 mm (WONG & MAK, 1997). In the present study, contamination of soils with particle size fractions below 2 μm was investigated using the pipette method (GEE & BAUDER, 1986), in which a sample is pipetted at different times and from various depths of the sample suspension 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 resulting solution 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 soils samples were analyzed in triplicate and mean values calculated for estimation of their precision. In addition, analytical blanks were run in the same way as

Table 2: Statistical summary of metal levels (in ppm) for the collected soil samples.

	N	Range	Minimum	Maximum	Mean	Std. Deviation	Variance	Skewness		Kurtosis	
	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic	Statistic	Std. Error	Statistic	Std. Error
Cr	30	1548.5	10.8	1559.3	392.9	611.9	374527	1.31	0.42	-0.25	0.83
Mn	30	2277	344	2621	1047	761	579141	1.06	0.42	-0.43	0.83
Fe	30	238851	16546	255398	65012	63783	4068293450	1.55	0.42	1.38	0.83
Ni	30	0.7	0.10	0.80	0.22	0.177	0.03	1.76	0.42	2.94	0.83
Cu	30	158.8	8.60	167.4	82.9	58.	3377	0.10	0.42	-1.60	0.83
Zn	30	389.8	44.8	434.6	174.3	118.9	14155	0.76	0.42	-0.66	0.8
Cd	30	0.7	0.10	0.80	.41	0.19	0.04	0.36	0.42	-0.92	0.83
Pb	30	96.2	18	114.2	55.3	30.8	954	0.81	0.42	-0.67	0.83
Valid N (listwise)	30										

the samples and concentrations were determined using standard solutions prepared with 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.

3. RESULTS AND DISCUSSION

3.1. General Trends

The average concentrations of the metals considered in the sampling in relation to the natural background values are listed in table 2. A wide range of values is observed for each metal. Also, spatial distribution maps for the various analyzed samples are presented in fig. 2. A comparison of the data shows that the average concentration of the investigated heavy metals in the analyzed soil samples are in many locations, higher than their corresponding values in the average world soils (Table 3).

3.2. Concentrations of Metals in Soil Samples

Minimum and maximum concentrations, mean values and standard deviations are presented in Table 2 for each of the analyzed metals in the collected samples from the industrial areas in the GTA, together with the corresponding background values. The mean concentrations for metals are as follows (in parts per million): Cd (0.41), Cr (392.95), Mn (1047.35), Fe (65.012), Ni (0.22), Cu (82.9), Zn (174.3), and Pb (55.37). In general, the concentrations of the metals vary widely in the studied locations. For some metals the mean

Table 3: Average crustal abundance of and average world soils concentrations.

Element	Element average in world soils (ppm) (ALLOWAY, 1990)	Average crustal soils abundance (ppm) (WEDEPHOL, 1969)
Pb	25	12.5
Cd	0.35	0.2
Zn	90	70
Co	15	25
Ni	40	75

concentrations for the soil samples collected in industrial locations are higher than their background values, suggesting that the presence of these metals in the collected samples around the GTA is influenced by anthropogenic sources, such as industrial activity and traffic flows. Kurtosis values (Table 2) for some of the studied metals are higher than zero, indicating that the peak in the distribution is sharper than expected, CHEN et al. (2012). The skewness values (Table 2) of some metals (Fe, Ni Cu) are larger than unity, demonstrating that these metals positively skew towards lower concentrations (LU et al., 2009; XIA et al., 2011). This observation is also confirmed by the fact that the arithmetic mean concentrations are greater than the corresponding median concentrations. As a result the geometric means for these metals provide more useful data than the arithmetic means. Particular elements are discussed in detail below:

3.2.1. Lead

Lead (Pb), a naturally occurring bluish-gray metal, is found in small quantities in the Earth's crust. Much of the lead in the environment is derived from human activities including fossil fuel combustion, mining and manufacturing (NAZZAL et al., 2012). Due to health concerns, the lead content in gasoline, paint and ceramic products and pipe solder have been dramatically reduced in recent years. When released into the air, lead can travel long distances before settling to the ground and it usually sticks to soil particles once it falls onto soils (HOWARI et al., 2004). In the study area, the Pb concentration ranges

Table 4: Principal component analysis results.

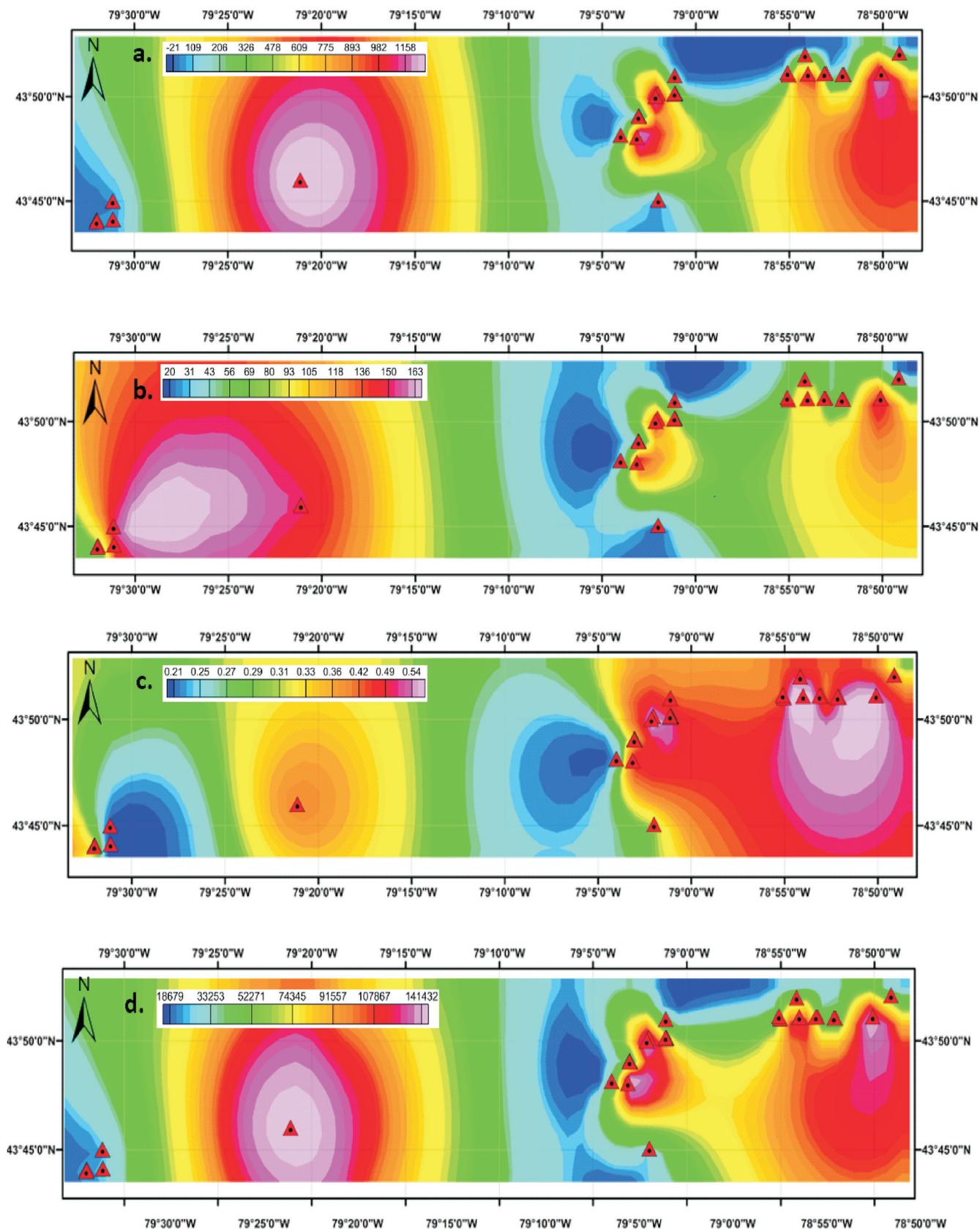|	Total variance explained						
	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings [a]
Component	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total
1	5.49	68.6	68.62	5.49	68.62	68.62	5.48
2	1.52	19.0	87.70	1.52	19.08	87.70	1.55
3	.47	5.88	93.58				
4	.27	3.45	97.04				
5	.09	1.14	98.18				
6	.07	.97	99.16				
7	.05	.72	99.88				
8	.009	.11	100.0				

Figure 2: Spatial distribution maps of metal concentrations (in ppm) for samples collected from different industrial locations in Greater Toronto. a) Cr, b) Cu, c) Cd, d) Fe, e) Mn, f) Ni, g) Pb, & h) Zn.
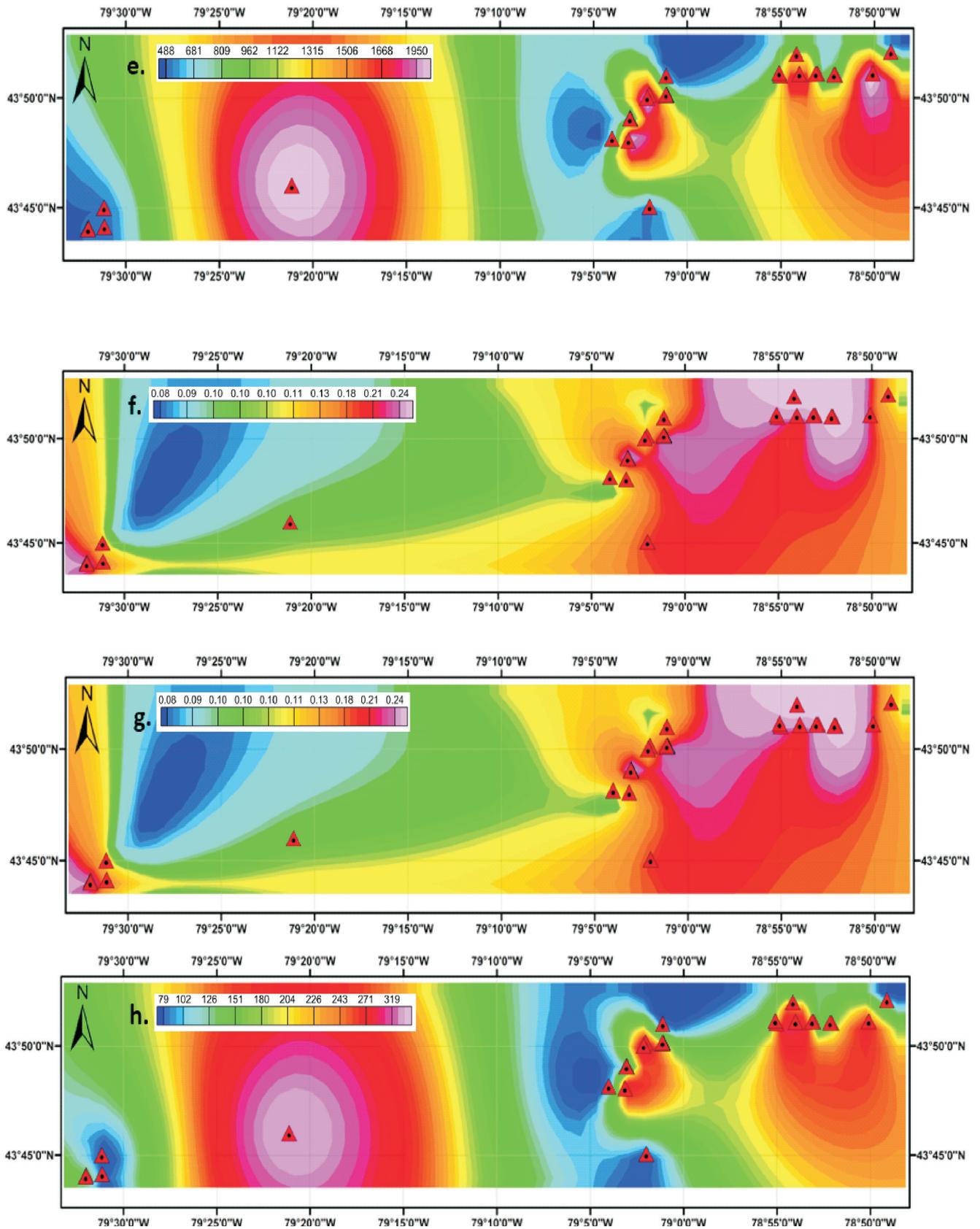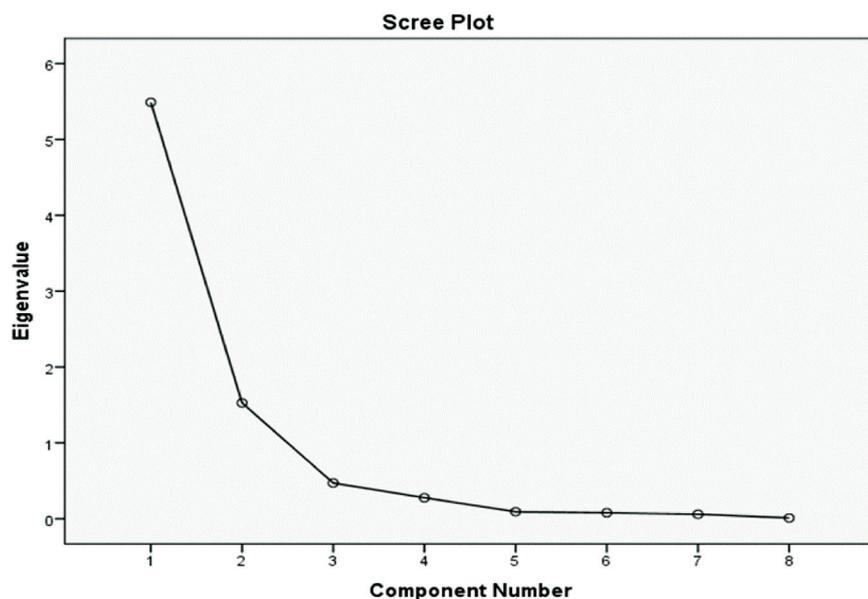
Nazzal et al.: Multivariate statistical analysis of urban soil contamination by heavy metals at selected industrial locations in the Greater Toronto area, Canada

153
Geologia Croatica

Figure 2: Continued.

between 18-114 ppm. The critical concentration in soils of lead is between 100 and 400 ppm, and the global measured lead concentration in surface soils is estimated as 25 ppm (ALLOWAY, 1990) (Table 3). Locations 5, 14, 17, 21 and 23 exhibit concentrations of more than 100 ppm and these values depend on such factors as industry type and size, traffic flows, prevailing winds and humidity (NAZZAL et al., 2014).

3.2.2. Zinc poor format here

Zinc, a heavy metal essential for life, acts biologically as a catalytic or structural component of numerous enzymes involved in energy metabolism and in transcription and translation (ALLOWAY, 1990); FORSTNER & WITTMAN, 1983). Zinc enters air, water and soils partly as a result of natural processes but mostly due to human activities (e.g., mining, zinc purification, steel production, burning of coal and wastes (NAZZAL et al., 2012). The zinc concentration in the investigated soil samples ranges from 45 to 435 ppm (Table 2). Most of the locations (13, 14, 15, 16, 17, 18, 20, 22, 24, and 29) exhibit higher values than the average world soil concentration value of 90 ppm (ALLOWAY, 1990). Locations 1, 5, 6, 7, 8, 9, 10, 11, 22, 24 and 29 exhibit maximum values exceeding 200 ppm. According to JIRIES et al. (2001), and ELLIS & REVITT (1982), zinc may be derived from mechanical abrasion and oil leaks from vehicles, so high concentrations in the study area are likely to be related to high traffic flows into and out of the industrial units.

3.2.3. Cadmium

Cadmium has no biological functions and is highly toxic. Environmental pollution from cadmium has increased rapidly in recent decades due to the rising use of cadmium by industry (ALLOWAY, 1990). The average natural abundance of cadmium in the earth's crust is normally reported to be 0.1-0.5 ppm, but much higher and much lower values have also been cited, depending on various factors (HOWARI et al., 2004). In the study area, the average concentration of Cd ranges be-

tween 0.1 and 0.8 ppm, with locations 1, 5, 6, 8, 13, 14, 15, 16, 17, 18, 20, 22 and 29 exhibiting higher than the permissible values (0.1–0.5 ppm). The presence of Cd in the studied samples is believed to be associated with tyre wear, a phenomenon described by ELLIS & REVITT (1982).

3. 3. Multivariate Geostatistics

Geostatistical methods are useful when data are normally distributed around a stationary mean and variances do not vary significantly spatially (SOUMYA et al., 2013). Significant deviations from normality and stationary means can cause problems. Initial plotting of a histogram of the data facilitates the checking of normality and position of the data values in space to determine any significant trends.

Data matrices were evaluated through Principal Component Analysis (PCA) allowing the summarized data to be further analyzed and plotted. Generally, three approaches are used: Catell Sree test, (CATTELL, 1966), Kaiser Criterion (KAISER & RICE, 1974), and variance explained criteria (percentage of variance).

We use the Scree plot method to assess the number of principal components (PCs) to be obtained (Fig 3). The plotting of eigenvalues (x axis) against PC numbers (y axis) provides insight into the maximum number of components to be extracted. According to the eigenvalues 5.490 and 1.527 respectively (Table 4), two principal components PC1 and PC2 are selected (Table 5) which explain 68.6 % and 19.1 % respectively of the total variance, (Table 4). The application of the rotation matrix method leads to an increase in PC1 and a reduction in PC2 (Table 5).

The application of Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity gives values of 0.82 and 315.9 (Table 6), respectively, and the significance level is <0.001. These values demonstrate that factor analysis for this study is suitable. Factor 1 should be industrial and traffic flow, which is also evident from the presence of various metal processing

Nazzal et al.: Multivariate statistical analysis of urban soil contamination by heavy metals at selected industrial locations in the Greater Toronto area, Canada

155

Geologia Croatica

Table 5: Component rotated matrix.

	Component	
	1	2
Cr	0.98	-0.11
Mn	0.96	0.08
Fe	0.95	-0.03
Ni	-0.13	0.94
Cu	0.77	-0.02
Zn	0.92	0.23
Cd	0.64	0.63
Pb	0.88	-0.41

Extraction Method: Principal Component Analysis.
Rotation Method: Oblimin with Kaiser Normalization.

Table 6: Kaiser- Meyer- Olkin (KMO) significance test.

KMO and Bartlett's Test		
Kaiser-Meyer-Olkin measure of sampling adequacy		0.82
Bartlett's test of sphericity	Approx. Chi-Square	315.9
	df	28
	Sig.	.00

industries in the area (i.e., the GTA has many metallurgical and chemical industries as shown in Table 1). The source of factor 2 is anthropogenic and natural, including weathering and erosion.

The correlation matrix for heavy metals in analyzed soil samples from the GTA is provided in Table 6. The results

here shows that, when p is 0.05 then the result is significant at the 95 % confidence level but highly significant would be p 0.01 (99%) confidence level.

A positive correlation between the metals is shown in Table 7. Cr is highly positively correlated with Mn, Fe, Cu, Zn, Cd and Pb. Mn positively highly correlated with Fe, Cu, Zn, Cd and Pb. Fe is highly positively correlated with Cu, Zn and Pb. Cu is positively correlated with Zn, while Zn is positively correlated with Cd and Pb. This highly positive correlation among metals may suggest a common origin, such as traffic flow or industrial activity in the study area. PCA is applied to assist in identifying sources of pollutants. By extracting the eigenvalues from the correlation matrix, the number of significant factors and the presence of variance explained by each of them, are calculated using the software package SPSS 15.

Table 4 displays two components. The first explains the majority of the total variance and is loaded heavily with Cr, Mn, Fe, Zn and Pb. The source of the component may be industrial activities and traffic flows. This observation is also evident from the presence of various metal processing industries in the study area in addition to traffic flow. Component 2 is loaded with Ni and Cd, the source of which could be lithology and traffic flow.

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. 4 as a dendrogram. This figure displays three major clusters, Mn–Zn, Pb–Cd–Cu – Cr and Fe–Ni, in agreement with PCA results.

Table 7: Correlation matrix.

		Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
Correlation	Cr	1.00	0.96	0.95	-.16	0.67	0.87	0.56	0.90
	Mn	0.96	1.0	0.91	0.002	0.70	0.91	0.69	0.79
	Fe	0.95	0.91	1.0	-0.07	0.63	0.85	0.59	0.85
	Ni	-0.16	0.002	-0.07	1.0	-0.07	0.10	0.42	-0.41
	Cu	0.67	0.70	0.63	-0.07	1.0	0.70	0.45	0.61
	Zn	0.87	0.91	0.85	0.10	0.70	1.0	0.80	0.69
	Cd	0.56	0.69	0.59	0.42	0.45	0.80	1.0	0.31
	Pb	0.90	0.79	0.85	-0.41	0.61	0.69	0.31	1.0
Sig. (1-tailed)	Cr		0.0	0.0	0.19	0.0	0.0	0.001	0.0
	Mn	0.0		0.0	0.49	0.0	0.0	0.0	0.0
	Fe	0.0	0.0		0.35	0.0	0.0	0.0	0.0
	Ni	0.19	0.49	0.35		0.34	0.28	0.009	0.012
	Cu	0.0	0.0	0.0	0.34		0.0	0.005	0.0
	Zn	0.0	0.0	0.0	0.28	0.0		0.0	0.0
	Cd	0.001	0.0	0.0	0.009	0.005	0.0		0.04
	Pb	0.0	0.0	0.0	0.012	0.0	0.0	0.045	

Figure 4: Hierarchical cluster analysis dendrogram.
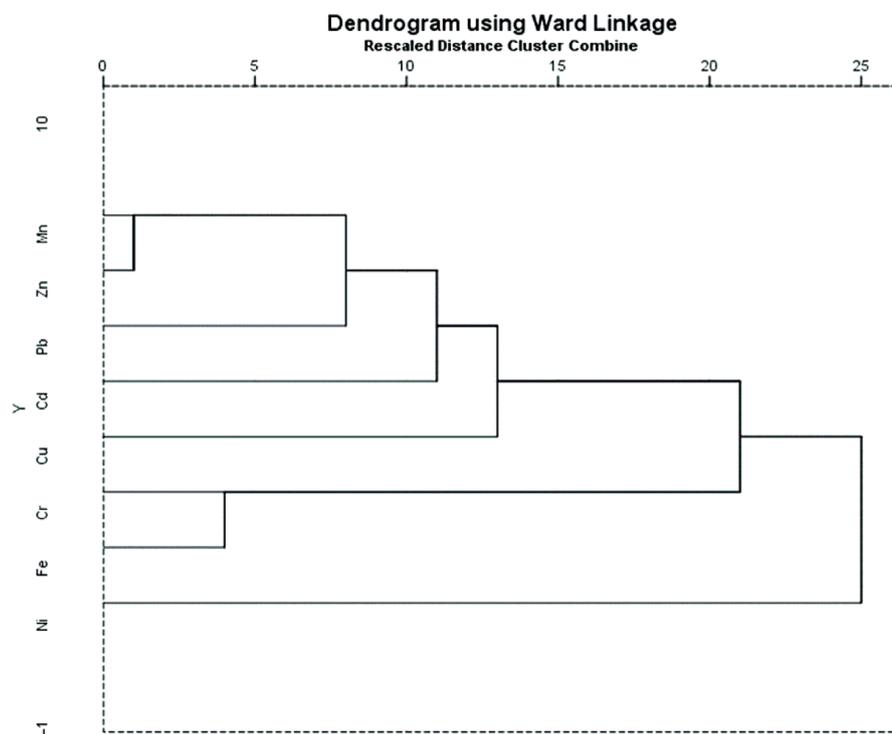
3.4. Geo-accumulation Index

The geo-accumulation index (I_{geo}), introduced by MULLER (1979), is used to assess the extent of pollution in the analyzed soil samples from industrial locations in the GTA, and can be calculated as follows:

$$I_{geo} = \text{Log}_2 \ (C_n/1.5B_n)$$

Here, C_n is the measured concentration of metal n in the soils, 1.5 is used as a factor to minimize possible variations in the background values, and B_n is the geochemical background value of metal n. Geochemical background values for the studied metals in soil media proposed by ALLOWAY (1990) were used as Bn.

Mean values of I_{geo} for each element are shown in Table 8. Based on the I_{geo} data and Muller's geo-accumulation index listed in Table 9, the main I_{geo} values are in the range of 0 to 1.67. The I_{geo} values indicate that the soil samples for the studied industrial locations in the GTA are slightly/moderately contaminated with Cr, Fe, Cu, Zn and Cd, and moderately contaminated with Pb. For Ni and Mn, I_{geo} falls in class 0, indicating that no pollution from these metals was recognized in the studied samples. These results indicate that the soil samples for the studied industrial locations in the GTA are enriched with potentially toxic metals from anthropogenic sources such as industry and traffic flow.

3.5. Pollution Load Index

The contamination extent by metals in soils is assessed using the Pollution Load Index (PLI) (TOMLINSON et al., 1980; SELVAMl et al., 2012) with heavy metal data and world shale average values (TUREKIAN & WEDEPOHL, 1961) of the metals, (BADR et al., 2009; RAY et al., 2006).

Table 8: Geo-accumulation index (I_{geo}) for contamination levels (adapted from MULLER, 1981).

I_{geo} class	I_{geo} value	Contamination level
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated/moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately/strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly/extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Table 9: Geo-accumulation index (I_{geo}) and contamination levels (in parentheses) for selected metals in Greater Toronto Area soil samples.

Metal	I_{geo}	Contamination level
Cr	0.99	Uncontaminated/Moderately contaminated
Mn	-0.75	Uncontaminated
Fe	0.27	Uncontaminated/Moderately contaminated
Ni	-7.64	Uncontaminated
Cu	0.93	Uncontaminated/Moderately contaminated
Zn	0.50	Uncontaminated/Moderately contaminated
Cd	0.65	Uncontaminated/Moderately contaminated
Pb	1.67	Moderately contaminated

157

Nazzal et al.: Multivariate statistical analysis of urban soil contamination by heavy metals at selected industrial locations in the Greater Toronto area, Canada   Geologia Croatica
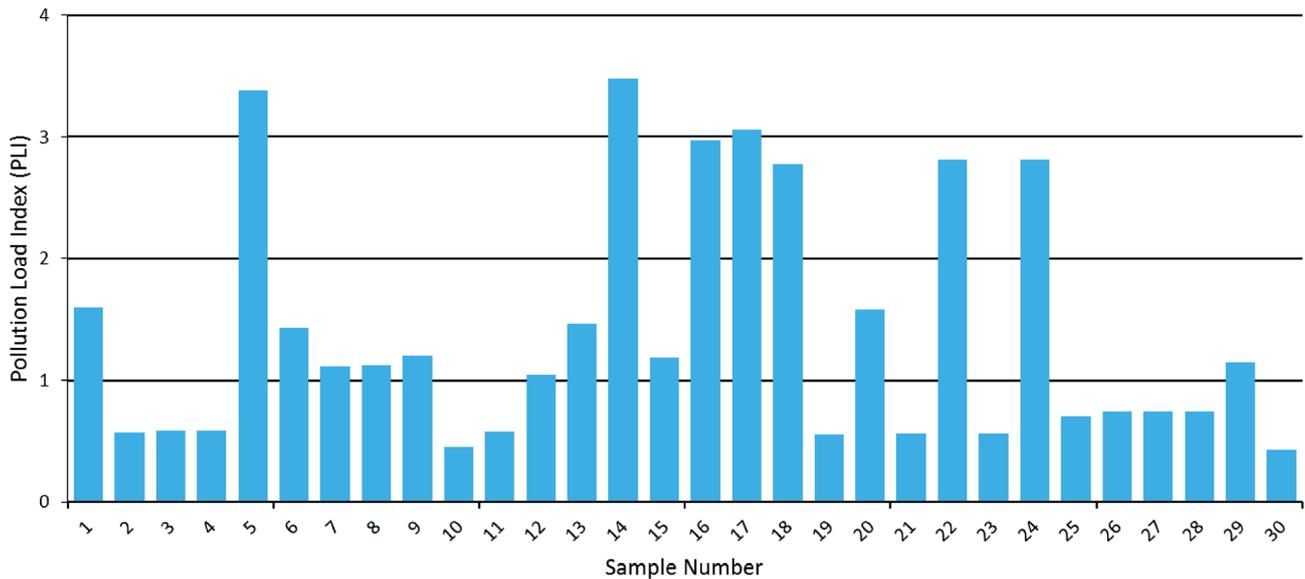

Figure 5: Pollution load index calculated for different locations in the study area.

The PLI provides a summative indication of the overall level of heavy metal pollution in a sample. The PLI was calculated for the investigation area for eight metals, considering the lowest toxicity of the most abundant metals. PLI values are calculated using the equation

$$PLI = \sqrt[n]{CF1 \cdot CF2 \cdot CF3 \cdot ... CFn}$$

Here, CF denotes the contamination factor and n is the number of metals. The contamination factor is calculated as follows:

$$CF = \frac{metal\ concentration\ in\ sample}{shale\ value\ /\ background\ of\ the\ metal}$$

The PLI values for all sites are found to range from 0.0-3.6 (Fig. 5). The lowest PLI values occurred at stations 6, 7, 8, 9, 10, 11, 12, 25, 26, 27 and 28, and the highest at stations 1, 5, 6,13,14,16, 17, 18, 20, 22 and 24, while stations 5, 13, 16, 17, 18, 22 and 24 exhibit very high PLI values. This confirms, as discussed earlier, the importance of the type of industries (especially metallurgical and chemical ones) in the area besides high traffic flows. Most of the industrial locations considered are close to the busiest highway in North America (Highway 401).

4. CONCLUSION

Heavy metal soil concentrations for industrial locations in the Greater Toronto area (GTA), Ontario, Canada have been investigated. The mean concentrations (ppm) for the metals assessed observed are Cd (0.41), Cr (392.95), Mn (1047.35), Fe (65012), Ni (0.22), Cu (82.9), Zn (174.3) and Pb (55.37). The use of a correlation matrix, cluster analysis and principal component analysis to estimate the variability of the chemical content of the soil reveals the impact of industrial

and anthropogenic activities on heavy metal concentrations in the soils of the study area. The geo-accumulation index and pollution load index results show that the main geo-accumulation index values are 0-1.67, suggesting that soil samples for the studied industrial locations in the GTA are slightly – moderately contaminated with Cr, Fe, Cu, Zn and Cd, and moderately contaminated with Pb, while Ni and Mn fall in class 0. The pollution loading index values are lowest at stations 6, 7, 9, 10, 11, 12, 25, 27 and 28, and highest values at stations 1, 5, 6, 13, 14, 16, 17, 18, 20, 22 and 24, while stations 5, 13, 16, 17, 18, 22 and 24 exhibit very high PLI values. It is concluded that the type of industry, especially those related to metallurgical and chemical activity, in the study area as well as traffic flows, are the main sources for the esnsuing soil pollution.

REFERENCES

ABU-RUKAH, Y.H. (2002): A study of soils along the Amman Aqaba highway contamination with heavy metal.– Freiberger Forschungshefte, Geowissenschaften, C49, 53–62.

AKHTER, M.S. & MADANY, I.M. (1993): Heavy metals in street and house dust in Bahrain.– Water, Air, and Soil Pollution, 66, 111−119.

AGRICULTURE AND AGRI-FOOD CANADA (1996): Soil Landscapes of Canada. Version 2.2, National Soil Data Base.– Ottawa, Ontario: Agriculture and Agri-Food Canada.

AGRICULTURE CANADA (1987): The Canadian System of Soil Classification.– 2nd ed. Publication No. 1646. Ottawa, Ontario: Agriculture Canada, Research Branch.

ALLOWAY, B.J. (1990): Heavy Metals in Soils.– Glasgow: Blackie and Sons.

BADR, N.B.E., EL-FIKY, A.A., MOSTAFA, A.R. & AL-MUR, B.A. (2009): Metal pollution records in core sediments of some Red Sea coastal areas, Kingdom of Saudi Arabia.– Environmental Monitoring Assessment, 155, 509–526.

BOSTOCK, H.S. (1970): Physiographic Subdivisions of Canada.– In: DOUGLAS, R.J.W. (ed.): Geology and Economic Minerals of Canada. Economic Geology Report No. 1. Ottawa, Ontario: Geological Survey of Canada, 10–30.

CALMANO, W. & WELLERHAUS, S. (1982): Dredging of contaminated sediments in Weser estuary: chemical forms of some metals.– Environmental Technology Letters, 3, 199–208.

CATTELL, R.B. (1966): The scree test for the number of factors.– Multiple Behavior Research, 1, 245–276.

CASTRIGNANO, A., COSTANTINI, A.C., BARBETTI, E.R. & SOLLITTO, D. (2009): Accounting for extensive topographic and pedologic secondary information to improve soil mapping.– Catena, 77, 28–38.

CHEN, X., XIA, X.H., ZHAO, Y. & ZHANG, P. (2010): Heavy metal concentration in roadside soils and correlation with urban traffic in Beijing, China.– Journal of Hazardous Materials, 181, 640–646.

CHEN & DONGMEI (2010): Geospatial analysis modelling of urban structure and dynamics.– Springer e Book, Springer.

CHEN, X., LU, X., & YANG, G. (2012): Sources identification of heavy metals in urban topsoil from inside the Xi'an Second Ring road, NW China using multivariate statistical methods. Catena, 98, 73–78.

DAO, L., MORRISON, L. & ZHANG, C. (2010): Spatial variation of urban soil geochemistry in a roadside sports ground in Galway, Ireland. Science of the Total Environment, 408, 1076–1084.

DE KIMPE, C.R. & MOREL, J.L. (2000): Urban soil management, a growing concern. Soil Science, 165, 31–40.

DYKE, A.S., VINCENT, J.S., ANDREWS, J.T., DREDGE, L.A. & COWAN, W.R. (1989): The Lauren tide ice sheet and an introduction to the quaternary geology of the Canadian Shield.– In: FUTTON, R.J. (ed.): Quaternary Geology of Canada and Greenland. Geology of Canada, publication No. 1 (178–189). Ottawa: Ontario Geological Survey of Canada.

ELLIS, J.B. & REVITT, D.M. (1982): Incidence of heavy metals in street surface sediments: solubility and grain size studies.– Water, Air, and Soil Pollution, 17, 87–100.

FACCHINELLI, A., SACCHI, E. & MALLEN, L. (2001): Multivariate statistical and GIS based approach to identify heavy metal sources in soils.– Environmental Pollution, 114, 313–324.

FERGUSSON, J.E., HAYES, R.W., YONG, T.S. & THIEW, S.H. (1980): Heavy metal pollution by traffic in Christchurch, New Zealand: lead and cadmium content of dust and soil, and plant samples.– New Zealand Journal of Science, 23, 293–310.

FERGUSSON, J.E. (1990): The Heavy Elements: Chemistry, Environment Impact and Health Effects, vol. 9.– Pergamon Press, Oxford.

FOREST LANDSCAPE ECOLOGY PROGRAM, ONTARIO MINISTRY OF NATURAL RESOURCES (1996): Surficial Geology of Ontario: Digital Database and Viewing Software [CD-ROM]. Sault Ste. Marie, Ontario: Ontario Forest Research Institute, Ontario Ministry of Natural Resources.

FORSTNER, U. & WITTMAN, G.T. (1983): Metal pollution in the aquatic environment.– Berlin-Springer.

GALLAGHER, F.J., PECHMANN, I., BOGDEN, J.D., GRABOSKY, J. & WEIS, P. (2008): Soil metal concentration and vegetative assemblage structure in an urban brownfield.– Environmental Pollution, 153, 351–361.

GEE, G.W. & BAUDER, J.W. (1986): Particle-size analysis.– In: KLUTE, A. (ed.): Methods of Soil Analysis, Part 1. American Society of Agronomy, Madison, 383–412.

GRATANI, L., TAGLIONI, S. & CRESCENTE, M.F. (1992): The accumulation of lead in agriculture soil and vegetation along a highway.– Chemosphere, 24, 941–949.

KAISER, H.F. & RICE, J. (1974): Little jiffy, mark IV Educ. Psychological Measurement, 34, 111–117.

HAJJI KOLSI, S., BOURI, S., HACHICHA, W. & BEN DHIA, H. (2013): Implementation and evaluation of multivariate analysis for groundwater hydrochemistry assessment in arid environment: a case study of Hajeb Elyoun-Jelma, Central Tunisia.– Environmental Earth Sciences, 70, 2215–2224.

HAMILTON, R.S., REVITT, D.M. & WARREN, R.S. (1984): Levels and physicochemical associations of Cd, Cu, Pb and Zn in road sediments.– Science of the Total Environment, 33, 59–74.

HARRISON, R.M., LAXEN, D.P.H. & WILSON, S.J. (1981): Chemical association of lead and zinc in street dust and road side soils.– Environ. Sci. Technol., 15, 1378–1381.

HOWARI, F.M. & BANAT, K.M. (2001): Assessment of Fe, Zn, Cd, Hg, and Pb in the Jordan and Yarmouk River sediments in relation to their physicochemical properties and sequential extraction characterization.– Water, Air, and Soil Pollution, 132, 43–59.

HOWARI, F.M., ABU-RUKAH, Y. & GOODELL, O.C. (2004): Heavy metal pollution of soils along North Shauna-Aqaba Highway, Jordan.– Int. J. Environment and Pollution, 22, 597–607.

GHREFAT, H.A., ABU-RUKAH, Y. & ROSEN, M.A. (2011): Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafrain Dam, Jordan.– Environmental Monitoring and Assessment, Vol. 178, 95–109.

LI, J.L., HE, M., HAN, W. & GU, Y.F. (2009b): Analysis and assessment on heavy metal sources in the coastal soils developed from alluvial deposits using multivariate statistical methods.– Journal of Hazardous Materials, 164, 976–981.

LU, X.W., WANG, L.J., LEI, K., HUANG, J.M. & ZHAI, Y.X. (2009): Contamination assessment of copper, lead, zinc, manganese and nickel in street dust of Baoji, NW China.– Journal of Hazardous Materials, 161, 1058–1062.

JIRIES, A.G., HUSSEIN, H.H. & HALASH, Z. (2001): The quality of water and sediments of street runoff in Amman, Jordan.– Hydrological Processes, 15, 815–824.

JOHNSTON, R.W., RALPH, J. & WISEN, S. (1985): The budget of Pb, Cu and Cd for a major highway.– Science of the Total Environment, 46, 137–145.

MORTON-BERMEA, O., ALVAREZl, E., GONZALEZ-HERNANDEZ, G., ROMERO, F., LONZANO, R. & BERAMENDI-OROSCO, L.E. (2009): Assessment of heavy metal pollution in urban topsoil's from three metropolitan areas of Mexico City.– Journal of Geochemical Exploration, 101, 218–224.

MULLER, G. (1979): Schwermetalle in den Sedimenten des Rheins – Veränderungen seit 1971. Umschau, 24, 778–78.

NAZZAL, Y., ROSEN, M.A. & AL-RAWABDEH, AM. (2012): Assessment of metals pollution in urban road dusts from selected highways of the Greater Toronto Area in Canada.– Environ Monit Assess J, Springer. doi: 10.1007/s10661-012-2672-3.

NAZZAL, Y., HABES, G. & ROSEN, M.A. (2014): Application of multivariate geostatistics in the investigation of heavy metal contamination of road side dusts from selected highways of the Greater Toronto, Canada.– J. Environ. Earth Sci., 71, 1409–1419.

NRIAGU, J.O. & PANCYNA, J.M. (1988): Quantitative assessment of worldwide contamination of air, water and soils by trace metals.– Nature, 133, 134–139.

POPULATION OF CENSUS METROPOLITAN AREAS (2006): Census boundaries. Statistics Canada. http://www40.statcan.ca/l01/cst01/ demo05a-eng.htm. Retrieved 2010–03–02.

RAY, A.K., TRIPATHI, S.C., PATRA, S. & SARMA, V.V. (2006): Assessment of Godavary estuarine mangrove ecosystem through trace metal studies.– Environmental International, 32, 2190–223.

SELVAM, A.P., PRIYA, L.S., BANERJEE, K.G., HARIHARAN, G., PURVAJA, R. & RAMESH, R. (2012): Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad Lake, Southwest Coast of India.– Environmental Monitoring and Assessment, 184, 5899–5915.

SOLLITTO, D., ROMIC, M., CASTRIGNANO, A., ROMIC, D. & BAKIC, H. (2010): Assessing heavy metal contamination in soils of Zagreb region (Northwest Croatia) using multivariate geostatistics.– Catena, 80, 182–194.

SUN, L.V., YANG, X.B., WANG, N.Q. & CHEN, S. (2008): Spatial distribution of Cd, and Cu, in soils in Shenyang Zhangshi irrigation area (SZIA).– China Journal of Zhejiang University, Science, B, 9, 271–278.

TOMLINSON, D.L., WILSON, J.G., HARRIS, C.R. & JEFFREY, D.W. (1980): Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index.– Helgolander Meeresuntersuchungen Helgolander Meeresunters, 33, 566–575.

THURSTON, P.C. (1991): Geology of Ontario: introduction.– In THURSTON, P.C., WILLIAMS, H.R., SUTCLIFFE, R.H. & SCOTT, G.M. (eds.): Geology of Ontario, special volume no. 4, 3–26. Toronto, Ontario Geological Survey.

TUREKIAN, K.K. &WEDEPOHL, K.H. (1961): Distribution of the elements in some major units of the earth's crust.– Geological Society of America, 72, 175–192.

WEBSTER, ATTEIA, O. & DUBOIS, J.P. (1994): Coregionalization of trace metals in the soil in the Swiss Jura.– Eur. J. Soil Sci., 45, 205–218.

WEDEPOHL, K.H. (1969): Composition and abundance of common igneous rocks. In: WEDEPOHL, K.H. (ed.): Handbook of geochemistry, , vol. I., 227–249. Berlin-Heidelberg-New York: Springer 1969.

WEI, B. & YANG, L. (2010): A review of heavy metal contamination in urban soils, urban roadside and agricultural soils from China.– Microchemical Journal, 94, 99–107.

WEI, B., JIANG, F., LI, X. & MU, S. (2009): Spatial distribution and contamination assessment of heavy metals in urban road dusts from Urumqi, NW China.– Microchemical Journal, 93, 147–152.

WONG, J.W.C. & MAK, N.K. (1997): Heavy metal pollution in children playgrounds in Hong Kong and its health implications.– Environmental Technology, 18, 109–115.

XIA, X., CHEN, X, LIU, R. & LIU, H. (2011): Heavy metals in urban soils with various types of land use in Beijing, China.– Journal Hazardous Materials, 186, 2043–2050.

XIAUYU, Li, LIJUAN, LIU, YUGANG, WANG, GEPING, LUO, XI, CHEN, XIAOLIANG, YANG, MYRNA, H. P. H., RUICHAO, GUO, HOUJUN, WANG, JIEHUA, CUI & XINGYUAN, HE. (2013): Heavy metal contamination of urban soil in an old industry city (Shenyang) in Northeast China.– Geoderma, 192, 50–58.