

# Trace metal assessment in soils in a small city and its rural surroundings, Pensacola, FL, USA

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**Abstract** This study assesses the origin and pollution of trace metals in surface soils in a region with contrasting land uses (urban vs. rural). Principal component analysis (PCA) reveals that Cr and Ni are predominantly of geogenic origin. These two trace metals are also the only ones with statistically significant correlations with soil particle size and organic matter content. Copper, Pb and Zn, and possibly Hg, are of anthropogenic origin, but their concentrations rarely reach levels described as strongly polluted by pollution indexes. The concentrations of these anthropogenic trace metals are statistically not different in urban and rural areas, except for Pb that is higher in the urban area. This general lack of a difference between the two land uses indicates that the influence of this small urban area on trace metal concentrations in soils is minor. Lead and Zn have the most, but still a modest number, of strongly polluted sites, mainly in an industrial part of the city. GIS analysis shows that, based on the pollution load index (PLI), overall concentrations of trace metals also reach their highest levels in that industrial area. These observations indicate that the influence of industry on trace metal pollution in soil exceeds that of other urban activities in the region. Local background concentrations were found to be very different from general crustal background concentrations. This demonstrates the importance of the careful selection of a background type in studies like this.

**Keywords** Soils · Trace metals · Pollution index · Geochemical background · Soil geography · GIS

## Introduction

Assessment of anthropogenic influences on soils has become necessary due to increasing human impacts on soil characteristics. These anthropogenic influences have most often been studied in the context of agriculture, but growing urbanization and industrialization call for more assessment of their effects on soils. One soil characteristic that is influenced by human activities is trace metal content. Trace metals are of great environmental and human health concern because of their toxicity, their release into the environment through a range of natural and human-induced processes, and their resistance to degradation under natural terrestrial surface conditions. Common anthropogenic sources of trace metals include mining, industry, wastewater, fossil fuels, and pesticides. Trace metals from these sources enter soils chiefly through the atmosphere (Simonson 1995; Nicholson et al. 2003), but also by direct land application of wastewater sludge and pesticides. The atmospheric input is often highest in urban and industrial areas and can overshadow geogenic trace metal input in those areas (Madrid et al. 2006). Many studies of urban soils have found elevated levels of trace metals (Pfeiffer et al. 1991; Kelly et al. 1996; Sanchez-Martin et al. 2000; Manta et al. 2002; Banat et al. 2005; Krishna and Govil 2008) and some have found trace metal concentrations that exceed national and international regulatory limits (Madrid et al. 2002; Imperato et al. 2003; Madrid et al. 2006). The trace metal pollution has been linked to city centers and historic districts, probably because human activities are more intense and older in these areas (Kahle 2000; Madrid

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et al. 2002; Chen et al. 2005). The most commonly identified specific sources for the trace metals in urban soils are vehicular traffic, road infrastructure, power plants, and industrial activities (Ritter and Rinefierd 1983; Banat et al. 2005; Moller et al. 2005; Crnkovic et al. 2006). Most studies of urban soil pollution have focused on larger cities such as Beijing, Bangkok, Hong Kong, and Palermo (Chen et al. 1997, 2005; Wilcke et al. 1998; Manta et al. 2002; Li et al. 2004). Few studies have assessed trace metal pollution in smaller cities, but limited results suggest trace metal concentrations may be lower there (Sanchez-Martin et al. 2000; Madrid et al. 2006). Geographic information systems (GIS) have been employed to help identify potential sources of soil pollution in some studies (Facchinelli et al. 2001; Imperato et al. 2003; Li et al. 2004; Lee et al. 2006). Most of these studies use one of a variety of spatial interpolation techniques to produce simple continuous surface maps to depict the spatial distribution of the concentration of metals. Few studies use more advanced spatial analysis to assess the potential origin of trace metals in soils, although some have generated maps showing the likelihood that a metal's concentration exceeds a given threshold (Lu et al. 2008).

Other studies have shown that pollutants are present in the air, water, and biota of NW Florida, USA, where the present study was conducted, and in some instances the pollutants exceeded national and state regulatory limits (Lewis et al. 2001; Karouna-Renier et al. 2007; Liebens et al. 2007). However, environmental research in the study area has rarely focused on soils. The only studies of soil pollution known to the authors are related to Superfund sites. These studies were very limited in spatial extent and usually concentrated on on-site pollution, although in some cases nearby off-site locations were examined (USEPA 1991; Black and Veatch Waste Science 1995; CDM Federal 1998; ATSDR 2005a, b). A limited number of surface soil samples from the study area were previously analyzed for trace metals as part of a study of storm water treatment systems (Liebens 2001). The samples were collected from sites that were thought to be relatively unaffected by direct release of pollutants and thus should approach background levels of trace metals. Results showed that some of these sites had Pb levels above Florida Clean Soil Criteria and all sites had As levels above EPA Soil Screening Levels.

The goal of the present study was to assess the concentrations of trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) in surface soils in a small city (Pensacola, FL, USA) in a region with contrasting land uses (urban vs. rural). To evaluate the possible origin of the trace metals and potential sources, a combination of principal component analysis and GIS-based hot spot analysis was used. Aluminum and Fe, two metals that are predominantly of natural origin, were analyzed as reference elements

because they can help show the origin of the trace metals. A secondary goal was to assess different methods to determine pollution indexes commonly used in soil pollution literature. Sampling focused on soils in public places because the influence of trace metal pollution on human health, especially that of children, is strong and well documented (Simpson 1996; Dor et al. 1998; Mielke et al. 1999). Consequently, sampling sites were in publicly accessible places such as parks, playgrounds, and sports fields where most interaction between humans and soils takes place.

## Study area

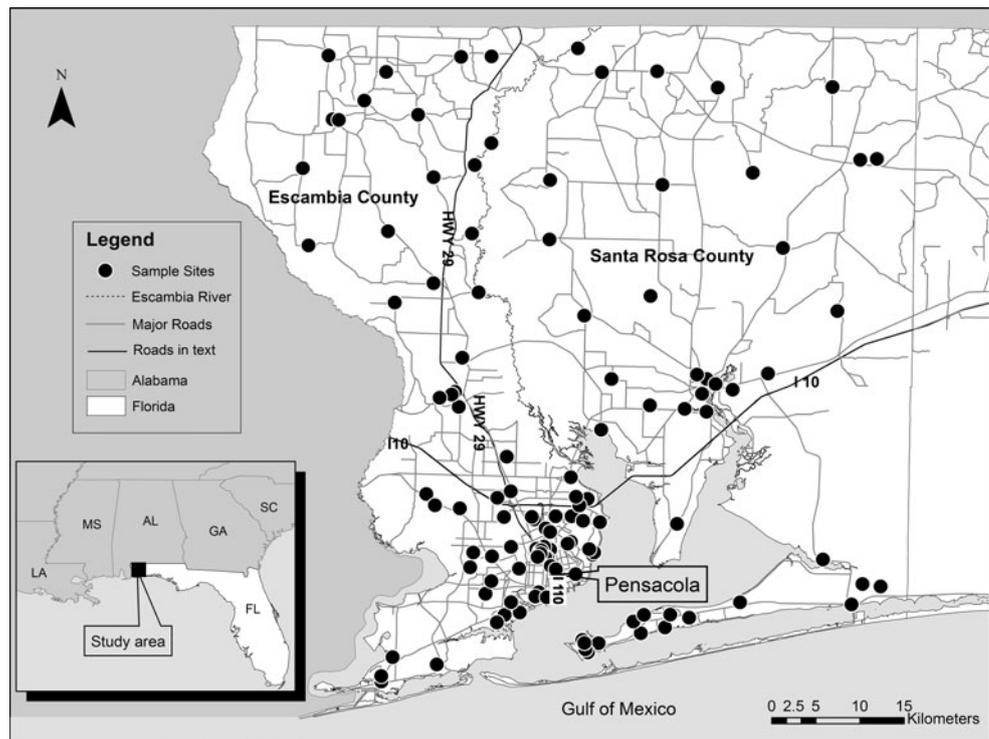
The study area comprised the two westernmost counties in Florida, USA (Fig. 1). The main urban area, the City of Pensacola, is in the SW of the study area and has grown by about 25% in the last two decades to close to 60,000 inhabitants. In and just outside Pensacola are several industrial facilities, including a paper mill, a large nylon plant, a coal-fired power plant, and several chemical facilities. In the north of Pensacola, there is a former industrial zone, the Palafox Industrial Corridor that used to have wood treating, fertilizer production, and scrap metal facilities. Currently, the corridor has a rail yard, an asphalt facility, light industry, and commercial services. The city is surrounded by agricultural (cotton, corn, peanuts, soybeans) and silvicultural land use, especially to the north. The two-county study area has about 450,000 inhabitants on 3,300 km<sup>2</sup>. Traffic on most highways (Fig. 1) is relatively light and in the rural areas annual average daily traffic (AADT) is usually below 5,000 vehicles. Secondary roads in the rural areas may see only a few cars each day. The main north–south thoroughfare (US29), in the western half of the study area, has an AADT of about 15,000. In the city, larger streets have an AADT of 15,000–25,000, and smaller ones between 5,000 and 10,000. The major north–south thoroughfare through the city (I-110) has an AADT of 52,000. Interstate I-10 (Fig. 1) crosses the southern half of the study area, including the urban area, in a roughly east–west direction and has an AADT between 30,000 and 55,000 depending on the segment under consideration.

## Methods

### Site selection and sampling

To facilitate sampling, a map of potential sampling sites was constructed from data about the location and type of public places obtained from local government agencies. The obtained data included a total of 270 public places.

**Fig. 1** Location of study area and distribution of sampling sites



The greatest concentration of public places was in the city (Pensacola). Because of the lower density of potential sites outside the city, all non-urban public places were retained as potential sampling sites. In the city, potential sampling sites were manually selected in a GIS so that a homogeneous spatial distribution of potential sampling sites resulted. All potential sampling sites were visited and visually evaluated for recent human disturbance of the surface, the proximity of major roads, or other features that could skew trace metal content, and to judge if the sites were in the urban or rural part of the study area. Sites were rejected if there were any perceived signs of human disturbance or if they were near mixed urban/rural land use. Ultimately, 112 locations were sampled (Fig. 1), 65 in urban areas and 47 in rural areas. Twelve of these sites were in the Palafox Industrial Corridor, in and beyond areas studied by previous investigators.

Soil samples were collected from 0 to 5 cm depth with a stainless steel scoop after removal of grass, weeds, and any loose surficial material. Within the general area of interest for each sample (the public place), an attempt was made to determine the area of least disturbance for sampling. Care was used to avoid areas that might have had anthropogenic influences such as filling, landscaping, traffic, or regular parking of vehicles, and thus might yield unrepresentative pollution levels. Samples were preserved in acid-washed glass jars on ice and shipped within 24 h to the analytical laboratory.

#### Analysis and data processing

The chemical analyses of the samples were carried out by a contracted NELAP-certified commercial laboratory (Columbia Analytical Services, Jacksonville, FL, USA) with standard USEPA procedures. Mercury was determined by Method 7471A for sediments by cold vapor atomic absorption. Most other project metals (As, Cd, Cr, Cu, Pb, Ni, Zn) were analyzed by ICP-MS (method 6020, Acid Digestion of Sediments, Sludges, and Soils). Aluminum and Fe were analyzed on ICP-OES (method 6010B). All laboratory QA/QC procedures had results within acceptable limits as specified in a USEPA approved QAPP and NELAP guidelines. The matrix spike and matrix spike duplicate showed recovery of between 87 and 112%, which was well within acceptance limits. The relative percent difference between the duplicates was generally <10% and never >20%. Laboratory control spikes were also within acceptance limits and were between 90 and 104%. Method blanks had BDL results for the trace metals, but occasionally had detected values for Al or Fe of up to 8 mg/kg.

For the particle size, organic matter and pH determination samples were manually mixed and homogenized in the laboratory while being air dried. After air drying, samples were crushed with mortar and pestle to break up aggregates. The pipette method was used for clay and dry ro-tap sieving for the sand fractions (procedure 3A1 of Burt (2004)). Organic matter was determined with the

loss-on-ignition method by heating at 400°C for 6 h. Soil reaction (pH) was measured in a 1:1 soil–water solution (method 4C1a2 of Burt (2004)).

Three site-specific indexes were calculated to aid in the assessment of the pollution levels and origin of the trace metals. These indexes compare observed concentrations to background concentrations and are thus indicative of the degree of anthropogenic pollution. The index of geoaccumulation (Muller 1969) is calculated as:

$$I_{geo} = \log_2 \left( \frac{\text{Conc. metal}_{\text{sample}}}{1.5 \times \text{Conc. metal}_{\text{background}}} \right)$$

The factor of 1.5 is intended to account for variations in background values and minimizes overestimation of pollution levels. Interpretation of index values in descriptive terms is challenging, but terms used herein are based on Ntekim et al. (1993), Banat et al. (2005) and Gonzalez et al. (2007).

The enrichment factor also employs a ratio of observed to background concentrations, but standardizes the trace metal concentrations with a stable metal of natural origin (Zoller et al. 1974). Aluminum is often used as the stable metal for standardization as it is usually unaffected by anthropogenic inputs and relatively immobile in most common soils (Covelli and Fontolan 1997; Teng et al. 2009). The use of Al for standardization would be inappropriate where specific anthropogenic input of Al into the soil environment exists such as near smelters or where alum was used, but these activities are not present in the study area. The enrichment factor is calculated as follows (Zoller et al. 1974):

$$EF = \frac{(\text{Conc. metal}/\text{Conc. Al})_{\text{sample}}}{(\text{Conc. metal}/\text{Conc. Al})_{\text{background}}}$$

The descriptive terminology used for EF is based on Banat et al. (2005) and Wang et al. (2006).

The pollution load index (PLI) (Tomlinson et al. 1980) is the geometric mean of the concentration factor (CF), which standardizes the trace metal's observed concentration with its background concentration. The PLI is a measure for the overall level of all trace metals combined at a given site. The PLI is calculated as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

in which  $CF = \text{Conc. metal}_{\text{sample}}/\text{Conc. metal}_{\text{background}}$  for all  $n$  metals in a sample.

Completely natural background concentrations for heavy metals may not exist anymore in surface soils as anthropogenic pollution has reached almost the entire world via atmospheric transport and deposition. Therefore, background concentration is used in this study for the combination of the original geochemical background plus a small component of large-scale diffuse anthropogenic

input. It is used in a sense largely equivalent to the term baseline, which is often found in the geochemical literature (Teng et al. 2009). A discussion of the definition and methods of determination for this type of background is available in Matschullat et al. (2000). In the present study, the background concentration for the indexes was established with a K-means cluster analysis with Euclidean distances to separate the bimodal distribution of the trace metal concentrations into two groups, one group of background concentrations and one of sites with concentrations significantly above these background values. Normality of the metal data was tested with the Lilliefors test. Because all metals failed the test, the data were log transformed. This resulted in all metals but Ni passing the Lilliefors test. Therefore, results for Ni have to be interpreted with caution. The mean concentration plus two times the standard deviation ( $\sigma$ ) of the background group for each metal was used as the background concentration in the calculation of the indexes. The principle of establishing a background population and using the mean plus  $2\sigma$  of that unpolluted group as the background for calculation purposes is often used, although there are various methods to establish the background group (Matschullat et al. 2000). The local background values obtained by the present study are more appropriate to evaluate pollution levels than the general crustal background concentrations that have often been employed in other studies and may or may not apply locally (Covelli and Fontolan 1997; Ray et al. 2006; Gonzalez et al. 2007).

The PLI was used for hot spot analysis in a GIS to evaluate quantitatively if samples with high levels of trace metals are grouped in any given part of the study area. Hot spot analysis assesses the value at each site within the context of values at neighboring sites and, using Z scores, identifies clusters of sites that have significantly higher values than the whole dataset (Mitchell 2005). As one of the approaches to assess the origin of the metals, a principal component analysis (PCA) with varimax rotation was performed on a log-transformed trace metal dataset that included Al and Fe. Cadmium was left out of the dataset because of its relatively large number of below detection limit (BDL) results. Similar PCA approaches have often been used to identify the potential origin of trace metals in soils and sediments (Kumru and Bakaç 2003; Loska and Wiechula 2003; Boruvka et al. 2005).

## Results and discussion

### Descriptive statistics

Descriptive statistics for the metals and for soil characteristics are provided in Tables 1 and 2, respectively. The

**Table 1** Descriptive statistics for trace metal concentrations (mg/kg) (*n* = 112)

	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Mercury	Nickel	Zinc
Geomean	5,595	1.33	0.04	6.69	4.33	3,585	12.01	0.019	1.97	17.35
Mean	7,281	1.87	0.13	9.01	6.26	4,914	23.98	0.026	2.48	33.22
Median	5,985	1.40	0.04	6.45	4.40	3,900	11.50	0.019	1.95	17.00
Minimum <sup>a</sup>	919	0.13(4)	0.02(55)	0.39(1)	0.27(1)	589	0.82(2)	0.005(4)	0.17(2)	0.53(1)
Maximum	31,800	14.00	1.80	60.00	54.00	18,000	325.00	0.380	8.00	289.00
Stand. dev.	5,075	1.81	0.28	8.25	6.86	3,316	46.16	0.038	1.61	46.48
Skewness	1.91	3.82	4.44	3.23	4.05	1.67	4.75	7.72	1.24	3.08
Min DL <sup>b</sup>	1.1	0.016	0.006	0.005	0.017	1.3	0.013	0.004	0.016	0.028
Max DL <sup>c</sup>	6.6	0.210	0.081	0.068	0.230	1.7	0.17	0.006	0.210	0.370
RSCTL <sup>d</sup>	80,000	2	82	210	150	53,000	400	3	340	26,000
# Exceeding RSCTL	0	34	0	0	0	0	0	0	0	0

<sup>a</sup> Listed minimum for trace metals is lowest detected concentration. All trace metals had BDL results. The number between parentheses is the number of samples BDL. Minimum for Al and Fe are detected concentrations

<sup>b</sup> Minimum detection limit

<sup>c</sup> Maximum detection limit

<sup>d</sup> Residential soil cleanup target level

minimum concentrations for the trace metals were BDL, but most trace metals had only a few analytical results BDL (Table 1). Cadmium had BDL concentrations at 55 sites. Other studies have substituted half the detection limit in place of BDL values in calculations (Nadal et al. 2004; Sharma et al. 2007). Because replacing a BDL result with a value introduces spurious data, the BDL results in this study were treated as missing data and pairwise omission of missing data was used for correlation and principal component analysis. For the descriptive statistics, BDL results were replaced with half the detection limit because omitting BDL results would skew the statistics, especially the measures of central tendency. In any case, given the very small number of BDL results, the treatment of BDL should have minimal effect for all metals but Cd. With the exception of Ni, the trace metal concentrations are strongly positively skewed, which is typical for environmental data and often, but not necessarily, reflects the existence of two populations of data. Aluminum and Fe are less skewed than the trace metals, which suggests, but does not prove, a natural origin for these metals. This origin is also suggested by the coefficient of variation (CV) that was calculated for the log-transformed data. This CV is lower (8.8%) for Al and Fe than for the trace metals (As 220%, Cd 44%, Cr 41%, Cu 60%, Pb 43%, Hg 17%, Ni 101%, Zn 39%). This smaller CV for Al and Fe points to their appropriateness for use as reference elements for the indexes (Zhou et al. 2007). The soils in the study area are generally coarse textured and on average have 86.5% sand and 2% clay (Table 2). In general, the most sandy soils occur in the southwest of the study area, while clay content is higher in

the north due to more intense weathering as a consequence of the greater age of the soils. The soils are acidic with an average pH of about 5.2, but with an extreme low of 3.8. These acidic soil pHs can be expected to favor mobility of many of the trace metals.

#### Comparison with regulatory guidelines and other cities

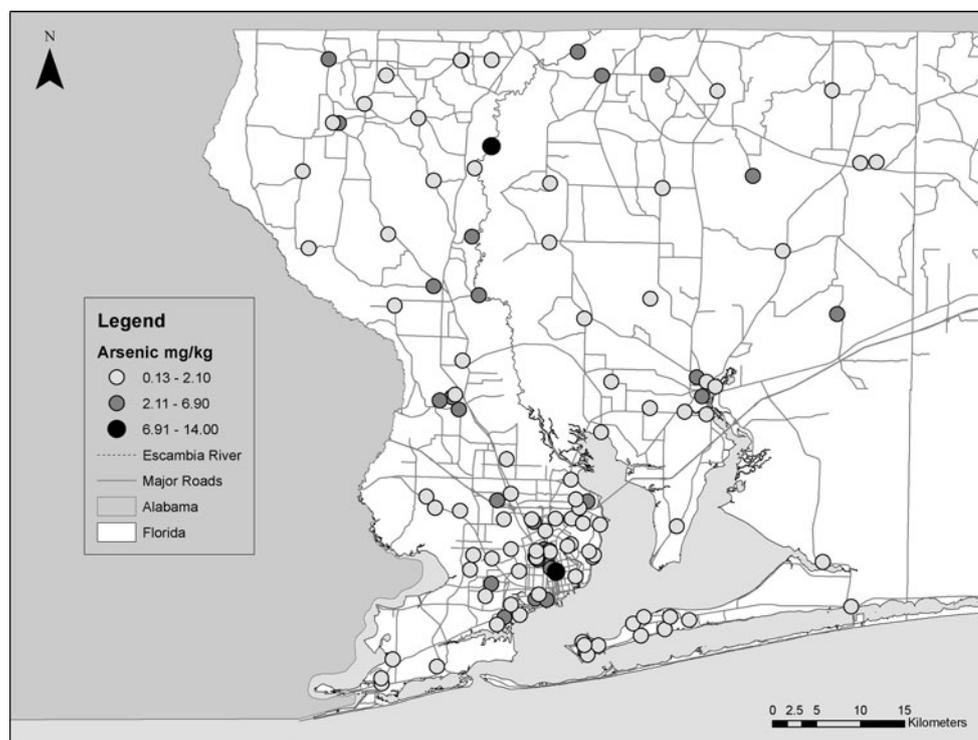
With the exception of As, trace metal concentrations in the study area do not exceed their respective State of Florida Soil Cleanup Target Level for residential areas (RSCTL) (Table 1). For arsenic, 34 of the samples (30.4%) exceed the RSCTL of 2.1 mg/kg, and thus are of environmental concern. These 34 samples are from locations throughout the study area in both rural and urban settings and do not show a clear spatial pattern (Fig. 2). This suggests that there is not a specific local point source for the As at surface level. The mean As concentration of 1.87 mg/kg is between the averages obtained in the urban settings of Gainesville, FL (0.40 mg/kg) and Miami, FL (2.81 mg/kg) (Chirenje et al. 2003), and thus is not exceptionally elevated in the present study area.

The average trace metal concentrations for the urban area are several times lower than those for larger cities (Table 3). Even compared to cities described as intermediate or small in size by the respective authors (Salamanca, Valladolid, Aveiro), the concentrations observed in the urban area of the present study remain low (Table 3). The only exception is Pb, which has a higher average concentration in Pensacola than in the small (70,000 inhabitants) Portuguese city of Aveiro (Madrid et al. 2006) and

**Table 2** Descriptive statistics for soil characteristics [%]

	Clay	Silt	Sand	OM <sup>a</sup>	pH
Geomean	2.08	8.56	86.45	4.13	5.17
Mean	2.72	10.27	87.01	4.70	5.22
Median	1.91	8.72	89.20	4.17	5.14
Minimum	0.26	2.04	45.03	1.10	3.80
Maximum	17.97	37.00	97.45	17.80	7.12
Stand. dev.	2.68	6.70	8.99	2.52	0.69
Skewness	3.62	1.70	−2.11	1.60	0.58

<sup>a</sup> Organic matter

**Fig. 2** Arsenic concentrations [mg/kg] in surface soils. Class breaks are RSCTL (2.1 mg/kg) and industrial/commercial SCTL (6.9 mg/kg)

Damascus. The data for these various cities may not be fully comparable due to discrepancies in sampling and analytical methods and soil characteristics, such as the relatively low pH for the soils in the present study, but the magnitude of the difference in concentrations suggests that the small city in the study area (Pensacola) has less influence on the concentrations of trace metals than large cities. This influence of city size was also suggested by Madrid et al. (2006) and is the result of the more intense land use in larger cities.

#### Assessment of influence of land use and potential origin

To assess the influence of land use on trace metal concentrations in the soils of the study area, the trace metal concentrations in the urban and rural parts were compared

with a *t* test for equality of means (Table 4). Mean concentrations for Pb and Zn, two trace metals that often have been linked to transportation sources, are higher in the urban areas than in the rural areas, but for Zn the difference of the means is only borderline statistically significant ( $P = 9\%$ ). Chromium and Ni concentrations are much higher in rural areas than in urban areas and the difference is statistically highly significant (Table 4). Arsenic, Cd, Cu, and Hg have very similar concentrations in and outside the urban area, suggesting that in the soils of NW Florida, these trace metals are not substantially influenced by land use. For As, this is consistent with the above made inference that there is no specific local source for As at surface level. The observation that with the exception of Pb, and possibly Zn, the trace metal concentrations are not significantly higher in Pensacola than in the surrounding rural

**Table 3** Comparison of trace metal concentrations [mg/kg] in urban soils for this and other studies

	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
This study—all sites	1.87	0.13	9.01	6.26	23.98	0.026	2.48	33.22
This study—urban	1.82	0.13	6.98	6.22	30.96	0.03	1.99	39.03
Naples <sup>b</sup>	na <sup>a</sup>	na	11	74	262	na	na	251
Seville <sup>b</sup>	na	na	39.4	68.2	137	na	21.9	145
Kowloon (Hongkong) <sup>b</sup>	na	0.62	23.1	23.3	94.6	na	12.4	125
Belgrade <sup>b</sup>	7.2 <sup>c</sup>	na	33.2	29.0	53.2	na	67.4	129
Salamanca/Valladolid <sup>b</sup>	na	0.41/0.28	na	na	165/151	na	na	na
Aveiro <sup>b</sup>	na	na	10	18	20	na	11	46
Beijing <sup>b</sup>	na	na	na	71.2	66.2	na	22.2	87.6
Addis Ababa <sup>b</sup>	19.9	3.22	64.7	31.8	31.4	na	52.4	85.4
Bangkok <sup>b</sup>	na	0.29	26.4	41.7	47.8	na	24.8	118
Damascus <sup>b</sup>	na	na	57	34	17	na	39	103

<sup>a</sup> Not available

<sup>b</sup> Sources: Naples: Imperato et al. (2003); Seville: Madrid et al. (2002); Kowloon: Li et al. (2004); Belgrade: Crnkovic et al. (2006); Salamanca/Valladolid: Sanchez-Martin et al. (2000); Aveiro: Madrid et al. (2006); Beijing: Chen et al. (2005); Addis Ababa: Demlie and Wöhnlich (2006); Bangkok: Wilcke et al. (1998); Damascus: Moller et al. (2005)

<sup>c</sup> Includes subsurface samples

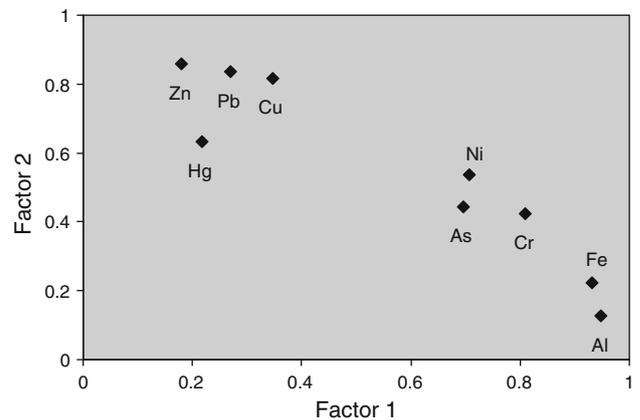
**Table 4** Average trace metal concentrations [mg/kg] for urban and rural parts of the study area

Metal	Urban	Rural	<i>P</i> <sup>a</sup> [%]
Arsenic	1.82	1.95	70
Cadmium	0.13	0.11	59
Chromium	6.98	11.81	0.6
Copper	6.22	6.31	95
Lead	30.96	14.31	3
Mercury	0.0270	0.0253	80
Nickel	1.99	3.14	0.01
Zinc	39.03	25.18	9
<i>n</i>	65	47	

<sup>a</sup> *P* value for *t* test for equality of means

areas corroborates the notion argued in section “Comparison with regulatory guidelines and other cities” that this small city has a minor influence on trace metal concentrations.

To evaluate the potential origin of the trace metals, a PCA was applied to a dataset that included the trace metals and Al and Fe. The PCA yielded two components with eigenvalues >1 that together explained 77% of the variance. The factor loading plot (Fig. 3) shows that Pb and Zn plot on the opposite site of the graph than Al and Fe, indicating that these two pairs of metals are not of the same origin. Iron and Al are most likely of geogenic origin. These metals have often been used in the literature as reference elements that are of natural (i.e., geogenic)



**Fig. 3** Factor loading plot. Metals plotting in the same part of the graph are assumed to be of common origin

origin (e.g., Daskalakis and O’Connor 1995; Weisberg et al. 2000; Sindern et al. 2007). In this study, a geogenic origin for these two metals is corroborated by their low CV that is mentioned above, their relatively strong and significant correlation with soil properties (Table 5), the lack of a clear spatial pattern of their concentrations other than what can be explained by variations in soil properties (e.g., Fig. 4 for Al), and the absence of specific known anthropogenic sources for these metals in the region. Lead and Zn have a clearly different origin, most likely anthropogenic, as was also suggested above by higher concentrations of these metals in urban areas than in rural areas. Chromium, Ni, and As are associated with Fe and Al (Fig. 3), and thus are also likely to be of geogenic

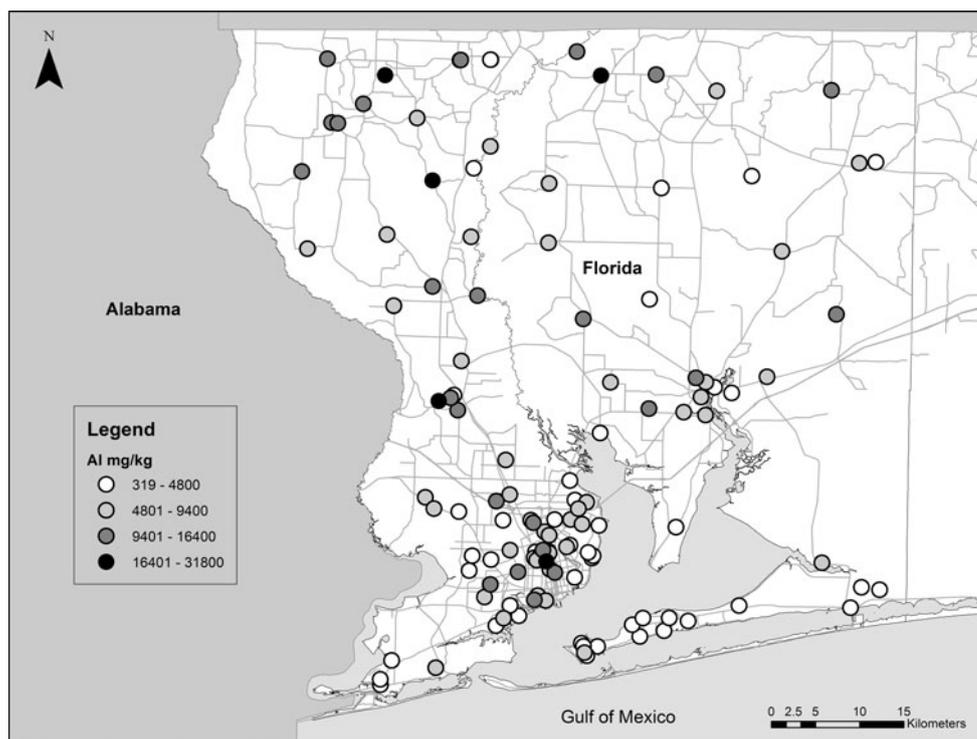
**Table 5** Pearson correlation coefficients between soil properties and trace metal concentrations

	Al	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
Clay	<b>0.71<sup>a</sup></b>	0.11	-0.14	<b>0.48</b>	0.10	<b>0.52</b>	-0.01	0.13	<b>0.57</b>	-0.06
Silt	<b>0.67</b>	0.24	-0.07	<b>0.46</b>	0.21	<b>0.63</b>	0.08	0.20	<b>0.62</b>	0.03
Sand	<b>-0.71</b>	-0.21	0.09	<b>-0.49</b>	-0.18	<b>-0.62</b>	-0.06	-0.19	<b>-0.63</b>	0.00
OM <sup>b</sup>	<b>0.49</b>	0.20	-0.17	<b>0.32</b>	0.25	<b>0.38</b>	0.03	0.14	<b>0.44</b>	0.10
pH	0.07	0.23	0.18	0.07	0.22	0.10	0.19	0.11	0.14	<b>0.37</b>

<sup>a</sup> Values in bold are statistically significant ( $p < 0.01$ ;  $p = 0.02$  for Zn vs. pH)

<sup>b</sup> Organic matter content

**Fig. 4** Aluminum concentrations (mg/kg) in surface soils. No clear spatial pattern is discernible except for some low concentrations in the extreme south that are consistent with the young, quartz-rich nature of the local soils



origin. For Cr and Ni, this is in line with the observation that they have higher concentrations in rural areas because the northern half of the study area, which is under rural land use, is characterized by intense weathering (Williams 2004) that may have released Cr and Ni from the soil parent material. The contention that Cr and Ni have predominantly the same origin as Al and Fe is consistent with the relatively large and statistically significant correlation with soil particle size fractions and organic matter content for all four of these metals (Table 5). Copper is not significantly higher in urban than rural parts of the study area (Table 4) but, nevertheless, the PCA shows that it is associated with Pb and Zn, suggesting Cu is also of anthropogenic origin. Mercury plots differently than the other metals, indicating a different origin. This is in line with what is known about sources of Hg in the environment which are largely different from those of Pb, Zn, and

Cu, and include mainly coal burning power plants and (medical) waste incinerators. Arsenic may also be released by coal burning power plants, but the PCA results suggest that this is not the primary source of both Hg and As in the study area.

#### Pollution indexes

To evaluate if the trace metal concentrations may represent anthropogenic pollution, two indexes that compare observed concentrations to background concentrations, the index of geoaccumulation (Igeo) and the enrichment factor (EF), were applied. Many other studies have employed general crustal background concentrations to calculate indexes like these (Covelli and Fontolan 1997; Ray et al. 2006; Gonzalez et al. 2007). These general background concentrations (Table 6) may or may not apply to any

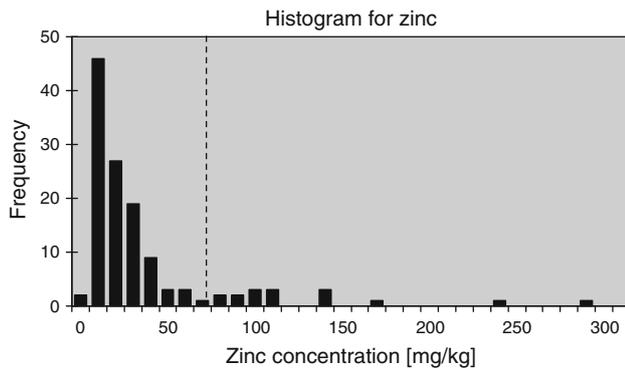
**Table 6** Comparison of crustal and local background values [mg/kg]

Source	Al	As	Cd	Cr	Cu	Fe	Pb	Hg	Ni	Zn
Shale <sup>a</sup>	80,000	2.1	0.3	90	45	47,200	20	0.4	68	95
Sandstone <sup>a</sup>	25,000	1	na	35	na	9,800	7	0.03	2	16
Crustal avg. <sup>b</sup>	82,300	1.8	0.2	100	55	56,300	12.5	0.08	75	70
This study	13,634	4.6	0.4	21	17	8,895	59	0.07	3.98	77

<sup>a</sup> Source Turekian and Wedepohl (1961)

<sup>b</sup> Source Taylor (1964)

na Not available



**Fig. 5** Histogram for Zn concentration [mg/kg]. Dashed line marks calculated background (77 mg/kg)

particular region due to differences in rock type, climate, and geochemistry, and thus local background values seem much more appropriate. The trace metal concentrations in the present study have a distinct skew and bimodal distribution (e.g., Zn, Fig. 5), and lend themselves to identification of a local background value. The resulting local background concentrations are substantially different from the general background values for most metals (Table 6), illustrating the importance of calculating a local background in this type of study. The general crustal values were obtained with sampling procedures and analytical methods that differed greatly from those used in the present study. Consequently, one would not expect to find very similar results, but the magnitude and variability of the discrepancies between the general and local background values show that the general crustal background values,

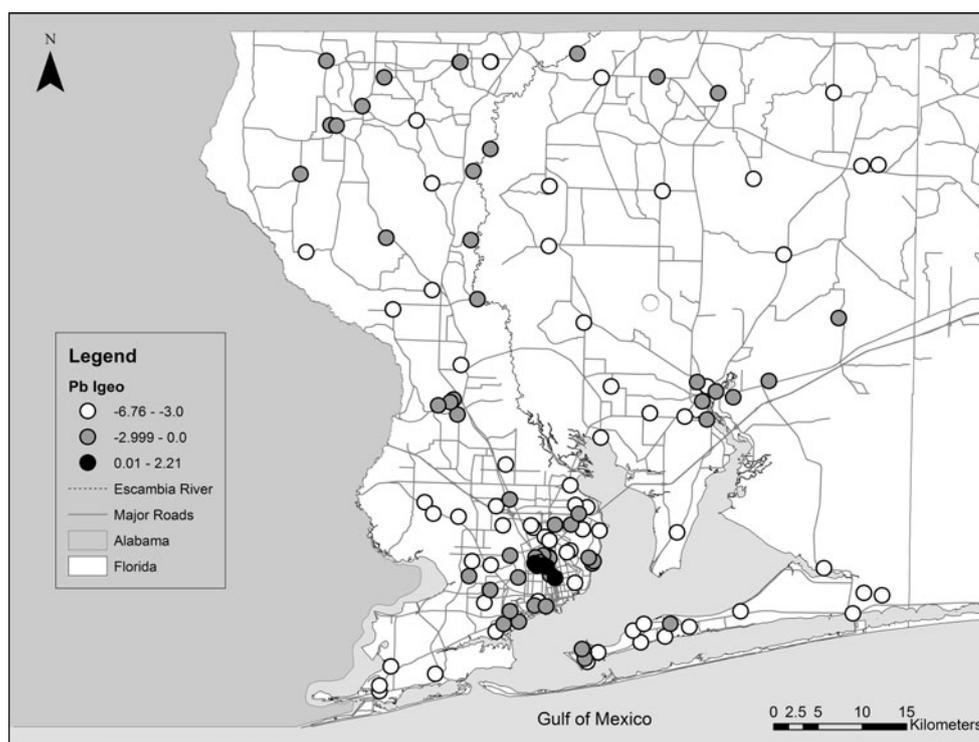
which are frequently used in the literature, should be employed with great caution. They are best suited for internal comparison in regions with homogeneous soil parent materials.

The enrichment factor identifies more sites as being polluted or strongly polluted than the index of geoaccumulation, but absolute differences between the two indexes are modest (Table 7). The indexes show that very few sites are strongly polluted. The trace metals with the highest proportion of strongly polluted sites are Pb and Cu, which were shown by several lines of evidence to be of anthropogenic origin, but even these metals reach that pollution level at no more than 1.6% of the sites based on the enrichment factor. These sites are mainly in the Palafox Industrial Corridor (Fig. 6 for Pb). The other trace metals with some albeit few strongly polluted sites (EF only) are Hg, Ni, and Zn. For Hg and Zn, this is consistent with the PCA-based observations that these two metals may also be of anthropogenic origin. Arsenic, which exceeds the RSCTL at the most sites (Table 2), has relatively few polluted or strongly polluted sites (Table 7). This observation indicates that very few As concentrations are above the local background, but that the background is close to the RSCTL. Comparison of the local and general crustal backgrounds also indicated that As has a high background (4.6 mg/kg) in the study area (Table 6). High As backgrounds have been reported previously for the region (Chen et al. 1999; Liebens 2001). Chromium and Ni are of geogenic origin according to the PCA and in principle should have the lowest proportions of (strongly) polluted sites.

**Table 7** Proportion [%] of samples at various pollution levels based on local background concentrations

Index value	Pollution level	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Index of geoaccumulation									
0–2	Polluted	2.4	1.6	3.2	2.4	4.0	1.6	4.0	4.8
>2	Strongly polluted	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0
Enrichment factor									
2–10	Polluted	5.6	5.6	2.4	7.1	8.7	7.9	13.5	11.1
>10	Strongly polluted	0.0	0.8	0.0	1.6	1.6	0.8	0.8	0.8

**Fig. 6** Spatial distribution of Igeo for Pb. Map shows “polluted” sites are concentrated in one particular area, an (former) industrial corridor



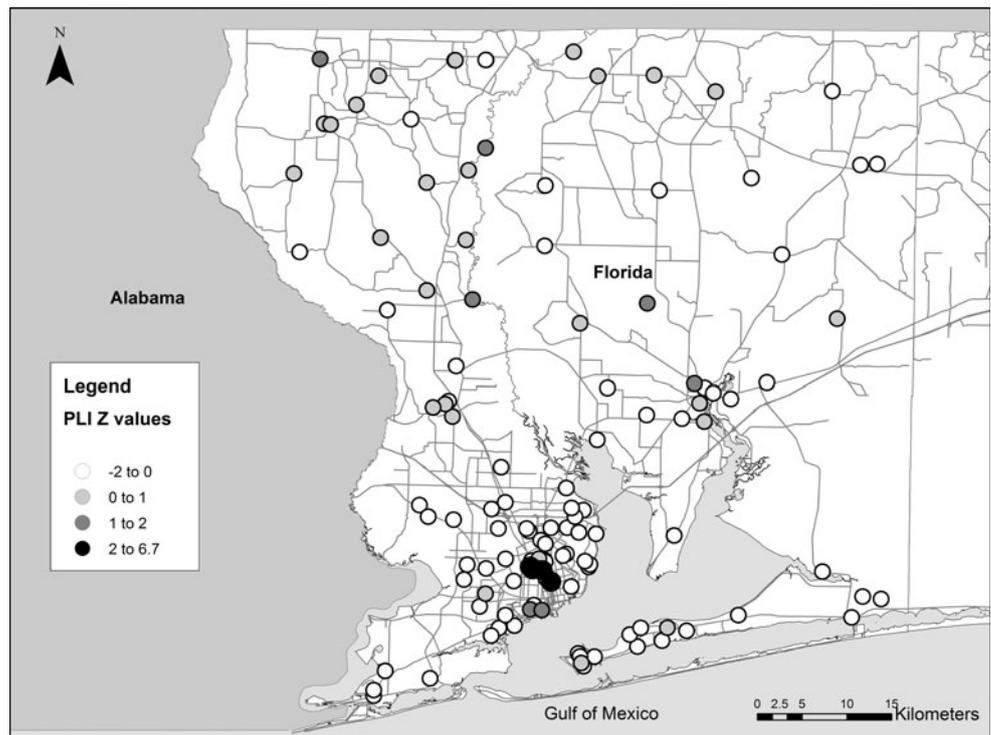
This is not the case for Ni, at least in part because this study’s approach forces part of the data into a polluted population. This is a drawback of this or any other method that separates a dataset into two populations and points to the need for careful consideration of trace metal characteristics when applying this type of method to determine background concentrations.

#### Hot spot analysis

Spatial clustering of high concentrations of trace metals, or any other pollutant, can point to the presence of local sources of pollution and can help reveal the origin of pollutants. Therefore, the trace metal concentrations were further examined in a GIS with hot spot analysis. Hot spot analysis is a quantitative technique to interpret spatial patterns and does not rely on interpolated data, making it superior to visual interpretation of continuous surface maps (Imperato et al. 2003; Li et al. 2004). The hot spot analysis was performed on the PLI, an index that is a measure for the overall magnitude of the trace metal concentrations at a given site (Tomlinson et al. 1980). Results show that a clear hot spot exists in the Palafox Industrial Corridor and that elsewhere in the study area the PLI is lower and of more-or-less comparable magnitude (Fig. 7). The hot spot is irregular in shape, but it is approximately 3 km in its widest dimension and 1 km in its shortest dimension and is

largely centered on the industrial corridor. This relatively small size implies that the trace metal pollution has spread only by local processes, such as potentially, short range atmospheric transport or surface runoff. The spatial concurrence of the hot spot and the industrial corridor does not necessarily represent a causal relationship, but given the well-documented pollution history in the industrial corridor (Geraghty and Miller 1992; Liebens et al. 2006), it seems reasonable to assume that this previously undocumented trace metal hot spot is due to the local (former) industry. The former industry included a wood treatment facility, a fertilizer manufacturing plant, and a scrap metal facility. Currently, there is an asphalt plant, a railroad yard, and other minor light industry. The relatively low Z scores elsewhere in the urban area indicate that in a small city like Pensacola, the influence of industry on soil trace metal concentrations exceeds that of traditional urban activities such as traffic. This observation is consistent with the spatial pattern of the pollution indexes, which showed a concentration of sites strongly polluted with Pb and Zn in the Palafox Industrial Corridor (Fig. 6 for Pb). The well-defined PLI hot spot and the co-located spatial concentration of elevated values for the other two pollution indexes suggest that the input of trace metals into the soils of the Palafox Industrial Corridor is locally high enough to mask the effect of the soil characteristics in the area. This provides a possible explanation for the lack of correlation between anthropogenic trace metal concentrations and soil

**Fig. 7** Z scores from hot spot analysis of PLI index. *Black site markers* show a cluster of points with high Z scores in the (former) industrial corridor



characteristics described in section “[Assessment of influence of land use and potential origin](#)”.

**Conclusions**

In the small city in the study area (Pensacola), trace metal concentrations are considerably lower than in large and intermediate cities. This suggests that trace metal concentrations in urban soils are related to the size of the city, presumably because of the more intense land use in larger cities. Differences in concentration between Pensacola and its rural surroundings are small for the anthropogenic trace metals and statistically significant only for Pb, a trace metal that has been clearly linked to traffic and other urban sources by this and other studies. The low concentrations and the lack of differentiation between urban and rural areas indicate that the influence of Pensacola on soil trace metal concentrations is small, except for Pb. With the exception of As, none of the trace metals exceeds its RSCTL. Arsenic exceeds its RSCTL not only in the city but throughout the study area, indicating that it is not predominantly of urban origin. These observations suggest that the influence of a city like Pensacola on soil trace metal concentrations may not be large enough to be of regulatory concern. Obviously, this is dependent on the natural concentrations of the trace metals in the area and the specifics of the applicable regulatory guidelines. These conclusions are based on a study of only one small city and

require confirmation by follow-up studies in other small cities, but the observations for Pensacola and the differences with large cities show that such studies are warranted.

Two pollution indexes were determined to assess the trace metal pollution level in the area. The EF and Igeo indexes led to generally similar conclusions about the proportion of polluted sites, which is relatively low in the study area. Local background concentrations were very different from general crustal values used in some other studies. These differences in backgrounds can result in major differences in outcomes for the indexes, underscoring the importance of careful consideration of methods in this type of study.

There was a notable agreement between the different approaches employed to assess the potential origins of the trace metals. Aluminum and Fe are generally accepted to be of geogenic origin and several lines of evidence suggest that this is the case in the present study, including relatively high correlations with soil properties, PCA loadings that are very different from those of anthropogenic trace metals, and low CVs. Simple descriptive statistics show that Ni, and to some degree Cr, have characteristics that are more similar to those of Al and Fe than those of the other trace metals, suggesting that Ni and Cr may at least in part also be geogenic. This is corroborated by PCA that indicates Ni and Cr are of similar origin as Al and Fe, and by high correlations between Ni and Cr and soil particle size distribution and organic matter content. The consistency of

the results of these three approaches leads to the conclusion that land use has little influence on Cr and Ni concentrations in soils in the study area. The PCA also indicates that Pb, Zn, Cu, and Hg have a different origin, presumably anthropogenic. These four trace metals have very low correlations with clay content. Low correlations have been interpreted by some as evidence for an anthropogenic origin of trace metals. Pb, Zn, Cu, and Hg have the highest pollution indexes, especially Pb and Zn, but none of the trace metals reaches strong pollution levels at more than 2.4% of the sites. Most of the sites with high concentrations and high index values for these trace metals are in the industrial part of the city, as indicated by visual interpretation of maps. More objective geostatistical analyses show that the overall trace metal concentrations, as expressed by the PLI, are also higher in the industrial part of the city. This pollution is spatially limited, suggesting that the sources are local, which points to the impact of the local (former) industry on the soil environment. These observations imply that in a small city like Pensacola, industrial sources of trace metals predominate other urban sources, as has been observed in larger cities.

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