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Spatial Distribution of Heavy Metals in Top Soils Around the Industrial Facilities of Cromatos de México, Tultitlan Mexico

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Abstract The environmental damage caused by industrial activities in Cromatos de México, (Tultitlán, México) has been evaluated in terms of heavy metal concentrations in topsoils of the surrounding area. The concentrations of lead, copper and zinc demonstrate a significant enrichment with respect to unpolluted levels. Their maximum enrichment factors are 37.7, 21.1 and 9.6 mg kg^{-1}, respectively; such increase is related to traffic emissions. Nickel concentrations show no significant difference in the analyzed samples. Total chromium concentrations show a significant decrease with distance from the industrial facilities, ranging from 15 to 1,837 mg kg^{-1}. The enrichment factors of chromium (total), with respect to the background values reach up to 40.8 mg kg^{-1}. In spite of this pronounced increase, only three analyzed samples show chromium (VI) concentrations over 0.5 mg kg^{-1} (instrumental detection limit) and do not exceed the values recommended by the Mexican official norm. The current results show that the chromium present in the studied area does not represent serious health risks and environmental damage in the zone, nevertheless, it is necessary to consider that the oxidation of chromium (III) is determinate by changes in redox and/or pH conditions which would imply significant impacts upon its toxic risk. This study suggests that the waste material generated during the industrial activities of Cromatos de Mexico represents a relevant metal pollution source for the area even 30 years after the closure of the industrial facilities.

Keywords Chromium · Pollution · Mexico · Industrial facilities

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The environmental deterioration due to anthropogenic activities has been a subject of numerous studies in many countries (Kabata-Pendias and Pendias, 2001; Wong et al. 2006). Heavy metals may come from many different sources in urbanized areas. The increase of heavy metal concentrations in environmental materials in industrial areas is frequently reported as industrial impact indicator (Shallari et al. 1998; Çelik et al. 2005; Zhou et al. 2007). These studies reported a negative impact from industrial activities with respect to heavy metals in the surroundings of the industrial complexes and showed that the levels of pollutants in soils decrease gradually as distance increases from the contaminant source (Nadal et al. 2004; Shukurov et al. 2005; Al-Khashman and Shawabkeh 2006). The study of the spatial distribution of heavy metals in urban soil samples is very important from the point of view of identifying hot-spot areas and assessing the potential sources of pollutants. The spatial distribution of heavy metal contamination can be studied based upon geographical information system technology (GIS). Geochemical maps produced using GIS, enable the analysis through the visualization of the information in a geographic context. Therefore GIS is a useful tool to simulate and present future scenarios in order to formulate appropriate proactive measures.

One of the most important Pb sources in an urban environment is vehicle emission. In recent years, numerous studies have assessed the influence of traffic emissions on the levels of Pb. Monna et al. (2006); Sun et al. (2006); Ligero et al. (2004) and Hernandez et al. (2003) show that the combustion of leaded gasoline was the primary source of Pb. In addition some workers have reported a positive correlation between Cu, Zn and Pb and have interpreted it as derivation of the same source of contaminants (Sezgin et al. 2003; Garcia and Millan 1998).

Similarly, the environmental chemistry of chromium has been widely studied (Richard and Bourg 1991). The two common oxidation states of Cr present in the environment, i.e. Cr(III) and Cr(VI), are drastically different in charge, physicochemical properties as well as chemical and biochemical reactivity. Chromium (III) is considered to be a trace element essential for the proper functioning of living organisms. Opposing party chromium (VI) exerts toxic effects on biological systems. The mobility and bioavailability of Cr depend fundamentally on its oxidation state. Chromium (VI) compounds are usually highly soluble, mobile and bio-available compared to sparingly soluble trivalent Cr species. Armienta et al. (1996), Isikli et al. (2003) and Bini et al. (2008) have reported an anomalous occurrence of Cr in soil samples surrounding the industrial zone. These studies are in agreement about the Cr(III)/Cr(VI) proportion in these samples being the dominant specie Cr(III) and in a lower proportion (Cr VI). An exact quantification of each species rather than the total Cr level is required to properly evaluate physiology and toxicological effects of Cr and its distribution and transport in the environment.

The high industrial growth rate in Mexico City has resulted in an increase of the levels of environmental pollution originated mainly from uncontrolled factory emissions and waste discharge. *Cromatos de México* was operating between 1870 and 1984 in the region of Tultitlan and was an important industrial centre located at ca. 20 km north of Mexico City. The industrial activities were principally related to the production of Na-chromate and K-chromate using chromites ($FeCr_2O_4$) as the main raw material. Industrial production was performed without considering any control over emission of contaminants and disposition of final residues. It is estimated that during this period about 120 tons of industrial waste were accumulated within the industry installations (Gutierrez et al. 1985). Since 1983, the residues have been confined in an area of 16,500 m^2, without an impermeable base and application of required technical specifications.

The objective of this study was to investigate the local distributions of Cr, Cu, Ni, Pb and Zn in soils from the vicinity of the industrial complex of *Cromatos de México* as well as to determine the metal pollution impact in this zone. These data will provide a basis for further investigations of the metal speciation and behavior to evaluate the potential for remobilization, transport, and biological uptake.

Materials and Methods

In transects of ca. 1 km around *Cromatos de México*, 30 different samples from the top layer (1 cm) of the soil profiles were collected during the summer of 2006. Sampling sites were selected to understand the pollution impacts of different trace elements on the topsoil. Samples were collected by stainless steel trowel and stored in plastic bags. Ten soil samples were selected from the surrounding rural areas at a distance of 10 km from the industrial zone as the background to define the unpolluted values. Samples were air-dried at 60°C and passed through nylon sieves of 200 mesh size. The concentrations of Cr, Cu, Ni, Pb and Zn were determined on bulk samples of <200 mesh size sediments by Siemens SRS 3000 sequential X-ray spectrometer. The accuracy of the procedure was determined by analyzing the certificated reference material NIST 2586 (National Institute of Standards and Technology, USA). The results obtained were in exact agreement with the certified concentrations.

Heavy metal concentrations in the bulk surface soil samples were used to construct contour maps using SURFER software (Golden Software Inc., Colorado) and the data were geographically managed and processed with the GIS software Arcview 3. Geochemical maps, generated using GIS, were used to identify sources of emission and to study the distribution and correlation of metals in the urban area.

Results and Discussion

The concentrations of Cu, Ni, Pb, Cr (total) and Cr(VI) in the bulk soil samples are shown in Table 1. The heavy metal concentrations show a wide range of variation with variable pattern. Cr (total) shows a significant effect with distance from the industrial facilities. It ranges from 15 to 1,837 mg kg^{-1}. The enrichment factors of Cr (total), with respect to the background values, reach up to 40.8.

Table 1 Concentrations (mg kg^{-1}) of heavy metals in the analyzed soil samples

Sample	Cr(VI)	Cr tot mg kg^{-1}	Cu mg kg^{-1}	Ni mg kg^{-1}	Pb mg kg^{-1}	Zn mg kg^{-1}
1	bdl	168.3	48.6	23.1	130.7	431.8
2	bdl	222.5	39.7	32.2	68.2	136.3
3	bdl	123.8	131.1	49.1	275.7	407.4
4	bdl	15	10.7	5	117.8	41.3
5	bdl	58.8	47.2	28.1	89.9	329.4
6	bdl	105	95.3	28	152.7	194.9
7	bdl	87.3	327.3	28.6	81.8	653
8	bdl	77.4	97.8	22.7	77.4	191
9	bdl	45.7	43.5	15.2	165.5	142.7
10	bdl	56.6	135.1	22.1	103.9	220.6
11	bdl	69.1	55.4	25.3	153.1	394.1
12	bdl	75.2	33.8	21.7	65.6	122.3
13	63.1 μg kg^{-1}	1,837	28.6	51.1	78.1	165.5
14	58.6 μg kg^{-1}	294.2	38.5	30.4	129	172.2
15	bdl	69.3	62.2	38.1	71.1	277
16	bdl	131.2	107	25.3	343.1	269.8
17	bdl	47.9	25.6	20.9	20.7	68.3
18	bdl	173.1	41.3	50	116.3	178.4
19	bdl	40.3	17.5	21.2	17.4	54.8
20	bdl	101.5	101.7	18.3	255.6	385.4
21	bdl	37.3	32.3	19.8	62.6	149.5
22	bdl	47.3	39.9	27.4	94.3	316.2
23	bdl	54.3	21.7	21.6	15.9	67.3
24	bdl	33.4	23.2	35.3	11	87.6
25	bdl	41.3	16.5	16.7	10.4	46.3
26	bdl	222.1	23.1	14.2	22.7	72.4
27	bdl	550.2	69	50.2	169	207.9
28	10.2 μg kg^{-1}	229.1	687.7	36.3	138.5	1,092.7
29	bdl	146.7	74.2	24.3	116.8	307.7
30	bdl	54.4	50.2	33	84.5	125.6
Min		15	10.7	5	10.4	41.3
Max		1,837	687.7	51.1	343.1	1,092.7
Mean		173.84	84.19	27.84	107.98	243.65
Background		45	20	28	12	69
Guidelinie	280[1]		3,100[3]	1,600[1]	400[1]	23,000[3]
EF		40.82	34.39	1.83	28.59	15.84

EF enrichment factor

bdl below detection limit

[1] Values recommended by the Mexican Ministry of Environment (2007)

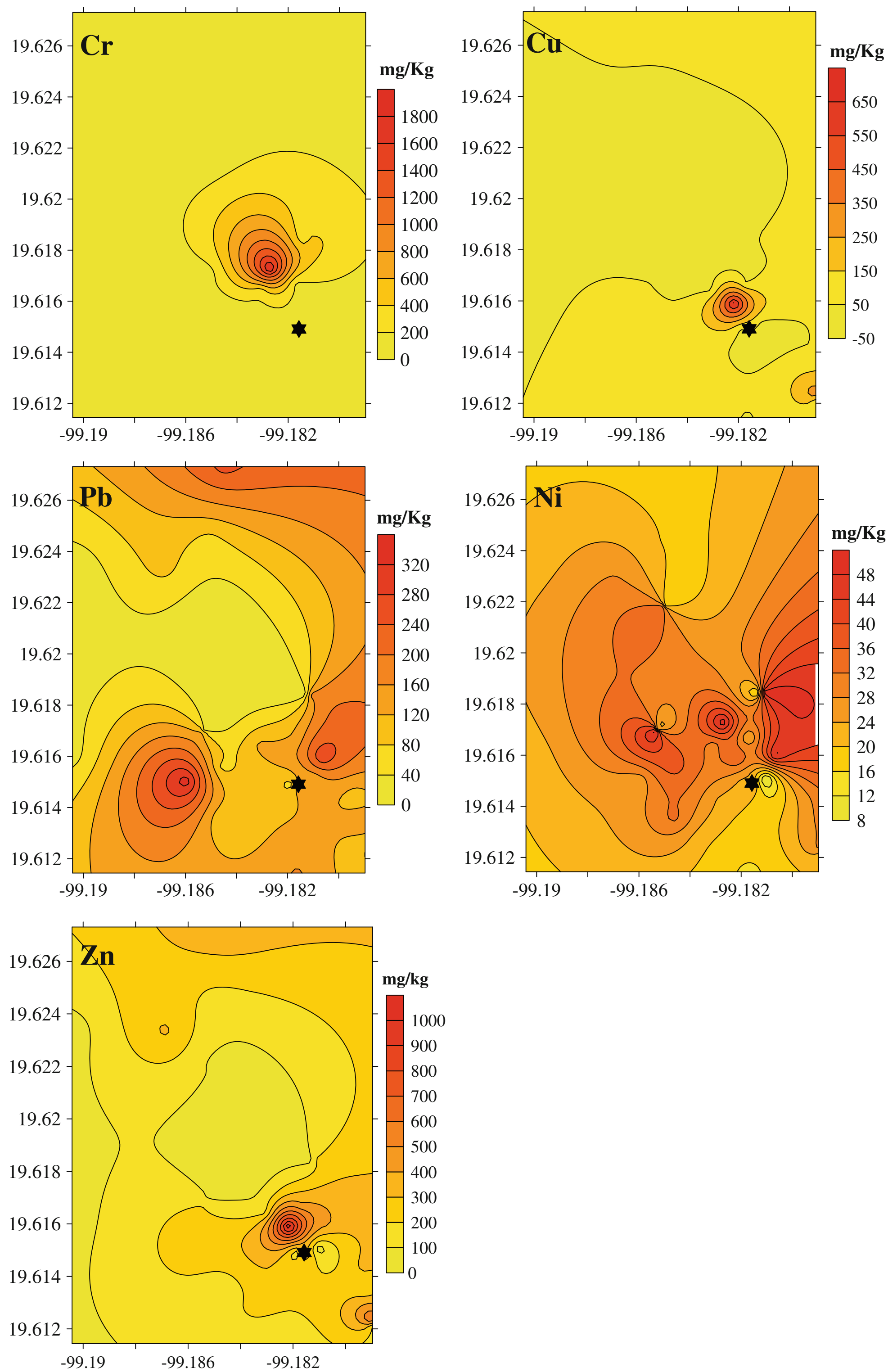
[2] Values recommended by the Mexican Ministry of Environment (2007) for Cr(VI)

[3] Values recommended by Environmental Protection Agency (Region 9)

However, Cr(VI) concentrations reach >0.5 mg kg^{-1} only in three analyzed samples and do not exceed the recommended concentrations. The concentrations of Pb, Cu and Zn demonstrate a significant enrichment with respect to unpolluted levels (Table 1). The maximum enrichment factors for Pb, Zn and Cu are 37.7, 21.1 and 9.6 mg kg^{-1}, respectively. Lead concentration ranges from 5 to 521.2 mg kg^{-1}. The increase of Pb is related to traffic emissions and the highest concentrations were found in soils exposed to heavy traffic conditions. Although the use of leaded gasoline has been prohibited since 1989 in Mexico, the Pb enrichment is attributed to decades of leaded gasoline use. Cu concentration varies between 14 and 397 mg kg^{-1}. Concentrations of Zn were found between 90 and 1,456 mg kg^{-1}. Ni and V concentrations show no significant difference in the analyzed samples and generally have low contents close to background levels.

Geochemical maps of Cr (total), Cu, Ni, Pb and Zn were produced based on geographical information system (GIS) software (Fig. 1). The spatial distribution of Cr can be attributed to the proximity of industrial discharge points showing a decrease of concentration as distance increases from the industry. Spatial distribution of Cu and Zn are very similar. An important hot-spot of both Cu and Zn is located close to the industrial site indicating that industrial activities might have contributed to the accumulation of

Fig. 1 Geochemical maps of *Cr* (total), *Cu*, *Ni*, *Pb* and *Zn* in the analyzed area



these heavy metals in the studied area. Several hotspots of high Pb concentrations were identified in the geochemical maps. The hot-spots were found at the junctions of roads and/or near major roads that have a heavy traffic density suggesting that vehicular emissions may be the major sources of Pb in the study area. The dispersal behavior of Ni suggests a natural input of this metal from mafic parental rocks present in the surroundings.

Table 2 shows the correlation coefficients of the analyzed metals at 95% significance level. Both Cu and Zn

Table 2 Correlation coefficients between heavy metal contents in the analyzed topsoils. Significant correlations at the $p < 0.001$ level are marked in bold

	Cr	Cu	Ni	Pb	Zn
Cr	1				
Cu	−0.0189	1			
Ni	**0.5323**	0.1937	1		
Pb	0.0127	0.2213	0.1978	1	
Zn	−0.0086	**0.9001**	0.2653	**0.3691**	1

show significant positive correlation. Between Ni and Cr (total), the correlation is positive. The remaining metals analyzed do not exhibit any significant correlation coefficient between them.

The present study aims to assess the extent of contamination that the soils around the industrial facilities that the company *Cromatos de México* (Tultitlan, Mexico) have taken up. Chromium concentrations in some soil samples are still high. However, the predominant chemical species in these samples is Cr(III). Cr concentrations above the instrumental detection limit were found only in three samples. The range of Cr(VI) concentrations is 10.2–63.1 mg kg^{-1}. Therefore it is considered that the present chromium concentrations in the environmental zone do not represent serious health and environmental risks. Nevertheless, it is necessary to consider that the oxidation of Cr(III) is determinate by changes in redox and/or pH conditions which would imply significant impacts upon their toxic risk.

The increase of Ni in the analyzed soil samples seems to be strongly correlated to Cr, however their concentration is very low and they are within the safety interval. The relatively high concentrations of Pb, Zn and Cu in the soil samples of the investigated area were related to other pollution sources, i.e. vehicle traffic.

The current results show the environmental damage in the zone, even 30 years after the closure of the industrial facilities of *Cromatos de México,* and suggest that the waste material generated during industrial activities represents a relevant metal pollution source for the area. Attention should be paid to the management of solid waste dumped in inappropriate sites inside of the industrial facilities. It is necessary to establish a specific management procedures, otherwise metal content may increase in the surrounding area, resulting in an irreversible environmental damage that will increase the health risk to the population of the region.

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