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Elemental Analysis of Soils as Possible Resuspended Dust Sources in Mexico City

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ABSTRACT: Soil samples were collected from seven sites in and around the Metropolitan Area of Mexico City. The locations were chosen as possible sources of fugitive dusts which contribute to suspended particulate matter in the atmosphere of Mexico City. X-ray Fluorescence (XRF) was used to determine the concentrations of several major elements (Si, K, Ca, Ti, Mn, and Fe), as well as of other trace elements that might be useful to identify the source of the airborne particles (Cr, Ni, Cu, Zn, Rb, Sr, Y, and Zr), while X-ray Diffraction (XRD) was employed to identify the most important mineral phases present in the samples. It was found that the concentrations of some elements and the presence of minerals (like albite, quartz, and calcite) show a certain similarity to those determined by other authors in samples of Total Suspended Particles (TSP) from this urban area. Also, a comparison is made with ratios of published elemental compositions of fugitive dust profiles for inhalable particulate matter (PM_{10} and $PM_{2.5}$). The ratio Mn/Fe obtained in this work is very similar to all other studies, suggesting a crustal origin, while the ratios Cr/Fe and Ni/Fe in the other studies may be affected by anthropogenic sources.

Key words: Airborne particles, Minerals, X-ray fluorescence, X-ray diffraction

INTRODUCTION

Many authors have shown the strong influence of dusts from several sources on the concentrations and composition of airborne particulate matter, either due to long range (Perry *et al.,* 1997) or to short range (Rojo *et al.,* 2008) transport towards other sites. Dust may be re-suspended in the atmosphere either by abrasion (when there is a disturbance on the surface like the passing of vehicle or the hopping motion of other particles, through a process known as saltation), or by means of the direct action of the wind on the surface (Ziskind *et al.,* 1995). Several works have demonstrated the impact of resuspended road dusts (Thorpe and Harrison 2008; Almeida *et al.,* 2006) on the composition of airborne particulate matter. There is also a direct impact of the resuspended dust on human health, consumed either by breathing or direct ingestion (Singh and Singh, 2010). Moreover, Đorđević et al. (2005) proved that local resuspended soil dust has a more important influence on atmospheric aerosols in an urban area, even though they may have a remote origin. Additionally, other sources, like traffic, may affect the composition of deposited dust, which will be resuspended later (Machado *et al.,* 2008).

Likewise, it is known that the Metropolitan Area of Mexico City (MAMC), besides being an emitter of many kinds of pollutants sent to other regions (Molina *et al.,* 2010), is also subjected to the effect of external or local sources. The origin of particulate matter related to soils (resuspended dusts) in the MAMC is not fully understood to date. For instance, Vega et al. (2002) found that geological material contributed to almost 40% of PM_{10}, and it was attributed to agricultural lands around MAMC in the north and northeast sectors of the basin. After that, Johnson et al.(2006) concluded that particle back-trajectories passing up the Rio Balsas valley and over Toluca to the west/southwest of the Mexico City basin increased the fine soil concentrations; that work also discards the dry Texcoco Lake as the dominant source of soil particles, as proposed by other authors (Moya *et al.,* 2003). The origin of the geological aerosols was not explicitly mentioned by Molina et al. (2010) in their MILAGRO summary, although during this program, Querol et al. (2008) inferred that in Southwest Mexico City, soil-derived aerosols are probably due to mineral dust re-suspension, not specifying the sources, but that they amounted up to 25% of total mass in the urban area. More recently, the development of receptor models (Barrera *et al.,* 2012) in conjunction with simulated back-trajectories showed that soil-derived aerosols are perhaps created in all of the aforementioned areas in

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*Corresponding author E-mail:miranda@fisica.unam.mx and around the MAMC. Thus, different studies are not in complete agreement about the origin of those particles.

In a related issue, almost no information is currently available about the elemental contents in soils in the MAM and in its neighbourhood; only the work by Ramos-Bello et al. (2001) about concentrations of several heavy metals in the Xochimilco area (southeast MAMC), associated with soil fertility, has been published. Correspondingly, only the paper by Gutiérrez-Castorena et al. (2005) presents data on the mineral phases found in the Texcoco Lake soils, and there has been no recent efforts neither to characterize the possible sources nor the minerals in the airborne particulate matter. As exemplified by Shen et al. (2009), the mineralogical characterization of soils may assist in the identification of sources contributing to atmospheric aerosols at a specific site. Therefore, this work is intended to determine the elemental contents and main mineral phases in samples of soils extracted from several locations inside and in the surroundings of the MAMC. This represents a first step in a more extensive characterization of geological sources of airborne particles. It is expected that the elemental concentrations and mineral phases found in the soils will be similar to those found in other works where analogous properties of atmospheric aerosols were studied.

MATERIALS & METHODS

Samples of soils were collected from seven sites, mostly within the boundaries of the MAMC (Fig. 1): Universidad Nacional Autonoma de México (UNAM) main campus (residential/school area, low vehicle traffic, 2 km from industry); Cerro de la Estrella National Park (recreational area, very high traffic load, 5 km from industry); Downtown (commercial/residential zone, very high traffic load, 15 km from industrial sources); UNAM Iztacala campus (school area, medium intensity traffic, in the middle of an industrial area); Santa Fe (commercial/residential zone, very high traffic load, 5 km from industry); Xalostoc (residential/industrial area, very high traffic load); and Texcoco Lake (rural area, medium traffic load, dry lake, 10 km from industry). The samples were taken from the surface (5 cm depth at most), using a plastic palette knife, previously wiped with high purity ethanol. If necessary, bushes and dry leaves were removed, to avoid contamination with other materials. The extracted material was deposited in 6 mL plastic vials, which were introduced and kept in sealed polyethylene bags during transport to the laboratory. At least three samples per site were collected. The temperature during storage varied between 20 °C and 25 °C, while relative humidity was in the range 30% to 40%. To process the samples for XRF analysis, soils were ground with a corundum mortar and pestle to produce a more uniform particle distribution. It was also necessary to heat them to 50 °C during 30 min, to reduce humidity, and then they were compacted as 1 g pellets, 7 mm in diameter. After this, the pellets (two per extracted sample) were analysed with an x-ray spectrometer built at the Institute of Physics, UNAM, mainly used for environmental studies (Espinosa *et al.,* 2012). An Oxford Instruments (Scotts Valley, CA, USA) x-ray tube (Rh anode, 50 kV operating voltage), was employed to irradiate the pellets, using a 5 mm lead collimator at the tube exit. A Si-PIN detector (Amptek Inc., Bedford, MA, USA), with a 5 mm Pb collimator at the entrance, registered the x-rays emitted by the samples, and an Ortec multichannel analyser collected the spectra, which were analysed with the QXAS computer code (IAEA, 2005). Spectra were obtained after irradiating each sample during 1200 s, with a current of 500 μA. The detection system was calibrated using pellets of certified reference materials with a similar matrix (IAEA SL-1, IAEA SL-7, NIST 2711, NIST 1648a and NIST 2646). An example of a calibration curve for an element (Mn) is shown in Fig. 2. Analogous curves were obtained for the major elements Si, K, Ca, Ti, Mn, and Fe, as well as for the trace elements Cr, Ni, Cu, Zn, Rb, Sr, Y, and Zr. It is expected that all these elements may assist to identify the sources contributing to airborne particulate matter. The X-ray powder diffraction patterns of the samples were measured in air at room temperature with a Bruker (Karlsruhe, Germany) D-8 Advance diffractometer with the Bragg-Brentano θ-θ geometry, Cu K_α line, a Ni 0.5 % Cu- K_β filter in the secondary beam, and a 1-dimensional position sensitive silicon strip detector (Bruker, Linxeye). The diffraction intensity as a function of the angle 2θ was measured between 6.5° and 110°, with a 2θ step of 0.039°, for 52.8 s per point.

RESULTS & DISCUSSION

The average elemental concentrations and the mineral phases determined for the soils from each site is presented in Table 1, together with the minimum detection limits (MDL) under the experimental conditions. A test of the reliability of the XRF results, presented elsewhere (Espinosa *et al.,* 2012), was obtained with data from a set of samples extracted from pluvial systems in Chihuahua (Northern Mexico), near the border with Texas, USA, by comparing them with the concentrations obtained with Particle Induced X-Ray Emission (PIXE) for Rb, Sr, and Zr (Domínguez-Acosta and Gill, 2007). The agreement with the latter results was reasonable, considering the uncertainty interval overlap. Additionally, when comparing with the elemental contents in the average earth crust (Lide, 2007), the coincidence is very good for most elements, except for a few of them (mainly trace elements). In all of the samples albite (feldspar) and quartz mineral phases were found; however some sites are characterised by the presence of other minerals: olivine

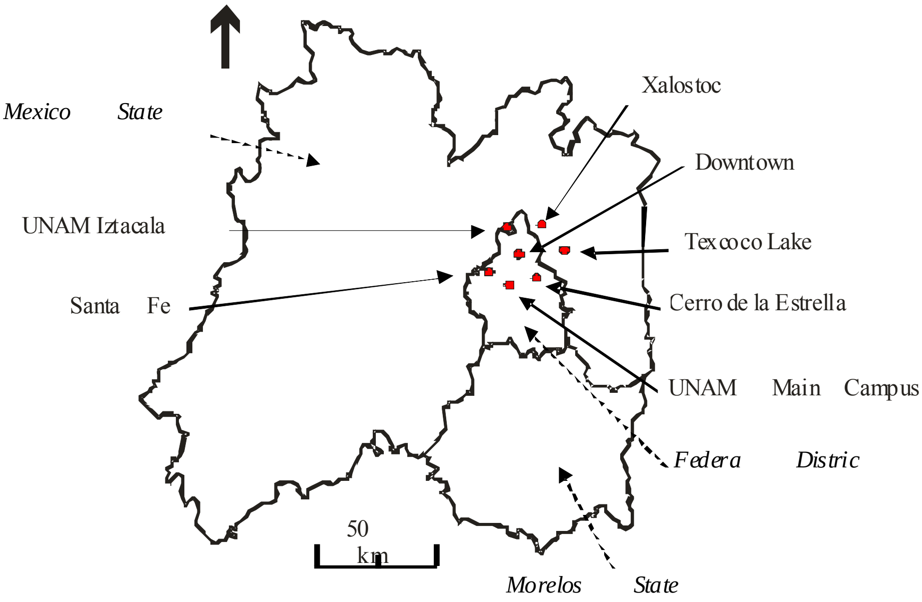

Fig. 1. Location of the sampling sites

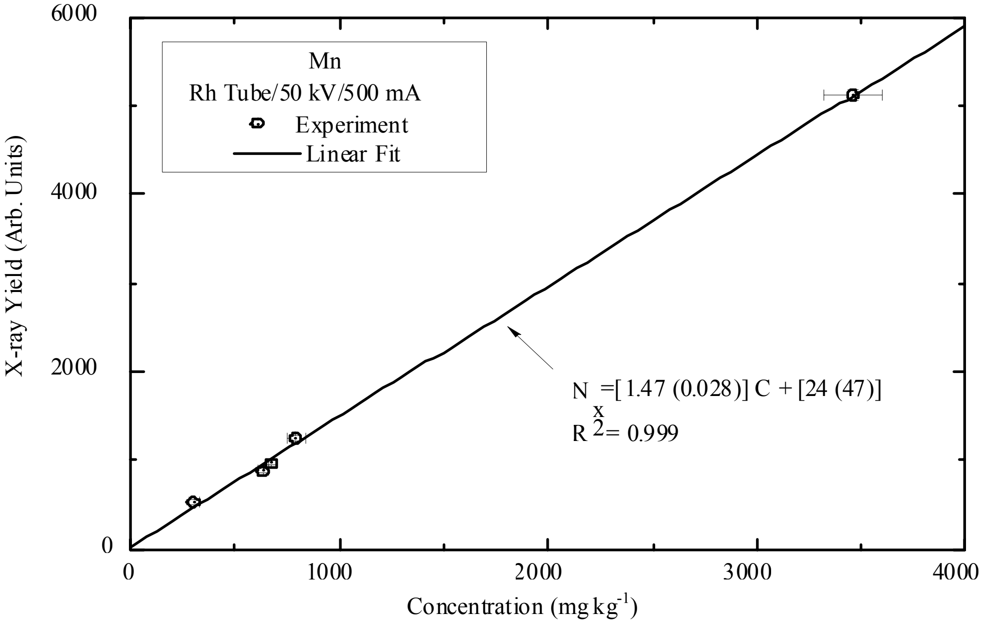

Fig. 2. Calibration curve for determination of Mn contents in pelletized soil samples, obtained after irradiation of certified reference materials with a Rh tube (50 kV, 500 μA), during 1200 s

at the UNAM and Xalostoc sites, calcite at Texcoco Lake, koninckite (hydrous ferric phosphate) at Cerro de la Estrella and Texcoco Lake, and kaolinite at Santa Fe. It is remarkable that in their mineralogical study of TSP at the UNAM site, Salazar et al. (1989) found quartz, albite, calcite, and kaolinite. These minerals, may be associated with the Texcoco Lake and the western site of Santa Fe, which may have a contribution from the Toluca valley, in full agreement with other works (Johnson *et al.*, 2006; Moya *et al.*, 2003; Barrera *et al.*, 2012). Additionally, Martínez et al. (2008) analyzed both TSP and PM_{10} from five sites in the MAMC using Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis, concluding that indeed alumino-silicates represent a very important mineralogical component in TSP, although no specific phases were described. A further test of the quality and usefulness of the results may be done if the measured concentrations in soils are compared to the elemental contents determined in airborne particulate matter (TSP or PM_{10}). This can be done if the ratio of the concentration of some elements determined in TSP or PM_{10} to that of Fe is calculated. Fe is chosen because it is frequently used in atmospheric aerosol analyses

Table 1. Average elemental concentrations, minimum detection limits (MDL), and mineral phases determined in soils from the MCMA. Concentrations in mg/kg for trace elements and in mass percent for major elements

Element	MDL	UNAM		Downtown		Cerro de la Estrella		Lago de Texcoco		Iztacala		Santa Fe		Xalostoc	
Si[a]	7.7	28	(2.7)[c]	28	(2.7)	26	(2.7)	19	(2.7)	26	(2.7)	22	(2.7)	22	(2.7)
K[a]	0.18	1.1	(0.13)	0.63	(0.11)	0.90	(0.12)	1.7	(0.16)	1.1	(0.13)	0.53	(0.11)	0.44	(0.10)
Ca[a]	0.32	2.7	(0.36)	2.4	(0.35)	3.0	(0.37)	6.6	(0.48)	5.8	(0.44)	1.1	(0.34)	1.4	(0.34)
Ti[a]	0.02	0.42	(0.04)	0.78	(0.05)	0.56	(0.04)	0.25	(0.03)	0.31	(0.03)	0.42	(0.04)	0.33	(0.03)
Cr[b]	31	79	(6)	87	(6)	52	(5)	34	(4)	37	(4)	43	(4)	48	(5)
Mn[b]	36	721	(42)	1090	(48)	842	(43)	442	(38)	520	(39)	740	(42)	571	(39)
Fe[a]	0.95	3.52	(0.49)	4.99	(0.50)	4.22	(0.49)	2.65	(0.48)	3.02	(0.48)	3.58	(0.48)	3.23	(0.48)
Ni[b]	5	84	(53)	150	(65)	98	(55)	72	(51)	108	(57)	82	(52)	106	(56)
Cu[b]	27	110	(10)	82	(8)	56	(7)	50	(7)	31	(5)	33	(6)	31	(5)
Zn[b]	27	530	(42)	275	(40)	325	(41)	282	(40)	199	(40)	228	(40)	153	(39)
Rb[b]	44	68	(10)	59	(10)	60	(10)	74	(10)	60	(10)	55	(10)	67	(10)
Sr[b]	77	453	(48)	498	(49)	467	(49)	839	(53)	729	(52)	408	(48)	442	(48)
Y[b]	14	26	(10)	47	(10)	-	-	-	-	33	(11)	-	-	17	(10)
Zr[b]	146	260	(23)	283	(26)	271	(25)	246	(21)	229	(18)	234	(19)	270	(24)
Mineral phases[d]	-	A, Q, O		A, Q		A, Q, K		A, Q, C, K		A, Q		A, Q, Kl		A, Q, O	

[a] Concentrations in mass percent.

[b] Concentrations in mg kg^{-1}.

[c] Numbers between parenthesis represent the combined uncertainty.

[d] A = albite, Q = quartz, O = olivine, K = koninckite, C = calcite, Kl = kaolinite.

and it is most frequently associated to a crustal origin. Table 2 displays this comparison for Cr, Mn, and Ni, using data taken from the works by García et al. for TSP at UNAM (2008); Querol et al. (2008) for TSP from a rural area North of the MAMC, and PM_{10} from urban sites at the Southeast and UNAM main campus; Vega et al. (2001) for PM_{10} from Texcoco Lake, used as one of the fugitive dust source profiles; and Barrera et al. (2012) for PM_{10} at the UNAM main campus site.

The first point to emphasize when looking at the concentration ratios is that the samples analysed in this work have a much wider size distribution than the airborne particulate matter, regardless of its type (TSP or PM_{10}). Therefore, an exact match in the ratios should not be expected, as each size may have a different elemental composition. Nevertheless, in the case of Mn/Fe the agreement is very good with all the other studies, a fact that can be explained because usually Mn in atmospheric aerosols has a crustal origin. In this case, the size distribution of the particles in the soils analysed in the present work seems to have no influence in the Mn/Fe ratio. In contrast, the ratios Cr/Fe and Ni/Fe are higher in two cases (TSP from García et al. (2008) and PM_{10} from Barrera et al. (2012)), because they must have an anthropogenic contribution. This human influence was also observed in the PM_{10} results published by Querol et al. (2008) when compared with the present results as an enrichment with Ni; the data for TSP from the rural site, although not directly related to the locations studied in this work, seem to be in full agreement with a crustal origin of the airborne particles. Furthermore, the conformity with the ratios obtained by Vega et al. (2001) is understood because their samples were directly obtained from crustal material extracted from the sites. Again, the particle dimensions seem to have no effect.

Table 2. Elemental concentration ratios determined in studies of airborne particles and for soils in the MCMA

Reference/Site	Cr/Fe		Mn/Fe		Ni/Fe	
Garcia, 2008, TSP UNAM Main Campus	0.022	(0.002)[a]	0.018	(0.002)	0.021	(0.002)
Querol, 2008, TSP[b] Rural site	0.0012		0.020		0.0021	
Querol, 2008, PM_{10} CENICA	0.0008		0.022		0.0033	
Querol, 2008, PM_{10} UNAM Main Campus	0.0019		0.023		0.0030	
Vega, 2001, PM_{10} Texcoco Lake	0.0040	(0.0003)	0.015	(0.0012)	0.0016	(0.0001)
Barrera, 2012, PM_{10} UNAM Main Campus	0.013	(0.0005)	0.026	(0.0017)	0.013	(0.0006)
UNAM Main Campus	0.0022	(0.0003)	0.020	(0.0028)	0.0024	(0.0003)
Downtown	0.0017	(0.0002)	0.022	(0.0022)	0.0030	(0.0003)
Cerro de la Estrella	0.0012	(0.0001)	0.020	(0.0023)	0.0023	(0.0003)
Texcoco Lake	0.0013	(0.0002)	0.017	(0.0030)	0.0027	(0.0005)
UNAM Iztacala	0.0012	(0.0002)	0.017	(0.0027)	0.0036	(0.0006)
Santa Fe	0.0012	(0.0002)	0.021	(0.0028)	0.0023	(0.0003)
Xalostoc	0.0015	(0.0002)	0.018	(0.0026)	0.0033	(0.0005)

[a] Numbers between parenthesis represent the combined uncertainty.
[b] No uncertainty was quoted in this work.

CONCLUSION

The results obtained in this work seem to support the assumption that elemental concentrations and mineral phases found in soils extracted from possible emitting sources show similarities with the composition of atmospheric aerosols in the MAMC as determined in previous studies. This should assist in the identification of the sources contributing to the pollution in certain sites at the MAMC. Nevertheless, care must be taken when extrapolating to airborne particulate matter composition, because of the particle dimensions of the soil samples analysed here, and for the possible presence of anthropogenic compounds in the collected samples. Although the elemental contents were determined for several possible emitting sources of geological airborne particles, it is necessary to sample at more sites (like the Toluca valley and the North/Northeast agricultural lands), as well as to measure the concentrations according to particle dimensions (like PM_{10} or $PM_{2.5}$), following similar procedures as those used by Vega et al. (2001). Moreover, it will be necessary to study the soil size distributions to better understand the dust resuspension effects on the particulate matter concentrations in the atmosphere of the MAMC.

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