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Integrating Multiple Spheres to Identify the Provenance and Risk of Urban Dust and Potentially Toxic Elements: Case Study from Central Mexico

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This section is 17 pages long.

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Text S1. Geochemical data are compositional variables that form part of a whole. Taking the geochemical data as if they were individual variables could generate spurious correlations, due to the presence of atypical values and the so-called closure or constant sum effect (Pawlowsky-Glahn et al., 2015). The application of logarithmic ratio transformations to compositional data makes statistical analysis more efficient (Filzmoser et al., 2009). The compositional data transformations most used are the additive logarithmic ratio (alr), the centered logarithmic ratio (clr), and the isometric logarithmic ratio (ilr) (Aitchison, 1982; Egozcue et al., 2003). The clr transformation has been widely applied in geochemical studies (Álvarez-Vázquez et al., 2020; Cicchella et al., 2022; Somma et al., 2021). Therefore, in this study we used CoDA.

Table S1. Reagents required to prepare 1 L of artificial lysosomal fluid (ALF) for the lung bioaccessibility test (Colombo et al., 2008).

Reagent	Chemical formula	Mass (gr)
Magnesium chloride	$MgCl_2$	0.05
Sodium chloride	$NaCl$	3.21
Disodium hydrogen phosphate	Na_2HPO_4	0.07
Sodium sulphate	Na_2SO_4	0.04
Calcium chloride dihydrate	$CaCl_2 \cdot 2H_2O$	0.13
Sodium citrate dihydrate	$C_6H_5Na_3O_7 \cdot 2H_2O$	0.08
Sodium hydroxide	$NaOH$	6.00
Citric acid	$C_6H_8O_7$	20.8
Glycine	H_2NCH_2COOH	0.06
Sodium tartrate dihydrate	$C_4H_4O_6Na_2 \cdot 2H_2O$	0.09
Sodium lactate	$C_3H_5NaO_3$	0.09

Table S2. Bioaccessibility (%) obtained for the NIST 2710a certified reference material (after 24 h, S: L of 1: 1000), using ALF solution, in this work compared to the results reported by other authors.

PTE	$Bio_{i,NIST,\ this\ study}$ (%)	$Bio_{i,NIST,\ another\ study}$ (%)	$R_{Bioi,NIST}$ (%)
As	49.0	60.1[1]	80
Fe	16.5	11.1[2]	150
Cu	62.0	72.3[3]	90
Mn	36.0	43.4[3]	80
Pb	44.6	50.6[1]	90
Zn	27.1	31.2[2]	90

[1] Kastury et al., (2018)
[2] Meza-Figueroa et al., (2020)
[3] Pelfrêne et al., (2017)

Table S3. PTE and REE concentrations (mg/kg) for zinc concentrate, rock, and urban dust samples (<20 µm) analyzed by ICP-MS.

	Zn concentrate samples		Rock samples				Urban dust samples									
Analyte	**Z1**	**Z2**	**R1**	**R2**	**R3**	**R4**	**5**	**8**	**12**	**17**	**18**	**21**	**28**	**35**	**36**	**38**
Fe	46004.32	34343.61	9486.79	6055.49	5494.44	11831.30	9590.03	9741.05	8645.42	10536.13	10609.15	12230.25	11753.80	8514.07	11906.54	10275.48
Zn	134200.55	134066.48	53.64	39.02	45.49	37.86	307.58	2524.08	361.07	1171.48	442.77	337.24	269.47	106.65	225.79	213.68
Mn	1062.06	1420.32	81.22	49.24	58.77	168.37	197.99	213.62	243.74	349.85	212.13	252.88	289.57	210.43	296.96	306.25
Cu	5748.21	4147.98	2.44	3.36	3.87	3.16	122.11	105.31	34.63	84.26	71.28	102.67	69.81	28.68	47.27	50.88
Pb	1815.99	1411.10	20.61	15.63	8.53	10.02	95.05	93.19	55.34	156.60	88.02	104.08	103.28	45.33	55.66	87.62
Sc	0.30	0.18	7.16	4.38	4.76	05.02	3.53	3.57	2.91	3.18	3.18	3.12	3.44	3.25	3.13	1.76
Sr	5.95	10.11	16.08	24.44	179.46	54.39	144.28	113.03	78.43	88.29	83.44	109.11	88.01	118.02	101.88	102.25
Zr	3.99	04.06	65.93	35.13	50.69	56.79	50.08	51.37	47.21	56.86	50.30	43.48	54.43	38.11	47.56	21.03
Cr	08.05	28.21	3.84	5.98	13.35	3.40	27.52	22.26	25.98	44.80	38.01	48.33	49.76	21.73	42.48	44.63
As	235.61	113.95	8.60	3.18	6.11	2.63	12.67	20.15	8.55	39.04	13.63	11.21	7.86	6.54	8.62	16.12
V	3.51	4.52	4.52	2.45	1.49	4.45	23.28	22.76	19.89	22.23	22.21	29.03	25.55	34.50	29.38	29.80
Al	1.92	0.72	38.60	35.13	29.41	39.14	25.85	24.85	20.67	20.80	18.88	18.89	21.66	21.89	22.23	10.10
Ni	3.91	10.30	03.01	3.59	6.44	2.11	10.67	9.96	8.56	9.76	11.69	15.60	12.25	8.68	15.21	12.44
Th	0.05	0.08	16.88	10.62	14.91	5.88	5.81	5.38	4.46	4.38	5.23	3.88	5.17	3.53	3.75	1.76
Nb	0.19	0.14	21.94	11.00	13.46	7.99	9.67	10.17	10.14	11.51	9.88	8.68	11.45	7.11	9.76	4.31
Y	0.52	0.54	64.06	50.80	36.86	19.99	16.85	17.03	12.07	12.54	12.48	11.03	14.14	12.74	13.21	5.83
Ti	113.00	85.94	531.47	326.21	320.01	747.51	998.82	1022.76	1052.12	1558.74	1257.65	1393.47	1276.39	1064.42	1188.78	734.04
TiO2	0.01	0.01	0.05	0.03	0.03	0.07	0.10	0.10	0.11	0.16	0.13	0.14	0.13	0.11	0.12	0.07
10*Th	0.46	0.80	168.80	106.18	149.07	58.81	58.13	53.85	44.59	43.76	52.32	38.77	51.65	35.26	37.48	17.57

Zr/Ti	0.04	0.05	0.12	0.11	0.16	0.08	0.05	0.05	0.04	0.04	0.04	0.03	0.04	0.04	0.04	0.03
Nb/Y	0.35	0.26	0.34	0.22	0.37	0.40	0.57	0.60	0.84	0.92	0.79	0.79	0.81	0.56	0.74	0.74
La	0.27	0.61	36.11	36.99	29.31	23.57	17.45	16.60	14.37	14.85	17.19	13.97	14.95	11.58	13.26	6.11
Ce	0.52	0.86	89.56	54.01	55.16	43.44	36.35	34.06	29.91	31.34	37.85	31.03	33.11	23.57	26.45	12.17
Pr	0.07	0.10	10.40	10.15	8.37	5.92	4.32	4.32	3.63	3.82	3.96	3.28	3.84	2.93	3.35	1.47
Nd	0.25	0.32	42.46	41.75	32.52	23.39	16.36	16.37	13.60	14.32	14.70	12.15	14.28	11.00	12.72	5.55
Sm	0.05	0.06	10.75	10.09	7.22	05.03	3.44	3.49	2.79	2.94	2.92	2.41	2.94	2.28	2.66	1.18
Eu	0.01	0.01	0.29	0.46	0.17	0.72	0.26	0.24	0.21	0.25	0.23	0.22	0.22	0.19	0.23	0.13
Gd	0.05	0.06	11.35	10.28	6.47	4.39	2.99	2.99	2.35	2.52	2.50	02.01	2.51	1.98	2.26	01.01
Tb	0.01	0.01	1.98	1.70	01.06	0.66	0.47	0.47	0.37	0.40	0.38	0.31	0.40	0.31	0.35	0.16
Dy	0.05	0.05	12.63	10.16	6.60	3.79	2.75	2.79	2.14	2.32	2.20	1.79	2.35	1.79	02.09	0.91
Ho	0.01	0.01	2.62	1.99	1.32	0.73	0.53	0.54	0.42	0.46	0.43	0.35	0.46	0.36	0.41	0.18
Er	0.03	0.03	7.85	5.69	3.83	02.04	1.54	1.57	1.22	1.32	1.26	01.01	1.35	01.03	1.19	0.52
Tm	0.00	0.00	1.10	0.76	0.51	0.27	0.21	0.22	0.17	0.18	0.17	0.14	0.19	0.14	0.16	0.07
Yb	0.02	0.03	7.23	4.90	3.15	1.69	1.37	1.42	1.11	1.21	1.15	0.92	1.23	0.91	01.08	0.47
Lu	0.00	0.00	01.03	0.71	0.46	0.25	0.21	0.22	0.17	0.19	0.18	0.14	0.19	0.14	0.17	0.07
∑REE	1.35	2.15	235.35	189.63	156.15	115.88	88.24	85.29	72.46	76.11	85.11	69.73	78.01	58.21	66.37	29.99
1.54*Ce	0.78	1.28	134.33	81.02	82.73	65.16	54.53	51.09	44.87	47.00	56.77	46.55	49.67	35.35	39.67	18.25
3.1*La	0.85	1.91	111.93	114.66	90.87	73.06	54.09	51.46	44.56	46.04	53.28	43.31	46.34	35.89	41.11	18.94

Table S4. PCA coefficients highlighting the largest contributions (in bold).

Variable	PC1	PC2
Sc	**-0.3**	0.2
V	-0.2	**-0.4**
Cr	-0.2	**-0.5**
Mn	**0.3**	0.1
Fe	0.1	**0.6**
Cu	**0.3**	-0.2
Zn	**0.3**	-0.0
As	**0.3**	0.1
Sr	**-0.3**	-0.1
Zr	**-0.3**	0.2
Pb	**0.3**	-0.1
REE	**-0.3**	0.2

Table S5. CoDA correlation matrix for ΣREEs and PTEs (Sc, Zr, Sr, Fe, As, Mn, Cr, Pb, V, Zn, and Cu). ΣREE showed statistically significant positive relationships ($p<0.05$) with Sc ($r=0.99$), Sr ($r=0.77$), and Zr ($r=0.98$), while it showed statistically significant negative relationships ($p<0.05$) with Zn ($r=-0.91$), Cu ($r=-0.98$), Pb ($r=-0.94$), As (-0.75), and Mn ($r=-0.78$). Zn showed statistically significant positive relationships ($p<0.05$) with As ($r=0.88$), Pb ($r=0.94$), Cu ($r=0.93$), and Mn ($r=0.70$). Positive relationships are shown in green, while negative relationships are shown in red.

	V	**Cr**	**Mn**	**Fe**	**Cu**	**Zn**	**As**	**Sr**	**Zr**	**Pb**	**REE**	**Al**
Sc	0.37	0.14	**-0.74****	-0.07	**-0.98*****	**-0.93*****	**-0.76*****	**0.79*****	**0.99*****	**-0.95*****	**0.99*****	**0.98*****
V	1	**0.63****	-0.38	**-0.63****	-0.4	**-0.62****	**-0.74****	**0.58***	0.43	-0.48	0.35	0.30
Cr		1	-0.37	**-0.73****	-0.21	-0.44	**-0.54***	**0.58***	0.21	-0.33	0.17	-0.01
Mn			1	**0.56***	**0.69****	**0.70****	**0.60***	**-0.71****	**-0.75*****	**0.73****	**-0.78*****	**-0.78*****
Fe				1	0.1	0.26	0.39	-0.46	-0.16	0.25	-0.11	-0.28
Cu					1	**0.93*****	**0.75*****	**-0.79*****	**-0.98*****	**0.95*****	**-0.98*****	**-0.97*****
Zn						1	**0.88*****	**-0.89*****	**-0.94*****	**0.94*****	**-0.91*****	**-0.94*****
As							1	**-0.85*****	**-0.81*****	**0.84*****	**-0.75*****	**-0.79*****
Sr								1	**0.82*****	**-0.92*****	**0.77*****	**0.76*****
Zr									1	**-0.92*****	**0.98*****	**0.95*****
Pb										1	**-0.94*****	**-0.94*****
REE											1	**0.95*****
Al												1

p-value = 0 (***) ; p-value = 0.001 (**) ; p-value = 0.01 (*).

Scenarios for hypothesis testing:

1. **Most studies:**

   According to only urban dust samples along with PCA and cluster analyses the provenance of PTEs is as follows:

   Geogenic provenance: Sc, Zr, V, Fe, Sr, Cr, Mn

   Anthropogenic provenance: Cu, Pb, Zn, As

   Null hypothesis (Ho): The concentrations of PTEs in urban dust samples, along with statistical and documentary analyses, accurately differentiate the geogenic and anthropogenic sources of PTE in urban dust.

   Alternative hypothesis (Ha): The concentrations of PTEs in urban dust samples, along with statistical and documentary analyses, does not accurately differentiate the geogenic and anthropogenic sources of PTE in urban dust.

2. **This study:**

   According to the integration of urban dust, geological, and pollution source samples, along with sound chemical analysis, the provenance of PTEs is as follows:

   Geogenic provenance: REE, Sc, Zr, Sr, V, Cr

   Anthropogenic provenance: Cu, Zn, Mn, Fe, As, Pb

   Null hypothesis (Ho): The integration of urban dust, geological, and pollution source samples, along with sound chemical analysis, does not accurately differentiate the geogenic and anthropogenic sources of PTE in urban dust.

Alternative hypothesis (Ha): The integration of urban dust, geological, and pollution source samples, along with sound chemical analysis, accurately differentiate the geogenic and anthropogenic sources of PTE in urban dust.

Table S6. Results of the Wilcoxon-Mann-Whitney analysis for hypothesis testing. Values of $p \geq 0.05$ indicate acceptance of the null hypothesis, while values of $p < 0.05$ indicate rejection of the null hypothesis and acceptance of the alternative hypothesis.

Wilcoxon – Mann-Whitney	
Scenarios for hypothesis testing	**p-value**
Most studies: Without integration urban dust, geological, and pollution source samples	0.58
This study: Integration urban dust, geological, and pollution source samples and sound chemical analyses.	5.28E-07

Table S7. One-way analysis of variance (ANOVA) results using Welch and Box for PTE concentrations in urban dust, particle size, and lung bioaccessibility between pre and post-rainy season sampling. p-values≤0.05 mean significant differences for the variables pre and post-rainy season, while p-values>0.05 mean not significant differences. Only Cu and Mn showed statistically significant differences between pre and post rainy seasons.

Variable	**p-value**	
	Welch's test	**Box's test**
Urban dust		
Zr	0.25	0.25
Sr	0.42	0.42
Pb	0.79	0.79
As	0.11	0.11
Zn	0.33	0.33
Cu	**0.00**	**0.00**
Fe	0.05	0.06
Mn	**0.01**	**0.01**
Cr	0.52	0.52
V	0.33	0.33
Sc	0.06	0.06
Particle size		
PM2.5	0.29	0.29
PM5.0	0.50	0.50
PM10	0.25	0.25
PM20	0.24	0.24
Lung bioaccessibility		
Sr	0.08	0.08
Cu	0.44	0.44
Zn	0.34	0.34
Fe	0.83	0.83
Mn	0.81	0.81

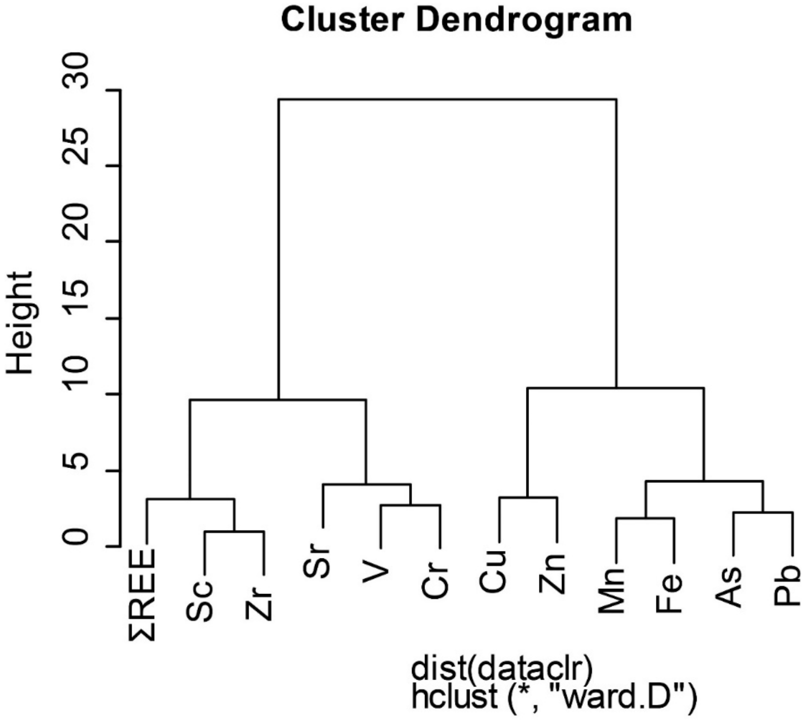

Figure S1. Cluster analysis showing the grouping of ΣREE-Sc-Zr with Sr-V-Cr and Cu-Zn-Mn with Fe-As-Pb according to geogenic and anthropogenic origins, respectively.

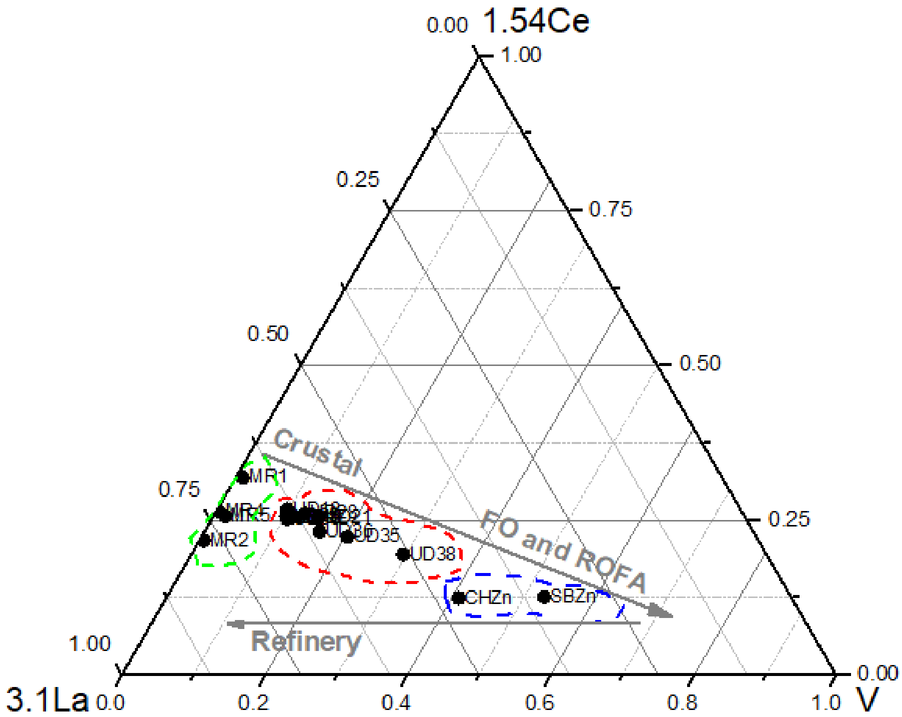

Figure S2. The 3.1*La–1.54*Ce–V ternary diagram (Moreno et al., 2008) commonly used to test the impact of V sources showing the distribution of rock (green circle), urban dust (red circle), and zinc concentrate (blue circle) samples from this study.

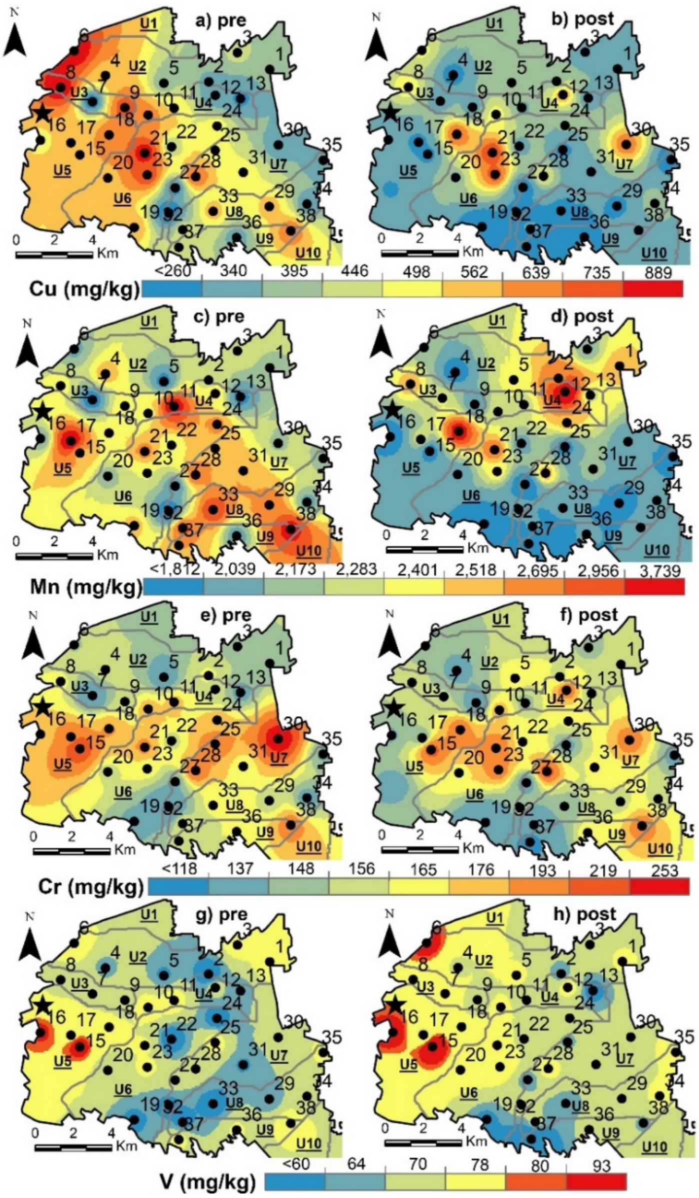

Figure S3. Spatial distribution Cu, Mn, Cr, and V in urban dust samples (n=38) pre and post rainy season. A defined pattern in the distribution of elements was not observed. However, high concentrations were found in the U5 urban basin, where the ZR is located (black star). The spatial distribution patterns of Cu and Mn were similar in both samplings. Canadian Cu guidelines account for 63 and 91 mg/kg for residential and commercial/industrial soils, respectively (CCME, 2007). Worldwide Mn average concentrations account for 500 to 900 mg/kg (WHO, 1981). Canadian Cr guidelines account for 64 and 87 mg/kg for residential and commercial/industrial soils, respectively (CCME, 2007). Mexican V guidelines account for 78 mg/kg for residential and commercial soils (DOF, 2007). Therefore, the concentrations of Cu, Mn, and Cr were high in urban dust in the SLPMA, while the concentrations of V exceed Mexican regulations.

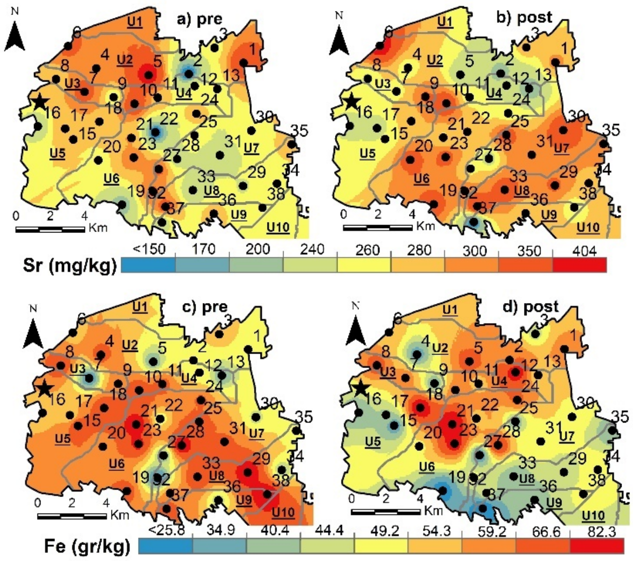

Figure S4. Spatial distribution of Sr and Fe in urban dust samples (n=38) pre and post rainy season. A defined pattern in the distribution of elements was not observed, which might result from a combination of area and geogenic sources.

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