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Evidence of Natural and Anthropogenic Impacts on Rainwater Trace Metal Geochemistry in Central Mexico: A Statistical Approach

D. M. Rivera-Rivera [1], D. C. Escobedo-Urías [2,*], M. P. Jonathan [1,*], S. B. Sujitha [3] and S. Chidambaram [4]

1 Centro Interdisciplinario de Investigaciones y Estudios sobre Medio Ambiente y Desarrollo (CIIEMAD), Instituto Politécnico Nacional (IPN), Calle 30 de junio de 1520, Barrio la Laguna Ticomán, Del. Gustavo A. Madero, Ciudad de Mexico (CDMX) C.P. 07340, Mexico; deni.mrr@gmail.com
2 Centro Interdisciplinario de Investigación para el Desarrollo Integral Regional (CIIDIR), Instituto Politécnico Nacional (IPN), Bulevar Juan de Dios Bátiz Paredes·250, Colonia San Joachin, Guasave, Sinaloa C.P. 81101, Mexico
3 Centro Mexicano para la Producción más Limpia (CMP+L), Instituto Politécnico Nacional (IPN), Av. Acueducto s/n, Col. Barrio la Laguna Ticomán, Gustavo A. Madero, Ciudad de Mexico (CDMX) C.P. 07340, Mexico; sbsujitha@yahoo.com
4 Water Research Centre, Kuwait Institute for Scientific Research, P.O. Box 24885, Safat 13109, Kuwait; sabarathinam.chidambaram@gmail.com
* Correspondence: durias@ipn.mx (D.C.E.-U.); mpjonathan7@yahoo.com (M.P.J.)

Received: 25 November 2019; Accepted: 6 January 2020; Published: 10 January 2020

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Abstract: Trace metals Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd, and As were determined on a monthly basis in a total of 52 rain samples collected from six different locations in the central region of Mexico during March 2016–April 2017. The average concentrations of trace metals (mg/L) in the rainwater samples showed an order of Zn (0.873) > Fe (0.395) > Mn (0.083) > Cr (0.041) ≥ Cu (0.041) > Pb (0.031) > Ni (0.020) > Co (0.013) > As (0.0003) > Cd (0.002). The differences observed in metal concentrations are related to variations in the influence of continental air masses, local transport, regional advection, and the solubility of trace metals. High concentrations of metals were observed in the months of March to May at all sites, probably due to the less extensive removal of air/air pollutants. The values obtained from the enrichment factor (EF) per metal showed relatively high values for Cd, Zn, Cu, Pb, Co, Ni, and Cr, suggesting anthropogenic origin. Pearson's correlation matrix validated the distribution of trace metal sources and their relationships with local/regional meteorological characteristics. This paper presents relevant basic information for the evaluation of the toxic potential of rainwater and the possible health risks when using this source of water for human consumption.

Keywords: rainwater; provenance; geochemistry; trace metals; Central Mexico

1. Introduction

Rainwater chemistry is extremely variable, both geographically and temporally responding to atmospheric circulation patterns [1], possessing particulates from local or long-range transport [2,3]. Naturally, rainwater comprises sea salt and soil dust, while anthropogenic sources include gases and particles associated with traffic emissions, road dust resuspension, nonferrous metal production, fossil fuel combustion, and residential heating [4–6]. The chemical composition of rainwater clearly reflects the degree of air pollution in urban, rural, and industrial biomes [7]. In recent times, increased levels of anthropogenic dusts have resulted in the incidence of acid rains, the most studied issue due to its lethal impacts on ecosystems including humans [8], even at the remotest sites. Additionally, rainwater proves to be a vector of nutrients and contaminants (including metals) in all biogeochemical cycles of aquatic and terrestrial ecosystems [9–12].

The atmospheric budget of trace metals is mainly controlled by emissions from anthropogenic/natural sources and deposition through wet/dry scavenging [13]. With reference to wet deposition, it includes two main mechanisms, namely in-cloud and below cloud scavenging [14]. The concentrations of trace metals in rainwater are mainly controlled air-mass origins, pollutant sources, transportation media, migration pathways, and types of aerosol particles [15,16]. Furthermore, high levels of trace metals in rainwater are perilous for terrestrial and aquatic ecosystems due to their toxicity, bioaccumulation/biomagnification, and carcinogenic properties. Globally, studies characterizing rainwater geochemistry have gained significant momentum since 1970s [17–26].

Lately, water scarcity has become a pressing issue worldwide, and rainwater harvesting is considered to be a potential water source for urban settings [27]. Henceforth, systems of collection and storage of precipitation waters for the supply of drinking water, crop irrigation, and the recharging of aquifers are widely used, proving to be the only viable way to obtain drinking water in many regions; however, the presence of dissolved contaminants in rainwater is often mysterious [28–34]. Trace metals in rainwater can result in various health disorders in humans, such as atrial fibrillation, arterial hypertension, psoriasis, and angina pectoris [35].

Rainwater geochemistry is indicative of local/regional temporal patterns of atmospheric emissions, and proves to be useful in identifying the source apportionment of trace metals. Most of the studies conducted in Mexico [36–38] refer to the chemical composition of rainwater in Mexico City, as it is one of most polluted cities in the world. The chemical composition of rainwater in the metropolitan Mexico City has been analyzed and reported for nearly a decade in distinct regions in terms of its physicochemical parameters and some dissolved geochemical elements. The results indicate a common external and crustal origin during different periods [15,39–41]. Therefore, the present study demonstrates the first direct measurements of trace metals in rainwater collected from six different localities of Central Mexico that encompass urban, rural, industrial, and mining settings.

The study mainly focuses on identifying the possible sources and associated risks of trace metals in rainwater using multivariate statistical techniques, indices, and elemental ratios.

2. Materials and Methods

2.1. Study Area

Composite mixed monthly rainwater samples were collected from six different localities (Table 1) in Central Mexico (Gustavo A. Madero: 19.4873° N–99.1236° W, Tula: 20.0522° N–99.3442° W, Pachuca: 20.1011° N–98.7591° W, Tulancingo: 20.0905° N–98.3691° W, Agua Blanca: 20.3465° N–98.3595° W, Molango: 20.7908° N–98.7288° W) during March 2016–April 2017. Among the sampling stations, Gustavo A. Madero (Figure 1), located in the northern part of the megalopolis Mexico City, is densely populated, with approximately 1,164,477 inhabitants [42]. The region also witnesses strong vehicular traffic and is home to numerous manufacturing industries, namely food products, textiles, leather industries, wood, paper, chemicals, nonmineral products, and metal industries. Tula, an important industrial locality in the Hidalgo state, hosts the Miguel Hidalgo Refinery of Petróleos Mexicanos (PEMEX) and the Francisco Pérez Ríos Thermoelectric Plant of the Federal Electricity Commission (CFE), in addition to chemical, cement, metalworking, and metal-mechanics industries, among others. Pachuca is the capital of Hidalgo State, and is one of the oldest and most productive silver mining districts in Mexico [43], whereas Tulancingo, located in the Southeast territory of Hidalgo, is the center of textile, clothing, and leather industry [44]. Two of the localities, namely Agua Blanca and Molango, are mainly rural areas, with lower impacts of urban and industrial activities. However, huge mountains, deep canyons, and dense vegetation distinguish the environmental locales of Molango.

Table 1. Description of the study area.

Location	Altitude (masl)	Average Temperature (°C/year)	Average Rainfall (mm/year)	Population	Geology	Industries
Gustavo A. Madero	2240	16	893	1,164,477	Igneous rocks (basalts)	Food products Textile, leather Wood Paper Chemical Nonmineral products Metal industries
Tula	2020	17.6	438	109,093	Igneous rocks (tuffs, andesites, rhyolites); Sedimentary rocks (sandstone, limestone)	Refinery and Thermoelectric Plant Chemical Cement Metalworking
Pachuca	2382	15.5	574	277,375	Extrusive rocks (rhyolites and andesites)	Silver mining Manufacturing
Tulancingo	2181	14	532	161,069	Extrusive igneous rocks (acid and basalt tuffs)	Textile Clothing and leather Food products, beverages, and tobacco Nonmetallic mineral products and basic metal industries.
Agua Blanca	2100	14.2	1061	9116	Igneous rocks (basalts and acid tuffs)	Food products Wood Production of nonmetallic and metallic minerals
Molango	1620	17	1438	11,587	Igneous rocks (basalt, acid tuff and traquita); Metamorphic rocks (gneiss); Sedimentary rocks (limestones, shales and sandstones)	Manufacturing Manganese extraction

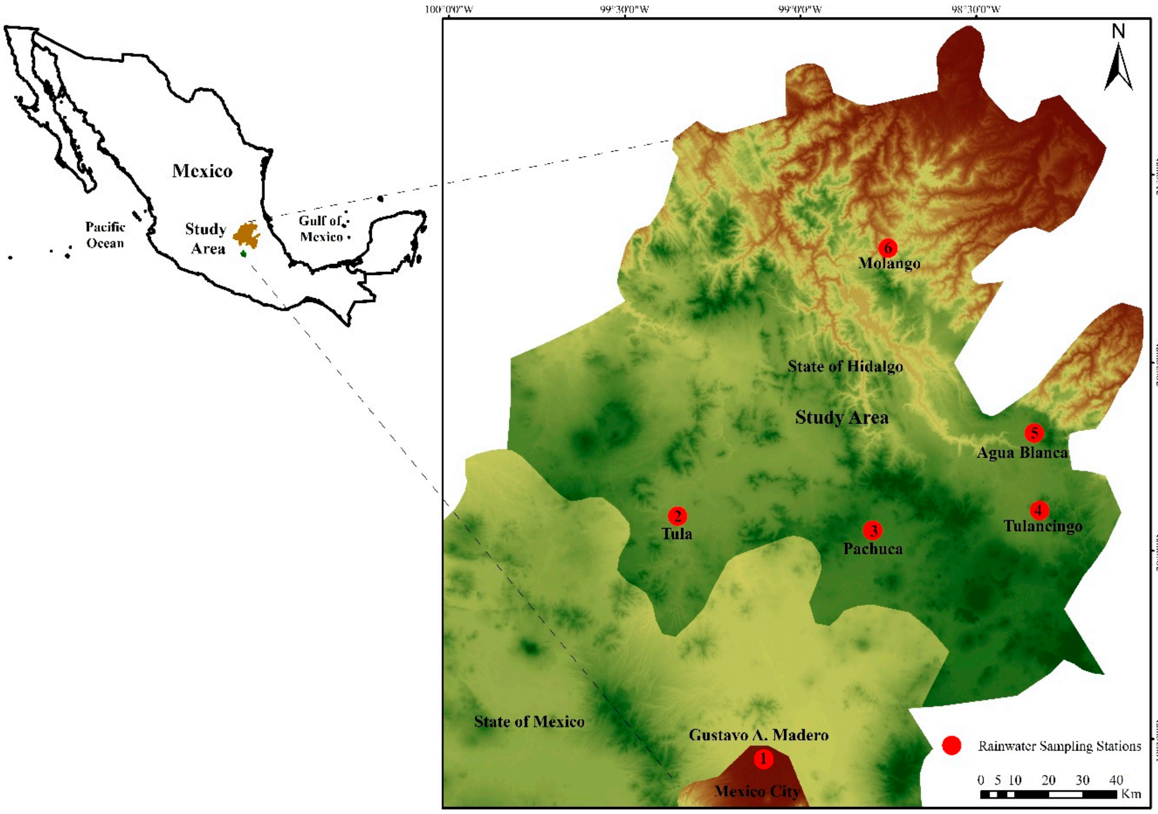

Figure 1. Study area map with the sampling locations in Central Mexico.

2.2. Meteorological Characteristics

Meteorological attributes, namely precipitation, wind velocity, air temperature, relative humidity, and barometric pressure, were assessed on a monthly basis (Supplementary Table S1). Heavy rain episodes were observed in the localities of Agua Blanca and Molango in the State of Hidalgo during May-October, when it is under the influence of tropical meteorological systems of the Pacific Ocean, the Caribbean Sea, and the Gulf of Mexico [45]. Likewise, the average amounts of rainfall collected during the aforementioned months in Agua Blanca were found to be 8564 and 5371 mm, respectively. Additionally, the high altitude of Hidalgo State plays a vital role in the development of natural atmospheric processes. However, Gustavo A. Madero mainly experiences relatively low humidity and a polar-type meteorological system or air mass, coming from the north of the American continent. The annual mean temperatures were more-or-less similar in all the stations; however, high temperatures were recorded in the month of May, while the lowest were recorded in the month of December. Wind directions presented similar behavior in most cases, and high wind speeds occurred in Tula (avg. 11.13 m/s) and Pachuca (avg. 11.51 m/s) throughout most of the sampling months (Supplementary Figure S1). Relative humidity in all the stations was less during the months of March–April (64.17%). The lowest mean barometric/atmospheric pressure value of 790.62 mb in September indicated cyclonic conditions and heavy rain incidences [25].

2.3. Analytical Procedures

Monthly rainfall samples, comprising accumulated daily rainwater, were collected (n = 52) from six localities in Central Mexico. The collected volume of rainwater was immediately measured and transferred to sterilize polypropylene bottles from all sampling sites. Subsequently, the samples were acidified using 0.1 mL of concentrated HNO_3, and transferred to the laboratory and refrigerated at 4 °C for further analysis.

The direct aspiration method, as described in [46], was employed for the determination of trace elements (Fe, Mn, Cr, Cu, Mo, Ni, Co, Pb, Cd, and Zn) using an Atomic Absorption Spectrometer (Perkin Elmer Model AAnalyst100). An internal standard of 2% analytical grade of HNO_3 was used for the analysis. Additionally, calibration curves for individual elements were set forth to upkeep the precision and accuracy of the analysis. For QA/QC, blanks and samples in duplicates were analyzed after every 10 samples. The recovery percentages of all the measured elements ranged between 91.23–108.54%.

2.4. Data Assessment

2.4.1. Statistical Analysis

Multivariate statistical techniques (correlation, factor and cluster analysis) were applied to the measured analytical and meteorological data to gauge the possible sources of trace elements. Statistical tests were conducted using the software STATISTICA (Version 12.0—Dell Software, Round Rock, Tx, USA). A Pearson correlation analysis ($p < 0.05$) was done to examine whether any significant relationships existed in the present study. Furthermore, factor scores were executed to evaluate potential locality-related differences [47].

2.4.2. Enrichment Factor

Surface soil is often a direct sink of toxic metals and man-made activities. The natural surface soil contains both natural and toxic elements [48–50]. Hence, the baseline concentrations are basically from these sources which are often harmful to human health and the surrounding ecosystem [51,52]. An Enrichment Factor (EF) was used to ascertain the possible sources of trace metals in rainwater. EF values were calculated based on the Equation (1) of [53].

$$\mathrm{EF} = \frac{\left(\frac{X}{Fe}\right)sample}{\left(\frac{X}{Fe}\right)Crust} \tag{1}$$

where (*X*/*Fe*) *sample* is the ratio of dry or wet deposition of a given element in the sample, while (*X*/*Fe*) *Crust* is the concentration ratio of the given element in the continental crust [54,55]. For the present study, *Fe* was used for the computation of EF because the element is mainly influenced by crustal sources rather than anthropogenic activities [56].

Calculated EF values are numerical, and they indicate different level of contamination. The values of $0.5 \leq \mathrm{EF} \leq 1.5$ suggest that the geochemical element could come from natural weathering processes [57]. An EF > 1.5 indicates that it is delivered due to noncrustal materials (i.e., external materials like nonpoint sources). Likewise, the deficiency to minimal enrichment of an element is indicated by an EF < 2; 2 < EF < 5 indicates moderate enrichment; 5 < EF < 20 indicates significant enrichment; 20 < EF < 40 indicates very high enrichment and EF > 40 indicates extremely high enrichment [58–60].

2.4.3. Elemental Ratios

Mostly world-wide, toxic metals (e.g., Pb, Zn, and As) are often derived from vehicle emissions, abrasion, tire wear, heavy traffic, mining activities, fuel combustion, metallurgical activities, the weathering of asphalt, and dust deposition [61–63]. Hence, in the present study, Pb and Zn elemental values were used to determine the external inputs. In order to assess the contribution of anthropogenic sources, the elemental ratio of Pb/Zn was examined for the present study. The Pb/Zn ratio has been widely used as a potential marker of industrial pollution from short (local and regional) and long-range transports [64,65].

3. Results and Discussion

3.1. Spatial Distribution of Trace Metals in Rainwater

Seasonal variation (all values in mg/L) (2016–17) of iron (Figure 2a) varied in Agua Blanca (0.11–0.96, avg. 0.38); in Gustavo A Madero (0.22–0.45, avg. 0.37); Molango (0.12–1.08, avg. 0.44); Pachuca (0.12–0.64, avg. 0.29); Tula (0.12–1.68, avg. 0.47); Tulancingo (0.15–1.17, avg. 0.41); manganese (Figure 2b) varied in Agua Blanca (0.002–0.288, avg. 0.059); in Gustavo A Madero (0.003–0.104, avg. 0.044); Molango (0.002–0.727, avg. 0.145); Pachuca (0.001–0.276, avg. 0.075); Tula (0.001–0.278, avg. 0.074); Tulancingo (0.002–0.372, avg. 0.098); chromium (Figure 2c) varied in Agua Blanca (0.02–0.20, avg. 0.06); in Gustavo A Madero (0.02–0.04, avg. 0.03); Molango (0.01–0.20, avg. 0.05); Pachuca (0.02–0.05, avg. 0.03); Tula (0.02–0.07, avg. 0.04); Tulancingo (0.02–0.05, avg. 0.04); copper (Figure 2d) varied in Agua Blanca (0.01–0.08, avg. 0.03); in Gustavo A Madero (0.01–0.11, avg. 0.04); Molango (0.01–0.09, avg. 0.05); Pachuca (0.01–0.09, avg. 0.04); Tula (0.01–0.10, avg. 0.05); Tulancingo (0.002–0.124, avg. 0.04); nickel (Figure 2e) varied in Agua Blanca (0.004–0.18, avg. 0.029); in Gustavo A Madero (0.01–0.037, avg. 0.019); Molango (0.005–0.019, avg. 0.012); Pachuca (0.005–0.021, avg. 0.012); Tula (0.003–0.11, avg. 0.033); Tulancingo (0.005–0.03, avg. 0.014); cobalt (Figure 2f) varied in Agua Blanca (0.002–0.03, avg. 0.014); in Gustavo A Madero (0.004–0.01, avg. 0.009); Molango (0.006–0.023, avg. 0.013); Pachuca (0.005–0.027, avg. 0.013); Tula (0.007–0.028, avg. 0.015); Tulancingo (0.005–0.031, avg. 0.017); lead (Figure 2g) varied in Agua Blanca (0.01–0.14, avg. 0.05); in Gustavo A Madero (0.01–0.06, avg. 0.03); Molango (0.01–0.06, avg. 0.03); Pachuca (0.002–0.04, avg. 0.02); Tula (0.01–0.06 avg. 0.03); Tulancingo (0.01–0.06, avg. 0.03); zinc (Figure 2h) varied in Agua Blanca (0.001–7.09, avg. 0.80); in Gustavo A Madero (0.09–2.76, avg. 0.95); Molango (0.01–0.78, avg. 0.28); Pachuca (0.03–6.36, avg. 1.17); Tula (0.01–0.41, avg. 0.14); Tulancingo (0.03–5.73, avg. 1.89); cadmium (Figure 2i) varied in Agua Blanca (0.001–0.008, avg. 0.002); in Gustavo A Madero (0.001–0.018, avg. 0.004); Molango (0.001–0.003, avg. 0.001); Pachuca (0.001–0.002, avg. 0.001); Tula (0.001–0.003, avg. 0.002); Tulancingo (0.001–0.003, avg. 0.002) and arsenic (Figure 2j) varied in Agua Blanca (0.001–0.007, avg. 0.003); in Gustavo A Madero (0.001–0.005, avg. 0.003); Molango (0.001–0.004, avg. 0.002); Pachuca (0.001–0.008, avg. 0.003); Tula (0.002–0.008, avg. 0.004); Tulancingo (0.001–0.007, avg. 0.003) respectively. The overall mean trace metal concentrations in rainwater samples (Figure 2a–j) collected at six different localities presented similar pattern, and were found to be in the order of (all values in mg/L), Zn (0.873) > Fe (0.395) > Mn (0.083) > Cr (0.041) ≥ Cu (0.041) > Pb (0.031) > Ni (0.020) > Co (0.013) > As (0.0003) > Cd (0.002).

Seasonally, total metal burdens were observed to be high in the summer months of March–May in all localities, which can be explained by the less extensive scavenging of pollutants from atmosphere/air [66]. During the study period, the localities presented average metal concentrations in the order of (all values in mg/L), Tulancingo (2.54) > Pachuca (1.66) > Gustavo A. Madero (1.50) > Agua Blanca (1.42) > Molango (1.04) > Tula (0.85). Regional differences of metal concentrations are probably due to the variations in the influences of continental air masses, local transport, regional advection, and the solubility of trace metals in a particular region [4,13]. Zn was observed to be the most abundant metal in the present study (0.873 mg/L), which is consistent with results reported worldwide [67–70].

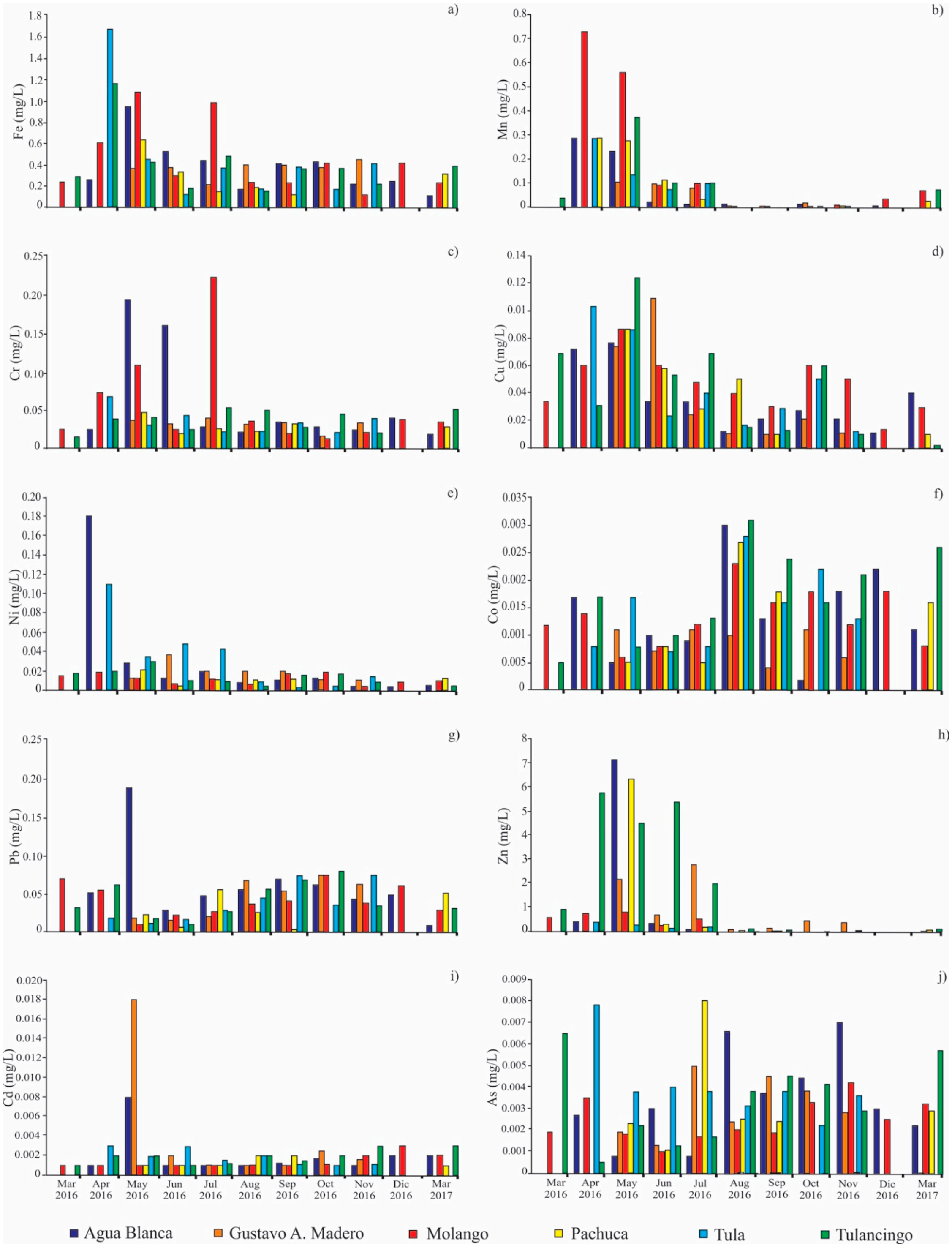

Figure 2. (**a**–**j**) Spatial and temporal distribution pattern of trace metals in precipitation of Central Mexico.

The relatively high concentrations of Zn measured in rainwater of Pachuca (1.174 mg/L) and Tulancingo (1.892 mg/L) were attributed to local sources, i.e., mine tailings and the textile industry, respectively [71,72]. Additionally, Zn can also be sourced from metallic roofs, storage tanks, road transportation, domestic heating, agricultural waste burning, and direct emission from polluted soils. The concentrations of Fe and Mn are mainly aeolian dusts from crustal/geological origin. However, high levels of Fe (0.448 mg/L) and Mn (0.148 mg/L) in Molango are probably related to the open-cast manganese mine that operates in the area [73,74]. Similar concentrations of Cr in Agua Blanca (0.058 mg/L) and Molango (0.055 mg/L) exhibit regional natural and anthropogenic sources, including smoke from forest fires, biogenic emissions from vegetation, wood industries, and fossil fuel combustion [75]. Cu, Ni, and Pb in rainwater display the characteristics of anthropogenic activities, comprising industrial pollution, vehicle emission, road dust [76], and the combustion of anthropogenic chemicals at high temperature [16,77]. However, the concentrations of toxic metals Cd (0.002 mg/L) and As (0.003 mg/L) presented similar levels in all localities, with no major toxicological risks in the region. In general, the Total Metal Burden (TMB) in rain episodes exhibited significant relationships with the meteorological data and topography of the area. Above all, factors such as the scavenging processes, sizes, and hydroscopic properties of particles considerably alter the concentration of metals in rainwater [78].

The results of the present study were also compared with the data reported from various locations around the world (Table 2). Daya Bay, China presented high concentrations of metals, probably due to the high degree of atmospheric contamination mainly sourced from sea salt/dust, fossil fuel combustion, and crustal sources [79]. Fe concentrations in the rainwater of the present study were higher than the permissible limits set by the Mexican Government [80] for domestic usage. The higher values of Cr and Pb were due to the strong influence of urban, industrial, and mining activities in the associated regions (Stations 1, 2, 5 & 6). However, the As and Cd levels were below the limits, posing no carcinogenic risks. Overall, the concentration levels in rainfall were influenced by city pollution and other industrial activities in the region.

Table 2. Comparison of the trace element concentrations (mg/L) with the data reported from various locations around the world.

Locations	Years	Description	Fe	Mn	Cr	Cu	Ni	Co	Pb	Zn	Cd	As
Nam Co [a*]	2007–2008	Remote	0.011	0.001	0.0002	0.001	0.0002	0.0001	0.0001	0.006	0.000004	-
Mexico City [b*]	2001–2002	Urban	-	0.008	0.0003	-	0.003	-	0.002	-	0.0004	-
Pretoria [c*]	2007–2009	Rural	0.045	0.001	-	0.002	0.001	0.0002	0.001	0.010	0.00003	-
Cape Point [d*]	2007–2009	Urban	0.049	0.002	-	0.001	0.009	0.0002	0.001	0.057	0.00002	-
Mersin [e*]	2003–2005	Urban	0.743	0.019	0.006	0.004	0.007	0.002	0.011	0.050	0.0008	-
S. Jordan [f*]	2003–2004	Rural	0.022	-	-	0.04	0.002	-	0.051	0.032	0.042	-
Matsuura [g*]	2003–2005	Remote	-	0.003	0.0002	0.001	0.001	-	0.004	0.011	0.0002	0.0005
Daya Bay [h*]	2015–2017	Urban	1.13	0.23	0.016	0.025	0.010	0.001	0.040	0.51	0.008	0.020
Jiaozhou Bay [i*]	2015–2016	Urban	0.017	0.028	0.001	-	-	0.0001	0.003	0.028	0.0002	-
Mt Heng [j*]	2009	Urban	0.118	0.013	0.001	-	-	-	0.008	-	0.0007	-
Present Study [+]												
Gustavo A. Madero		Urban	0.371	0.044	0.035	0.037	0.019	0.009	0.033	0.952	0.004	0.003
Tula		Industrial	0.472	0.074	0.036	0.045	0.033	0.015	0.028	0.137	0.002	0.004
Pachuca	2016–2017	Urban/Mining	0.292	0.075	0.030	0.041	0.012	0.013	0.020	1.174	0.001	0.003
Tulancingo		Peri-urban	0.406	0.098	0.038	0.046	0.014	0.017	0.031	1.892	0.002	0.003
Agua Blanca		Rural/Remote	0.379	0.059	0.058	0.032	0.029	0.014	0.045	0.799	0.002	0.003
Molango		Rural	0.448	0.148	0.055	0.047	0.012	0.013	0.031	0.282	0.001	0.002
Permissible limits												
Mexico [k]			0.3	0.15	0.05	2	-	-	0.025	5	0.005	0.005

* Values in VWM concentration: [+] Values in mg/L: [a] [81]; [b] [38]; [c,d] [31]; [e] [82]; [f] [83]; [g] [65]; [h] [79]; [i] [84]; [j] [85]; [k] [80].

3.2. Statistical Analysis

A Pearson correlation matrix ($p < 0.05$) revealed significant correlations between the meteorological characteristics and total metal burden at each site (Table 3). A positive correlation (r^2) of RH vs precipitation in Pachuca (0.92), Molango (0.76), and Agua Blanca (0.66) indicate that high RH is often a predictor of precipitation events [86]. Specifically, Tula presented substantial interrelationships between TMB and WV (r^2 = 0.91), RH (r^2 = −0.90) and BP (r^2 = 0.77). The results showed that wind speeds in the region are highly influential, by transporting particulate matter from adjoining regions to the sampling location, and thereby, contributing to the TMB, whereas negative correlation with RH is probably due to the wash out processes by rains [87]. Significant correlations (r^2 = 0.41–0.78) of TMB vs AT found in all the localities were attributed to the fact that more favorable atmospheric dispersion conditions and photochemical reactions prevail under warm conditions [88].

Table 3. Correlation matrix of total metal burdens and meteorological conditions for each site.

	Total Metal Burden (TMB)	Precipitation (P)	Wind Velocity (WV)	Air Temperature (AT)	Relative Humidity (RH)	Barometric Pressure (BP)
Gustavo A. Madero (*n* = 7)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	-	-	1.00			
Air temperature	0.52	-	-	1.00		
Relative humidity	-0.56	-	-	−0.64	1.00	
Barometric pressure	0.65	-	−0.65	0.71	−0.89	1.00
Tula (*n* = 8)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	0.91	-	1.00			
Air temperature	-	-	-	1.00		
Relative humidity	−0.90	-	−0.88	−0.66	1.00	
Barometric pressure	−0.77	-	−0.70	−0.64	0.88	1.00
Pachuca (*n* = 6)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	-	−0.65	1.00			
Air temperature	0.78	-	-	1.00		
Relative humidity	-	0.92	-	-	1.00	
Barometric pressure	-	-	-	-	-	1.00
Tulancingo (*n* = 10)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	-	-	1.00			
Air temperature	0.65	-	-	1.00		
Relative humidity	-	0.60	−0.91	-	1.00	
Barometric pressure	-	-	−0.92	-	0.84	1.00
Agua Blanca (*n* = 10)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	-	-	1.00			
Air temperature	-	-	0.66	1.00		
Relative humidity	-	0.76	−0.80	-	1.00	
Barometric pressure	-	-	−0.89	−0.69	0.70	1.00
Molango (*n* = 11)						
Total Metal burden	1.00					
Precipitation	-	1.00				
Wind velocity	-	-	1.00			
Air temperature	0.66	-	-	1.00		
Relative humidity	-	0.66	-	-	1.00	
Barometric pressure	-	-	−0.65	-	0.86	1.00

Positive correlations of Mn vs Cu (r^2 = 0.83) and Zn (r^2 = 0.76), when $p < 0.05$ in the rainwater collected at the urban center of Gustavo A. Madero (Table 4), indicated the influence of local road traffic and automobile exhausts [89]. The negative relationship of Mn and Pb (r^2 = −0.94) was probably due to the Pb mostly originating from rooftop sources such as lead flashing roofs and leaded roofing nails, rather than industry and cars in the region [90], whereas the discrepancies of Fe vs Zn (r^2 = −0.84) indicate a crustal/geological origin of Fe compared to Zn. Likewise, in Tula, the significant correlations (r^2) were observed between Ni and Zn (0.93), Fe (0.84), Mn (0.96), As (0.92), and Zn vs Fe (0.80), Mn (0.99), As (0.84) were related probably due to local industrial sources, particularly the cement [91] and petroleum refineries that operate in the area. Moreover, the evidence on the presence of Fe and As also indicates their sources to be the limestone deposits of the region [92].

Strong positive correlations in the rainwater of Pachuca were found between Ni vs Cr (r^2 = 0.94), Zn vs Cr (r^2 = 0.87), Ni (r^2 = 0.83), indicating their origin to be from mine tailings [93]. The presence of fabric and leather industries in the region of Tulancingo led to a positive correlation of Mn vs Zn (r^2 = 0.81) [94], whereas strong associations of Cd vs Pb (r^2 = 0.90) and Zn (r^2 = 0.97) in Agua Blanca explain the potential impact of dust from the local wood processing industries [95].

Site-specific factor analysis (Table 5) was performed for the entire dataset in order to indicate the potential fingerprints of metal sources. In this study, the principal component method was used to extract the factors; the cumulative% at each site ranged between 75.84–95.34%. The locality of Gustavo A. Madero presented four factors (F1–F4), where F1 presented positive loadings on Zn (0.85) and Co (0.75), signifying anthropogenic sources, i.e., mainly from traffic emission [96]. In contrast, negative loading on Fe (−x0.95) indicate crustal origin. F2, with a total variance of 23.30% with positive loadings on Cu (0.97), Ni (0.70), Mn (0.70), is mainly from anthropogenic chemicals [15]. Two factors (F1 & F2) with total variances of 71.71% and 12.34% respectively were extracted in Tula. Significant positive loadings on Cr (0.93), Ni (0.77), Fe (0.86), and As (0.92) clearly exhibit their origin, i.e., the local refinery that operates in the region [97]. In the rainwater samples of Pachuca, F1 explains the total variance of 52.61%, F2 of 23.20%, and F3 accounts for a total variance of 14.16%. Negative loadings on Cd (−0.92) and Co (−0.87) exhibit their dissimilarity in origin, being from both natural and anthropogenic sources [98] in Pachuca, whereas strong positive loadings of Cr (0.96), Ni (0.98), and Zn (0.87) clearly indicate their source as the dusts blown from the mine tailings present in the region [93]. Likewise, the factors and loadings of metals extracted in the rainwater samples of Tulancingo, Agua Blanca, and Molango clearly explain the influences of industrial, crustal, and traffic emissions, and are also highly site specific.

Table 4. Correlation matrix values of six studies sites from Central Mexico.

Site		Cu	Cd	Cr	Ni	Pb	Zn	Co	Fe	Mn	As
Agua Blanca ($n = 10$)	Cu	1.00									
	Cd	0.58	1.00								
	Cr	0.55	0.71	1.00							
	Ni	0.69	-	-	1.00						
	Pb	0.65	0.90	0.64	-	1.00					
	Zn	0.71	0.97	0.77	-	0.93	1.00				
	Co	-	-	-	-	-	-	1.00			
	Fe	0.66	0.78	0.85	-	0.84	0.84	−0.62	1.00		
	Mn	0.93	0.51	-	0.82	0.56	0.61	-	-	1.00	
	As	−0.52	-	-	-	-	-	0.57	−0.53	-	1.00
Molango ($n = 11$)	Cu	1.00									
	Cd	−0.58	1.00								
	Cr	-	-	1.00							
	Ni	-	-	-	1.00						
	Pb	-	-	-	-	1.00					
	Zn	0.58	−0.50	0.59	-	-	1.00				
	Co	-	-	-	-	0.56	-	1.00			
	Fe	0.59	-	0.86	-	-	0.70	-	1.00		
	Mn	0.63	-	-	-	-	0.77	-	0.63	1.00	
	As	-	-	-	-	-	-	-	-	-	1.00
Gustavo A. Madero ($n = 7$)	Cu	1.00									
	Cd	-	1.00								
	Cr	-	-	1.00							
	Ni	0.64	-	-	1.00						
	Pb	−0.76	-	−0.63	−0.52	1.00					
	Zn	-	-	0.51	-	−0.73	1.00				
	Co	-	-	-	-	-	0.57	1.00			
	Fe	-	-	-	-	0.57	−0.84	−0.56	1.00		
	Mn	0.83	0.58	-	-	−0.94	0.76	-	−0.58	1.00	
	As	−0.69	-	-	-	-	-	-	-	-	1.00
Tula ($n = 8$)	Cu	1.00									
	Cd	-	1.00								
	Cr	-	0.66	1.00							
	Ni	0.70	0.79	0.82	1.00						
	Pb	−0.64	−0.71	-	−0.62	1.00					
	Zn	0.85	0.68	0.67	0.93	−0.70	1.00				
	Co	-	-	−0.60	−0.66	-	−0.58	1.00			
	Fe	0.75	-	0.83	0.84	-	0.80	-	1.00		
	Mn	0.86	0.71	0.74	0.96	−0.67	0.99	−0.55	0.86	1.00	
	As	0.65	0.67	0.91	0.92	-	0.84	−0.58	0.94	0.89	1.00
Pachuca ($n = 6$)	Cu	1.00									
	Cd	-	1.00								
	Cr	-	-	1.00							
	Ni	-	-	0.94	1.00						
	Pb	-	-	-	-	1.00					
	Zn	0.77	-	0.87	0.83	-	1.00				
	Co	-	0.83	-	-	-	-	1.00			
	Fe	0.76	−0.56	0.67	0.60	-	0.90	-	1.00		
	Mn	0.84	−0.53	0.69	0.59	-	0.94	−0.65	0.94	1.00	
	As	-	-	-	-	0.73	-	-	-	-	1.00
Tulancingo ($n = 10$)	Cu	1.00									
	Cd	-	1.00								
	Cr	-	-	1.00							
	Ni	0.72	-	-	1.00						
	Pb	-	-	-	-	1.00					
	Zn	-	-	-	-	-	1.00				
	Co	−0.81	0.58	-	−0.61	-	−0.53	1.00			
	Fe	-	-	-	-	-	0.52	-	1.00		
	Mn	0.62	-	-	0.69	-	0.81	-	0.60	1.00	
	As	-	-	-	-	-	−0.76	-	-	−0.57	1.00

Table 5. Factor loading normalized with VARIMAX rotation.

	Gustavo A. Madero				Tula		Pachuca		
	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 1**	**Factor 2**	**Factor 1**	**Factor 2**	**Factor 3**
Cu	-	0.97	-	-	-	0.74	-	-	-
Cd	-	-	0.88	-	-	-	−0.92	-	-
Cr	-	-	-	0.93	0.93	-	-	-	0.96
Ni	-	0.70	-	-	0.77	-	-	-	0.98
Pb	-	-	-	-	-	−0.98	-	−0.89	-
Zn	0.85	-	-	-	-	0.74	-	-	0.87
Co	0.75	-	-	-	-	-	−0.87	-	-
Fe	−0.95	-	-	-	0.86	0.71	-	-	-
Mn	-	0.70	-	-	-	-	-	-	-
As	-	−0.80	-	-	0.92	-	-	-	-
Expl. Var	2.99	3.10	1.65	1.79	4.74	3.66	2.96	2.31	3.73
Prp. Totl	0.30	0.31	0.17	0.18	0.47	0.37	0.30	0.23	0.37

	Tulancingo			Agua Blanca			Molango			
	Factor 1	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**
Cu	-	−0.75	-	-	0.78	-	0.86	-	-	-
Cd	-	-	-	0.92	-	-	-	-	−0.75	-
Cr	-	-	-	0.79	-	-	-	-	-	0.93
Ni	-	-	-	-	0.98	-	-	0.83	-	-
Pb	-	-	0.85	0.93	-	-	-	0.81	-	-
Zn	0.86	-	-	0.94	-	-	-	-	-	-
Co	-	-	-	-	-	−0.88	-	-	-	-
Fe	-	-	-	0.82	-	-	-	-	-	0.88
Mn	0.89	-	-	-	0.90	-	0.77	-	-	-
As	−0.83	-	-	-	-	−0.80	-	-	−0.86	-
Expl. Var	3.29	2.90	1.40	4.46	2.57	1.94	2.73	1.85	1.52	2.36
Prp. Totl	0.33	0.29	0.14	0.45	0.26	0.19	0.27	0.18	0.15	0.24

3.3. Enrichment Factor

Enrichment factors in rain water samples were determined using sea-salt aerosols, which are often produced directly on sea surfaces, where the main sources are marine particulate matter and the coastal atmosphere playing a major role in the conversion of compounds [99,100]. In the case of terrestrial aerosols, they often give a good correlation for the seasonal distributions, as they are often generated in the lower atmospheric levels and are absorbed during the rainy season due to the washout effect [101,102]. In the present study, as all the regions are, in one way or another, influenced by industrial activities, we used the upper continental crustal values to identify the natural and external sources influencing the precipitation [103]. Generally, metals with an EF value close to unity indicate a strong influence of natural sources, whereas high values of EF indicate potential anthropogenic activities [81]. In the present study, site specific EF values were found to be:

- Gustavo A. Madero: Cd (4095) > Zn (2475) > Cu (296) > Pb (201) > Co (39) > Cr (30) > As (13) > Mn (11).
- Tula: Cd (2798) > Cu (367) > Zn (264) > Pb (232) > Co (82) > Ni (66) > Cr (38) > As (18) > Mn (14).
- Pachuca: Cd (2700) > Zn (1656) > Cu (415) > Pb (212) > Co (105) > Cr (42) > Ni (37) > As (24) > Mn (14).
- Tulancingo: Zn (4155) > Cd (2402) > Cu (385) > Pb (228) > Co (94) > Cr (38) > Ni (27) > Mn (18) > As (16)
- Agua Blanca: Cd (2314) > Zn (766) > Pb (287) > Cu (267) > Co (91) > Ni (67) > Cr (44) > As (20) > Mn (12).
- Molango: Cd (1754) > Zn (461) > Cu (376) > Pb (236) > Co (66) > Cr (36) > Ni (24) > Mn (19) > As (11).

Substantial differences are observed in the order of EF values, and are highly site specific. Based on the calculated values, the high EF values of Cd, Zn, Cu, Pb, Ni, Cr, and Co fall into the moderate to very high enrichment classes, indicating that external (anthropogenic), man-made activities are clearly affecting the region. The extremely high EF values confirm the role of local anthropogenic and industrial sources in the ambient atmosphere. Moreover, in rural sites, namely Agua Blanca and Molango, high enriched EF values (10–1000) of elements are due to long-range transport by atmospheric circulation. The presence of Mn in all the studied localities was attributed to crustal sources. Moreover, Mn is one of the most abundant trace elements in atmospheric waters [104]. However, Mn and As occurred in the moderate enrichment class in all the studied regions, i.e., mainly from the sedimentary terrain and dust particles.

3.4. Elemental Ratios

Seasonally, Pb/Zn ratios were observed to be higher (Figure 3) during the winter period and much lower during the summers. The observed high values were probably due to the favorable atmospheric conditions (e.g., lower mixing layer height, boundary layer dynamics, local transport processes, and thermal inversion) [105] that resulted in the accumulation of metals. The mean concentration ratio of Pb/Zn in Agua Blanca (rural site) was found to be three-fold higher (3.84) than that of other sites; the values ranged between 0.23–1.06. High Pb/Zn in the rural site is strongly influenced by the wood industries and local transport processes that bring urban contamination into the region.

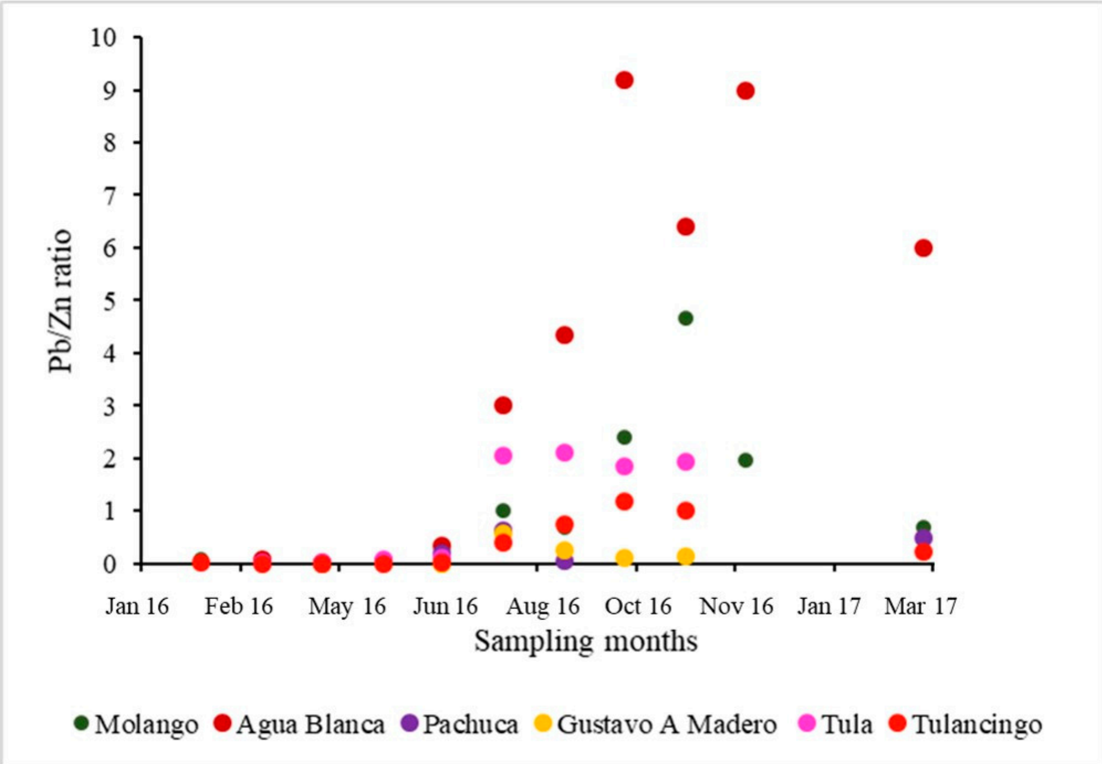

Figure 3. Pb/Zn concentration ratio in the study area during March 2016–2017.

Given the overexploitation of state aquifers, as well as the lack of use of rainwater, it is necessary to obtain water from rainwater collection systems. In certain regions of the state, scarcity forces the population living in rural areas to collect and use of rainwater. However, due to different elemental concentrations in the rainwater from the study area, this water is not suitable for direct human consumption or for domestic use without prior treatment. In order to regularize this rainwater for human consumption, filtration processes are required using activated carbon filters or sands, or ion exchange resins. Recently, it has been shown that advanced oxidation induces the change from reduced species to oxidized species, where metals become oxides that will be susceptible to precipitation [106–108].

It is also necessary that public and private sector institutions invest resources in generating solutions according to the specific characteristics of the hydrological cycle of each locality or climatic zone. Some of the variables that define the selection of techniques (soil, terrain, and dry period, and social and cultural aspects) are not repeated from one region to another. Each precipitation event occurs in unique conditions, and is based on circumstances such as the time during the day, geographical area, the environment, and the method of collection/conservation that will substantially alter its quality. Therefore, if people use rainwater as a resource and not as waste, it is vital to make measurements to define its use in a sustainable way, which can be achieved in real time by applying relatively simple technologies [109].

4. Conclusions

The annual monitoring of the rainwater geochemistry in six different locations in central Mexico during 2016–2017 showed that the concentrations of trace metals in the precipitation were significantly determined by local/regional meteorological characteristics, as well as by natural and anthropogenic sources. Statistical relationships provided an essential insight into the source apportionment of trace metals in both urban and rural sites. The high total metal burden in the precipitation in Tulancingo, a periurban region, indicates the influence of continental air mass movements that carry urban plumes, or by long-range transport. In general, the magnitudes of trace metal concentrations in all the localities were highly site- and month-specific. These types of findings are of great importance in water-stressed countries, where rainwater is considered a potential source for drinking and domestic purposes. Additionally, the study represents an essential tool for assessing the toxic potential of rainfall, notably linking rainfall chemistry with health risk evaluations.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/1/192/s1, Table S1: Monthly climate data for the studied locations of Central Mexico.

Author Contributions: M.P.J. and D.C.E.-U. conceived and directed the project; D.M.R.-R. performed the experiments; D.M.R.-R., S.B.S. and S.C. wrote the paper; D.C.E.-U., M.P.J. and S.C. further improved the concept, structure, contents and writing of the manuscript and also contributed to the discussion. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: D.M.R.-R. thanks CONACyT for the research fellowship. D.C.E.-U., M.P.J. and S.B.S. thank the Sistema Nacional de Investigadores (SNI), CONACyT, México. D.C.E.-U. and M.P.J. wishes to express their gratitude to IPN (COFAA, EDI) Mexico. This work is dedicated to (Late) C. Unnikrishnan Warrier, Senior Scientist, Center for Water Resources Development and Management (CWRDM), Kerala, India who passed away initiating the collaborative research work in Mexico. This article is 105th contribution (partial) from Earth System Science Group (ESSG), Chennai, India.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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