EnvironmentAsia
The international journal published by the Thai Society of Higher Education Institutes on Environment

Available online at www.tshe.org/EA
EnvironmentAsia 5(1) (2012) 39-47

Acid Rain Examination and Chemical Composition of Atmospheric Precipitation in Tehran, Iran

Mohsen Saeedi [a] and Seyed Pejvak Pajooheshfar [b]

[a] *Environmental Research Laboratory, School of Civil Engineering, Iran University of Science & Technology, Tehran, 16846, Iran*
[b] *Post Graduate in Environmental Engineering, School of Civil Engineering, Iran University of Science & Technology, Tehran, 16846, Iran*

Abstract

Air pollution is one of the most important environmental problems in metropolitan cities like Tehran. Rain and snow, as natural events, may dissolve and absorb contaminants of the air and direct them onto the land or surface waters which become polluted. In the present study, precipitation samples were collected from an urbanized area of Tehran. They were analyzed for NO_3^-, $PO4_3^-$, SO_4^{2-}, pH, turbidity, Electrical Conductivity (EC), Cu, Fe, Zn, Pb, Ni, Cr, and Al. We demonstrate that snow samples were often more polluted and had lower pH than those from the rain, possibly as an effect of adsorption capability of snow flakes. Volume weighted average concentrations were calculated and compared with some other studies. Results revealed that Tehran's precipitations are much more polluted than those reported from other metropolitan cities. Cluster analysis revealed that studied parameters such as metals and acidity originated from the same sources, such as fuel combustion in residential and transportation sectors of Tehran.

Keywords: wet deposition; heavy metals; acid rain; chemical composition; Tehran

1. Introduction

Air quality problems in urban areas mainly arise from fuel combustion in transportation, residential and commercial sectors and industrial activities. Metals in the atmosphere originate mainly from metal refining, fossil fuel combustion, vehicle exhausts, and other human activities, and stay there until they are removed by a variety of cleansing processes including dry deposition, scavenging and washout by wet deposition (Church *et al*., 1990; Alloway, 1990; Sillapapiromsuk and Chantara, 2010). Heavy metals emitted by combustion processes usually have relatively high solubility and reactivity, because of the small sizes of particles on which they are carried (Nriagu, 1984). Thus, they dissolve readily in rain, especially under low pH conditions caused by nitrogen and sulfur oxides in the urban atmosphere, resulting in polluted rainwater.

Sulphur dioxide (SO_2) and oxides of nitrogen are the primary causes of acid rain. These pollutants originate from human activities such as waste incineration and fossil fuels combustion in power plants, automobiles, mineral processing, refineries and industries. The levels of NOx are small in comparison to SO_2, but its contribution in the production of acid rain is increasing (Singh and Agrawal, 2008; Sillapapiromsuk and Chantara, 2010).

Some studies examined acidity of rainfalls in conjunction with concentrations of chemical species which influence the pH value of rain. All of them considered the rain with pH values lower than 5.6 as acid rain (Kobori *et al*., 2005; Sillapapiromsuk and Chantara, 2010; Smith *et al*., 1984; Singh and Agrawal, 2008).

Monitoring the concentrations of heavy metals in the atmosphere (aerosols and rain events) can provide important information about the sources of these metals and enables budget and flux calculations to be made (Alloway, 1990). Large volumes of various types of pollutants from different sources are emitted into the Tehran's atmosphere. However, there have not been any reports on average concentrations and environmental geochemistry of wet depositions in Tehran, the most populated and polluted city of Iran. In the present study, contents of dissolved metals (Al, Cr, Ni, Pb, Zn, Fe, and Cu) and ions (SO_4^{2-}, PO_4^{3-}, NO_3^-) along with Electrical Conductivity (EC), Turbidity, and pH of rain and snow samples from an urbanized area of Tehran from December 23, 2008 to July, 1 2009 were investigated. There was no precipitation event from July 1, 2009 to December 23, 2009.

2. Materials and Methods

2.1. Sampling

Samples were obtained at Elahieh located in north Tehran near Gholhak valley which is one of the polluted areas of Tehran (Fig.1). The samples were collected using a bulk sampler equipped with a plastic funnel that was set on the roof of a building at about 30 meters from ground level and separated from other buildings and structures to avoid undesirable effects. After a precipitation event, the samples were immediately transported to the laboratory keeping them at 4°C. Snow samples were collected in the sampling funnel and allowed to melt at room temperature. All sampling apparatus (buckets and funnels) were acid washed and rinsed with distilled water prior to sampling.

2.2. Chemical analyses

pH and Electrical Conductivity (EC) of the samples was measured by a pH-EC meter (Cyberscan 510 model) following calibration. A HACH 2100N Turbidimeter (USA) was used to measure samples turbidity. Concentrations of Fe^{2+} and anions (SO_4^{2-}, PO_4^{3-}, and NO_3^-) were measured by a DR/4000U HACH Spectrophotometer.

Acidifying samples, concentrations of metals (Al, Cr, Ni, Pb, and Zn) were determined by Graphite Furnace Atomic Absorption Spectrophotometer (Buck Scientific 210 VGP).

3. Results and discussion

3.1. Concentrations

Twenty one precipitation events occurred from July 2008 to October 2009 at Elahieh-Tehran. Samples of rain were collected in a plastic bucket during the first hour of a rainfall. Each rainfall was treated as one sample and the samples were not a mixture of different rains of the same day. Annual precipitation in Tehran province in the studied year 2008 and 2009 was about 307.41 and 297.2 mm respectively and a fifty year average is 232.8 mm. Heavy metals along with other studied parameter concentrations are presented in Table 1.

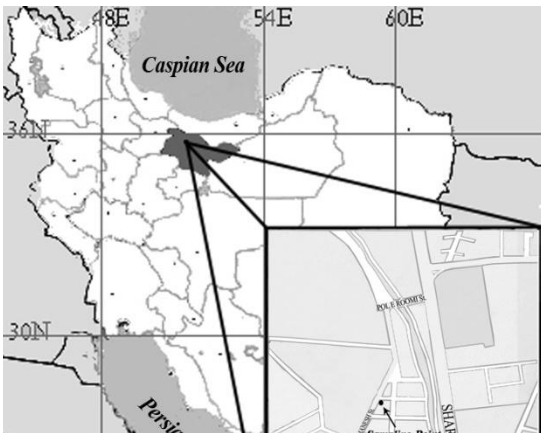

Figure 1. Sampling site for rain and snow collections in Tehran

Some samples were highly polluted in terms of almost all studied contaminants. This may be due to a long time gap between precipitations and heavy air pollution. For instance, on July 1, 2009, rain had 21.5 NTU turbidity, 167 µs EC, 0.21 mg/L Ni, 1.61 mg/L Al, and 1.19 mg/L PO_4^{3-}. This was one of the most polluted precipitations of the studied time period. Snow samples were usually more polluted than rains. Mean pH value of snow samples was lower than those of rain. In most of the samples the pH value was less than 5.5 in autumn and winter time while it was in higher values in spring time. This could be explained by the fact that the air pollution in Tehran is more extensive in cold seasons of the year (i.e. autumn and winter) than that of warm seasons. Fossil fuel combustion in autumn and winter in Tehran is increased during cold seasons to warm the homes and the traffic is heavier during this time. Inversion frequently occurs in cold seasons in Tehran preventing vertical mixing of the atmosphere. Overall, the rain and snow in Tehran within the time period of study was nearly acidic (mean rain pH; 5.9 and mean snow pH; 5.08) which may have negative impact on structures, soils and quality of groundwater and surface waters in the area. Acid precipitation in Tehran is primarily caused by a mixture of strong acids, H_2SO_4 and HNO_3, resulting from fossil fuel combustion mainly by transport sector.

3.2. Precipitation volume weighted-average concentration of elements

The precipitation volume weighted – average values for pH, studied elements and three ions are summarized in Table 2. SO_4^{2-} has the highest value. Nitrate is the second most concentrated pollutant. Aluminum, Cu, Ni, Zn and Pb have much higher values in comparison with other parts of the world (Galloway *et al*., 1982; Barrie *et al*., 1987; Horvath *et al*., 1994; Landis and Keeler, 1997; Takeda *et al*., 2000). Therefore, we consider Tehran as a highly polluted city in the world.

A comparison of concentration of trace elements in the wet deposition samples reported in the literature is presented in Table 3. The higher concentrations of studied elements in Tehran may be mainly due to emissions from residential and transportation sectors and

Table 1. Sampling date of Tehran precipitations and their chemical and physical compositions

Sample	NO_3 (mg/L)	PO_4 (mg/L)	SO_4 (mg/L)	pH	Tur. (NTU)	EC (mg/L)	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Pb (mg/L)	Ni (mg/L)	Cr (mg/L)	Al (mg/L)
Jan 8, 2009	1.1	0.046	12	4.65	4.78	56.7	0.19	0.141	0.123	0.877	0.077		0.740
Jan 12, 2009	0.7	0.045	5.5	4.99	1.12	20.6	0.12	0.085	0.023	0.409	0.101	0.008	0.966
Jan 15, 2009	2.2	0.095	30.7	5.03	2.6	107.2	0.21	0.197	0.298	0.649	0.048	0.007	1.095
Jan 21, 2009	0.8	0.018	2.3	5.45	1.25	22	0.137	0.022	0.153	0.950	0.100	0.003	0.891
Jan 29, 2009	1.4	0.037	13.6	5.29	2.2	42.5	0.371	0.078	0.079	0.425	0.132	0.079	1.517
Mean Snow	1.24	0.048	12.820	5.082	2.390	49.800	0.206	0.105	0.135	0.662	0.091	0.024	1.042
Max	2.2	0.095	30.700	5.450	4.780	107.200	0.371	0.197	0.298	0.950	0.132	0.079	1.517
Min	0.7	0.018	2.300	4.650	1.120	20.600	0.120	0.022	0.023	0.409	0.048	0.003	0.740
Dec 23, 2008	0.9	0.057	6.9	5.88	1.6	23.6	0.222	0.063	0.052	0.497	0.121	0.033	0.497
Dec 25, 2008	0.7	0.028	2.7	5.55	2.15	20.8	0.125	0.062	0.009	0.363	0.030	0.016	0.106
Jan 25, 2009	0.5	0.036	6.2	5.52	1.55	11.3	0.115	0.051	0.042	0.128	0.014		0.451
Feb 4, 2009	0.9	0.042	13.1	5.72	2.15	42.4	0.198	0.037	0.071	0.621	0.138		0.157
Feb 7, 2009	0.9	0.202	12.4	5.89	2.9	49.6	0.124	0.026	0.065	0.309	0.026	0.038	0.206
Feb 8, 2009	0.5	0.035	3.1	4.73	3	39.3	0.156	0.072	0.042	0.280	0.053	0.042	0.469
Feb 8, 2009	0.5	0.043	2.3	5.66	0.8	12.69	0.12	0.03	0.024	0.262	0.085	0.009	1.055
Feb 14, 2009	0.8	0.34	16.3	5.81	4.3	43.5	0.326	0.181	0.019	0.406	0.099		0.435
Feb 15, 2009	0.6	0.066	8	5.51	1.4	19.03	0.229	0.002	0.022	0.454	0.014		0.928
Mar 28, 2009	0.6	0.058	5.2	5.89	0.9	39.8	0.125	0.012	0.004	0.096	0.037	0.019	0.443
Mar 29, 2009	0.6	0.091	4.6	5.93	0.87	25.6	0.256	0.052	0.020	0.190	0.088	0.010	1.360
Apr 26, 2009	1.4	0.894	18.4	6.48	ND	101.4	0.269	0.055	0.090	0.900	0.166	0.016	1.301
Apr 26, 2009	0.9	0.28	8.7	6.13	39	75.7	0.321	0.147	0.059	0.358	0.011	0.011	1.476
Apr 26, 2009	0.8	0.253	10.6	5.98	11.7	63.6	0.316	0.177	0.016	0.288	0.084	0.038	0.910
May 17, 2009	4.5	0.266	74.3	7.75	26	521	0.459	0.296	0.275	0.829	0.147	0.063	4.404
July 1, 2009	3.1	1.191	25.5	6.51	21.5	167	0.29	0.134	0.094	0.781	0.213	0.045	1.611
Mean Rain	1.138	0.243	13.644	5.934	7.988	78.520	0.228	0.087	0.056	0.423	0.083	0.028	0.988
Max	4.500	1.191	74.300	7.750	39.000	521.000	0.459	0.296	0.275	0.900	0.213	0.063	4.404
Min	0.500	0.028	2.300	4.730	0.800	11.300	0.115	0.002	0.004	0.096	0.011	0.009	0.106

utilization of heavy liquid fuel oil in many industries and power plants within and around Tehran. It should be pointed out that lower precipitation in Tehran compared to most of the other studied sites would eventually results in higher metal concentrations. Lower rain volumes in Tehran and longer time periods between rain and snow events in addition to the high amounts of pollutants in the air would result in higher dissolution and absorption of contaminants in lower volumes of water making rain and snow highly polluted in terms of metals and acidic ions.

3.3. Acid rain comparisons

Acid rain occurs in Tehran, Iran (Table 1). A rainfall of pH 4.65 was measured on Jan 8, 2009. It is shown that all snow samples have lower pH than rainfalls and all of them are acidic with the pH value of 5.6. Forty three

Table 2. Precipitation volume weighted-average concentrations of elements and ions in Tehran's wet depositions

	Mean Volume Weighted	(Min)	(Max)
pH	5.4741	4.65	7.75
NO_3^- (mg/L)	0.8376	0.5	4.5
PO_4^{3-} (mg/L)	0.1026	0.018	1.191
SO_4^{2-} (mg/L)	8.0640	2.3	74.3
Cu (mg/L)	0.1849	0.115	0.459
Fe (mg/L)	0.0721	0.002	0.296
Zn (mg/L)	0.0519	0.0043	0.2977
Pb (mg/L)	0.4057	0.0957	0.95
Ni (mg/L)	0.0659	0.0105	0.2134
Cr (mg/L)	0.0164	0.0031	0.0789
Al (mg/L)	0.7612	0.1058	4.4038

percent of all samples showed to have pH values lower than 5.6. The average pH value in of samples was about 5.7 and the mean volume weighted value was around 5.47. All of these results showed that precipitation in Tehran is acidic and it must be considered as a risk that has to be taken care in the view of atmospheric corrosion and its effects on structures, impacts on soil and waters, impacts on plants and crops. Fig. 2 shows the scatter plot of pH values of samples.

3.4. Relationships between precipitation volume and concentrations of chemical species

The relationships between the concentrations of Al and SO_4^{2-} and the volume of precipitation per event are shown in Fig. 3. Increasing volumes of precipitation would result in a decrease of pollutant concentrations which may be reasonable due to dilution effect.

All correlation coefficients between chemical data and the volume of precipitation were -0.4148, -0.3921, -0.42866, -0.49027, -0.32529, -0.34134, -0.28432, -0.43522, -0.33402, -0.47766, -0.2258 and -0.34672 for NO_3-, PO_4^{3-}, SO_4^{2-}, Cu, Fe, Zn, Pb, Ni, Al, pH, Turbidity and Electrical conductivity, respectively. It means that higher volume of precipitation led to lower concentrations in precipitations.

3.5. Relationship between anions and metals

Linear regression was computed amongst anions (NO_3^-, SO_4^{2-} and PO_4^{3-}) and metals in samples. Almost all of them had good R-squared values indicating reasonable relationships between quantities of measured parameters. For instance, relationships between metals against the ions are shown in Fig. 4 and Fig. 5. A direct correlation among the ions and elements may be indicative of existence of same sources of their emission into Tehran's atmosphere.

3.6. Relationship between rainfall intervals and concentrations

Our data (Table 1) clearly show that concentrations of metals and ions increase whenever the time lap between two precipitations is longer. Therefore, the correlation coefficients between rainfall intervals and quantity of parameters were calculated. Results showed that some parameters like NO_3-, PO_4^{3}-, pH, and Ni had significant correlation coefficients which are 0.49, 0.66, 0.45, and 0.52 respectively. The obtained data reveal that snow has higher metal, but lower ion, concentrations when compared with rain. This may be explained by the adsorption capacity of snow flakes to uptake metals and capability of rain (especially in lower pH valued) to dissolve ions. The pH, turbidity and electrical conductivity (EC) of rain are also higher than of snow. Probably ions are more easily soluble in rain than snow.

3.7. Cluster analysis

Data in Table 1 are used to portrait cluster a dendrogram of ions and heavy metals in all the samples those were collected (Fig. 6). All studied parameters have positive similarity coefficients as coefficients between NO_3^- and SO_4^{2-}, Al and Cu, Al and Fe, Fe and Cu, and Zn and Pb are 0.939, 0.725, 0.675, 0.675, and 0.662, respectively. Nitrate, SO_4^{2-}, Al, Fe and Cu form a cluster with higher similarities. Nickel-PO_4 and Pb-Zn also form other clusters with similarities higher than

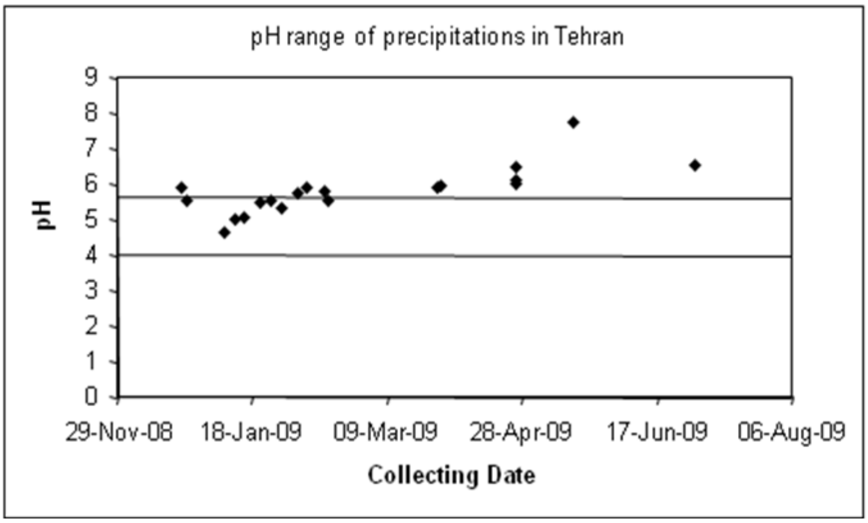

Figure 2. Scatter plot of pH values in Tehran precipitation (2008-2009)

Table 3. Comparison of concentration of trace elements in the wet deposition reported in literature (μg/L)

Sites (rural or urban, bulk or wet)	Al	Fe	Cu	Pb	Ni	Zn	Annual precipitation volume (mm/ yr)
Rural area (Galloway *et al*., 1982)			5.4	12	2.4	36	
Rural area (Barrie *et al*., 1987)			0.68 - 24	3.0 - 14.0	0.79 - 17	4.7 - 50	435 - 659
Hungary 3 sites Rural (Horvath *et al*., 1994)			3.6 - 11	13 - 17	1.7 - 4.6	34 - 51	
Dexter Michigan, USA semi-rural (Landis and Keeler, 1997)	57		0.86	1.4	0.23	7.7	
Hiroshima Japan (Takeda *et al*., 2000)	0.06		0.62	1.24	0.29	4.77	1433
Ajlune, Jordan Rural (Al-Momani, 2003)	382	92	3.1			6.5	
Paradise, New Zealand Rural (Halstead *et al*., 2000)		2.1	0.013			0.038	
New Castle, USA Urban (Pike and Moran, 2001)	24	23	1.3			26	
Montreal Island, Canada Urban (Poissant *et al*., 1994)	18	91	4.0			28	
Singapore Urban (Hu and Balasubramanian, 2003)	18.4	24	5.6			7.2	
North Atlantic Ocean (Church *et al*., 1990)	47	25	0.38			1.7	
Tsukuba, Japan Suburban (Hou *et al*., 2005)	34	7.5	2.5			18	
Tehran, Iran (This study)	761.17	72.1	184.94	405.71	65.88	51.89	232.8

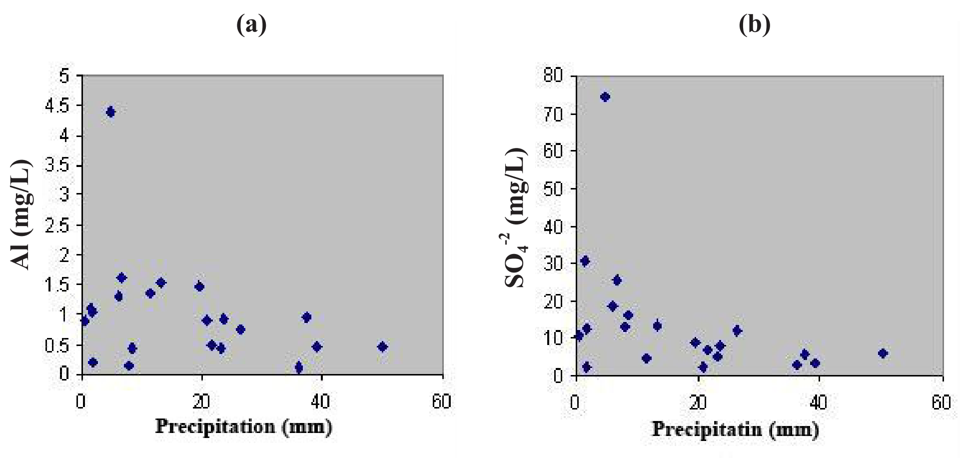

Figure 3. Relationship between precipitation volumes and concentrations of (a) Al, (b) SO_4^{2-}

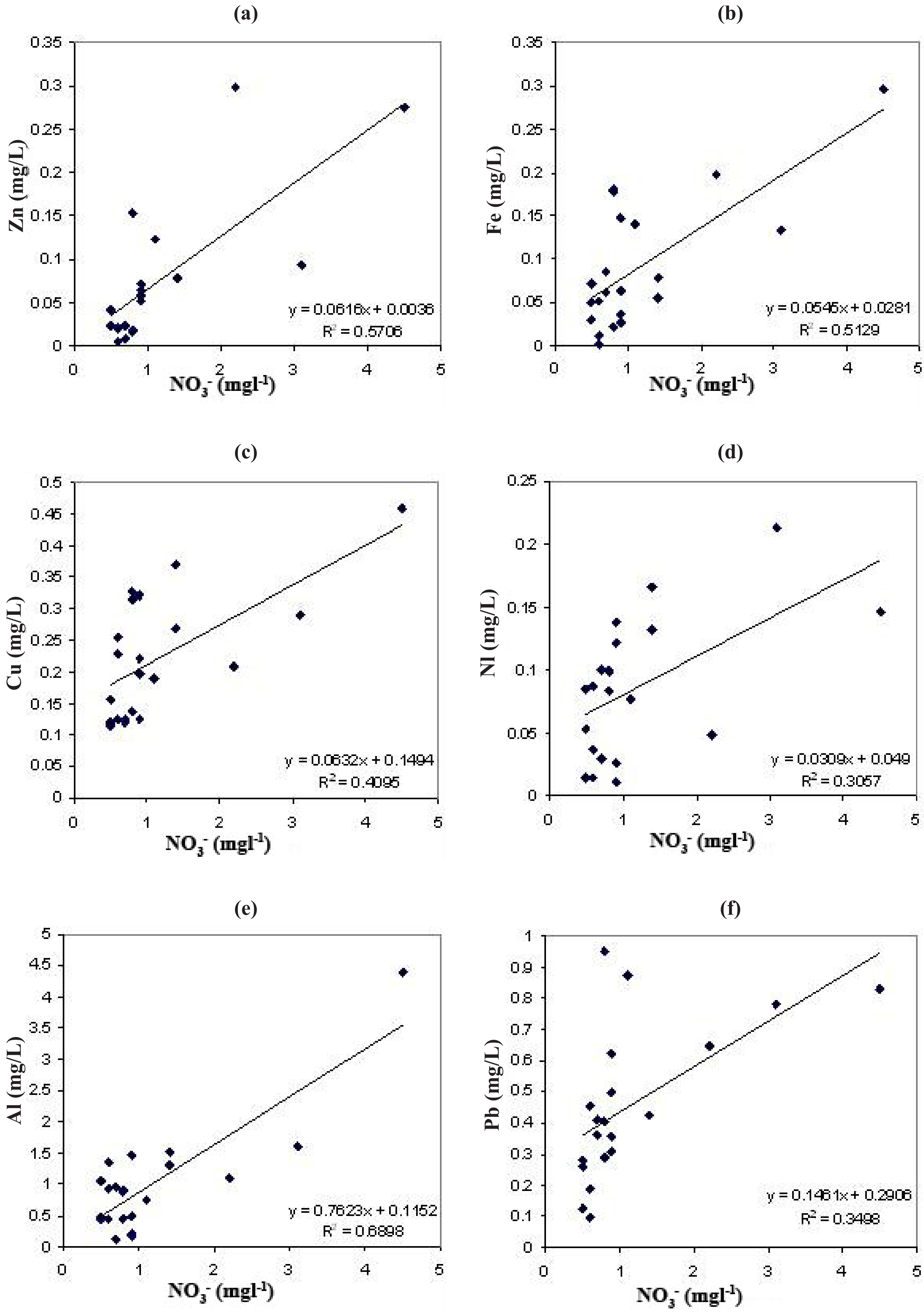

Figure 4. Relationship between NO_3^- and metals concentrations

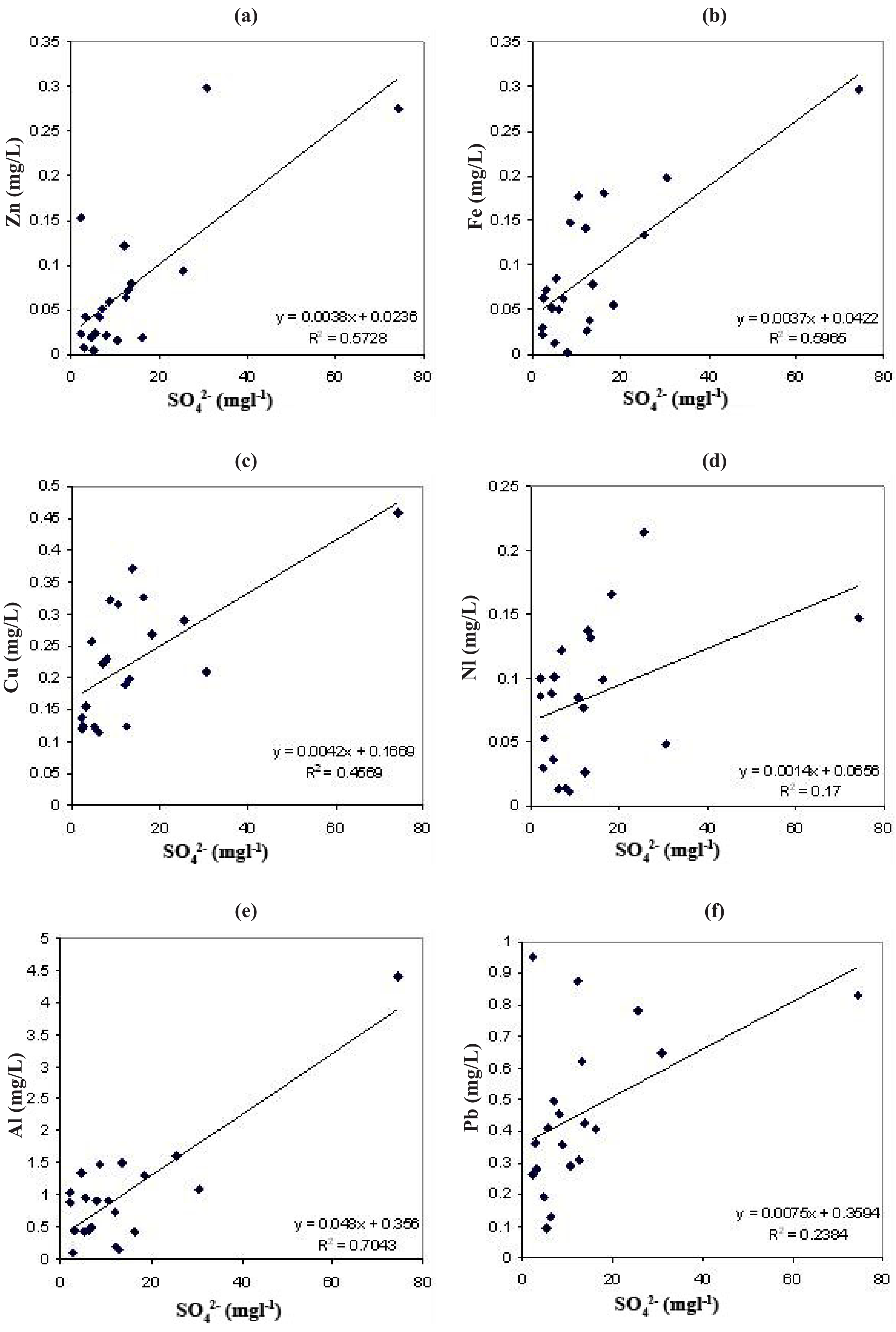

Figure 5. Relationship between SO_4^{2-} and metals concentrations

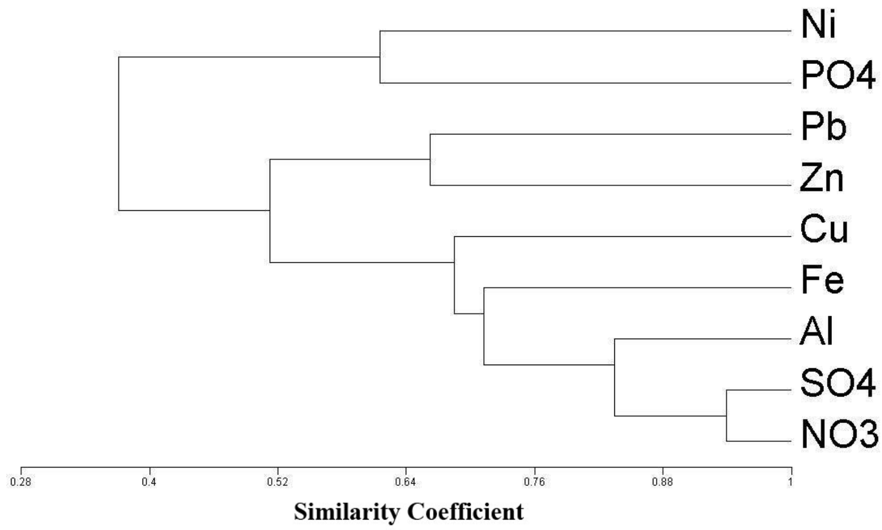

Figure 6. Dendrogram of studied parameters in Tehran precipitation samples

0.6 which connect to ions cluster in 0.4-0.5 similarity coefficients. On the basis of similarity coefficients all studied parameters may originate from same sources which seem to be the combustion of fossil fuels (particularly liquid fuels) in Tehran.

4. Conclusions

Twenty one precipitation samples were collected and analyzed for different constituents within a half year period of time in Tehran. Results revealed that rain and snow samples are more polluted than those of other studies around the world. Snow samples are mostly more polluted than rain samples in terms of heavy metal contents. Long intervals between precipitations result in increased pollution. The pH of snow samples had more acidity than that of rain. Larger precipitations resulted in dilution of contaminant concentrations in samples and lower concentrations. We show that Tehran's precipitations are considerably more polluted than that of other metropolitan cities of the world. Based on the results of this study and negative effects of polluted/acidic rains, some measures like more efficient energy consumption and air pollution control of transportation vehicles should be taken in Tehran.

Acknowledgement

This study was partially supported by deputy of research and Enviro-hydroinformatics center of excellence, Iran University of Science and Technology.

References

Alloway BJ. The origins of heavy metals in soils. In: Heavy metals in soils (*Ed*: Alloway BJ) Blackie and Son Ltd. 1990; 29-39.

Al-Momani IF. Trace elements in atmospheric precipitation at Northern Jordan measured by ICP-MS: acidity and possible sources. Atmospheric Environment 2003; 37: 4507–15.

Barrie LA, Lindberg SE, Chan WH, Ross HB, Arimoto R, Church TM. On the concentration of trace metals in precipitation. Atmospheric Environment 1987; 21: 1133–35.

Church TM, Veron A, Patterson CC, Settle D, Erel Y, Maring HR, Flegal AR. Trace elements in the North Atlantic troposphere: shipboard results of precipitation and aerosols. Global Biogeochemical Cycles 1990; 4: 431–43.

Galloway JN, Thornton JD, Norton SA, Volchok HL, McLean RA. Trace metals in atmospheric deposition: a review and assessment. Atmospheric Environment 1982; 16: 1677–700.

Halstead JRM, Cunninghame GR, Hunter AK. Wet deposition of trace metals to a remote site in Fiordland, New Zealand. Atmospheric Environment 2000; 34: 665–76.

Horvath Z, Lasztity A, Varga E, Meszaros E, Molnar A. Determination of trace metals and speciation of chromium ions in atmospheric precipitation by ICPAES and GFAAS. Talanta 1994; 41: 1165–68.

Hou H, Takamatsu T, Koshikawab MK, Hosomi M. Trace metals in bulk precipitation and throughfall in a suburban area of Japan. Atmospheric Environment 2005; 39: 3583–95.

Hu GP, Balasubramanian R. Wet deposition of trace metals in Singapore. Water Air & Soil Pollution 2003; 144: 285–300.

Kobori H, Kumazawa M, Kai Y, Ham Y. Monitoring Study on Acid Rain in Kanagawa Prefecture, Central Japan. Journal of Environmental and Information Studies 2005; 6: 97-101.

Landis M, Keeler GJ. Critical evaluation of a modified automatic wet-only precipitation collector for mercury and trace element determinations. Environmental Science & Technology 1997; 31: 2610–15.

Nriagu JO. Changing Metal Cycles and Human Health. (*Ed*: Nriagur JO). Springer-Verlag, Heidelberg. 1984; 445-28.

Pike SM, Moran SB. Trace elements in aerosol and precipitation at New Castle, NH, USA. Atmospheric Environment 2001; 35: 3361–66.

Poissant L, Schmit JP, Beron P. Trace inorganic elements in rainfall in the Montreal Island. Atmospheric Environment 1994; 28: 339–46.

Singh A, Agrawal M. Acid rain and its ecological consequences. Journal of Environmental Biology 2008; 29: 15-24.

Sillapapiromsuk S, Chantara S. Chemical composition and seasonal variation of acid deposition in Chiang Mai, Thailand. Environmental Engineering Research 2010; 15: 93-98.

Takeda K, Marumoto K, Minamikawa T, Sakugawa H, Fujiwara K. Three-year determination of trace metals and the lead isotope ratio in rain and snow depositions collected in Hiroshima, Japan. Atmospheric Environment 2000; 34: 4525–35.

Smith SJ, Sharpley AN, Menzel RG. The pH of rainfall in the southern plains. Proceedings of the Oklahoma Academy of Science 1984; 64: 40-42.

Received 20 August 2011
Accepted 18 September 2011

Correspondence to
Professor Dr. Mohsen Saeedi
Environmental Research Laboratory,
School of Civil Engineering,
Iran University of Science & Technology,
Tehran, 16846,
Iran
Email: msaeedi@iust.ac.ir