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Determination of Trace Elements Concentration in wet and dry Atmospheric Deposition and Surface soil in the Largest Industrial city, Southwest of Iran

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ABSTRACT: Dry and wet atmospheric depositions as well as urban surface soil samples were collected in eight different land use zones (during 2010) of the most important and largest industrial city, southwest Iran for determining Cadmium, Chromium, Lead and Zinc. The average of Cd, Cr, Pb and Zn concentrations in the study area for wet precipitation were 17.8 µg/L, 49.97 µg/L, 2.31 µg/L, and 0.53 µg/L, respectively. Also, the mean levels of mentioned elements were 0.144 mg/m^2.day, 0.457 mg/m^2.day, 0.091 mg/m^2.day, and 0.0017 mg/m^2.day, respectively in dry deposition samples. Moreover, the average amounts of Pb, Zn, Cr, and Cd were recorded for soil samples as a value of 64.2 mg/kg, 197.3 mg/kg, 61.24 mg/kg and 0.73 mg/kg. As a result, the trend of metal concentrations in all media were similar and decreased as Zn> Pb> Cr> Cd. The high contamination levels of heavy metals indicate that they have been significantly impacted from anthropogenic activities (non-ferrous metal smelting, fossil fuel combustion, pit burning, gas flaring and traffic sources). According to analysis results, the significantly positively correlations between Cd-Pb, Pb-Zn and Zn-Cd were shown in all three environments.

Key words: Atmospheric chemistry, Heavy metals, Suspended particle matter, Wet precipitation, Urban surface soil

INTRODUCTION

The suspended particulate matters are one of the primary air pollutants encompass a wide spectrum of elements with different degree of toxicity, harmfulness (Sherwood, 2002; Sekhavatjou *et al.*, 2010) and severe impact on the respiratory system (Seinfeld & Pandis, 2006; Parr *et al.*, 1994) resulting in increased morbidity and mortality rates (Gotschi *et al.*, 2005; Valavanidis *et al.*, 2006; EEA, 2005; WHO, 2003; Sekhavatjou *et al.*, 2011). Trace metals are part of a major concern due to their toxic and potentially carcinogenic characteristics (Cao *et al.*, 2009; Chiou, 2009) and their persistent in the environment (Sherwood, 2002; Hosseini Alhashemi *et al.*, 2012; Taghinia Hejabi *et al.*, 2010). They enter the environment through atmospheric deposition, erosion of the geological matrix, and from anthropogenic sources arising from both stationary (power plants, industries, incinerators, and residential heating) and mobile sources (road traffic) (Giordano *et al.*, 2005; Bilos *et al.*, 2001; Pacyna, 1984; Sweet & Vermette, 1993; Sullivan & Woods, 2000; Chen *et al.*, 2010; Lara *et al.*, 2001; Safai *et al.*, 2004; Das *et al.*, 2005; Song & Gao, 2009).

Dry and wet precipitations play important roles in carrying chemical species from the atmosphere to the surface (Al-Khashman , 2005; Zheng *et al.*, 2005; Goncalves *et al.*, 2000; Tanga *et al.*, 2005; Lara *et al.*, 2001), thus they can bring potential adverse effects on the continents as well as in the oceans (Kim *et al.*, 2000; Gao *et al.*, 2003; Boyd *et al.*, 2004; Sow *et al.*, 2006).

There have been several recent studies of chemical composition and concentration of heavy metals in dry and wet depositions in both urban and rural areas (Khare *et al.*, 2004; Kulshrestha *et al.*, 2003; Seung-Muk *et al.*, 2006; Garcia *et al.*, 2006; Green & Morris, 2006; Michael & Christos, 2006; Zhong *et al.*, 1994; Cheng & You, 2010) furthermore. Also, Chudaeva et al. (2008), Melaku et al. (2008), Li et al. (2007) and Itoh et al. (2006) were reported the concentration of heavy metals in wet precipitation in urban areas of Russia, Washington, China and Japan, respectively (Chudaeva *et al.*, 2008; Melaku *et al.*, 2008; Li *et al.*, 2007; Itoh *et al.*, 2006). In addition, heavy metal amounts in dry

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deposition and soil were measured by Leung Anna et al. (2009), Wang *et al.,* (2009), Wei et al. (2009) in China, Deboudt et al. (2004) in western Europe, Preciado and Loretta (2006) in British Colombia, Al-Khashman et al. (2005) in Jordan (Leung Anna *et al.,* 2009 ; Wang *et al.,* 2009 ; Wei *et al.,* 2009 ; Deboudt *et al.,* 2004; Preciado & Loretta, 2006; Al-Khashman *et al.,* 2005).

Ahvaz is a capital city of the Khouzestan province, Iran. It is built on the banks of the Karun River and is situated in the middle of Khouzestan Province (31°19’45" N and 48°41’28" E). The city had a population of 1,338,126 in 2006. Ahvaz has a desert climate with long, extremely hot summers and mild, short winters. It is an industrialized city and the major parts of oil industries which are located there. So, the main sources of potentially toxic metals (Cr, Cd and Pb) which are especially high temperature processes such as non-ferrous metal smelting, fossil fuel combustion vehicle exhaust, and other human activities, which are located in the city (Sekhavatjou *et al.,* 2011; Herrera *et al.,* 2009). So the present study has researched the following aims in an important industrialized city in the southwest of Iran:

a. To determine trace elements levels (Cd, Cr, Pb and Zn) in wet precipitation, dry deposition and urban surface soil and to investigate seasonal variation of studied elements in mentioned media

b. To determine relationship between trace elements concentration in settling particles, amount of these metals in wet precipitation and surface soil of studied urban area

c. To identify the probably effects of emission sources on increasing and accumulation of trace elements in different media

The results obtained from this study will provide a useful databank of metal concentrations in the three studied media in Ahvaz that contribute to have an effective monitoring on both environmental quality and the human health.

MATERIALS & METHODS

The eight sampling sites have been selected according to several parameters such as industries locations, residential area, traffic zones, access and representativeness in the city of Ahvaz that their characteristics are given in Table 1. Also the map of the study area is presented in Fig. 1.

Wet precipitation samples were collected immediately after precipitation events. Wet deposition sample containers were cleaned before sampling with distilled water and a final rinse with a 10% nitric acid solution to eliminate particle deposition or adsorption onto container. All collected samples were passed through a membrane filter pore size 0.45 micron. Then, the nitric acid was added to filtered samples to adjust the pH to less than 2.0 and to dissolve most of the particles. The acidified samples were then preserved in a refrigerator for further analysis (Singh & Mondal, 2008; Desboeufs *et al.,* 2001; Sandroni & Migon, 2002). The collection of dry deposition was according to ASTM 1739D, using polyethylene cylindrical containers. The sampling containers were placed in elevation of 2 meters above surface and far from any pollution sources. The sampling period was 30 days in both winter and spring 2010 (ASTM, 2004). The preparation and chemical analysis of dry deposition was same as soil samples that are mentioned as a below (Wei & Yang, 2010; USEPA, 1996). About 50 g of

Table 1. Characteristics of selected sampling sites in the area of the study

Station code	Land use	Elevation (m)	Location	Distance from road (m)	Distance from industrial and commercial area (m)	Distance from residential area	Population
S1	High traffic	3	City center	10	2500	adjacent	20000
S2	Industrial	5	Eastern margin	10	500	adjacent	12000
S3	Residential-industrial	2	Southeast	10	450	adjacent	35000
S4	Residential-industrial	2	Southwest	12	500	adjacent	45000
S5	Residential	2	Southwest	450	7000	adjacent	1000
S6	Light traffic-residential	3	Western margin	200	3000	adjacent	7000
S7	Residential-industrial	2	Northern margin	10	300	adjacent	12000
S8	Residential	3	Northern margin	250	4000	adjacent	5000

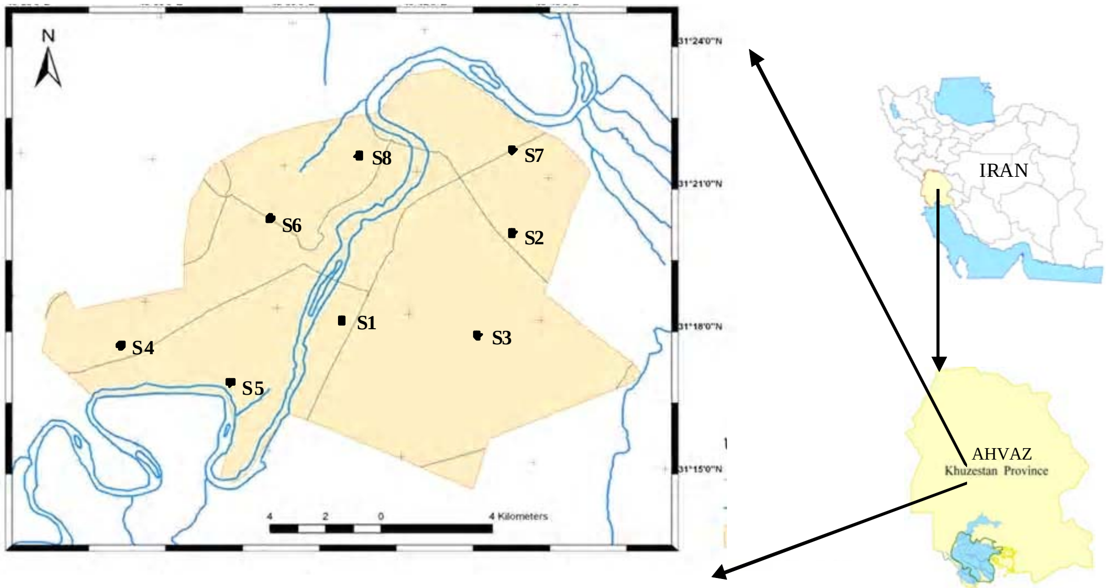

Fig. 1. Position of sampling sites in Ahvaz city

composite soils were taken from 0-5 cm of surface, both before and after rainfalls, from each site and were kept in polyethylene bags. The air dried soils were passed through a 63-µm mesh (sieve No. 230) and were powdered by an agate mortar and pestle. About 0.5 g of the powdered sample was placed in a beaker containing 5 mL of 3:1 HNO_3 to HCl and covered with a watch glass. Then samples were heated until most of the liquid evaporate, and were allowed to cool before 3 mL of Per-chloric acid ($HClO_4$) repeatedly. The heating was continued till the evaporation of most of the liquid. Finally samples were filtered and diluted to 50 with 1 N HCl and analyzed (Hosseini Alhashemi *et al.*, 2010; Hosseini Alhashemi *et al.*, 2011). The total concentration of Cd, Cr, Pb, and Zn were determined by ICP-AES, model Ultima 2C. The standard errors were in the range 0.2% to 0.5%.

RESULTS & DISCUSSION

The descriptive statistics results of heavy metals in wet and dry deposition and soil samples are presented in Table 2. The highest concentration levels of Pb for wet precipitation, dry deposition and soil were shown in S2, S1 and S7 sampling sites, respectively. Also the most concentration levels of Zn in all media were recorded in site S1. Moreover, the highest amounts of Cr for wet deposition (5.4 µg/L), dry deposition (0.175 $mg/m^2.d$) and soil (80.42 mg/kg) were reported in site S3. The similar trend was observed for Cd in S1 sampling site. The trend of studied metals were as Zn (49.893 µg/L)> Pb (17.817 µg/L)> Cr (2.3 µg/L)> Cd (0.53 µg/L), Zn (0.457 mg/m2.d)> Pb (0.1444 mg/m2.d)> Cr (0.09141 mg/m2.d)> Cd (0.00176 mg/m2.d) and Zn (197.385 mg/kg)> Pb (64.2 mg/kg)> Cr (61.24 mg/kg)> Cd (0.7387 mg/kg) for wet precipitation, dry deposition and soil, respectively.

The levels of Pb and Zn are high in both dry deposition and soil samples. Lead which is one of the most hazardous metals revealed widely high levels in all studied media in the area of study. This is due to several emission sources in the adjacent city such as Carbon Black plant, non-ferrous metal smelting, steel and pipe manufacturing plants, gas flare burning and heavy traffic of vehicles. These amounts were between 2.56 - 91.18 µg/L in wet precipitation samples. Concentration of studied elements showed meaningful differences in sampling points ($P<0.01$).

The concentrations of Zn and Cr in wet precipitation were between 7.31-127.46 µg/L and 0.7-7.43 µg/L, respectively. The highest levels of Zn and Cr were shown in traffic and industrial stations, respectively. Totally, the concentrations of heavy metals in wet precipitations are highly dependent to emission sources and this point is an important role of pollutant's transferring from air to soil via wet depositions.

The Fig. 2 has showed the significant correlation between Pb and Zn ($r^2=0.459$, $P<0.01$), Cd and Pb ($r^2=0.601$, $P<0.01$) and Zn and Cd ($r^2=0.436$, $P<0.05$) in wet precipitation due to the effects of industrial and traffic activities on rain chemistry in urban area.

Trace elements amounts in industrial and terrific zones are higher than other sites in dry deposition

Table 2. Heavy metal concentrations in wet precipitation, dry deposition and soil collected from Ahvaz city

Elements / Station	Pb			Zn			Cr			Cd		
	Wet precipitation µg/lit	Dry deposition $mg/m^2.d$	Soil mg/kg	Wet precipitation µg/lit	Dry deposition $mg/m^2.d$	Soil mg/kg	Wet precipitation µg/lit	Dry deposition $mg/m^2.d$	Soil mg/kg	Wet precipitation µg/lit	Dry deposition $mg/m^2.d$	Soil mg/kg
S1	10.725^{b}	0.209^{b}	89.4^{a}	90.22^{a}	0.769^{a}	401.6^{a}	3.58^{b}	0.126^{ab}	65.6^{b}	0.87^{a}	0.0049^{a}	1.51^{a}
S2	62.97^{a}	0.207^{b}	84.8^{a}	89.23^{a}	0.735^{ab}	302.4^{b}	1.76^{c}	0.108^{b}	52.9^{c}	1.2^{a}	0.0023^{b}	1.27^{a}
S3	18.695^{b}	0.201^{b}	54.5^{b}	28.12^{b}	0.4055^{bc}	156.3^{c}	5.4^{a}	0.175^{a}	80.42^{a}	0.606^{b}	0.0016^{bc}	0.5^{b}
S4	17.827^{b}	0.114^{bc}	82.4^{a}	70.62^{a}	0.5315^{bc}	159.8^{c}	1.61^{c}	0.111^{b}	64.2^{b}	0.33^{c}	0.0018^{bc}	1.21^{a}
S5	4.427^{c}	0.089^{bc}	42.9^{c}	15.33^{b}	0.0861^{d}	65.6^{d}	1.7^{c}	0.0153^{c}	52.6^{c}	0.196^{c}	0.0002^{c}	0.27^{c}
S6	5.378^{c}	0.0461^{c}	43.3^{c}	22.77^{b}	0.337^{c}	144.1^{c}	1.84^{c}	0.039^{c}	50.3^{c}	0.261^{c}	0.0003^{c}	0.35^{c}
S7	16.33^{b}	0.255^{a}	75.9^{a}	61.6^{a}	0.619^{ab}	276.6^{b}	1.39^{c}	0.123^{ab}	70.2^{ab}	0.448^{c}	0.0023^{b}	0.51^{b}
S8	6.185^{c}	0.0344^{c}	40.4^{c}	21.26^{b}	0.1735^{d}	72.68^{d}	1.12^{c}	0.034^{c}	53.7^{c}	0.335^{c}	0.0007^{bc}	0.29^{c}
Min - Max	5.378 - 62.97	0.0344 - 0.255	40.4 - 89.4	15.33 - 90.22	0.0861 - 0.769	65.6 - 401.6	1.12 - 5.4	0.0153 - 0.175	50.3 - 80.42	0.196 - 1.2	0.0002 - 0.0049	0.27 - 1.51
Mean	17.817	0.14443	64.2	49.89375	0.457075	197.385	2.3	0.091413	61.24	0.53075	0.001763	0.73875
SD	19.12887	0.083908	20.9712729	31.54249	0.251116	118.2403	1.454436	0.055647	10.66815	0.346191	0.001519	0.504365

samples. Average amounts of Pb, Zn, Cr, and Cd in dry deposition samples are 0.144 mg/m^2.day, 0.457 mg/m^2.day, 0.0017 mg/m^2.day,respectively.The concentration of studied elements in dry deposition samples has shown meaningful differences in sampling points ($P<0.01$). The highest concentration of Pb was shown near flares and burning pits. In addition the most concentration levels of Zn and Cd were recorded in traffic zone. There were significant correlation between Pb and Zn (r^2=0.734, $P<0.01$), Cd and Cr (r^2=0.518, $P<0.05$), Cd and Pb (r^2=0.649, $P<0.01$), Cr and Pb (r^2=556, $P<0.05$), Zn and Cr (r^2=0.587, $P<0.05$) and Cd and Zn (r^2=0.515, $P<0.01$) in settled particle samples (Fig.3). Due to high correlation between heavy metals and high concentration levels of studied elements in traffic and industrial zones, the anthropogenic activities can lead to increasing the metal amounts. The mean concentration of Pb, Zn and Cr were 64.2 mg/kg, 197.3 mg/kg and 61.24mg/kg in surface soil samples in the study area. The highest levels of Pb and Zn in surface soil were shown in traffic and industrial stations, respectively. On the contrary the highest level of Cr was recorded near non-ferrous metal smelting factory. Therefore, it seems that the main emission sources of Cr are industrial activities. Concentration of studied elements in surface soil samples showed meaningful differences in various sampling points ($P<0.01$). Also, there were significant correlation between Pb and Zn (r^2=0.44, $P<0.05$), Cd and Pb (r^2=0.34, $P<0.05$), and Cd and Zn (r^2=0.41, $P<0.01$) in surface soil samples (Fig. 4). According to statistical analysis, there were significant correlation between Zn (r^2=0.551, $P<0.01$), Cr (r^2=0.648, $P<0.05$), and Cd (r^2=0.542, $P<0.05$) in wet precipitation and urban surface soil. Also Pb concentration in wet precipitation had weak correlation with Pb in surface soil in the study area (r^2=0.204, $P<0.05$) (Fig. 5). *Dry deposition - Urban surface soil correlation shows the following pattern* Pb (r^2=0.55, $P<0.05$), Zn (r^2=0.73, $P<0.01$) and Cd

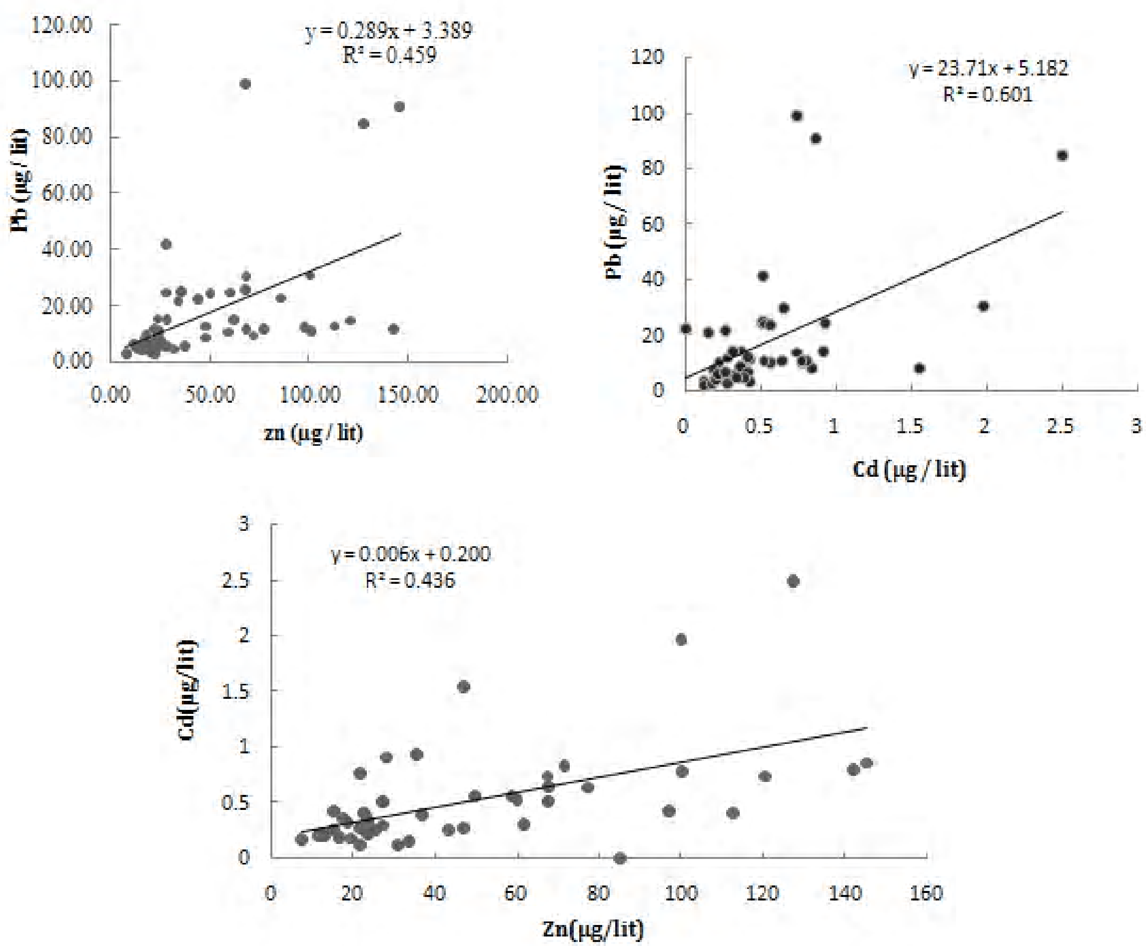

Fig. 2. Correlation of heavy metals in wet precipitation

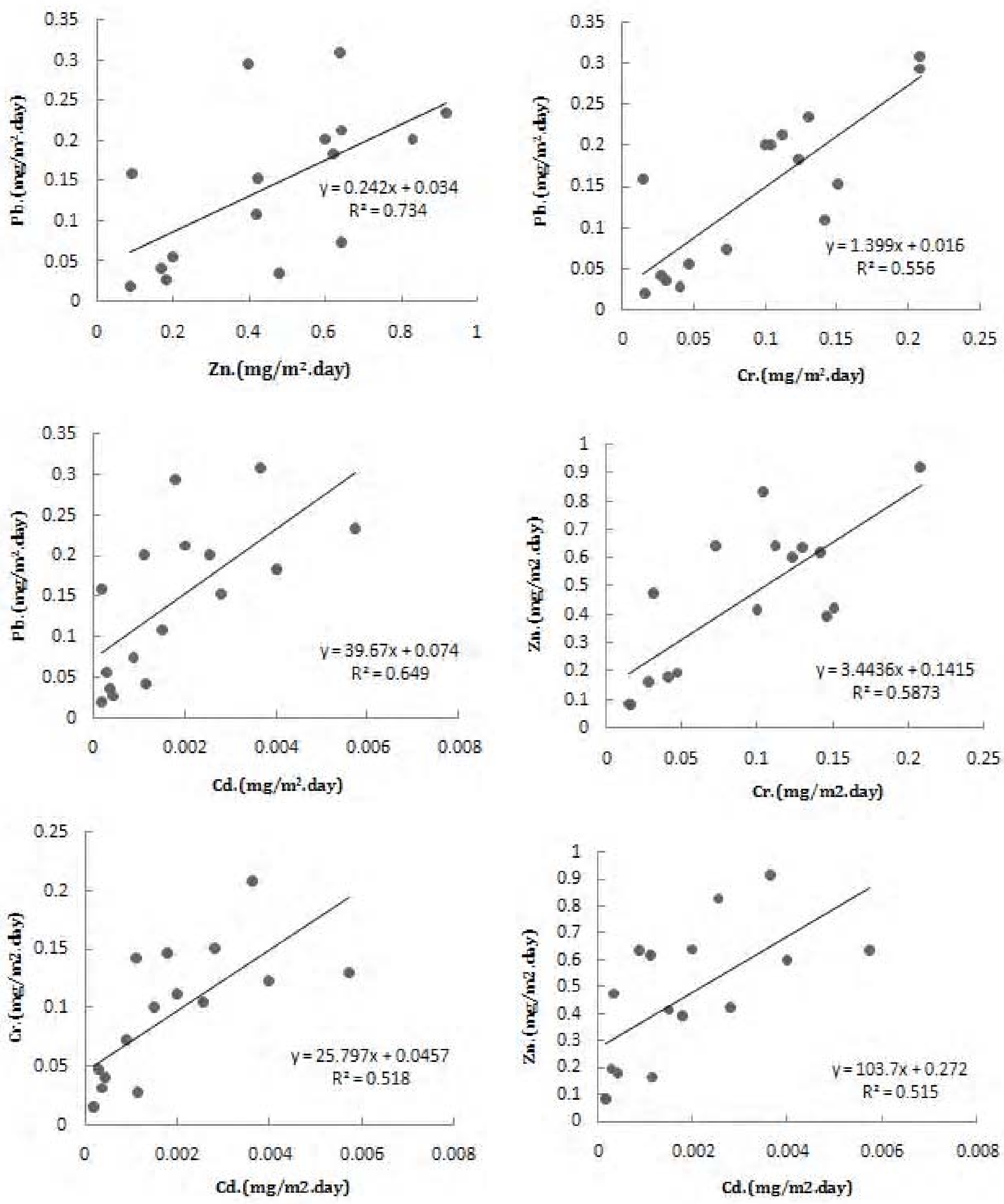

Fig. 3. Correlation of heavy metals in dry deposition

(r^2=0.645, $P<0.05$) had meaningful relationship in particle settled samples and surface soil of studied area as shown in Fig.6. Zn concentration in dry and wet deposition samples revealed meaningful correlation (r^2=0.88, $P<0.01$), while other elements had no significant correlation (Fig. 7).

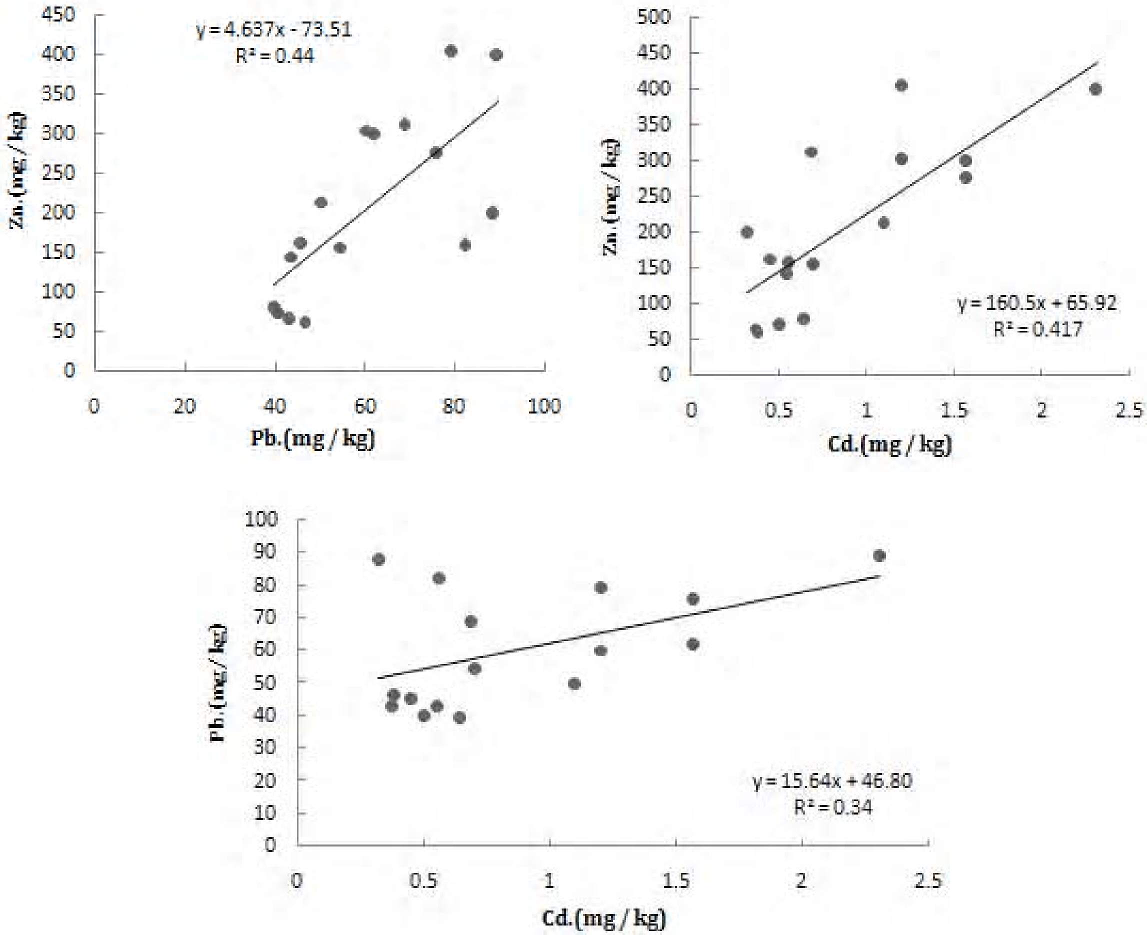

Fig. 4. Correlation of heavy metals in surface soil

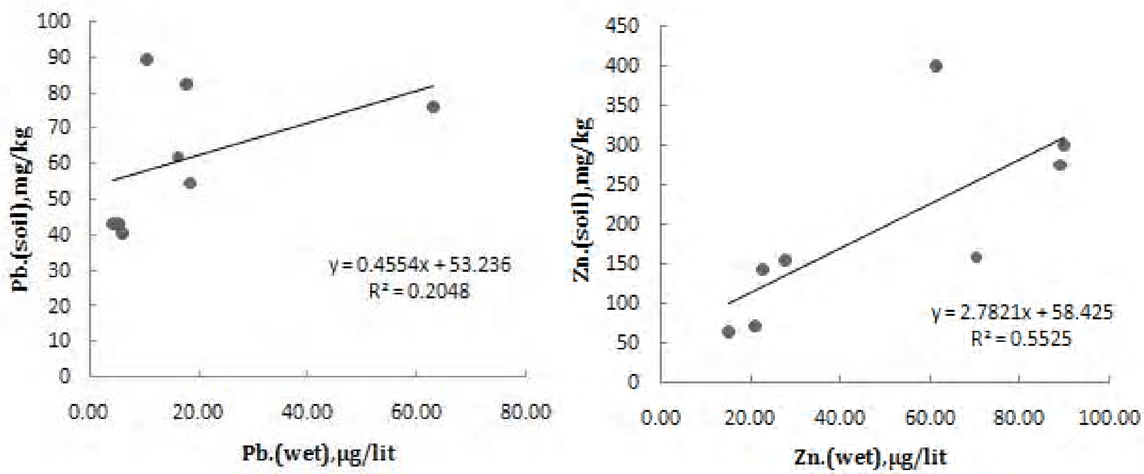

Fig. 5. Correlation of heavy metals between wet precipitation and urban surface soil

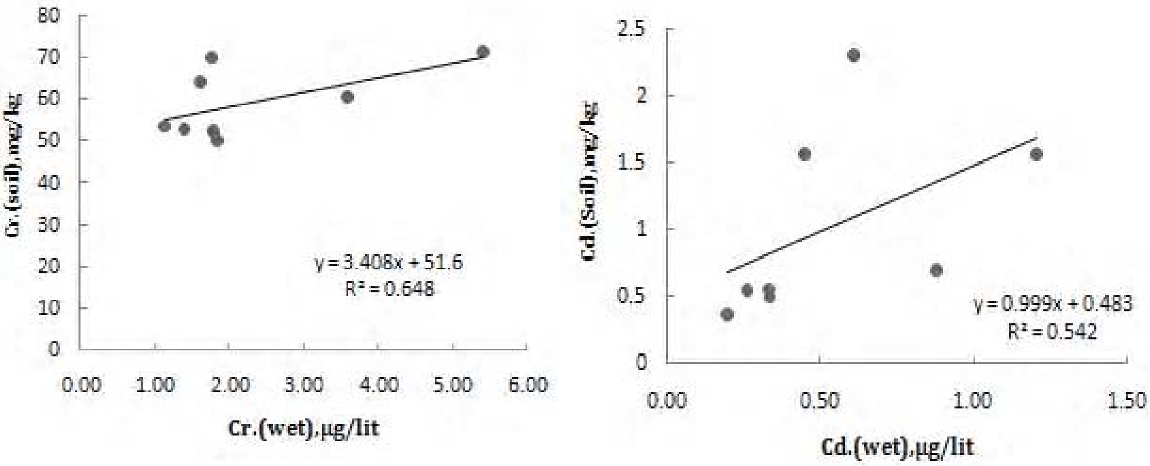

Fig. 5. Correlation of heavy metals between wet precipitation and urban surface soil

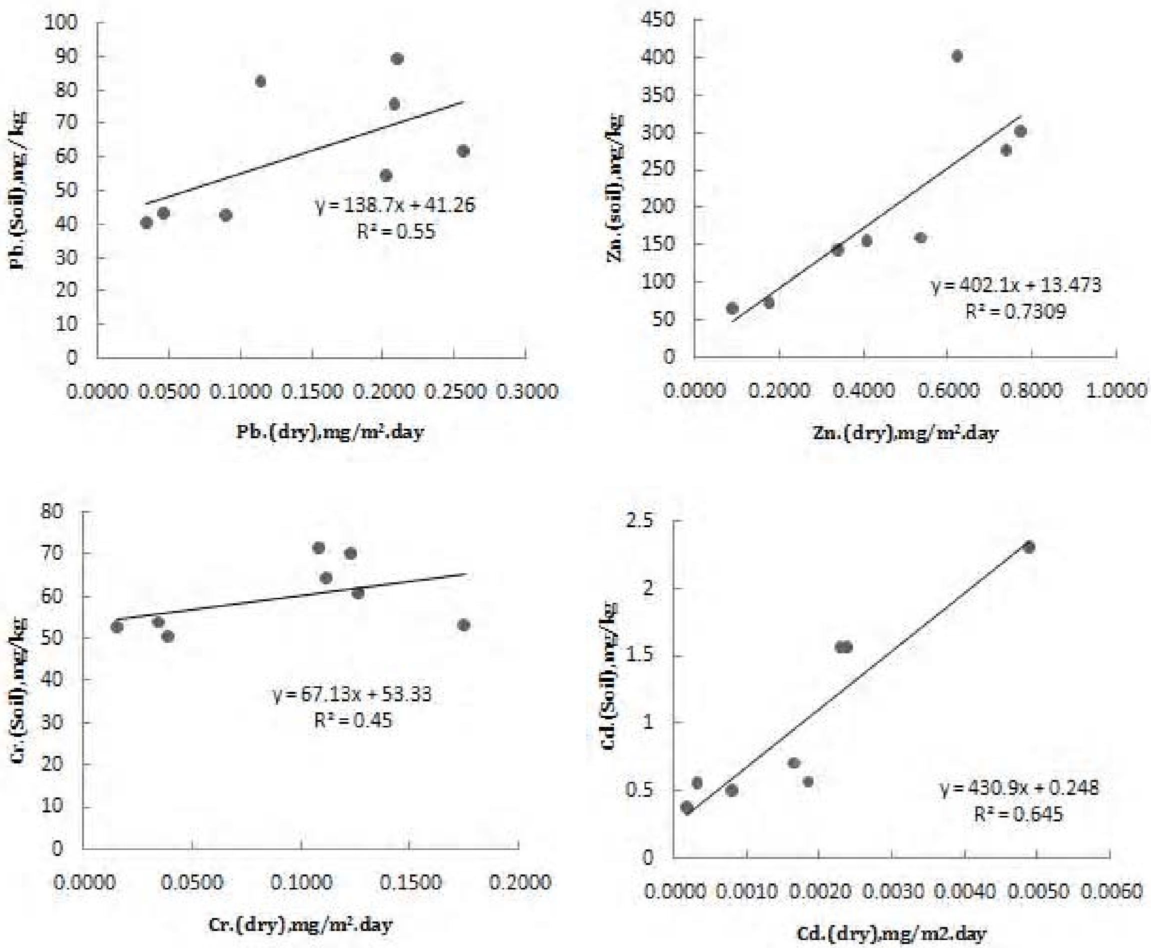

Fig. 6. Correlation of heavy metals between dry deposition and urban surface soil

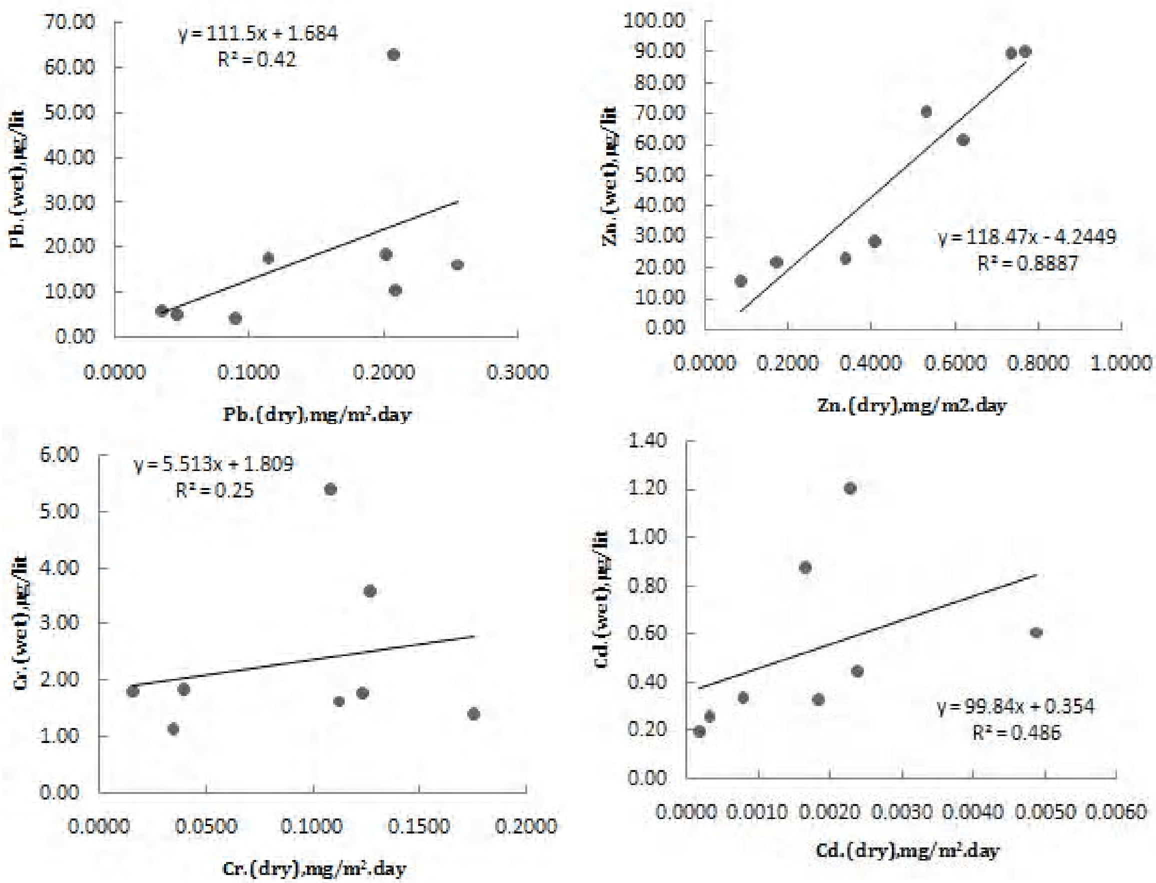

Fig. 7. Correlation of heavy metals between dry deposition and wet precipitation

Table 3. Mean of worldwide concentration of trace elements in different environments

Media	Site	Pb (µg/l)	Zn (µg/l)	Cr (µg/l)	Cd (µg/l)	Reference
wet depositio n (Precipit	Ahvaz -Iran	2.56- 91.18	7.31-127.4	0.7-7.43	0-1.97	This study
	Zanjan – Iran(14)	0.99-1.55	6.01-145	0.47-14	0.05-3	(Farahmand kia et al., 2009)
	South of Jordan(102)	0.012-0.85	2.82-110	-	0.02-0.54	Wedyan et al., 2009)
	Washington,DC, USA(70)	0.11-3.2	-	0.062-4.6	0.06-5.1	(Melaku *et al*., 2008
	Athens,Greece(58)	0.0-3.6	2.85-155	0.26-4.47	0.02-0.54	Kanellopoulou , 2001)
Dry Deposition	**Site**	**Pb** (mg/m^2.day)	**Zn** (mg/m2.day)	**Cr** (mg/m2.day)	**Cd** (mg/m2.day)	**Reference**
	Ahvaz -Iran	0.019-0.309	0.084-0.918	0.0149-0.208	0.0001-0.0057	This study
	Western Europe(41)	0.049-0.157	0.1420.540	-	0.0005-0.0035	(Deboudt et al., 2004
	Central Ontario(54)	0.032-0.956	0.022-1.317	-	0.002-0.0097	(Jeffries DS. J. & Snyder, 1981)
Soil	**Site**	**Pb** (mg/kg)	**Zn** (mg/kg)	**Cr** (mg/kg)	**Cd** (mg/kg)	**Reference**
	Ahvaz, Iran	64.2	197.38	61.24	0.73	This study
	Beijing, China	35.4	92.1	61.9	0.215	(Chen et al., 2010)
	Jeddah,Saudi Arabia(56)	47.5	222.2	53.3	-	(kadi., 2009)
	Shanghai,China(85)	70.69	301.4	107.9	0.52	(shi et al., 2008)
	Luoyang, China(38)	65.92	215.75	71.42	1.71	(Lu et al., 2007)
	Background values of the world	35	90	70	0.35	(CNEMC, 1990)

CONCLUSION

Comparison between trace elements concentrations in surface soil and dry and wet deposition in other sites of the world and this study are presented in Table 3. As this table shows, Pb and Cr levels of wet samples in Ahvaz city were higher than other studies in the world. Also, Pb and Zn concentration in dry deposition were very higher than other sites of the world. According to soil sample results, amounts of trace elements concentration in the studied area were higher than literature cited and also Pb, Zn and Cd showed higher levels than background values of the world. It seems that the main reason of high level concentration of studied elements in Ahvaz city is related to a various industrial emission sources activities such as non-ferrous metal smelting, fossil fuel combustion, pit burning and gas flaring around this area. As a results, it should be mentioned that general pattern of elemental concentrations in dry deposition, wet precipitation and urban surface soil decrease as Zn>Pb>Cr>Cd. In addition, the concentrations of studied elements in industrial and traffic zones were more than other sites in this area. Totally, results indicate high contamination levels of heavy metals in urban soils, wet and dry deposition that have been significantly impacted from anthropogenic activities.

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