

## Characterization and metals fractionation of street dust samples from Tehran, Iran

Salmanzadeh, M.<sup>1</sup>, Saeedi, M.<sup>2,3\*</sup>, Li, L.Y.<sup>3</sup> and Nabi-Bidhendi, Gh.<sup>4</sup>

<sup>1</sup>Graduate Student, School of Civil Engineering, Iran University of Science and Technology, Iran

<sup>2</sup>School of Civil Engineering, Iran University of Science and Technology, Iran

<sup>3</sup>Department of Civil Engineering, The University of British Columbia, Canada

<sup>4</sup>Faculty of Environment, University of Tehran, Iran

Received 18 June 2014;

Revised 4 Sep. 2014;

Accepted 5 Nov. 2014

**ABSTRACT:** Fifty street dust samples were collected from Southern and Eastern parts of Tehran, the capital of Iran. Samples were collected during summer under dry and stable weather conditions. Total concentrations of copper (Cu), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), iron (Fe), manganese (Mn) and lithium (Li) were determined. Ten samples were then selected for characterization, metals fractionation and single stage extraction studies. X-ray diffraction (XRD) and X-ray fluorescence (XRF) were utilized to study the crystalline forms of metals and chemical compositions. In addition, sequential and single extraction procedures were used to determine the concentrations of six heavy metals (i.e. Cu, Cd, Pb, Cr, Ni and Zn), and also the mobility and bioavailability of elements. The risk assessment code (RAC) and  $I_{\text{POLL}}$  were employed for the risk assessment and pollution intensity of metals, respectively. Results showed that the single extraction procedure could be used to estimate the total concentrations of most metals as an appropriate alternative for total digestion. The mobility and potential availability of metals in Tehran street dust followed the order of  $\text{Cd} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Cr}$ . The risk assessment code results showed high risk for Pb, Cd and Zn and low-medium risk for Ni, Cr and Cu, and correlated positively with  $I_{\text{POLL}}$  result.

**Key words:** Heavy metals, Risk, Sequential extraction, Single extraction,  $I_{\text{POLL}}$ , Dust, Tehran

### INTRODUCTION

Street dust is one of the sources of heavy metals that may originate from either anthropogenic such as high vehicle traffic volumes, building materials, fuel burnings, corrosion of different parts of vehicle (e.g. tires, batteries, and alloys) or natural sources such as local soil. There are many published studies about the concentrations of heavy metals in street dust of developed countries; however inadequate researches have been conducted in developing countries. Most studies were performed on total concentration of heavy metals without adequate focus on chemical fractions. Some studies on the mobility and different geochemical phases of heavy metals and their effects on the urban environment have been conducted (Banerjee, 2003; Kubova *et al.*, 2008; Rao *et al.*, 2010). In this context, various extraction methods such as Tessier's sequential extraction (Tessier *et al.*, 1979; Li *et al.*, 2001; Banerjee, 2003; Barreto *et al.*, 2004; Rath *et al.*, 2009), the European Community Bureau of References (BCR) three-step sequential extraction (Tokalioglu *et al.*, 2003; Kartal *et al.*, 2006; Kubova *et al.*, 2008; Rao *et al.*, 2010) were

carried out to assess the bioavailability of metals in soil, sediments and street dust samples. A few researchers also used single extraction procedure by different reagents (e.g. 0.5M HCl or EDTA) as leach tests (Garrabrants *et al.*, 2000; Saeedi *et al.*, 2009). Single extraction methods are more simple and easier to operate in comparison to total digestion.

Barreto *et al.*, (2004) employed Tessier and 0.1 M HCl extraction methods to estimate the bioavailability of metals (Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) in sediments. The metal concentrations in the first four fractions of sequential extraction procedure were compared with results of HCl extraction. Pb, Ni, Al, Cr and Fe showed more contents in sequential extraction. For Co the results of both extraction methods were similar but the concentrations of Cu and Mn in HCl extraction method were more than those of sequential extraction. Gibson and Farmer (1984) used six-step sequential procedure and a single extraction method (0.07 M HCl) to evaluate the chemical partitioning of Pb, Zn, Cu and Cd from urban street dirt. The comparison of metal concentrations in the first three

\*Corresponding author E-mail: msaeedi@iust.ac.ir

sequential fractions and 0.07 M HCl showed that Zn, Cd and Cu were more released in HCl, while Pb had more concentration in sequential extraction.

Most studies about the chemical fractionation of metals have been performed on sediments and soils (Rath *et al.*, 2009; Rao *et al.*, 2010; Wu *et al.*, 2011); therefore studies on the chemical fractionation of heavy metals in street dusts can yield useful results on interpretation of their pollution and risks in dust. In the present study, after determination of the total concentration of metals in 50 street dust samples, chemical and mineralogical characterizations of ten samples were examined, in summer 2011. Samples were also subjected to chemical portioning of six metals (Cu, Cd, Pb, Cr, Ni and Zn) by using Tessier's extraction method and the results of single, total and Tessier's extraction method were compared.

## MATERIALS & METHODS

Tehran, is the biggest and the most populated city in Iran. It is also among the biggest and contaminated cities around the world. Population and vehicle traffic in Tehran have been increasing continuously during the last decades. Tehran covers an area of 730 km<sup>2</sup> with a population density of about 11,000 person km<sup>-2</sup>. It is the most densely populated area in Iran and one of the highest between the Middle Eastern countries (SCI, 2011). Precipitations are usually occurred during fall and winter, thus samples were collected in August 2010, the driest month of the year. Fifty sampling sites were chosen from eastern and southern parts of Tehran (Fig. 1).

At every sampling site, about 500 g dust composite sample was collected using a broom and suction from six points on the sides of roads and pavements. Samples were stored in closed polyethylene bags at temperature < 4°C. Samples were air dried at room temperature and then screened through # 10, 35, 60 and 230 (63µm) sieving sets. Particles smaller than 63 µm were subjected to chemical analysis. Samples of all 50 sites were analyzed for total metal contents (Cu, Cd, Pb, Cr, Ni, Zn, Fe, Mn and Li) according to USEPA 3050B (USEP, 1996) and loss on ignition (LOI). Total digestion results provide data only about heavy metal contents but detailed information about bioavailability and different fractions of metals in dust samples can be obtained from sequential extraction. Ten samples (from sites 1, 9, 22, 27, 28, 32, 33, 37, 46 and 50) were selected randomly for more detailed studies (chemical fractionation, single extraction and X-ray analyses). Chemical and mineralogical composition of ten selected samples were determined by XRF (PHILIPS PW1480) and XRD (PHILIPS PW1800). Metal concentrations were determined using Atomic Absorption Spectrometer (Buck Scientific-210 VGP) equipped with Deuterium lamp background correction according to USEPA 7000s series methods (USEPA, 1992). Five-step sequential chemical extraction method was performed on ten selected dust samples according to Tessier *et al.*, (1979):

1. Exchangeable: approximately 1.0 g dust sample was extracted at room temperature for 1 h with 10 ml of 1.0 M MgCl<sub>2</sub> (pH 7.0) with continuous agitation.

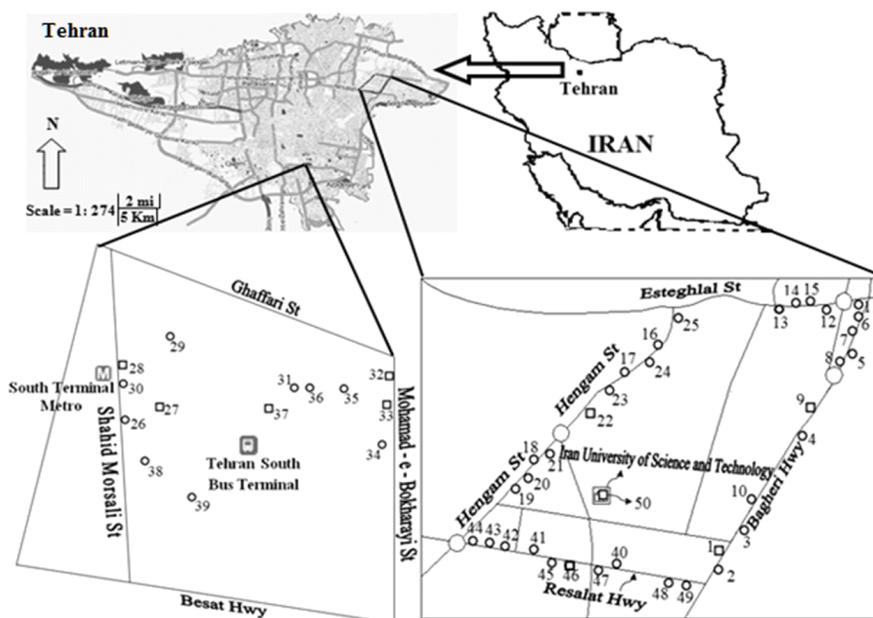


Fig. 1. Street dust samples collection sites; (o) Samples for total digestion (□) Samples for total digestion, single and sequential extraction and X-ray analyzes

**Table 1. Classifications of risk assessment code (RAC) (Perin *et al.*, 1985)**

| Risk classification | Metals in carbonate and exchangeable fractions (%) |
|---------------------|--|
| No risk             | <1   |
| Low risk            | 1-10   |
| Medium risk         | 10-30  |
| High risk           | 30-50  |
| Very high risk      | >50  |

**Table 2. Contamination classes according to  $I_{POLL}$  index (Karbassi *et al.*, 2008)**

| $I_{POLL}$          | Pollution intensity |
|---------------------|---------------------|
| Extremely polluted  | > 5                 |
| Strongly polluted   | 4-5                 |
| High polluted       | 3-4                 |
| Moderately polluted | 2-3                 |
| Low polluted        | 1-2                 |
| Unpolluted          | < 0-1               |

**Table 3. Metals (ppm) and LOI contents in street dust of Tehran (n=50) and other selected cities**

| Contaminant <sup>a</sup>   | Cu   | Cd   | Pb   | Cr   | Ni   | Mn   | Zn   | Fe    | Li   | LOI  |
|--|------|------|------|------|------|------|------|-------|------|------|
| Mean (this study)  | 222  | 10.7 | 254  | 33.3 | 34.5 | 1212 | 863  | 47763 | 9.3  | 14.8 |
| Min (this study)   | 58.6 | 9.9  | 64.7 | 15.2 | 12.6 | 721  | 399  | 26602 | 3.4  | 8.2  |
| Max (this study)   | 778  | 11.1 | 764  | 58.0 | 73.0 | 2231 | 1935 | 96427 | 16.8 | 22.0 |
| Median (this study)  | 201  | 10.7 | 188  | 31.2 | 30.8 | 1168 | 790  | 45013 | 8.9  | 14.6 |
| St. Dev. (this study)  | 149  | 0.2  | 158  | 11.3 | 15.1 | 324  | 280  | 12729 | 2.8  | 3.2  |
| Birmingham <sup>b</sup>  | 466  | 1.6  | 48.0 |      | 41.1 |      | 534  |       |      |      |
| Kuala Lumpur <sup>c</sup>  | 35.5 | 2.9  | 2466 |      |      | 153  | 344  | 1790  |      |      |
| London <sup>d</sup>  | 155  | 3.5  | 1030 |      |      |      | 680  | 26000 |      |      |
| Mutah <sup>e</sup>   | 69.0 | 1.3  | 143  |      | 1.7  | 136  | 132  | 5362  |      |      |
| Madrid <sup>f</sup>  | 188  |      | 1927 | 61.0 | 44.0 | 362  | 476  | 19300 |      |      |
| Oslo <sup>f</sup>  | 123  | 1.4  | 180  |      | 41.0 | 833  | 412  | 51452 |      |      |
| Ottawa <sup>g</sup>  | 188  | 0.6  | 68.0 | 59.0 | 19.0 | 534  | 184  | 25660 | 9.0  |      |
| Kavala <sup>h</sup>  | 172  | 0.2  | 386  | 232  | 67.9 |      | 354  |       |      |      |
| Earth Crust Content <sup>i</sup>                                 | 50   | 0.2  | 14   | 100  | 80   | 950  | 75   | 41000 | 20   | ---  |
| Background values of heavy metals in soils of China <sup>j</sup> | 26.7 | 0.1  | 19.4 | 49.3 | 26.6 | 688  | 68.8 | ---   | ---  | ---  |

2. Bound to carbonates: The residue obtained from first step was leached at room temperature with 10 ml of 1.0 M sodium acetate adjusted to pH 5.0 with acetic acid. The mixture was shaken for 5 h.

3. Bound to Fe–Mn oxides: The residue obtained from second step was refluxed at 100°C with 20 ml of 0.04 M NH<sub>2</sub>OH HCl in 25% (v/v) acetic acid for 6 h.

4. Bound to organic matter: 3 ml of 0.02 M HNO<sub>3</sub> and 5 ml of 30% H<sub>2</sub>O<sub>2</sub> were added to the residue obtained from third step and pH adjusted to 2.0 with HNO<sub>3</sub>. The mixture was refluxed at 100°C for 2 h. A second 3 ml aliquot of 30% H<sub>2</sub>O<sub>2</sub> (pH 2 with HNO<sub>3</sub>) was then added and the sample was again refluxed for 3 h. After cooling, 5 ml of 3.2 M ammonium acetate in 20% (v/v) HNO<sub>3</sub> was added. The sample was diluted to 100 ml and stirred continuously for 30 min.

5. Residual: The residue obtained from fourth step was digested according to USEPA 3050B (USEPA, 1996). Extracts then analyzed for six heavy metals (Cu, Cd, Pb, Cr, Ni and Zn).

Different materials such as EDTA, DTPA, CaCl<sub>2</sub>, NaNO<sub>3</sub>, and HCl have been used for single extraction of metals from soil, dust and sediment (Rao *et al.*, 2010;

Wu *et al.*, 2011). In this study 0.5 M HCl single extraction was applied on ten selected samples according to Kubova *et al.*, (2008).

All dust and blank samples were analyzed in duplicates for quality assurance/quality control of laboratory analyzes. MESS-3 from Institute for National Measurement Standards, National Research Council of Canada (NRC) was used as the standard sediment sample for quality control. The measured concentrations of metals were within the published metal contents given by NRC (NRC, 2000).

Risk assessment code (RAC) was introduced by Perin *et al.*, (1985) according to equation (1) to assess the availability of metals in sediments, and then has been used in other studies to estimate the metal availability in soil (Mashal *et al.*, 2009; Liu *et al.*, 2011; Miretzky *et al.*, 2011).

$$RAC = f_1 + f_2 \quad (1)$$

Where  $f_1$  and  $f_2$  show the metal concentrations in the first and second fractions of Tessier sequential extraction method. In the present study, RAC was used to assess the risk of Cu, Pb, Cd, Cr, Ni and Zn in street dust of Tehran. Different RAC categories are illustrated in Table 1.

Karbassi *et al.*, (2008) introduced  $I_{\text{POLL}}$  index for metal pollution assessment in water and sediment (equation 2). In this research, this method has been used to assess the pollution of metal in street dust.

$$I_{\text{POLL}} = \text{Log}_2(B_c/L_p) \quad (2)$$

Where  $I_{\text{POLL}}$  is the pollution intensity,  $B_c$  shows the bulk concentration and  $L_p$  shows the lithogenous portion from the results of sequential extraction method.

## RESULTS & DISCUSSION

Concentrations of heavy metals in street dust samples of Tehran comparing to some other selected cities around the world are presented in Table 3.

<sup>a</sup>metals are in ppm and LOI is in %. <sup>b</sup>Charlesworth *et al.* (2003), <sup>c</sup>Ramlan and Badri (1989), <sup>d</sup>Schwar *et al.* (1988), <sup>e</sup>Manasreh (2010), <sup>f</sup>De Miguel *et al.* (1997), <sup>g</sup>Rasmussen *et al.* (2001), <sup>h</sup>Christoforidis and Stamatis (2009), <sup>i</sup>(Karbassi *et al.* 2005; Niencheski *et al.* 2002), <sup>j</sup>CEPA and CGSEM (1990).

According to Table 3, the concentrations of Cu, Cd, Pb and Zn were substantially more than those of the earth crust. In case of Cu, Cd, Pb and Zn, even the minimum contents detected in samples exceeded those of the crust, while maximum values were much greater. While, mean contents of Cr and Ni were less than half of corresponding earth crust values, Cd, Cu and Zn concentration in Tehran dust were more than those of other cities even more than those of major cities in developing countries such as Mutah in Jordan, Kuala Lumpur in Malaysia, and Kavala in Greece. Concentrations of all metals except for Cr were much more than the background amount of metals in Chinese soil. Among cities of developed countries London dust had less amount of metal than Tehran (except for Pb). The largest amounts of pollutants except for Cd were detected in Baghery highway samples (one of the high traffic loaded places in Tehran). It seems that vehicular emissions such as fossil fuel combustion, lubricants and corrosion of vehicle covers were the most probable sources of such pollutants. Cd concentration was quite high and almost constant in sampling locations.

Table 4. Street dust characterization from XRD analysis

| Sample | Major components                  | Minor components                                 | Trace components |
|--------|-----------------------------------|--|------------------|
| 1      | Quartz, Calcite, Albite, Dolomite | Orthoclase, Chlorite, Montmorillonite            | ----             |
| 9      | Quartz, Calcite, Albite           | Orthoclase, Chlorite, Dolomite                   | Muscovite-illite |
| 22     | Quartz, Calcite, Albite           | Orthoclase, Chlorite, illite                     | Dolomite         |
| 27     | Quartz, Calcite, Albite           | Orthoclase, Chlorite, Dolomite, Muscovite-illite | ----             |
| 28     | Quartz, Calcite, Albite           | Orthoclase, Chlorite, Dolomite, Muscovite-illite | ----             |
| 32     | Quartz, Calcite, Albite           | Orthoclase, Dolomite, Muscovite-illite           | ----             |
| 33     | Quartz, Calcite, Albite           | Orthoclase, Chlorite, Muscovite-illite           | ----             |
| 37     | Quartz, Calcite, Albite           | Orthoclase, Chlorite, Dolomite, Montmorillonite  | ----             |
| 46     | Quartz, Calcite, Albite           | Orthoclase, Dolomite, Muscovite-illite           | ----             |
| 50     | Quartz, Calcite, Albite           | Orthoclase, Dolomite, Muscovite-illite, Chlorite | ----             |

Table 5. Chemical composition of Tehran street dust from XRF analysis

| Chemical (%)   | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | MgO | TiO <sub>2</sub> | MnO  | P <sub>2</sub> O <sub>5</sub> | SO <sub>3</sub> |
|----------------|------------------|--------------------------------|--------------------------------|------|-------------------|------------------|-----|------------------|------|-------------------------------|-----------------|
| Station number |                  |                                |                                |      |                   |                  |     |                  |      |                               |                 |
| S-1            | 44.6             | 8.1                            | 5.6                            | 13.0 | 1.1               | 1.9              | 2.5 | 0.7              | 0.1  | 0.3                           | 2.1             |
| S-9            | 41.5             | 7.5                            | 5.7                            | 14.6 | 1.3               | 2.0              | 2.2 | 0.8              | 0.1  | 0.3                           | 2.2             |
| S-22           | 45.9             | 8.5                            | 5.7                            | 12.7 | 1.1               | 2.0              | 2.4 | 0.6              | 0.1  | 0.3                           | 1.5             |
| S-27           | 42.6             | 8.3                            | 5.0                            | 14.6 | 1.1               | 2.2              | 2.8 | 0.6              | 0.1  | 0.3                           | 1.3             |
| S-28           | 40.1             | 8.4                            | 5.2                            | 14.0 | 1.2               | 2.4              | 2.9 | 0.5              | 0.1  | 0.4                           | 2.5             |
| S-32           | 44.2             | 7.9                            | 5.4                            | 13.0 | 1.2               | 2.0              | 2.3 | 0.6              | 0.1  | 0.4                           | 2.4             |
| S-33           | 46.1             | 10.2                           | 5.5                            | 11.9 | 1.0               | 2.2              | 3.2 | 0.6              | 0.1  | 0.4                           | 0.9             |
| S-37           | 46.2             | 7.8                            | 5.3                            | 12.0 | 1.0               | 2.1              | 2.3 | 0.5              | 0.1  | 0.4                           | 2.2             |
| S-46           | 42.5             | 7.8                            | 5.7                            | 13.0 | 1.2               | 2.1              | 2.5 | 0.6              | 0.1  | 0.4                           | 2.0             |
| S-50           | 48.7             | 8.2                            | 4.6                            | 14.9 | 1.3               | 1.9              | 2.5 | 0.6              | 0.1  | 0.3                           | 0.7             |
| Mean           | 44.2             | 8.3                            | 5.4                            | 13.4 | 1.1               | 2.1              | 2.5 | 0.6              | 0.1  | 0.3                           | 1.8             |
| Min            | 40.1             | 7.5                            | 4.6                            | 11.9 | 1.0               | 1.9              | 2.2 | 0.5              | 0.1  | 0.3                           | 0.7             |
| Max            | 48.7             | 10.2                           | 5.7                            | 14.9 | 1.3               | 2.4              | 3.2 | 0.8              | 0.1  | 0.4                           | 2.5             |
| St. Dev.       | 2.6              | 0.7                            | 0.4                            | 1.1  | 0.1               | 0.1              | 0.3 | 0.07             | 0.01 | 0.04                          | 0.6             |

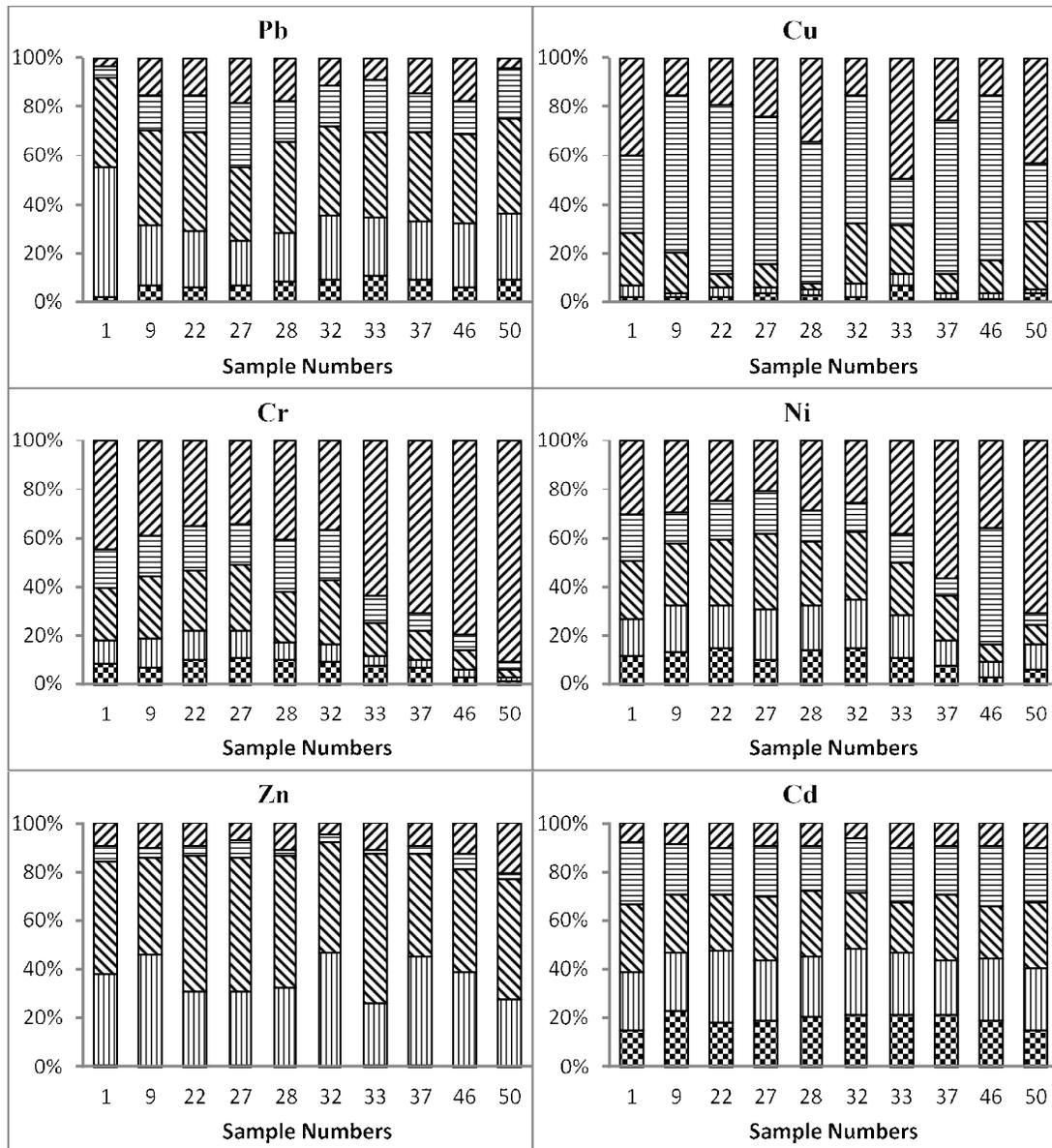


Fig. 2. Heavy metals fractionation in ten street dust samples

According to the results of particle size analyze, on average the size of %12 of dust particles was lower than  $63 \mu\text{m}$  and according to USDA were silt and clay (subjected particles to chemical analyzes). Silt and clay have high amount of organic matter (Das, 2009); therefore the considerable amount of LOI was expected in dust samples (Table 3). The high surface area of smaller particles (i.e.  $\phi < 63 \mu\text{m}$ ) and high contents of LOI can lead to high sorption capacity of dust for metals in the study area. XRD analyzes results showed that Quartz ( $\text{SiO}_2$ ), Calcite ( $\text{CaCO}_3$ ) and Albite ( $\text{NaAlSi}_3\text{O}_8$ ) were major phases of street dust samples (Table 4). Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) was among minor components of dust in Tehran, however in sample 1

dolomite was the major phase. Orthoclase ( $\text{KAlSi}_3\text{O}_8$ ), Chlorite ( $(\text{Mg,Fe})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ ), Montmorillonite ( $\text{CaO} \cdot 2(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ ), Muscovite-illite ( $\text{KA}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$ ) were minor or trace components of street dust samples. The minerals of different phases particularly major phases in dust samples were somehow similar to each other in all 10 sampling stations indicating that they should majorly be originated from same sources. High amounts of calcite and quartz were evidence of detrital sources for street dust samples of Tehran (Zarasvandi, 2009) such as corrosion of street surface materials (Harrison *et al.*, 1981). XRF results are demonstrated in Table 5 and showed that the dominant component of dust samples

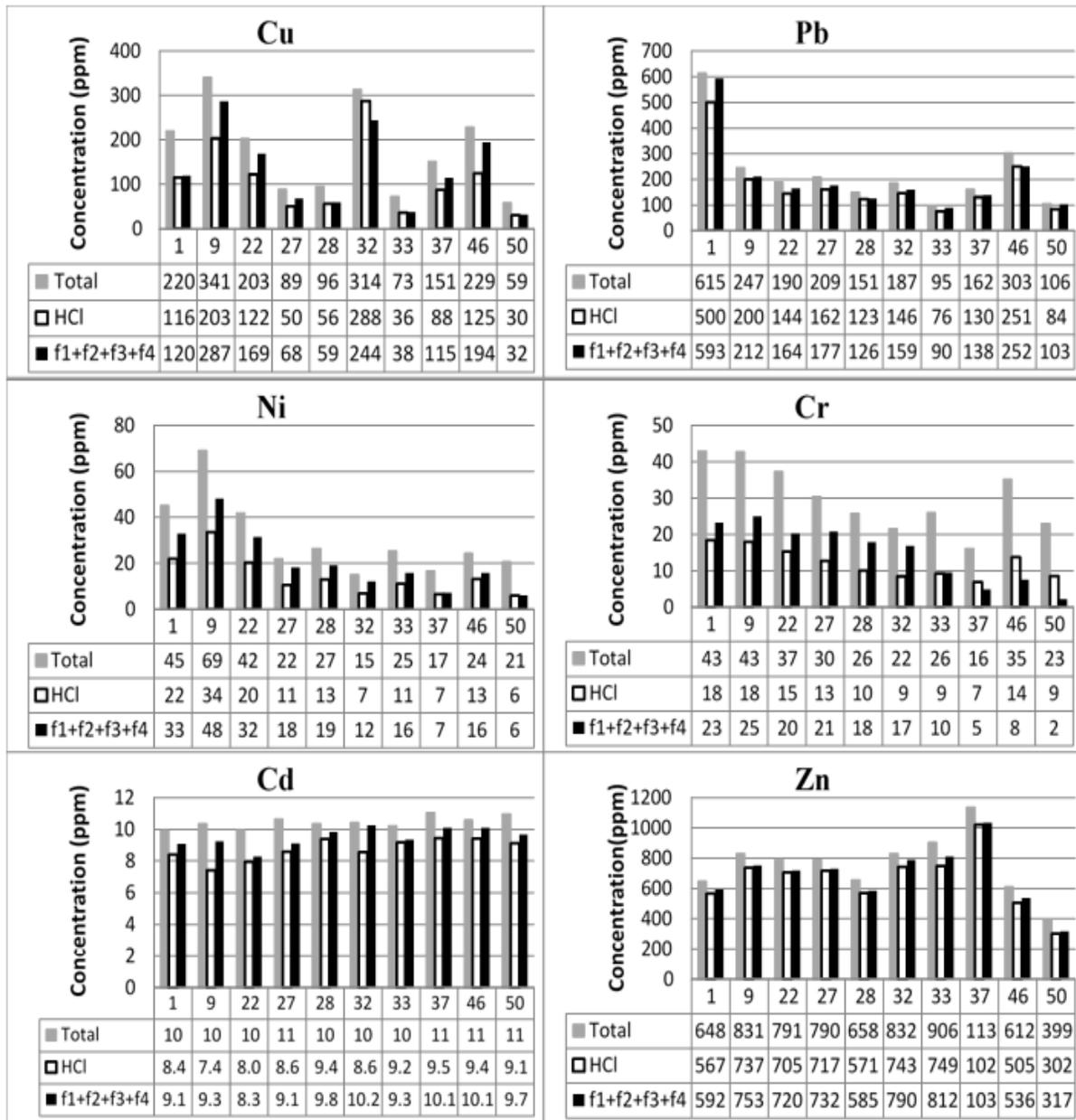


Fig. 3. Concentrations of heavy metals in three extraction methods (ppm)

was  $\text{SiO}_2$ , which is mainly from quartz (Soltan *et al.*, 2005). The concentration of quartz was shown to be mostly greater than other constituents in XRD analysis. CaO was the second dominant component in street dust samples, which originates mainly from calcite (the second major constituent of street dust samples from XRD analysis). The third major component of XRF analyze was  $\text{Al}_2\text{O}_3$ . Albite and some other minor and trace components from XRD analyzes contain Aluminum. The lowest amount of  $\text{Fe}_2\text{O}_3$  was observed in sample No. 50 from IUST campus with much lower traffic loads around. According to XRD results,

potassium and magnesium were the components of minor or trace phases of street dusts (e.g. Muscovite-illite, Orthoclase, Chlorite, Montmorillonite and dolomite contain K and Mg), therefore lower amount of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and MgO in samples was expected. Results of five step sequential extraction in ten selected samples of Tehran dust are depicted in Fig. 2. Chemical association of Pb in street dust samples is as follows: Fe-Mn oxide > carbonate > organic > residual > exchangeable. 63% of Pb was associated with Fe-Mn oxide and carbonate fractions. Similar results acquired in previous research on street dusts (Harrison *et al.*,

1981; Gibson and Farmer, 1984; Fergusson and Kim, 1991; Li *et al.*, 2001). Fe-Mn oxides are effective scavenger for Pb (Tessier *et al.*, 1979; Rath *et al.*, 2009) and the dominant association of this element with Fe-Mn bound may be a result of Pb adsorption onto colloids of Fe-Mn (Banerjee, 2003; Rath *et al.*, 2009). The second important fraction of this element was carbonate because of lead carbonate formations (McAlister *et al.*, 2006). High percentage (87%) contribution of Pb in non-residual fractions is an indicator of anthropogenic source for this metal in street dust such as traffic (trucks and big vehicles are operated with gasoil in Iran which consist of considerable amounts of Pb). Sample 1 showed the highest non-residual content of Pb among all ten samples, which was located in Baghery highway, a highly traffic loaded highway in Tehran and confirms the contribution of traffic on the contamination of study area. The average fractionation pattern of Cu showed the following order: organic > residual > Fe-Mn oxide > carbonate > exchangeable and about 60% of Cu was associated with organic phase. Similar results were obtained by Harrison *et al.*, (1981), Gibson and Farmer (1984), Fergusson and Ryan (1984), Fergusson and Kim (1991), Li *et al.*, (2001) and Banerjee (2003) in street dusts. Adamo *et al.*, (1996) also demonstrated strong correlation between Cu and organic matter in soil sample. Because of Cu incorporation in clay minerals, residual fraction was an important phase of fractionation pattern (Pickering, 1986). The second non-residual dominant fraction for Cu was Fe-Mn oxide bounds (%16). According to McLaren and Crawford (1973), because of sorption capacity and surface area of Fe-Mn, Fe<sup>2+</sup> in Fe-Mn combination can be replaced by Cu (Taylor, 1965; Banerjee, 2003). On average 71% of Cu was associated with non-residual fraction indicating the high risk and mobility of this metal and anthropogenic origins such as erosion of vehicle covers for copper in Tehran dust. The average chemical association of Cr in street dust samples showed the following order: residual >> Fe-Mn oxide > organic > exchangeable > carbonate. Averagely 54% of Cr was bound to residual fraction. This result could be due to detrital sources for this element (Rath *et al.*, 2009), joining to silicate lattice (Tokalioglu and Kartal, 2006), tied to minerals and resistant components or tight organic components (Tessier *et al.*, 1979). Similar results were obtained in previous studies on street dusts (Banerjee, 2003; Tokalioglu *et al.*, 2003; Tokalioglu and Kartal, 2006). Because of the low percentage of non-residual fractions of this metal, Cr was not a highly available element in this study. 40% to 90% of Cr in dust samples was associated with residual fraction and also according

to total digestion results the concentration of Cr was lower than earth crust indicating that in addition to anthropogenic sources Cr may have natural origins. Sample 50 showed the highest concentration of Cr in residual fraction among all ten samples. This sampling station is located at IUST campus, with the lowest traffic volume (the only significant difference between this point and other stations) in comparison to other sampling locations, and thus the main anthropogenic source of Cr might be related to vehicles traffic.

The average fractionation pattern of Ni in street dust samples showed this order: residual > Fe-Mn oxide > organic ~ carbonate > exchangeable. The percentage of non-residual (63% on average) fractions demonstrated a combination of some natural and some anthropogenic (dominant) sources for this element. Fossil fuel combustion and vehicle oils are anthropogenic sources of Ni. Similar results were obtained in other studies on street dust samples (Banerjee, 2003). Fe-Mn oxide was the second dominant fraction of Ni and confirmed that Fe-Mn oxides were efficient scavengers for this element (Tessier *et al.*, 1979). A combination of anthropogenic and natural origins could be considered for Ni in dust samples of Tehran. Same as Cr, the highest residual content of Ni was detected in sample 50. This may indicate that the main anthropogenic source of Ni could also be related to traffic in Tehran. Different fractions of Zn showed the following order: Fe-Mn oxide > carbonate > residual >> organic > exchangeable. The same results were obtained in previous studies (Harrison *et al.*, 1981; Gibson and Farmer, 1984; Fergusson and Kim, 1991; Banerjee, 2003) on street dusts. The main fraction of Zn was Fe-Mn oxide, maybe because of solidity of Zn oxides (Fergusson and Ryan, 1984; Banerjee, 2003) or Fe-Mn oxide might act as scavengers for this element (Rath *et al.*, 2009). Carbonate phase was an important fraction, probably due to the effect of calcite on street dust samples (Li *et al.*, 2001). CaCO<sub>3</sub> may adsorb Zn and form CaCO<sub>3</sub>.ZnCO<sub>3</sub> as a salt (Banerjee, 2003). Averagely the proportion of Zn in non-residual fractions was 90%, represented mobility and anthropogenic resources for this metal such as erosion of alloys in vehicle components and car covers (Jiries, 2003; Wei *et al.*, 2010).

The average chemical associations of Cd in Tehran street dusts samples showed the following order: Fe-Mn oxide ~ carbonate > organic > exchangeable > residual. Similar results were obtained in previous studies on street dusts (Fergusson and Kim, 1991; Li *et al.*, 2001). Carbonate

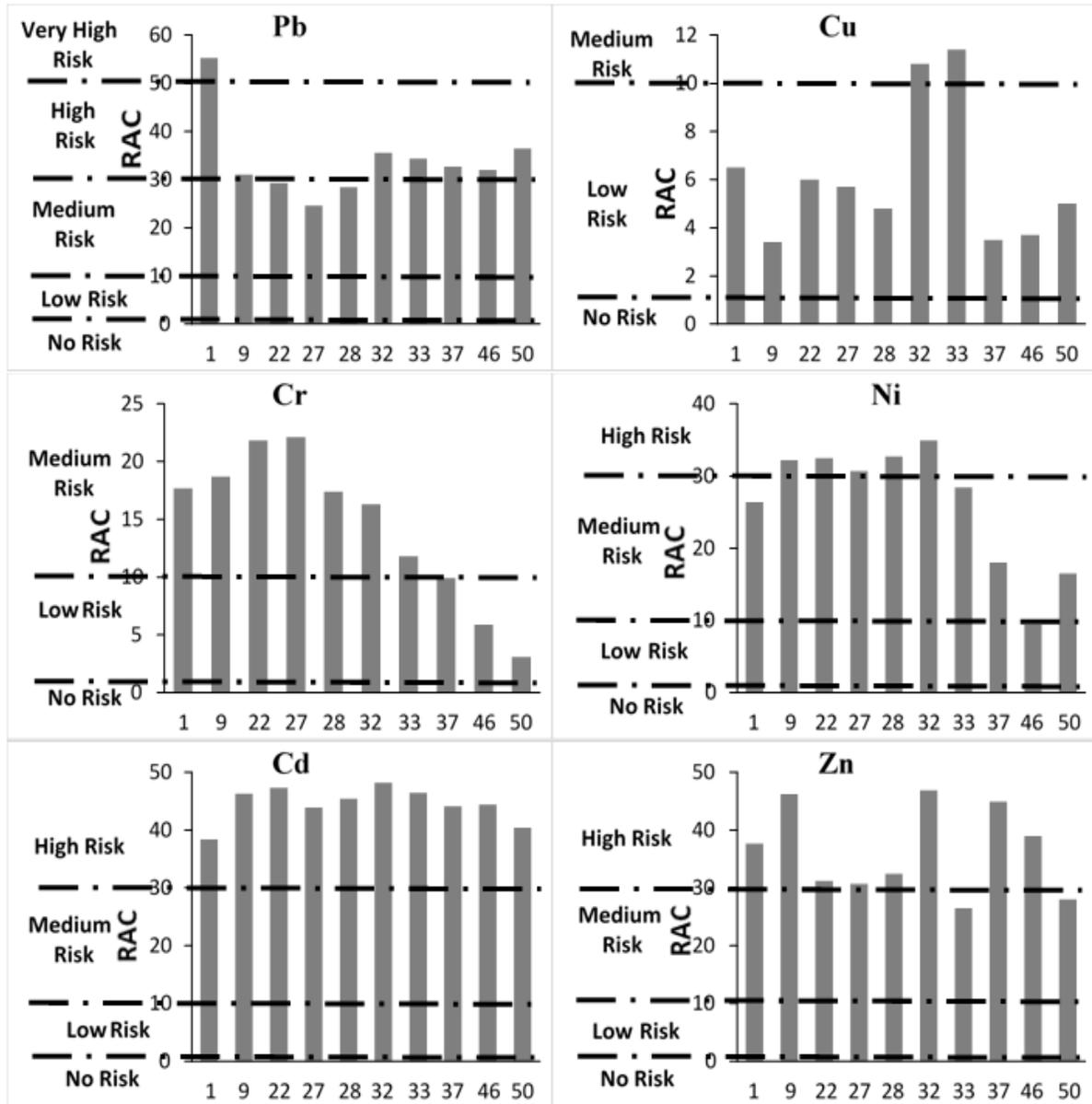


Fig. 4. RAC amounts of metals in different sampling sites

was the dominant fraction in some studies on Cd fractionation of street dust samples (Harrison *et al.*, 1981; Tokalioglu and Kartal, 2006). Cd had a greater proportion in exchangeable phase (%19) in comparison to other elements and thus this metal is more mobile than other elements. The distribution pattern of Cd was nearly similar to Pb in this study. The high percentage (91%) of non-residual fractions demonstrated high mobility, availability and anthropogenic resources for this element. Cd is mainly from plastic, batteries and building materials (Wei *et al.*, 2010). Many administrative and residential buildings were near the sampling sites of

this study; therefore, erosions of tires, car batteries and building materials were the main possible resources of Cd. The most concentrated fraction of Cd was carbonate fraction maybe because of containing alkali, lime or calcium in samples. Fe-Mn oxide was a dominant fraction of Cd illustrated that Fe and Mn oxides were powerful scavengers for this metal (Rath *et al.*, 2009). In another study on Tehran street dust (Saeedi *et al.*, 2012) the ecological risk of Cd was considerable and despite the fact that this element had very high ecological risks, it had different sources from other metals. Thus, Cd may have a regional anthropogenic source for whole

**Table 6. Pollution intensity of metals in Tehran street dust according to  $I_{\text{POLL}}$  values**

| Element | $I_{\text{POLL}}$ | Element pollution intensity |
|---------|-------------------|-----------------------------|
| Cu      | 0.35              | Unpolluted                  |
| Cd      | 1.74              | Low polluted                |
| Pb      | 1.82              | Low polluted                |
| Cr      | 0.61              | Unpolluted                  |
| Ni      | 1.16              | Low polluted                |
| Zn      | 2.48              | Moderately polluted         |

Tehran. According to obtained results, the bioavailability of metals in street dust shows following order: Cd > Zn > Pb > Cu > Ni > Cr. Similar results were acquired in other studies on street dust (Harrison *et al.*, 1981; Fergusson and Kim, 1991; Li *et al.*, 2001). Except for Pb the highest proportion of elements in residual fraction occurred in sample taken from the university campus. This result sounds reasonable due to lower traffic and anthropogenic resources in this sampling site. The high proportion of metals in carbonate fraction may lead to the abundance of calcite in street dust (Harrison *et al.*, 1981). According to XRD results, calcite was a major phase of dust samples, thus high concentration of metals in carbonate phase seems reasonable. Also regarding XRF and sequential extraction results,  $\text{Fe}_2\text{O}_3$  was a major component of dust sample and Fe-Mn oxide was an important phase in metal fractionation; therefore X-ray and sequential extraction results are positively correlated. All ten selected samples were extracted by 0.5 M HCl. The molarity of human's stomach acid is about 0.1 M (Day *et al.*, 1979) therefore by using of 0.5 M HCl extraction an estimation of the uptaken amount of pollutants by human from ingested street dusts could be calculated. Some researchers estimated lead uptake by young children using dilute HCl (Day *et al.*, 1979; Gibson and Farmer, 1984) as an extractant for dust contamination assessment. On average, the concentrations of Cu, Cd, Pb, Cr, Ni and Zn extracted with 0.5 M HCl were about 85%, 92%, 90%, 120%, 72% and 96% of concentrations of these metals in non-residual fractions of Tessier method. Metal concentrations in total, single and sequential extraction (non-residual fraction) are displayed in Fig. 3. Cr concentration in single stage extraction is more than non-residual fractions of Tessier method in samples 37, 46 and 50.

Therefore, single extraction method may err on the mobility of Cr (Barreto *et al.*, 2004). The greater extractability of Cd, Zn and Pb by HCl extraction might be because of higher sorption of these metals onto carbonates. It also demonstrates that there are higher risks for Cd, Zn and Pb in Tehran dust (Wu *et al.*,

2011). On average, 0.5M HCl could extract 53%, 84%, 47%, 40%, 80% and 87% of total concentrations of Cu, Cd, Ni, Cr, Pb and Zn from dust samples, respectively. Consequently, the results of single extraction significantly correlated with total digestion results especially for Cd, Pb and Zn. Since HCl extraction method is more cost-effective, easier to operate and less extraction time is required in comparison to total digestion, this single stage extraction seems to be useful in dust pollution assessment. However, the single extraction method cannot provide detailed information about fractionation, mobility and related risk of heavy metals in dust. To summarize the results of three extraction methods, the metal concentration in dust samples showed this order: total digestion: Zn > Pb > Cu > Ni ~ Cr > Cd, sequential extraction ( $f_1 + f_2 + f_3 + f_4$ ): Zn > Pb > Cu > Ni > Cr > Cd, and single extraction: Zn > Pb > Cu > Ni > Cr > Cd. Therefore, the results of all three methods showed the same order for metal concentrations in dust samples. RAC amounts in ten street dust samples are shown in Fig. 4. RAC results showed high risk of Pb, Cd and Zn in dust samples of Tehran. Cr and Ni medium to high risk at most sampling stations. Cu showed low risk at all stations except for samples from stations 32 and 33 at which the risk was at medium level. Zn, Cr and Ni risk from IUUST campus samples were relatively lower than those from other sampling sites, which reconfirms the effect of vehicles traffic and other local anthropogenic sources for metals contamination in street dust of Tehran. In the case of Pb, the station number 1 (from Bahery highway) had the highest risk and the other sampling locations showed high risks except for sample 22, 27 and 28 which were very close to high risk level. Pb is the only element with a very high risk in one sample station; therefore this metal has potentially the most serious adverse effect on the environment and human health in Tehran. Cu had lower risk in comparison to other metals. Cr showed low risk in samples No. 46 and 50 while others had medium risks. Ni had high risk at stations number 9, 22, 27, 28 and 32 and other stations had medium risk. Cd showed high risk in all street dust sampling stations, which is a sign that highlights the need for further investigations on the origin and effects of Cd in Tehran. Regarding RAC results and significant risk of metals in Tehran dust, anthropogenic origins were the main sources of Cd, Pb and Zn, while Cr, Ni and Cu might have been originated from both anthropogenic and natural sources. The results of metals pollution intensity according to  $I_{\text{POLL}}$  index are shown in Table 6. According to Table 6, Zn showed moderately polluted level, while Pb and Cd showed a low pollution level close to moderate pollution. Therefore the pollution

intensity results were significantly correlated with RAC results (Zn, Pb and Cr were among the metals with high level of risk). Also Cu followed by Cr had the lowest amount of pollution intensity which reconfirmed the results of RAC.

## CONCLUSIONS

The results of this study provided essential information about the quality of street dust in Tehran. Some metal concentrations in Tehran street dust were more than earth crust and those of other cities around the world. Quartz, Calcite and Albite were major components of street dust, while Orthoclase, Chlorite, Dolomite and Muscovite-illite were minor ones. The chemical fractionation results demonstrated high proportion of Pb, Zn and Cd in carbonate/Fe-Mn oxide phases. Cu was highly associated with organic fraction while Cr and Ni were moderately extracted in residual fraction. The considerable proportion of Cd, Pb, Cu and Zn in non-residual fractions confirmed pollution, mobility and anthropogenic sources for these elements. The fractionation pattern of Ni showed a combination of natural and anthropogenic sources for this element while Cr was probably from lithogenic and natural origins. Results also revealed that the single extraction procedure could be applied as an appropriate alternative for total digestion. RAC results showed high risks and in sequence high bioavailability for Cd, Zn and Pb and medium to low risks for Ni, Cr and Cu. Anthropogenic sources were contributed to Cd, Pb and Zn while both sources of human activities and natural origins were expected for Ni, Cr and Cu. The results of pollution intensity and RAC were significantly correlated, and metals with higher risk showed higher level of pollution. Regarding high toxicity and negative health effects of dusts and heavy metals (particularly Cd and Pb) further detailed studies are required to assess the environmental risks of street dust in Tehran.

## REFERENCES

- Adamo, P., Dudka, S., Wilson, M. J., McHardy, W. J. (1996). Chemical and mineralogical forms of Cu and Ni in contaminated soils from the Sudbury mining and smelting region, Canada. *Environ. Pollut.*, **91**, 11-19.
- Banerjee, A. D. K. (2003). Heavy metal levels and solid phase speciation in street dusts of Delhi, India. *Environ. Pollut.*, **123**, 95-105.
- Barreto, S. R. G., Nozaki, J., Oliveria, E. D., Filho, V. F. D. N., Aragao, P. H. A., Scarminio, I. S. and Barreto, W. J. (2004). Comparison of metal analysis in sediments using EDXRF and ICP-OES with the HCl and Tessie extraction methods. *Talanta.*, **64**, 345-354.
- CEPA and CGSEM, (1990). Chinese Environmental Protection Agency and Chinese Station of Environmental Monitoring, Soil chemical element background values of China, Beijing.
- Charlesworth, S., Everett, M., McCarthy, R., Ordonez, A. and De-Miguel, E. (2003). A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. *Environ. Int.*, **29**, 563-573.
- Christoforidis, A. and Stamatis, N. (2009). Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. *Geoderma.*, **151**, 257-263.
- Das, B. M. (2009). Principles of geotechnical engineering. Cengage Learning, Stanford, USA.
- Day, J. P. H., Fergusson, J. E. and Chee, T. M. (1979). Solubility and potential toxicity of lead in urban street dust. *B Environ. Contam. Tox.*, **23**, 497-502.
- De Miguel, E., Llamas, J. F., Chacon, E., Berg, T., Larssen, S., Royset, O. and Marit, V. (1997). Origin and patterns of distribution of trace elements in street dust: unleaded petrol and urban lead. *Atmos. Environ.*, **31**, 2733-2740.
- Fergusson, J. E. and Kim, N. D. (1991). Trace elements in street and house dusts: sources and speciation. *Sci. Total Environ.*, **100**, 125-150.
- Fergusson, J. E. and Ryan, D. E. (1984). The elemental composition of street dust from large and small urban areas related to city type, source and particle size. *Sci. Total Environ.*, **34**, 101-116.
- Garrabrants, A. C. and Kosson, D. S. (2000). Use of a chelating agent to determine the metal availability for leaching from soils and wastes. *Waste Manage.*, **20**, 155-165.
- Gibson, M. J. and Farmer, J. G. (1984). Chemical partitioning of trace metal contaminants in urban street dirt. *Sci. Total Environ.*, **33**, 49-57.
- Harrison, R. M., Laxen, D. P. H. and Wilson, S. J., (1981). Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils. *Environ. Sci. Technol.*, **15**, 1378-1383.
- Jiries, A. (2003). Vehicular Contamination of Dust in Amman, Jordan. *Environmentalist.*, **23**, 205-210.
- Karbassi, A. R., Monavari, S. M., Nabi Bidhendi, Gh. R., Nouri, J. and Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environ. Monit. Assess.*, **147**, 107-116.
- Karbassi, A. R., Nabi-Bidhendi, G. R. and Bayati, I. (2005). Environmental geochemistry of heavy metals in a sediment core off Bushehr, Persian Gulf. *Iranian J. Environ. Health Sci. Eng.*, **2**, 225-260.
- Kartal, S., Aydin, Z. and Tokalioglu, S. (2006). Fractionation of metals in street sediment samples by

- using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *J. Hazard. Mater.*, **132**, 80-89.
- Kubova, J., Matus, P., Bujdos, M., Hagarova, I. and Medved, J. (2008). Utilization of optimized BCR three-step sequential band dilute HCL single extraction procedures for soil-plant metal transfer predictions in contaminated land. *Talanta*, **75**, 1110-1122.
- Li, X., Poon, C. S. and Liu, P. S. (2001). Heavy metal contamination of urban soils and street dusts in Hong Kong. *Appl Geochem.*, **16**, 1361-1368.
- Liu, J., Zhang, X. H., Tran, H., Wang, D. Q. and Zhu, Y. N. (2011). Heavy metal contamination and risk assessment in water, paddy soil, and rice around an electroplating plant. *Environ. Sci. Pollut. Res.*, **18**, 1623-1632.
- Manasreh, W. A. (2010). Assessment of trace metals in street dust of Mutah city, Kurak, Jordan. *Carpath J. Earth Environ.*, **5**, 5-12.
- Mashal, K., Al-Qinna, M. and Ali, Y. (2009). Spatial Distribution and Environmental Implications of Lead and Zinc in Urban Soils and Street Dusts Samples in Al-Hashimeyeh Municipality. *Jordan J. Mech Ind Eng.*, **3**, 141-150.
- McAlister, J. J.; Smith, B. J.; Torok, A., (2006). Element partitioning and potential mobility within surface dusts on buildings in a polluted urban environment, Budapest. *Atmos. Environ.*, **40**, 6780-6790.
- McLaren, R. G. and Crawford, D. V. (1973). Studies on soil copper I. The fractionation of copper in soils. *J. Soil Sci.*, **24**, 172-181.
- Miretzky, P. Avendano, M. R. Munoz, C. and Carrillo-Chavez, A. (2011). Use of partition and redistribution indexes for heavy metal soil distribution after contamination with a multi-element solution. *J. Soils Sediments.*, **11**, 619-627.
- NRC, (2000). National Research Council of Canada. Institute for National Measurement Standards. <http://www.nrc-cnrc.gc.ca/eng/rd/mss/index.html>
- Niencheski, L. F. H., Baraj, B., Franca, R. G. and Mirlean, N., (2002). Lithium as a normalizer for the assessment of anthropogenic metal contamination of sediments of the southern area of Patos Lagoon. *Aquat. Ecosyst. Health.*, **5**, 473-483.
- Perin, G., Craboledda, L., Cirillo, M., Dotta, L., Zanette, M. L. and Orio, A. A. (1985). Heavy metal speciation in the sediments of northern Adriatic sea. A new approach for environmental toxicity determination. In: International Conference of Heavy Metals in the Environment, Edinburgh, UK.
- Pickering, W. F. (1986). Metal ion speciation - soils and sediments (a review). *Ore Geol Rev.*, **1**, 83-146.
- Ramlan, M. N. and Badri, M. A. (1989). Heavy metals in tropical city street dust and road side soils: a case of Kuala Lumpur, Malaysia. *Environ. Technol. Lett.*, **10**, 435-44.
- Rao, C. R. M., Sahuquillo, A. and Lopez-Sanchez, J. F. (2010). Comparison of single and sequential extraction procedures for the study of rare earth elements remobilization in different types of soils. *Anal. Chim. Acta.*, **662**, 128-136.
- Rasmussen, P. E., Subramanian, K. S. and Jessiman, B. J. (2001). A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. *Sci. Total Environ.*, **267**, 125-140.
- Rath, P., Panda, U. C., Bhatta, D. and Sahu, K. C. (2009). Use of sequential leaching, mineralogy, morphology and multivariate statistical technique for quantifying metal pollution in highly polluted aquatic sediments – a case study: Brahmani and Nandira Rivers, India. *J. Hazard. Mater.*, **163**, 632-644.
- Saeedi, M., Hosseinzadeh, M., Jamshidi, A. and Pajooheshfar, S. P. (2009). Assessment of heavy metals contamination and leaching characteristics in highway side soils, Iran. *Environ Monit Assess.*, **151**, 231-241.
- Saeedi, M., Li, L. Y. and Salmanzadeh, M. (2012). Heavy metals and polycyclic aromatic hydrocarbons: Pollution and ecological risk assessment in street dust of Tehran. *J. Hazard. Mater.*, **227-228**, 9-17.
- Schwar, M. J. R., Moorcroft, J. S., Laxen, D. P. H., Thomson, M. and Armorgie, C. (1988). Baseline metal in dust concentrations in Greater London. *Sci. Total Environ.*, **68**, 25-43.
- SCI, (2011). Statistical Center of Iran. <http://www.amar.org.ir>
- Soltan, M. E., Rageh, H. M., Rageh, N. M. and Ahmed, M. E. (2005). Experimental approaches and analytical technique for determining heavy metals in fallen dust at ferrosilicon production factory in Edfu, Aswan, Egypt. *J. Zhejiang Univ-Sc. B.*, **6**, 708-718.
- Taylor, S. R. (1965). The application of trace element data to problems in petrology. In: *Physics and Chemistry of the Earth* (Aherns, L. H., Press, F., Runcorn, S. K. and Urey, H. C., Eds.). Pergamon Press, New York, USA, pp. 133-213.
- Tessier, A., Campbell, P. G. C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem.*, **51**, 844-851.
- Tokalioglu, S. and Kartal, S. (2006). Multivariate analysis of the data and speciation of heavy metals in street dust samples from the Organized Industrial District in Kayseri (Turkey). *Atmos. Environ.*, **40**, 2797-2805.
- Tokalioglu, S., Kartal, S. and Birol, G. (2003). Comparison of three sequential extraction procedures form partitioning of heavy metals in car park dusts. *Environ. Monit. Assess.*, **5**, 468-476.
- USEPA, (1992). Test methods for evaluating solid waste physical/chemical methods, SW-846. Washington, USA.

USEPA, (1996). Test methods for evaluating solid waste physical/chemical methods, SW-846. Washington, USA.

Wei, B., Jiang, F., Li, X. and Mu, S. (2010). Heavy metal induced ecological risk in the city of Urumqi, NW China. *Environ. Monit. Assess.*, **160**, 33-45.

Wu, G. H., Cao, S. S., Chen, S. R. and Cao, F. T. (2011). Accumulation and remobilization of metals in superficial sediments in Tianjin, China. *Environ. Monit. Assess.*, **173**, 917-928.

Zarasvandi, A. (2009). Environmental impacts of dust storms in the Khuzestan province. Environmental Protection Agency (EPA) of Khuzestan province, Internal Report.