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Spatial and temporal distribution of heavy metals in dust fallout in Basra city/ Iraq

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Abstract. This study examined the distribution and dominance of some heavy metals in samples of dust fallout from Shaibah area in the province of Basra/ Iraq. The fallen dust collected by special containers of metal (diameter of 15 cm and height of 30 cm) via bags of polyethylene monthly between June 2011 and November 2012. An acid mixture of nitric and Perchloric acids (1:1) was used to digest the samples, then heavy metals (Ni, Cd, Pb, Fe Zn and Cr) analysed by using a Flame Atomic Absorption Spectrophotometer. The program SPSS was used to analyse data statistically using model 19. The mean of Cd concentration was a range from 0.0002 during May in St7 and 0.0158 mg/m³ September and St8. The result showed that the concentration of Cr ranges from 0.0046 to 0.4598 mg/m³. Ni conc. showed significant differences (0.871-0.0012 mg/m³), Pb range from 0.008 to 1.9042 mg/m³. Contamination of Cd, Pb and Cr might accumulate from different areas along with local pollution because of the high occurrence in whole locations, whereas Ni seems polluted locally because of high rates only at St2. The heavy metals above the reference value become seriously polluted according to WHO2008 and ATSDR, (2002), but below the target value in other studies.

Keywords: Monitoring, Heavy Metal, Fallen Dust, Basra

1. Introduction

Atmosphere composition was changed when larger amounts of gases were burning, particles can be accumulation in the air. Dust particles could stay suspended for long times and transported for long distances in the air, causing changes in local, global climate and weather [1]. So that air becomes the source of many risks that threaten all aspects of living and non-living life [2, 3]. Some respiratory disease like asthma, lung cancer, bronchiolitis, COPD (Chronic Obstructive Pulmonary Disease) as will central nervous system dysfunctions, and cutaneous diseases result from heavy metals, Chronic poisoning or poisoning occur when heavy metals absorbed into the human body, depending on the severity and time of the exposure [4].

Saleh et al [5] have investigated heavy metals (Al, Ba, Hg, Mn and V, Mn, Pb and Zn) in the blood of men who have worked in crude oil fields, they found that the concentration of these metals increases by twice compared to people outside the pollution boundaries. Ahmed et al [6] Show that the trend of heavy metals toxicity in human blood as follows: Pb > Zn > Ni > Cd there were higher conce. of Mn, Pb, Cr, Ni in blood samples come from dust when agitated, and the plastic factory workers are at risk of being contaminated with heavy metals. Heavy metals damage the immune system, by inhibit and compete with protein and enzymes for binding sites. "Chronic exposure to toxic metals can increase the body's production of reactive oxygen species (ROS), leading to oxidative stress induction, induce mitochondrial DNA mutations, reduces the mitochondrial respiratory chain functions, the



permeability of cellular membrane being altered which causes the deterioration of mitochondrial antioxidant system and causing significant damage to cellular components such as lipids, proteins, and deoxyribonucleic acid (DNA)" [6].

Dust considered a significant heavy metal pollution source in the environment of urban, these tiny particles made up of many compounds, including silica, sulphates and heavy metals on the study of sources of dust storms over Iraq showed that the clay and silt particulates form about 86.9% and sand particles 13.2%, of a dust storm, the major mineral dust components were kaolinite, gypsum, albite, quartz and calcite, also dust particles have a high amount of Zn and Pb. [1]. Heavy metals such as Pb, Cr, Cu, and Zn in particle dust have higher concerns due to particles as tiny ones ability to deeply travel to the lungs causing much more damage compared to particulate matter being large [2, 7, 8]. According to Hashim [9], in Iraq, depositing average dust is approximately 4 times and $\frac{1}{2}$ higher compared to limits as allowable. As regards to dust deposits quantity, he found that increases in the quantities of deposits dust at Babylon governorate, where average annual deposits of dust through 2008 was (32.9 g/m²/month); whereas WHO recommending deposits of dust must no more than (9 g/m²/month). Al-Hassen [2] pointed out that the highest amount of dust falling in the city is increasing compared with the countryside and found that the amount of dust falling in Basra, up to (21.5g/m²) during (2009). Hassan et al [10] show the Pb and Cr conce. mean about 14.70 mg/m³ and 7.91 mg/m³ in stations southwest of Basra city. Heavy metals originating from anthropogenic sources include fuel and industrial activities combustion emission, responsible for the extent bulk of toxic metals in urban areas [11].

The health impact of the dust falling does not depend on the quantity, whereas some studies revealed that the falling particles of dust have heavy metals (Cd, Zn, Ni) concentrations [8, 12, 13]. Basra city receives the pollution origin from heavy traffic, petrochemical factory, and also, oil refinery, which may increase heavy metals like Pb, Cd, Ni and Zn into the atmosphere were particularly high in the dust [14].

Because of the nature of the climate in Basra city, there is a wide variation in the amount of falling dust, as well as the industrial activity in southern Basra, which has the largest oil industry in Iraq. Therefore, this study aims to monitor the concentrations of heavy metal in falling dust monthly during one year in some stations representing this region.

2. Methods and materials

Sites and areas for the study were elected from nearby areas of a refinery of oil at the governorate of Basra, Iraq. These stations are; St1 (gas or electric), St2 (houses of Shuaiba), St3 (staff break house), St4 (refinery of oil), St5 (Project of FCC), St6 (control of the military), St7 (Al-Kassed, oil station), St8 (stores of Alkziza), and St9 (Anas Ibn Malik Mazar) which illustrated at Figure 1 map.

2.1. Sampling

Samples were collected between June 2011 and November 2012, by utilizing a container of metal (diameter of 15 cm and height of 30 cm) via bags of polyethylene were covered which replacing every month to collect dust samples by taking the old one and transferred to the lab in Marine Science Centre. In the lab, the samples wash with distilled water to collect all dust in the glass beaker (from the polyethylene bags) and then dried in an oven at (105–110) ° C to drive out moisture. The beaker weighed before (W1) and after (W2) dry to evaluate the weight difference (ΔW). The concentration of dust falls calculated as showing in equation 2.

$$\Delta W \text{ g} = W2 - W1 \quad (1)$$

$$\text{Fall dust Conc. g/m}^2 = \Delta W / A \quad (2)$$

A: container area m²

The digestion procedure of the dust samples was done according to Sparks et al. [15] in which 6 ml of 1:1 acid mixture of nitric and Perchloric acids were added to the total weight of each dust sample in a Teflon beaker for the digestion near dryness. The sample transferred to a 50 ml volumetric flask and

completed the volume to the mark with distilled water. Heavy metals (Ni, Cd, Pb and Cr) mature by using flame Atomic Absorption Spectrophotometer Model Phoenix-986. The data Results were analysed statistically using the program SPSS model 19 by adopting the procedure of relative LSD along with level $P \leq 0.05$.

$$\text{Heavy metal conc. (mg/m}^3\text{)} = (c \cdot v_i) / v_t$$

c: element concentration;

v_i : sample volume =50 ml.

v_t : container total volume (m^3).

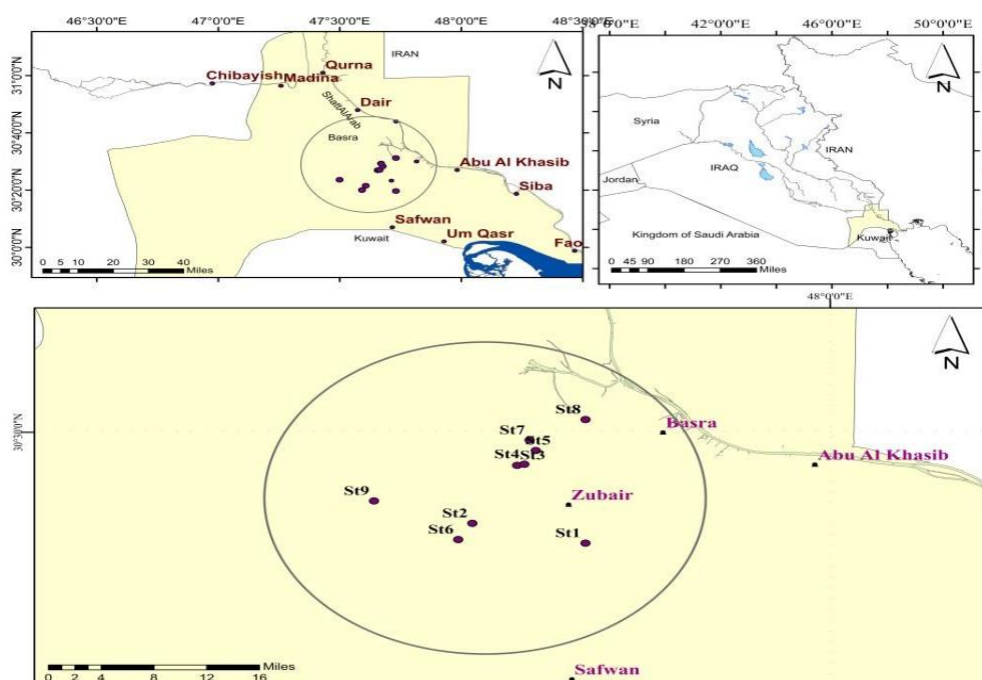


Figure 1: Map of Southern Iraq showing sampling sites within Basra governorate

3. Results and discussion

The concentration of heavy metals among study stations is shown in table 1, their monthly disruption is shown in table 2 and season and stations, interference in Fig 2 for Cd, Cr, Ni and Pb concentration in the study area. There is no significant difference in the concentration of Cd between stations or during the months. The mean of Cd concentration was a range from 0.0002 during May in St7 and 0.0158 mg/m^3 September and St8. (Table 1 and Fig 2). September achieved the highest concentrations in all stations it's mean was 0.0058 mg/m^3 , also St8 dominated during the study months, except April (table 2 and Fig 2). The Cd has the lowest levels in all stations, the mean was less than the range of the earth's crust (0.2 mg/g) [15,16]. But the mean metal concentration in the particulate was seen to be over the limits proposed by WHO or USEPA standards for atmospheric [17,18] which about 6 ng m^{-3} . Basra city receives pollution originating from an oil refinery, petrochemical factory and heavy traffic may contribute to increasing heavy metal such as Pb, Cd, Zn, Ni [14,13].

Cadmium has a toxic property, it is non-essential metal, some of its compounds can be soluble in water that leads to an increase in its availability in the environment also it has the ability of accumulation in tissue and thus it transfers to humans through the food chain. Cadmium in soil and sediment adsorbed on the clay minerals, carbonates, organic matter iron and manganese hydrous oxides of and depended on pH conditions of soil and sediment [3]. Abdalnabi et al. [19] records that

Cd strongly polluted with sediment from Basra environment (the highest value 5.5905 $\mu\text{g/g}$) that cloud be a source of air pollution [20].

Table 1: the concentration of heavy metaled (mg/m³) among study stations

| Metal | Stations | St1 | St2 | St3 | St4 | St5 | St6 | St7 | St8 | St9 | Total Mean |
|----------------|----------------|--------|--------|--------|--------|------------|--------|--------|--------|--------|------------|
| Cd | Mean | 0.0016 | 0.0016 | 0.0002 | 0.0006 | 0.0006 | 0.0002 | 0.0004 | 0.0058 | 0.002 | 0.0016 |
| | Std. Deviation | 0.0018 | 0.0016 | 0.0002 | 0.0006 | 0.0008 | 0.0002 | 0.0004 | 0.0086 | 0.0016 | 0.0032 |
| | Minimum | 0.0004 | 0.0002 | 0.0002 | 0.0002 | 0.0002 | 0.0002 | | 0.0002 | 0.0004 | 0.0002 |
| | Maximum | 0.003 | 0.004 | 0.0004 | 0.0012 | 0.0012 | 0.0004 | 0.001 | 0.0158 | 0.0038 | 0.0158 |
| | | | | | | | | | | | |
| Cr | Mean | 0.0692 | 0.1198 | 0.04 | 0.0828 | 0.028 | 0.0764 | 0.0532 | 0.0686 | 0.101 | 0.0712 |
| | Std. Deviation | 0.0404 | 0.1908 | 0.0214 | 0.0622 | 0.0182 | 0.0428 | 0.0354 | 0.0666 | 0.062 | 0.0774 |
| | Minimum | 0.0306 | 0.0144 | 0.0108 | 0.0302 | 0.014 | 0.0462 | 0.029 | 0.0046 | 0.0234 | 0.0046 |
| | Maximum | 0.127 | 0.4598 | 0.0706 | 0.173 | 0.0486 | 0.1066 | 0.104 | 0.178 | 0.164 | 0.4598 |
| | | | | | | | | | | | |
| Ni | Mean | 0.0284 | 0.4404 | 0.0012 | 0.0108 | 0.1028 | 0.0118 | 0.0292 | 0.022 | 0.0202 | 0.0784 |
| | Std. Deviation | 0.0006 | 0.609 | | | | | 0.0088 | 0.0168 | 0.0196 | 0.2126 |
| | Minimum | 0.028 | 0.0098 | 0.0012 | 0.0108 | 0.1028 | 0.0118 | 0.023 | 0.0102 | 0.006 | 0.0012 |
| | Maximum | 0.0288 | 0.871 | 0.0012 | 0.0108 | 0.1028 | 0.0118 | 0.0354 | 0.0338 | 0.0424 | 0.871 |
| | | | | | | | | | | | |
| Pb | Mean | 0.321 | 0.2136 | 0.0832 | 0.0774 | 0.0412 | 0.0306 | 0.0306 | 0.2094 | 0.1946 | 0.1502 |
| | Std. Deviation | 0.6996 | 0.245 | 0.1132 | 0.071 | 0.014 | 0.0172 | 0.0126 | 0.2812 | 0.1878 | 0.3184 |
| | Minimum | 0.017 | 0.008 | 0.0148 | 0.0136 | 0.0226 | 0.0184 | 0.0174 | 0.0222 | 0.0308 | 0.008 |
| | Maximum | 1.9042 | 0.5262 | 0.3066 | 0.193 | 0.0554 | 0.0428 | 0.0456 | 0.6968 | 0.4158 | 1.9042 |
| | | | | | | | | | | | |
| LSD $p < 0.05$ | | Cd NS | | Cr NS | | Ni = 0.093 | | Pb NS | | | |

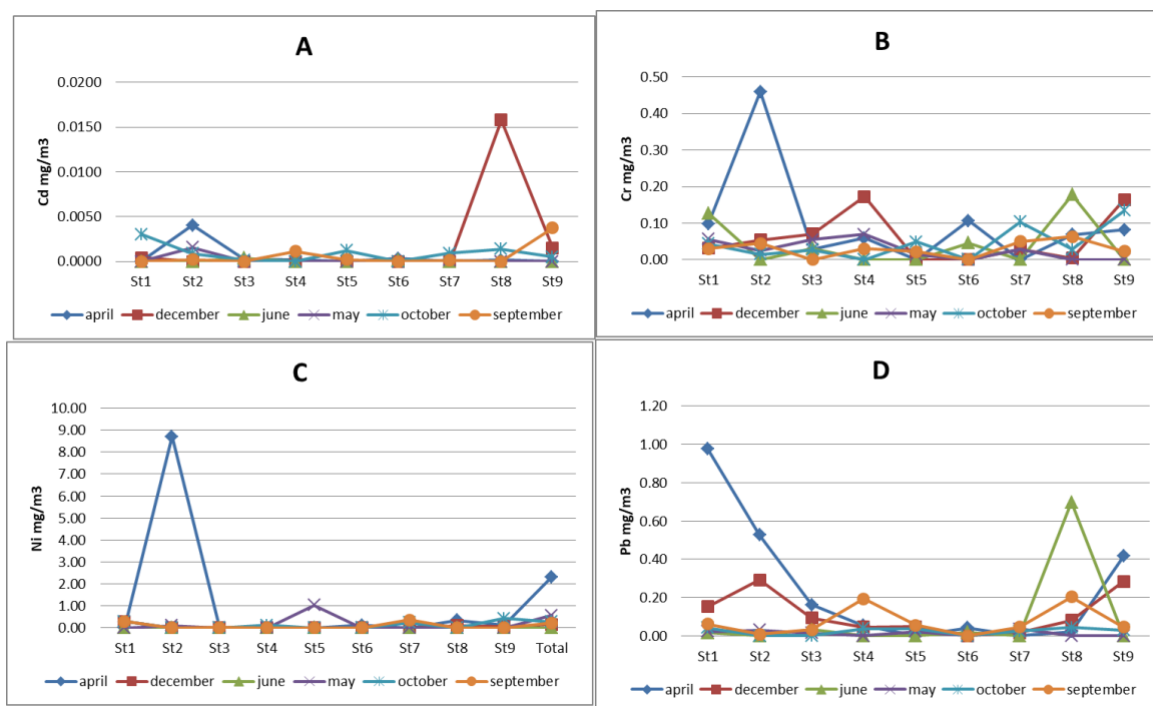


Figure 2: distribution of Cd (A), Cr (B), Ni(C) and Pb (D) mg/m³ in stations during six months

Table 2: the concentration of heavy metaled during months mg/m3

| | | Months | | | | | | | LSD p<0.05 |
|----|----------------|--------|----------|--------|--------|---------|-----------|--------|------------|
| | | April | December | June | May | October | September | Total | |
| Cd | Mean | 0.001 | 0.0058 | 0.0002 | 0.0008 | 0.0012 | 0.001 | 0.0016 | NS |
| | Std. Deviation | 0.0018 | 0.0086 | 0.0002 | 0.001 | 0.001 | 0.0016 | 0.0032 | |
| Cr | Mean | 0.1142 | 0.0752 | 0.0954 | 0.0416 | 0.0572 | 0.0378 | 0.0712 | NS |
| | Std. Deviation | 0.1336 | 0.067 | 0.0692 | 0.0214 | 0.0448 | 0.0154 | 0.0774 | |
| Ni | Mean | 0.2322 | 0.0146 | | 0.0562 | 0.0262 | 0.0218 | 0.0784 | 0.1758 |
| | Std. Deviation | 0.426 | 0.0116 | | 0.0658 | 0.0132 | 0.0182 | 0.2126 | |
| Pb | Mean | 0.3392 | 0.1268 | 0.1912 | 0.025 | 0.0364 | 0.0808 | 0.1502 | NS |
| | Std. Deviation | 0.5806 | 0.1072 | 0.337 | 0.0078 | 0.0078 | 0.074 | 0.3184 | |

The mean concentration of Cr was 0.0774 in the study area. It rang from 0.0046 to 0.4598 mg/m3. The highest value recorded during April in St2 is Shuaiba house station, and the lowest value of Cr in St8 during December, there are considerable spatial variations and heterogeneous between sites (table 1and Fig2). The result in table 2 shows the maximum Cr concentration in Abril (0.1142mg/cm3). The standards for atmospheric Cr ware 110 and 100 ng m⁻³ respectively [17,18]. So, there is a wide range between standard and measured values. According to Hassan et al [13] Cr concentrations one of the most abundant metals, in Shuaiba region.

Results of the statistical analysis indicated only Ni conc. showed significant differences among stations of this study the maximum value in St2 (0.871 mg/m3) and the minimum in St3(0.0012 mg/m3) (Table 1). Data in Fig 2 shows the lowest mean in St2 during September (0.0014 mg/m3) and the highest was observed at St3 (8.71 mg/m3) during April. The monthly distribution also showed variation in Ni concentration in December (0.0058 mg/m3) and in June (0.0002 mg/m3). Petroleum manufacturing processes to separate its derivatives such as kerosene, gasoline gas, medium and derivatives, heavy derivatives, etc. As a result of these operations gaseous compounds lead to air pollution (Hassan et al 2017). These Ni concentrations are higher than and ATSDR [17] WHO [18] its 20 ng m⁻³, but it's less than the value of Attiya and Jones [1] the found 40 and 114 ppm of Ni concentration in Basra and Iraq dust. Fossil fuel combustion and exhaust gases main sources of Ni in the atmosphere. Both Hassan et al [13] and Kadhum [14] found that Cd, Ni, were from the same pollution sources, while the Pb element was from the different pollution sources.

The mean Pb concentrations were 0.1502 mg/m3. There is a high difference between station studies ranged from 0.008 in St1 to 1.9042 mg/m3. Fig 2 displays the minimum value in St2 during September (0.0014 mg/m3) and the highest was observed at St3 (8.71 mg/m3) during April. The monthly distribution also showed variation in Ni concentration in December (0.0058 mg/m3) and in June (0.0002 mg/m3). Both Cr and Pb have dominated at all stations except at St2 and St5 the Ni and Pb have the highest value (see Figure 2).

Pb and Cr concentrations were the most abundant metals (Tables 1,2). Pb contamination may be coming from other areas as well as pollution locally due to the high prevalence in all locations as well as chromium and cadmium, while nickel appears locally polluted due to its high rates in only two stations (St2 and St5). However, heavy metals coming from different areas due to transporting via dust storms or wind, which considered as essential trace elements source for dust [20]. High heavy metals concentrations in Zubair soil, particularly in city West and North West sides which indicating prevailing consensus wind direction at the area of study and the resulting transfer of heavy elements

amounts via wind to Zubair town along with dust through storms of dust [8]. The amount of heavy metal during the dust storms in central and southern Iraq was studied by Attiya and Jones [1] who find that dust storms hold high polluted element concentrations including Cd, Pb, Zn and Ni.

Table 3: Dust and soil reference values

| | | WHO [18] | ATSDR [17] | Attiya and Jones [1] | | | | Swartjes [21] Ppm | Kadhum [14] In Basra ppm |
|----|---------------------------------------|--------------------|---------------|----------------------|--------------------------------|----------------------|-----------------------------|-------------------------|-----------------------------------|
| | percent study mg/m ³ | ng m ⁻³ | | Basra dust ppm | Mean in Iraq dust ppm | Basra soil ppm | Mean in Iraq soil ppm | | |
| Cd | 0.0016 | 6 | 6 | | | | | 0.8 | 3.47 |
| Cr | 0.0712 | 110 | 100 | | | | | 100 | |
| Ni | 0.078 | 20 | 20 | 42 | 114 | 30 | 122 | 35 | 233.6 |
| Pb | 0.1502 | 500 | 1500 | 7 | 40 | 6.4 | 12 | 85 | 102 |

In Table 3, it can be found the heavy metals above the reference value become seriously polluted according to ATSDR [17] and WHO [18] but below the target value in. In other studies, like Kadhum [14] and Attiya and Jones 2020 this variance may be due to the different methods of measurement and methods of expressing them. It is very important to identify the concentrations of heavy metals which can be harmful to human health. The heavy metal concentrations in Basra city were compared with ATSDR [17] and WHO [18] and other studies in Iraq and Basra city. Because there are no guidelines on this metal at the department of quality control in Iraq.

4. Conclusions

Results show Cr, Cd, Pb and Ni concentration in Shuaib at Basra city during study months considered the source of the main pollutants as industrial where samples were collected from the refinery area since gas wind conveyed as well as vapors and fumes resulting from certain operations production. Distillation processes for derivatives separating are variations in points of boiling, i.e. kerosene, gasoline gas, derivatives as heavy and medium resulting in operations compounds gaseous causing pollution of air. Such is one basic reason for a high trace elements concentration in falling particles of dust, which is in agreement with many studies at the area as local. However, heavy metals coming from different areas due to transporting via dust storms or wind which considered as essential trace elements source for dust. High heavy metals concentrations in Zubair soil, particularly in city West and North West sides which indicating prevailing consensus wind direction at the area of study and the resulting transfer of heavy elements amounts via wind to Zubair town along with dust through storms of dust. The amount of heavy metal during the dust storms in southern Iraq and its central were studied by Attiya and Jones [1] who find that dust storms hold high polluted element concentrations including Cd, Pb, Zn and Ni.

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