Assessment of Heavy Metal Contamination in the Soil of Fellujah City

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1. INTRODUCTION

Since the year 2005, numerous reports were revealed by the medical authorities in Fallujah, a 750,000 inhabitant city northwest of Baghdad. which dealt with the appearance of peculiar health symptoms, such as repetitive new and abortion of pregnant women, maldeformations of new born babies, an increased number of children blood cancer, an increase in the adult cancer cases....etc, [1-3]. The amount of these medical cases was almost epidemic. The kind of symptoms and medical cases were similar to those encountered formerly in the Chernoble and Fukushima catastrophies [3]. In fact, Fallujah had been the site of heavy military combat operations in the years 2004-2005. Besides, It is the location of moderate land traffic and includes an industrial area. A thorough study was called for the ecological causes of these health problems in the city [3].

Considering the kind of health abnormalities reported in Fallujah and their similarities to those of Chernoble and Fukushima, one may suggest a kind of radioactive contamination to be their cause. However it was reported that Pb, Cd, Cr contaminations as well as those of other heavy metals may induce similar health deteriorations [4,6].

ABSTRACT

Inductively coupled Plasma- Atomic Emmision Spectroscopy (ICPE-AES) was applied for the analysis of the soil of Fallujah city. The samples were taken from 50 different locations in the city and at the depths 20, 40 and 60 cm. No Cd ions were detected in the soil. Yet significant contamination was dtected with elements, Pb, Cr, Ni, Co, Zn and Cu. Fe concentration value was found to be less than the international average concentration value. The results showed a diffusion of the contaminating elements into the soil (at 20, 40 and 60 cm) of the sampling locations

In the present paper we report the results of soil analysis carried out in the years 2014-2015, applying the highly sensitive, Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) for the assessment of heavy metals, Pb, Cd, Fe, Co,Ni, Co, Cr, Cu and Zn in the soil of the city.

2. MATERIALS AND EXPERIMENTS

Soil samples were randomly collected from 50 different locations at different areas of Fallujah, 5 samples for each location, and at the depths 0-20, 20-40 and 40-60 cm from the surface of the soil. They were chosen either near a mosque or a school as a marking signal, Figure 1.

After removing any unwanted waste material, the samples were dried at 105°C for 24 hours in preparation for the chemical analysis.



Fig :1: Fallujah map indicating the sampling locations with (S) resembling the schools and (J) the mosques.

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2.1 .DIGESTION OF HEAVY METALS SALTS IN THE SOIL [7]

10ml of (1:1) concentrated nitric acid were added to 1g of the soil sample in a 100 ml beaker glass. The mixture was heated to 95°C and left for 15 minutes. As then 5ml of concentrated nitric acid were added and the mixture refluxed for 30 minutes with successive gradual addition of 5ml portions of concentrated nitric acid. The addition of the acid was stopped when the formation of brown fumes terminated. The mixture was refluxed then at 95°C for 2 hours. As then 2ml distilled water plus 3ml hydrogen peroxide (30%) were added and the mixture heated at 30–40°C. After cooling to room temperature, 10ml H₂O₂ were added gradually, followed by refluxing at 95°C for two hours too. It was cooled down then to room temperature followed by the addition of 10ml concentrated HCl acid. The formed reaction mixture was refluxed then at 95°C for 15 minutes.

The final solution was filtered through a 0.45 μ m filter paper into a 50ml volumetric flask and the filtrate diluted with distilled water to the mark. It was kept then in polyethylene flasks at 4°C and prepared for the analytical measurements.

All applied chemicals were of analytical grade and supplied by internationally recommended producers, Merck, Fluka and BDH.

Perkin-Elmer ICP-AES, USA, instrument was applied for the measurement of the heavy metal concentrations in the soil samples. The mapping of the plot diagrams and the contour pictures were done applying the SPSS program of IBM, USA.

3. RESULTS AND DISCUTION

A general inspection of the obtained results show that: a- a significant part of the detected elements concentrations did diffuse down the soil of the city, Table 1, and b- the absence of any traces for Cd in the soil.

3.1. Cu Results

The concentration values for this element, measured at the surface of the soil, ranged from 8.64 - 114.5ppm, depending on the sampling location, with an average value of 46.34ppm. Compared with the tolerated international value of 30.0ppm [8], it indicates that, the city is significantly contaminated with cupper, Figure 2. The contamination appears much more pronounced on adding the ppm values measured at the soil depth to those of the soil surface, Figure 3.

Table 1: Measured concentration values (**ppm**) for the heavy metals at the depths **a**-10-20 cm, **b**- 20-40 cm and **c**- 40-60 cm at 2 different locations in Falluja.

S1	Cu	Zn	Fe	Pb	Cr	Ni	Со	Cd
a-	42.12	96.22	26453	19.2	123.4	88.47	26.84	N.D
b-	39.7	77.84	21619	25.63	118.6	79.03	21.5	N.D
c-	34.7	71.32	17580	32.51	88.47	7.7	17.52	N.D
S2	53.5	98	24300	9.84	161.5	68.18	30.14	N.D
a-	58.2	112	32320	12.7	152.1	78.23	21.11	N.D
b-	72.67	125	36200	16.3	148.3	94.55	13.8	N.D
c-								

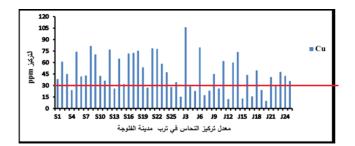


Fig:2: Plot diagram of the measured concentration values (ppm) at the different locations in Falluja, Si represent school locations and Ji represent the mosque locations. The red horizontal line depicts the average international Cu ppm value for the uncontaminated soils [8].

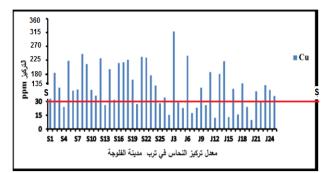


Figure:3: Plot diagram of the measured cumulative concentration values (ppm), summed by the addition of the concentration values at the 3 different depths, at the different locations in Fallujah, Si represent school locations and Ji represent the mosque locations. The red horizontal line depicts the average international Cu ppm value for the uncontaminated soils [8].

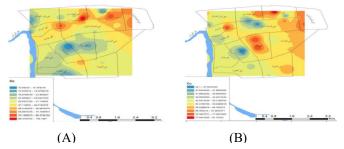


Fig: 4: Contour pictures for the measured Cu concentrations in Fallujah soil, (A) with Ji locations and (B) with Si locations.

3.2.Zn Results

The measured Zn concentration values for the Falluja soil surface ranged from 24 to 205 ppm, Figure 5. The average value of 79.68 ppm is higher than the international value of 50 ppm for the uncontaminated soil [8].

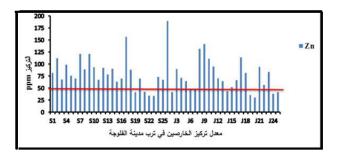


Fig :5: Plot diagram of the measured Zn concentration values (ppm) at the different locations in Falluja, Si represents school locations and Ji represent the mosque locations. The red horizontal line depicts the internationally tolerated Zn ppm value for the uncontaminated soils [8].

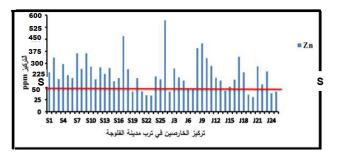


Fig :6: Plot diagram of the measured cumulative concentration values (ppm) of Zn, summed by the addition of the concentration values at the 3 different depths and at the different locations n Falluja, Si represent school locations and Ji represent the mosque locations. The red horizontal line depicts the average international Zn ppm value for the uncontaminated soils [8].

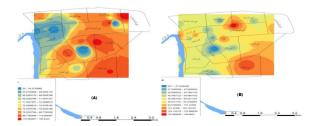


Fig:6a: Contour pictures for the measured Zn concentration in Fallujah soil, (A) with Ji locations and (B) with Si locations indicated .

3.3. Fe Results

The measured iron concentrations at the surface of Fallujah's soil falls in the range 6900 – 36200ppm. Compared with internationally average value, 38000ppm, it suggests a

deficiency of the element and thus a non-contaminated soil with iron, Figure 7.

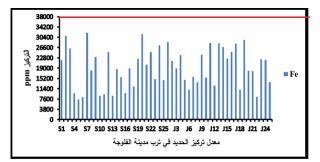


Fig :7: Plot diagram of the measured Fe concentration values (ppm) at the different locations in Falluja, Si represents school locations and Ji represents the mosque locations. The red horizontal line depicts the average international Zn ppm value for the uncontaminated soils [8].

3.4. Pb Results

The measured Pb concentration value for the soil surface of Fallujah range from 5.67-59.2ppm, Figures 8, 9 and 10, indicating a strong contamination in some areas of the city when compared with the internationally tolerated value of 10ppm [8].

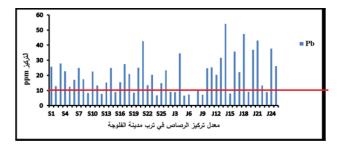


Fig:8: Plot diagram of the measured Pb concentration values (ppm) at the soil surface in different locations in Falluja, Si represents school locations and Ji represents the mosque locations. The red horizontal line depicts the average international Zn ppm value for the uncontaminated soils [8].

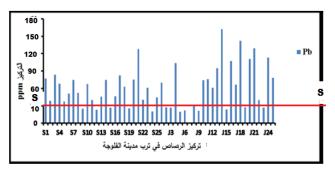


Fig:9: Plot diagram of the measured cumulative Pb concentration values (ppm), formed by the addition of the concentration values at the 3 different depths and at the different locations in Falluja, Si represents school locations and Ji represents the mosque locations. The red horizontal line

depicts the average international Pb ppm value for the uncontaminated soils [8].

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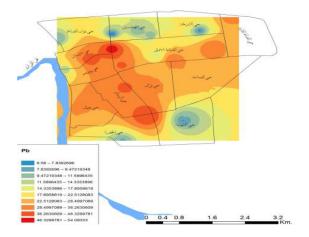


Fig:10: Contour mapping of the measured Pb concentration for the soil surface of Falluja. Only Ji marking locations are considered in this mapping

3.5. Cr Results

The measured Cr ion concentration for the surface of Fallujah soil ranged from 34.8 to 270ppm Figure 11. These values indicate, that in some areas of the city considerable Cr contamination exists. The acceptable value for the uncontaminated soil is 100ppm [8].

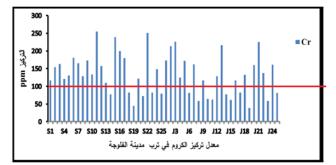


Fig:11: Plot diagram of the measured Cr concentration values (ppm) at the different locations in Fallujah, Si represent school locations and Ji represent the mosque locations. The red horizontal line depicts the average international Cr ppm value for the uncontaminated soils [8].

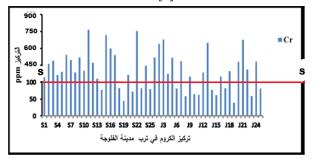


Fig:12: Plot diagram of the measured cummulative Cr concentration values (ppm) at the different locations in Falluja, Si represents school locations and Ji represents the

mosque locations. The red horizontal line depicts the average international Cr ppm value for the uncontaminated soils [8].

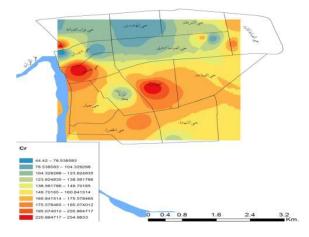


Fig:13: Contour mapping of the measured Cr concentration for the soil surface of Falluja. Only Si marking locations are considered in this mapping.

3.6. Ni Results

The measured Ni concentration at the surface of the soil of the city ranged from 12.6ppm to 196.30ppm, depending on the location of the sampling, Figures 14 and 15. Compared with the acceptable concentration of 40ppm, [8], it suggests a significant contamination with Ni in various locations of the city.

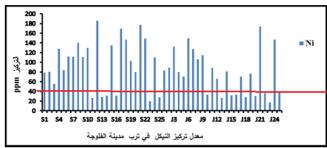


Fig:14: Plot diagram of the measured Ni concentration values (ppm) at the different locations in Falluja, Si represent school locations and Ji the mosque locations. The red horizontal line depicts the average international Ni ppm value for the uncontaminated soils [8].

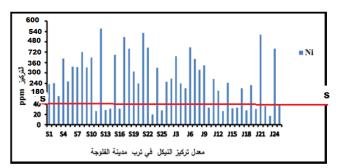


Fig:15: Plot diagram of the cummulated Ni concentrations (ppm) at the different locations in Falluja, Si represents school locations and Ji the mosque locations. The red horizontal line

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depicts the average Ni ppm value for the uncontaminated soils [8].

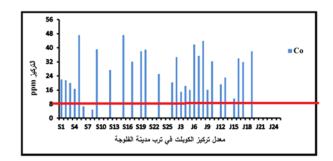


Fig:16: Contour mapping of the measured Ni concentration for the soil surface of Falluja. (A) are the Si marking locations and (B) are the Ji marking locations.

3.7. Co Results

For Co the measured soil concentration values at its surface ranged from 4.35ppm to 53.40ppm depending on the location of the sampling, Figures 17 and 18. The average value of the concentration is 27.26ppm. Compared with the international, acceptable concentration of 8ppm [8], it suggests a significant contamination of the soil with Co.

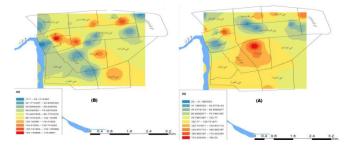


Fig:17: Plot diagram of the measured Co concentration values (ppm) at the different locations in Falluja, Si represents school locations and Ji represents the mosque locations. The horizontal red line depicts the average international Co ppm value for the uncontaminated soils [8].

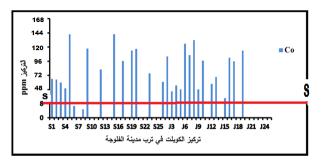


Fig:18: Plot diagram of the measured Co cummulative concentration values (ppm) at the different locations in Falluja, Si represent school locations and Ji represent the mosque locations. The red horizontal line depicts the average international Ni ppm value for the uncontaminated soils [8].

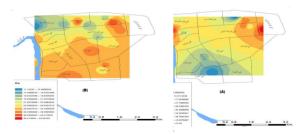


Fig:19: Contour mapping of the measured Co concentration for the soil surface of Falluja. (A) are the Si marking locations and (B) are the Ji marking locations .

Table 2 shows the Pearson's correlation coefficient values for the different heavy metals as detected by the present analysis. It is seen that positive correlations are found for the elements. Cu (Zn, Fe, Cr, Ni, Co); Zn (Fe, Cr, Ni, Co); Fe (Cr, Ni, Co) and Cr(Ni). The positive correlation values suggest that all these elements have the same origin of contamination with the exception of Pb. Naturally two positive sources for the Pb contamination are probable, a- the emission gas from the automobile combustion engines and the b- military combat operations of the years 2004, 2005.

Cu Ni Zn Fe Pb Cr Co 1.000 Cu Zn 0.908 1.000 Fe 0.953 0.934 1.000 Pb -0.947 -0.924 -0.966 1.000 0.421 0.339 0.351 -0.282 Cr 1.000 0.349 Ni 0.419 0.357 -0.282 0.301 1.000 0.298 0.221 0.158 -0.139 -0.394 Co -0.153 1.000

Table 2: calculated Pearson's correlation coefficient values for the different heavy metals as detected by the present analysis of the Falluja soil

Finally, the apparent significant contamination of Fallujah's soil with the heavy metals might be related to the following factors;

- **a**-the daily traffic in the streets of Falluja, J13, J12, J18, J16, S24, S8, S6 and S4
- **b**-the industrial activity in the areas, S5, S3, S2, J24, J23, J21, J18, J16, J14, J11, J9, J6, J3, S22, S14, S9.
- **c**-the waste deposited in the trading and commercial areas of the city,

d-the military operations in the years 2004, 2005.

4. CONCLUSIONS

The obtained results indicate a general contamination of the Fallujah soil with the corresponding heavy metals, exception is Cadmium. This fact might be clearly seen on comparing the measured maximal concentration values with the internationally tolerated values, i.e.; Cu (114.5ppm vs. 30.0ppm), Zn (205ppm vs. 79.68ppm), Pb (59.2ppm vs. 10ppm), Cr (270ppm vs. 100ppm), Ni (196.3ppm vs. 40ppm), Co (53.4ppm vs. 27.2ppm). Pearson's correlation factors show that all these elements have positive correlation values with each other with the exception of Pb, having negative values, suggesting that Pb has an independent source of emission from all the other heavy metals in the city. The results call for serious cleaning operations of the Falluja's soil, too.

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تقييم التلوث بالمعادن الثقيلة في تربة مدينة الفلوجة مثنى شنشل¹ وسجى سعدون فارس² وعمر حمد شهاب³ ¹ قسم الكيمياء، كلية العلوم، جامعة بغداد، الجادرية، بغداد، العراق

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الخلاصة:

تم تحليل عينات من تربة مدينة الفلوجة غي محافظة الانبار في العراق باستخدام مطياف الانبعاث الذري المستحث البلازموي.اخذت العينات من 50 موقع في المدينة وعلى الاعماق 20 و 40 و 60 سم في الارض. بينت النتائج خلو التربة من عنصر الكادميوم السام، مع تواجد تلوث عال لكل من العناصر (Pb, Cr, Ni, Co, Zn). وكانت نسبة الحديد في التربة اقل من المعدل العالمي. كما اظهرت نتائج التحليل نفوذ الفلزات الى الاعماق 20 و 40 و 60 سم تحت سطح الارض.

الكلمات المفتاحية: تربة الفلوجة، الفلزات الثقيلة، ICP-AES