RESEARCH PAPER

Heavy metals evaluation in soil of agricultural field around a pond of gas plant in the Kurdistan Region of Iraq.

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ABSTRACT:

This study was carried out to evaluate the limits of the heavy metals in soil around a produced water pond and the effect of the produced water on soil heavy metals in a gas facility in the Kurdistan Region of Iraq. The heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Hg and Pb) were analyzed from soil samples taken from different distances of (5, 10, 15, 20 and 25) meters from the pond. The experiment was designed in complete randomized design with 4 replications. The results showed that there were significant differences of mean values for some of the heavy metals in relation to the distances (Ni, Zn, Cu, Pb, Co). The limits of the heavy metals were then compared to maximum permissible limit (MPL) values of the heavy metals in soil by World Health Organization and Environmental Baseline Survey. It was evident that some of the heavy metals were within the normal range (Pb, Hg, Cd and Cu) and the others exceeded the normal range in the soil (Zn and Cr).

KEY WORDS: Heavy metal; Produced water; Soil, Oil and gas facility.

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1. INTRODUCTION:

Heavy metal contamination and accumulation is a serious problem around the world due to the potential threat to food safety and its detrimental effects on human and animal health. (Morais et al., 2012) Heavy metals are natural constituents of soil, therefore they can be find naturally in soils and rocks with a variety of regular concentrations in soils, rocks and water (Bello. et al., 2016). Human doings like industrial, agricultural, domestic, petroleum and other man made practices have effect to increase the levels of heavy metals to toxic levels when likened to those effects from lithological processes(Pam. et al., 2013, Siti Norbaya Mat Ripin, 2014). Soil may become polluted by the addition of heavy metals over spillage of hydrocarbons, wastewater irrigation, disposal of metal wastes, leaded gasoline and paints, pesticides, fertilizers and sewage sludge (Yaylali-Abanuz, 2011, Velea et al., 2009). It is important to evaluate the heavy metals in soil before cropping and harvesting crops. Heavy metal may pose a huge risk on human, crop, animal and water which may come from the oil and gas production activities such as drilling, construction, production, transportation and utilization. When using the contaminated soil to produce food by various crop plants, as the easy entry of these elements in the food chain which increases the risk to human health(Khudkur. et al., 2016). Heavy metals threaten human health through vegetable consumption and chronic low level intake of soil heavy metals through ingestion

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or inhalation (Abou-Shanab et al., 2007). Chronic exposure to Cd can have a harmful effect such as lung cancer, chronic effect of As include kidney and skin cancer and exposure to Pb may lead to gastrointestinal colic (Singh and Kalamhdad, 2011). Some heavy metals known as non-toxic heavy metal, uptake of excessive amount of those heavy metals are not known while but low intake of some heavy metals have adverse effect on human health such as zinc, the most important elements must disappeared from the soil are lead and cadmium, as they are very significant impact on human health(Toma., 2008). Heavy metal toxicity in plants varies with plant species, specific metal, concentration, chemical form and soil composition and pH, as many heavy metals are considered to be essential for plant growth. Some of these heavy metals like Cu and Zn either serve as cofactor and activators of enzyme reactions e.g., informing enzymes/substrate metal complex (Emurotu and Onianwa, 2017). Plants are often sensitive both to the deficiency and to the excess availability of some heavy metal ions as essential micronutrient, while the same at higher concentrations and even more ions such as Cd, Hg, As are strongly poisonous to the metabolic activities (Tiwari and Lata, 2018). Heavy metals establish an indistinct group of inorganic chemical hazards, and those most commonly found at polluted areas are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni). Soils are the main sinks for heavy metals released into the environment by man-made activities but different from organic contaminants which are decompose by microbial action, most metals do not undergo microbial or chemical degradation, and their total concentration in soils remain for a long time after their introduction (ChromaT.M. et al., 2014, Velea et al., 2009). However, changes in their chemical forms are possible (Munzi et al., 2015). The presence of toxic metals in soil can strictly prevent the biodegradation of organic pollutants (Zhou et al., 2016). From the foregoing, it is evident that considerable works have been done on the contamination of soil by anthropogenic sources in the world, but there is not any previous scientific work in the area of this scientific research, the primary objectives of the present study were to investigate the characteristic levels of heavy metals and some physicochemical properties of the produced water and its effect on soil heavy metal contamination, started from August 2018 to February 2019.

2. MATERIALS AND METHODS

2.1 Sample Collection

20 soil samples were collected in August 2018 at a gas facility in Kurdistan/Iraq around the Produced Water Pond, which uses to collect produced water during the operation, by means of complete randomized design with 4 replications, 5 samples at different distances by 5 meters for each sample at one direction. The soil samples were collected by using clean stainless-steel hand auger from the depth of 0-20 cm, they were thoroughly mixed and put into a clean and labeled polyethylene bag and transferred to laboratory for analysis.

2.2 Sample Preparation

The samples were air dried for 72 hours, then crushed and sieved through 2 mm sieve, in the gas facility’s laboratory, to obtain a representative sample.

2.3 Sample Analysis

The samples were taken for heavy metal analysis by using Genius 9000 XRFSkyray instrument at advanced laboratory of Environmental sciences department, college of science, university of Salahaddin. The data was statistically analyzed using SPSS program. The comparison among the means of soil heavy metals were done using Duncan multiple comparison (Harter, 1960). The particle size distribution was determined by the hydrometer method (USDA, 1095), the soil texture was silty loam. Seven water samples in Produced Water Pond have been taken and analyzed for determination of some chemical properties as described by (Agoro et al., 2018) in the gas facility’s laboratory. In the last 10 years, many oil and gas production, agriculture and other industrials companies have emerged in the Kurdistan Region of Iraq. Some of these companies have reportedly released a large amount of pollutants such as heavy metals into water and soil.
3. RESULTS AND DISCUSSION

Heavy Metals

Table (1) describes the mean values of the heavy metals.

The results of statistical analysis indicated to significant effect of distance factor on some heavy metal content of the soil. The concentration of heavy metals series was arranged as follow:

Mn > Cr > Ni > Zn > Cu > Pb > Co > As > Fe > Cd > Hg in a successive form.

Table (1): mean values of heavy metals

| Sample No. | Mean of Cr | Mean of Mn | Mean of Fe | Mean of Co | Mean of Ni | Mean of Cu | Mean of As | Mean of Zn | Mean of Cd | Mean of Hg | Mean of Pb |
|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| D5         | 76.00^a    | 294.65^a   | 1.97^a     | 7.42^b     | 60.43^a    | 18.28^c    | 3.62^a     | 49.38^a    | 0.13^a     | 0.03^a     | 6.50^b     |
| D10        | 67.06^a    | 249.41^a   | 2.17^a     | 8.19^ab    | 51.45^b    | 18.30^bc   | 2.63^a     | 35.74^b    | 0.12^a     | 0.03^a     | 7.84^ab    |
| D15        | 81.25^a    | 299.41^a   | 2.25^a     | 8.37^ab    | 51.17^b    | 24.17^a    | 3.63^a     | 50.11^a    | 0.15^a     | 0.02^a     | 12.22^ab   |
| D20        | 69.43^a    | 320.29^a   | 2.30^a     | 8.72^ab    | 48.37^b    | 23.15^ab   | 2.79^a     | 48.51^ab   | 0.14^a     | 0.01^a     | 14.67^ab   |
| D25        | 75.72^a    | 282.72^a   | 2.51^a     | 9.49^a     | 55.88^ab   | 17.39^c    | 3.02^a     | 48.65^ab   | 0.13^a     | 0.02^a     | 21.94^a    |

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The data reflects that Pb and Co are those heavy metals which were affected significantly by distance factor through all 25 meters, the mean value of Pb and Co is increasing by the increase of the distance, but comparing to Environmental Baseline Survey for heavy metals which has been done to the company by MapCom Company in 2010. The amount of Pb has not increased, so that the increasing of Co may be due to effect of the Produced Water Pond through evaporation of the produced water, and the silt loam soil allow the heavy metals to disperse through it and having the maximum adsorption capacity within the soil. While Zn and Cu have a significant difference and the mean has the highest value at 15 m and then decrease by increasing the distance, this may be because of medium adsorption capacity of the soil to Zn and Cu and it may collect in a distance and cannot go longer as the capacity of the adsorption is limited and comparing to Environmental Baseline Survey (Velea et al.) (Table 2), Cu has not increased since the EBS has been done which means that there is not any effect on Cu in the soil by byproducts. In addition, Ni has the highest mean value in 5 m and the value decrease with increasing distance till arrives 20 m, which may be linked to limited affinity of Ni through soil. However, the mean value increases from the distance of 25 m, which may be attributed to using fertilizer and pesticide some years ago by the local farmers as it was an agricultural land (Aydinalp. and Marinova., 2003). This could also be related to burning of some byproducts through the plant flare and then deposit the heavy metals on the surrounding soil.

**Table (2) Environmental Baseline Survey for Heavy Metals.**

| Elements | EBS Results |
|----------|-------------|
| Cd       | 1.1         |
| Cr       | 23          |
| Cu       | 42          |
| Ni       | 34          |
| Pb       | 8.5         |
| Hg       | 6.6         |
| Zn       | 23.8        |

However, heavy metals’ mean values of the Cr, Mn, Fe, As, Cd, Hg did not affected significantly by the distance factor which may be due to limited amount of those heavy metals in the produced water and all the amount which is present in the soil may naturally existed from the soil formation.

The produced water pH was in the range of (6.62 - 7.17), EC (1369 - 2512 µS) TDS (975.3 - 1879 ppm), TSS (730 to 748 ppm) and total hardness was (90 – 180 ppm).
Comparison

Figure (1) showed linear charts of some heavy metals (Pb, Zn, Hg, Cd, Cr and Cu) mean values compare to standard maximum allowable limit of the heavy metal by World Health Organization (Table 4). Figure (1) (A,C,D and F) indicate that Pb, Hg, Cd and Cu despite of being present in the soil and surrounding the Produced Water Pond are within the normal range in accordance to the World Health Organization standard for heavy metals, and don’t have a dangerous effect on leaching to underground water and on living organisms in the soil, while figure 1 (B and E) which are Zn and Cr have exceeded the normal range of the standard under effect of the produced water and other activities in surrounding soil.

![Comparison of heavy metals mean values and WHO standard limits](image)

A                                                                B
Figure (1) compare heavy metals mean value to World Health Organization standard limit.
Table (4) Guideline for the maximum permissible limit (MPL) values of the heavy metals in soil. (WHO, 1996)

| Elements | MPL value of soil (mg.kg⁻¹) |
|----------|-----------------------------|
| Cd       | 0.8                         |
| Cr       | 50                          |
| Cu       | 36                          |
| Ni       | 100                         |
| Pb       | 85                          |
| Hg       | 1                           |
| Zn       | 35                          |

4. CONCLUSION:

It is evident that there is a gradual buildup of some heavy metals in the soil around the gas plant area compared to Environmental Baseline survey which conducted 9 years ago and PEL of WHO. This reflects intense anthropogenic activities around the gas plant areas. Metal build up is gradual process, constant monitoring of the levels of these metals is required to safeguard farmlands and water bodies around these facilities. Also, burning byproducts have a role in increasing heavy metals. In addition, the heavy metals which were added to the soil in form of fertilizer and pesticide by local farmers some years ago, persist in the soil and increase the heavy metal levels. We recommend to performing a further research on effect of produced water on soil heavy metal by depth factor in future to detect the effect in the depth of the soil.

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