Contamination of Some Heavy Metals in Soil at Diyala/Sirwan River Banks

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Abstract. This study investigated contamination of a number of heavy metals including (Cadmium, Cupper, Lead, Nickel, Zink and Cobalt) in the soils of agricultural lands within Sirwan/Diyala River Banks. To determine the soils contamination by the mentioned heavy metals, sampling process was conducted in different points of the river banks. The evaluation of soil contamination in the current area was conducted by using some indices such as ecological risk factor (ER), enrichment factor (EF), contamination factor (CF), and geo-accumulation factor (Igeo). The outcome indicated that the levels of these elements were with the following order: Ni>Zn>Pb>Co>Cu>Cd. The values of enrichment factor were ranged from deficiency of Cu with a value of $(EF = 1.04)$ to significant enrichment of Ni ($EF = 18.87$). However, the values of contamination factor indicated low contamination of soil by Cu, Cd, Pb, Co and Zn with mean values of (0.15) , (0.56) , (0.65) , (0.72) and (0.76) respectively, to significant contamination by Ni (3.07). In terms of ecological risk factor, the average values of (Er) of all the observed elements were under low ecological risk category. The values of (Igeo) index for Cd, Pb, Cu, Zn and Co were under (unpolluted) category; while, Ni was under (unpolluted to moderate) category with a mean value of $(0.94 \ldots)$

Keywords. Sirwan/Diyala River Banks, heavy metals, contamination, Soil indices.

Introduction

Soil is considered as a fundamental part of the global ecosystem as it is an essential natural beside air, water and living things. Generally, the production of food and raw materials are its primary purpose [1]. Increasing the world population dramatically in last decades led to increase the need of huge amounts of food. While, soil production around the world has been influenced by the development of industrial production, road infrastructure and global warming [2]. It is thought that soil pollution, degradation and yield reduction are caused by chemical pollution, and as a result of using of irrigation water with poor quality, using excessive quantities of pesticides and herbicide as well as fertilizers [3-5]. The soil can be considered as contaminated when the concentrations of heavy metals in its horizons

exceed the acceptable levels [6]. Pollution by heavy metals forming a significant threat to the ecosystem security of river basins around the world, which has led to attract the attention of scholars over the world [7]. Two major sources of heavy metals in soil have been observed including: natural sources and manmade or anthropogenic sources [8]. The natural sources consist of rock weathering, atmospheric sedimentation, forest fire and volcanic eruption which all suspend heavy metals in the environment and thus falling and interring soil system[9]. On the other hand, the man-made sources include mining processes, transportation, irrigation by wastewater, electronic waste, using chemical pesticides, herbicides and fertilizers which all lead to accumulate heavy metals in soil [10]. Also, it has been illustrated that the man-made activities are the major cause of pollution by heavy metals especially in agricultural lands [11]. There are two factors that make heavy metals poisonous and dangerous which are their non-biodegradability in nature and their tendency to accumulate in soil causing deterioration of land productivity and harmful effects on crops quality [12,13]. Furthermore, the accumulation of heavy metal in soils can easily passing into the food chain and causing harmful effects. Thus, some heavy metals cumulate in human body and lead to cause chronic diseases regarding brain, liver, spleen, etc. Some heavy metals with high concentrations like lead, cadmium and mercury are dangerous for all living things, and some them considered as carcinogenic including arsenic, cadmium, chromium and beryllium which causing different diseases to children [2,14,15]. However, some other heavy metals like copper, cobalt, zinc are essential micronutrients and significant for human [16 J]

Sirwan River's banks are considered as important agricultural areas; while, limited researches were conducted regarding its contamination by heavy metals. The objective of the current study is to conduct an assessment of some heavy metals contamination in agricultural lands of Sirwan River Banks, Iraq. In the current study also, integrated pollution indices including ecological risk factor (Er), geo-accumulation factor (Igeo), contamination factor (CF) and enrichment factor (EF) have been utilized to estimate the level of pollution.

Materials and Methods

Study Area

It is located at the northern east of Iraq, and extends from Darbandikhan District to Jalawlaa sub-district, figure (1). The Sirwan

River receives huge quantities of wastewater from residential, industries, poultry projects and agricultural lands without any treatment. This is one of the main reasons for the pollution of the river and its banks.

Figure 1. The study area including sampling points.

Sampling and Analysis

Thirty samples of surface soil at depths 0–30 cm were collected from different locations at Sirwan River banks, figure (1) and table (1). All the samples were taken from wheat and barley fields which both are widely grown in the study area. A device of (GPS) has been used to determine the coordinates. The sampling process was conducted in December 2021, near the Sirwan riverbed at distances up to (50-100) m. All the samples were transferred to laboratory at Garmian University and were subjected to air-dry and then were sieved by a (2 mm) sieve. The heavy metals levels including (Pb, Ni, Zn, Cu, Cd and Co) were determined by (ICP-OES) device .

Table 1. The details of sampling stations within Sirwan/Diyala River Bank.

Soil Indices

Enrichment Factor (EF)

This is considered as one of the most significant indexes that indicate the environmental contamination degree. Also, it measures the possible effects of man-made activity on heavy metals concentrations in soil [17,18]. This factor was calculated by the following equation [19,20:]

 $EF = (\text{[(Me/Fe)]} \text{ (sample)}/(\text{[(Me/Fe)]}$ background)) (1)

Where, (Me/Fe)samples is the concentration of an observed heavy metal divided by the concentration of iron (Fe) in observed sample, and (Me/Fe)background is the natural

background of the same heavy metal and iron (Fe). As normalization element, Fe was selected as natural sources dominate its inputs [21]. Enrichment factor can be classified into five categories, table (2 .)

Contamination Factor

This index also can be carried out to evaluate soil contamination. It is calculated by the following equation [22:]

 $CF = (Cm_{sample})/(Cm_{background})$ $(2($

(Cm)sample represents the heavy metals concentration in an observed sample. (Cm)background represents the background value of the same heavy metal. Values of contamination factor can be classified into four classes, table $(2)($

Potential Ecological Risk (Er)

This factor is usually used to evaluate the soil ecological risk that caused by concentrations of heavy metals. The following equation was introduced by Hakanson (1980:)

 E_r^{\wedge} =T_r^ \times PI $(3($

Where, Tr represents the (toxic response factor), each metal has an individual Tr value. PI represents Single Pollution Index [22.]

Geo-Accumulation Index (Igeo)

This factor was proposed to evaluate the contamination of sediments by heavy metals [23]; then, it has been utilized in soil pollution researches [24]. It can be calculated by the equation below:

Igeo = $log_{10}^{(1)}$ 2Cm_(sample)/(1,5 Cm background ()) $(4($

Cmsample is the concentration of an observed heavy metal in a sample; Cmbackground is the same heavy metal's concentration in uncontaminated sample. While, (1.5) represents the factor that that used to modification the influence of any possible variations regarding the permissible values[25][26][27]. This index is also classified the heavy metal pollution into seven $(0 to 6)$ categories as mentioned in table (2) .

Table 2. The classifications of (CF), (EF), (Er) and (Igeo) indices [22,24,28,29.]

 $= 1$ >No contamination 2>Deficiency to minimum 30>Low 0>Unpolluted \geq 1CF<3 = Reasonable \geq 2EF<5 Reasonable 60–30Reasonable 1–0unpolluted to moderate

 \geq 3CF<6 = Significant \geq 5EF<20 Significant 120–60Moderate to high 2–1Moderate

 $CF>6$ = Very high $>20EF<40$ Very high 240–120High 3–2moderate to strong

EF >40 Extremely high 240 \leq Extremely high 4–3Strong

5–4strong to extreme

6>Extreme

Results and discussion

3.1

Concentrations of Heavy Metals

The heavy metals concentrations in the soil of Sirwan River Banks in the sampling stations were ranged Cd (0.12-0.41mg/kg), Cu (2- 8.65mg/kg), Pb (3.23-13.2mg/kg), Ni (101.55318mg/kg), Zn (47.98-102.1mg/kg) and Co (2.13-11.9mg/kg). The average values of the observed heavy metals have been calculated and found to be (0.229, 4.54, 6.74, 153.58, 68.24 and 5.74mg/kg) respectively as presented in table (3) and figure (2) .

Table 3. The concentrations of the heavy metals in the samples along Sirwan River banks.

Heavy Metal Min. Max. Ave. World median soil [30]

World average soil [31]

Earth crust [32]

It is very difficult to distinguish the anthropogenic from the natural sources of increasing metals in soil samples. The natural sources generate stronger imprint compared to anthropogenic sources for instance Ni, Co and Cu are developed from basaltic rocks into soil as a result of soil forming and rock weathering processes. The natural local background must be taking into account to estimate the heavy metals concentrations that are produced from the man-made sources. Since there is no available data or any study regarding the heavy metals in soils of the current area; therefore, the authors have been compelled to compare the present results with the world average soil, world median soil and the normal composition of earth crust. The results clearly demonstrated that the observed heavy metals concentrations from different sources (natural and man-made) were with the following order: Ni>Zn>Pb>Co>Cu>Cd.

The results of comparison revealed that Ni has abnormally high concentration; while, Cd has lower concentration in comparing with the other observed heavy metals. The average content of heavy metals in the soils of the current area differs from the average of world median, world average soil and the content of earth crust. This is normal due to the difference in the parent materials, processes of weathering and leaching [33,34]. The table (3) illustrates that the average values of Cu, Cd, Zn, Pb and Co are lower than the world average values; this indicates their poor sources of lithogenic. However, it is noted that there is slight increasing in the concentrations of Cd, Zn and Co which could be as a result of man-made activities .

Figure 2. The concentrations of observed heavy metals along Sirwan/Diyala River Banks.

Contamination Assessment

The table (4) below, shows that the assessment of studied factors and indices including contamination, enrichment factor, ecological risk and geo-accumulation index.

Table 4. Contamination index of the observed heavy metals in soil along Sirwan River banks.

The values of enrichment factor ranges from deficiency of Cu $(EF = 1.04)$ to significant enrichment of Ni at all the sampling stations $(EF = 18.87)$. The EF of Zn also considered as significant enrichment with an average of (5.02). However, the EF of Cd, Pb and Co considered as moderate enrichment with mean values of (4.4) , (3.81) and (4.9) respectively. The values of contamination factor indicate low contamination of soil by Cu, Pb, Cd, Co and Zn with mean values of (0.15) , (0.56) , (0.65), (0.72) and (0.76) respectively, to significant contamination by Ni with a mean value of (3.07) .

Regarding ecological risk factor, the mean values of all the observed metals are fall under low ecological risk category. The values are ascending order Cu<Zn<Pb<Ni<Cd<Co with mean values of (0.75), (0.76), (2.81), (15.36), (19.64) and (21.5) respectively. Regarding geo-accumulation index values, Cd, Cu, Pb, Zn and Co are fall under (unpolluted) category; while, Ni falls under (unpolluted to moderate) category with a mean value of (0.94) .

Discussion

In terms of Ni, it is noted that its average level is higher than the soil world average, world median and the composition of earth crust. This could probably be as a result of both natural and man-made sources; while, the natural sources of Ni could be stronger than anthropogenic sources. The contamination from municipal sewage, wastewater discharging and landfill stations are the anthropogenic sources of Ni in the present area. Also, the high concentrations of Ni may connected to the region's geochemical characteristics; weathering of the parent materials and hydrological erosion are the possible geogenic sources of Ni [3-37]. Fertilizers, pesticides, fungicides, animal manure, pigments and batteries are regarded as main sources of soil pollution by Zn [38,39]. A number of study observed that most of agricultural practices are significant sources of Zn, and it is as one host directly related to Fe and clay minerals[40]. The slightly high levels of Pb are attributed to the excessive application of fertilizer and insecticide as well as wastes of batteries [41]. Despite some sampling stations indicated abnormally high Pb concentrations; however, most of the sampling stations have moderate

concentrations of Pb which almost delegating slight contamination either due to anthropogenic or natural sources.

Cobalt is not considered as an essential nutrient for plants; while, it is one of the most pollutants that present in sewages [42]. It is accumulated in agricultural areas through using wastewater for irrigation and then causing toxic effects on plants [43,44]. As mentioned before, large amounts of wastewater are discharged daily into Sirwan River and this could be a source of increasing Co in some sampling station within the study area. Cadmium has a relative mobility, which make it to be less contaminant from both manmade and natural sources in the environment. Phosphate fertilizers, burning of oil, plastics, ceramics, glass and pigment are the most common sources of Cd in the environment $[45, 46]$

In contrary, lower concentrations of Cu in the study area indicate absence of both natural and man-made sources of pollutants. The soil content of copper relies on parent materials, clay content, organic matter and the value of soil's pH [47 .]

Conclusion

The objective of this research is to assess the contamination of a number of heavy metals in agricultural lands within Sirwan/Diyala River Banks. Integrated pollution indices have been used including (Er), (Ef), (CF) and (Igeo) factors. The outcomes indicate that the concentrations of the observed heavy metals are with the following order: Ni>Zn>Pb>Co>Cu>Cd.

The values of enrichment factor ranges from deficiency of Cu $(EF = 1.04)$ to significant enrichment of Ni at all the sampling stations ($EF = 18.87$). However, the values of (CF) indicate low contamination of soil by Pb, Cu, Cd, Co and Zn with mean values of (0.15), (0.56), (0.65), (0.72) and (0.76) respectively,

to significant contamination by Ni with a mean value of (3.07). Regarding the ecological risk factor, the mean values of all the observed metals are fall under low category. The values of (Igeo) index of Cd, Cu, Pb, Zn and Co are fall under (unpolluted) category; while, Ni falls under (unpolluted to moderate) category with a mean value of (0.94) .

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