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Impact of Using Aldanfeeli Valley Water on the Pollution of Soils with Heavy Metals

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ABSTRACT

The current study included collecting samples of water and soil from three main agricultural sites on Aldanfeeli Valley in Mosul city (North Iraq), where soil samples included two from each location, one for agricultural soil watered with untreated Valley water, and the second sample was from the adjacent uncultivated soils. A fourth site was chosen for the purpose of comparison at the end of Aldanfeeli Valley where the cultivated soil was watered with water of the Tigris River before the confluence of the River Valley. In addition to estimating the concentrations of heavy metals (Zn, Cd, Pb, Cu, Fe) in both water and soils, the present study aimed to identify some chemical and physical properties of the soils, namely: electrical conductivity, pH, organic matter, calcium carbonate, cations and anions, soil texture, and specific gravity. Despite the fact that the waters of Aldanfeeli Valley are poor for agricultural purposes in terms of salinity and total concentrations of both chloride and half of sulphate ions, the results showed that all soils do not suffer from the problems of salinity and alkalinity. Regarding the concentrations of heavy elements (Zn, Pb, Cd, Cu, Fe), their averages in the cultivated soils (23.86, 5.98, 75.14, 7.53 and 140.18) p.p.m. respectively, were higher than their counterparts in non-cultivated ones (18.70, 5.47, 36.82, 6.17 and 114.63) p.p.m. respectively. All soil samples especially the cultivated ones indicated higher concentrations than those of the irrigation waters (6.47, 4.87, 8.87, 2.27 and 7.07 p.p.m. respectively. The iron recorded at all sites higher means when compared to the rest elements. These were (140.18 and 114.63) p.p.m. in both the cultivated and noncultivated soils respectively. In both the second and the third sites of the cultivated soils; lead concentration averages of (114.25 and 91.06) $\mu g\ g^{-1}$ respectively, have exceeded its standard limit (50 $\mu g\ g^{-1}$); whereas, cadmium concentration averages in these two sites were (8.23 and 6.88) $\mu g\ g^{-1}$ respectively, have exceeded its critical limit (5 $\mu g\ g^{-1}$).

KEY WORDS:

heavy metals, soil pollution, wastewater

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1. INTRODUCTION:

In the past, the human contribution to contaminate his local environment does not form a great problem due to the low population, but with the steady increase in the numbers of the world's population and declining land productivity, the need of fresh water has become highly pressing, which prompted many countries to resort to the use of wastewater for agricultural purposes. In California alone, an estimated amount of wastewater treatment limits of 432 million cubic meters in which 260 million cubic metres are used for agricultural activities (Pescod, 1992). In Japan, more than 13 million cubic metres of treated sewage is reused in 1996 for agricultural activities (Taniyama and Adachi,

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1999). In Iraq, sewage waters are used to irrigate orchards and fields near sewage streams. This is clear in many farms located near Aldanfeeli Valley, Alkhouser River, and many other valleys in Mosul city that move large quantities of discards from the adjacent hospitals and residential buildings. In general, the process of using sewage for agricultural activities has some advantages and disadvantages (Massoudinejad *et al.*, 2006):

Heavy elements are all elements which have densities more than (6) g cm^{-3}. They are the most hazardous environmental pollutants and their severity is due to their cumulative property in the bodies of organisms (Sadik and Kamel, 2008; and Mohsen and Mohsen, 2008). Human and animal needs for a certain percentage of these elements that may get a part from the plants through the food chain (Azita and Seid, 2008), so the high concentrations of these elements in plant more than the allowed limits will subject the consumer life to danger (WHO, 2003). The increase in concentrations of these elements occure as a result of plant growth in a soil contaminated with these chemicals, or as a result of the excessive use of chemical fertilizers and pesticides, and often as a result of irrigation water contaminated with residues of plants, factories, drainage and sewage wastewater (Azita and Seid, 2008; Sadik and Kamel, 2008). Azita and Seid (2008) added to that, there are large areas of farmlands around the world are currently using untreated wastewater for irrigation due to the lack of the good quality water for this purpose.

Constantinescu (2008) studied soil contamination caused by mining in Romania, and had concluded that the concentrations of pollutants in forest soils were (199, 171, 65, 4.66) p.p.m. of zinc, lead, copper and cadmium, respectively; whereas, in the nearby agricultural soils the quantities of pollutants has increased to (749, 514, 113, 7.7) p.p.m. of the same elements, respectively.

Studies on vegetable-fed contaminated water indicated that these vegetables are containing high concentrations of heavy elements that make them invalid for consumption (Delibacak *et al.*, 2002; Lone *et al.*, 2003; and Durdana *et al.*, 2007). The industrial residues that contain heavy elements form the most serious pollutants affecting agricultural soils, and these could discharge in waterways and reused for irrigation once again. The most serious industrial elements that contaminate the soil are Zn, Cd, Pb, Cu, and Fe (Bowen *et al.*, 1969; Al-Rawi and Asheer, 1989; Al-Omer, 2000; Alhayali, 2001; Kabata-Pendias and Mukherjee, 2007; Mirsal, 2008; Vaalgamaa and Conley, 2008; Shereen, 2010; Al-Taie, 2012). Some of these elements are toxic even in low concentrations, such as lead, cadmium, copper (WHO, 2001). Table (1) shows the criteria adopted for the concentrations of heavy elements in soils (Aziz, 1995; and WHO, 2001).

Table 1: Criteria Adopted for Levels of Heavy Elements in Soils (Aziz ، 1995 ; WHO, 2001).

Element	Standard Soil $\mu g\ g^{-1}$	Critical Limit $\mu g\ g^{-1}$	Polluted Soil $\mu g\ g^{-1}$
Pb	50	150	600
Fe	/	/	/
Zn	70	300	/
Cu	20	50	/
Cr	100	250	800
Ni	50	100	500
Cd	1	5	20

Aldanfeeli Valley form one of the main vallies in Mosul city that carry large quantities of liquid wastes (1463 - 2106) $m^3\ h^{-1}$ into the Tigris River (Al-Assaf, 2009). Added to that, the presence of several farms on both sides of the valley are irrigated by its wastewaters. Therefore, in addition to some chemical and physical properties of the valley's water and the adjacent soils, the present study aimed to investigate the impact of using these untreated wastewaters on the concentrations of some heavy metals including (Zn, Cd, Pb, Cu, and Fe) on the nearby agricultural soils.

2. MATERIALS AND METHODS:

2.1 Sites of Collecting Soil and Water Samples:

On 29th of November 2012, samples of water and soil took from three main agricultural sites on Aldanfeeli Valley in the city of Mosul, where soil samples included two from each location, one for agricultural soil in which had been cultivated at least for the last ten years with different field crops like radish, cauliflower, and tomatos. This soil was watered directly with the Valley untreated water, while the other one was from the adjacent uncultivated soil. A fourth site is located at the end of Aldanfeeli Valley, in which the soil was planted and watered by the Tigris River water before the confluence of the Valley with the River. Figure (1) shows the sampling sites, and these are as follows:

Site (1): represents the region following the Green District Treatment Plant about (100 m).

Site (2): represents the area beyond both the industrial region and the sheep market in the left side of Mosul city. The region include significant areas of farmland irrigated by Valley's water.

Site (3): forms the beginning of the farms region that is irrigated with Valley's water before its confluence with the Tigris River of about (1 km).

Site (4): represents the water of the Tigris River before the confluence of the River Valley stream, and the agricultural soil sample was irrigated by the Tigris River water.

2.2 Chemical and Physical Tests of Water and Soil Samples:

2.2.1 Water Samples: Measurements of waters' electrical conductivity (EC) and (pH) were taken in situ time samples. Whereas, tests of sodium, calcium, magnesium, chloride, nitrate, sulfate, and bicarbonat were made by the same ways as in soil extracts.

2.2.2 Soil Sampling: Soil samples were collected from the abovementioned sites at a depth of about (25 cm), and were placed in polyethylene bags. They were dried naturally, then milled and sieved by (2.00 mm) openings before being preserved for the following tests.

Electrical conductivity for soil water extract (1:1) was measured using a HI-99301 E.C. meter measured in units of (ds m^{-1}), pH with a pH meter PB-11, the organic matter using ferrous and ammonium sulphate solution (0.5 M) and diphenyl amine indicator in an acidic media (Jackson, 1958). Calcium carbonate has been measured by adding specific volume of 1N HCl solution to a specific weight of dry soil, then the extra HCl was calibrated with 1N NaOH solution using phenol-phthalene indicator (Richards, 1969). Total carbonates and bicarbonates were measured through calibration with 0.01 N H_2SO_4 solution using phenol-phthalene and methyl orange indicators (Richards, 1969).

The specific gravity of the soil, which represents the ratio between actual density of soil and water density, has been measured using 100 ml volumetric flask (pycnometer) and following the American Standard Method for testing materials (Das, 1982). Using the hydrometer method, the particles size distribution for soils were estimated by determining the percentages of sand, silt and clay and extrapolating the results of analysis on soil texture triangle (Richards, 1969).

The concentration of sodium ions were measured for soil water extract (1:5) using a PFP7 Flame Photometer, calcium and magnesium ions by titration with 0.01 N ethylene di amine tetra acetic acid (EDTA) solution and using Eriochrom Black T. indicator. The concentration of chloride ions have been measured by titration with silver nitrate solution 0.01 N AgNO3 and by using potassium dichromate 5% K_2CrO_4 indicator, both nitrates and sulphates by UV – 9200 Spectrophotometer (Richards, 1969).

Concentrations of trace elements (Zn, Cd, Pb, Cu, Fe) were measured according to the method proposed by (Hendershot *et al.*, 2008) using calcium chloride solution 0.01 M $CaCl_2$ for the purpose of extracting elements from soil samples. The Atomic Absorption Spectrometer device type NOVAA was used for elements readings.

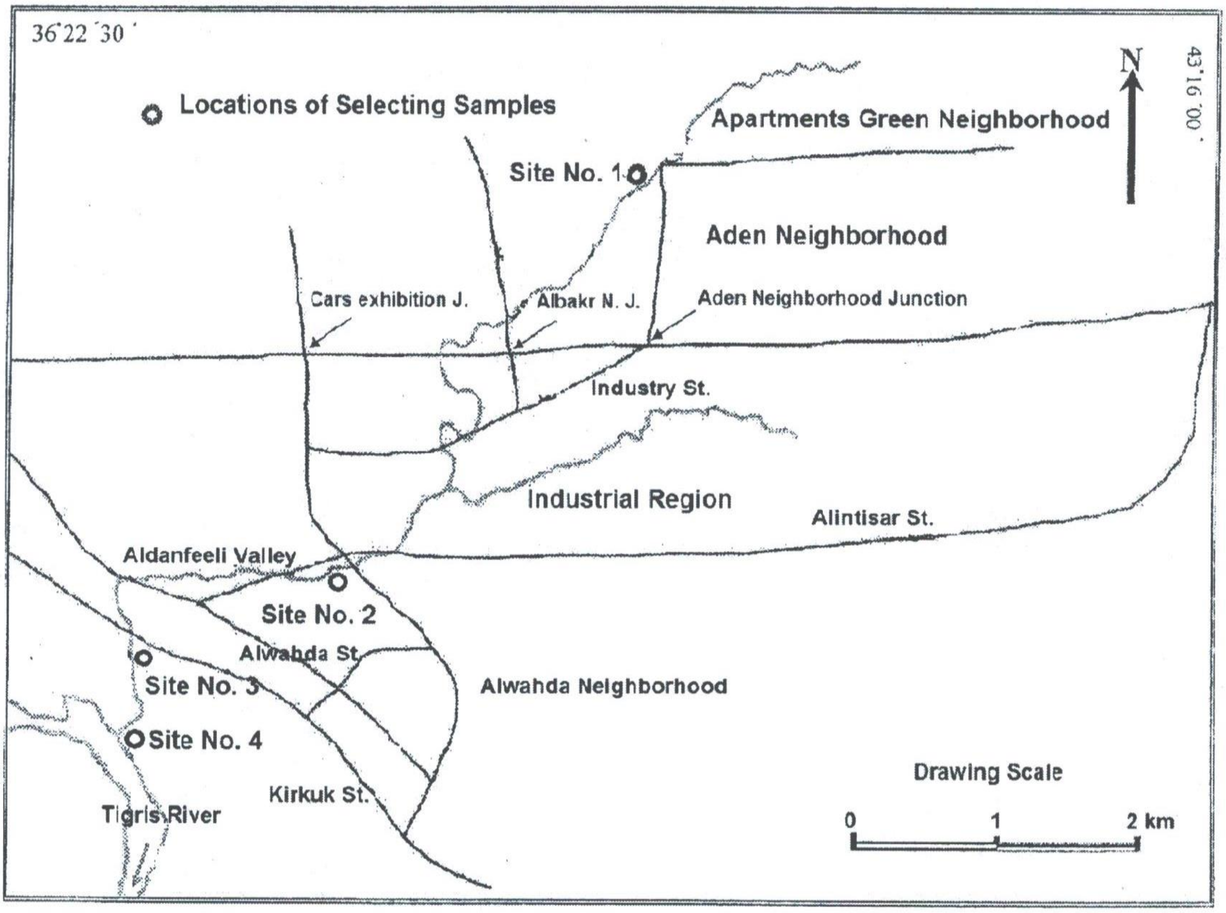

Figure (1): Shows the study area and the sites of collecting samples (Al-Assaf, 2009).

3. RESULTS AND DISCUSSION:

3.1 pH:

Table (2) indicated that pH values of the soils under study are ranged (7.2-7.9). Although this range is not too high, it could be responsible for the precipitation of phosphorus as calcium phosphate (Tisdale and Nelson, 1975). They indicated also that the availability of phosphorus could be the highest at soil pH (5.5 – 7). Jones and Fox (1978) found that corn plants gave the highest growth in soils of pH (6.3, 6.7 and 7.2) when there was enough phosphorus in soil solution.

3.2 Electrical Conductivity (E.C.):

Table (2) indicated that the EC values for soils studied are ranged between 1.088 ds m^{-1} in the uncultivated soil (site No. 2) to 4.184 ds m^{-1} in the cultivated soil (site No. 3). These values, except in the cultivated soil of site 3, are all pointing to the fact that these soils are natural due to the fact that the conductivity of the soils extracts in all sites are less than 4.0 ds m^{-1} (Table 3) (Ryne *et al*., 2003). Moreover, table (2) showed that the agricultural soils have relatively higher salinity compared with those on the shoulders of the Valley. This is due to the accumulation of salts in agricultural soils as a result of irrigation by waters polluted with salts (Table 4).

Table 2: Chemical Characteristics of the Studied Soils Samples.

Soil Character	Sample No.						
	1A	1B	2A	2B	3A	3B	4B
pH	7.20	7.68	7.80	7.90	7.50	7.70	7.70
EC (ds m^{-1})	1.164	3.685	1.088	3.222	1.382	4.184	1.406
Organic Matter (gm kg^{-1})	18.3	28.3	21.4	34.8	27.6	28.4	36.0
$CaCO_3$ (gm kg^{-1})	320	320	350	330	230	200	170
Clay (%)	38.4	40.0	30.3	29.4	21.1	20.3	20.6
Silt (%)	47.2	45.2	58.1	59.8	47.9	47.4	42.8
Sand (%)	14.4	14.8	11.6	10.8	31.0	32.3	36.5
Texture	SiC	SiC	SiCL	SiCL	L	L	L
Specific Gravity	2.782	2.835	2.760	2.801	2.714	2.754	2.480
Na^+ (ppm)	65	200	63	210	74	215	48
Ca^{+2} (ppm)	170	550	90	275	140	400	168
Mg^{+2} (ppm)	20	57	42	145	70	195	62
NO_3^- (ppm)	40	166	110	397	108	315	46
Cl^- (ppm)	202	640	140	435	262	760	292
SO_4^{-2} (ppm)	230	723	170	490	245	726	244
HCO_3^- (ppm)	30	35	34	107	19	52	62
* S.A.R. $(meq./L)^{0.5}$	1.257	2.172	1.374	2.552	1.276	2.203	0.805

* SAR (Sodium Adsorption Ratio) $(meq./L)^{0.5} = Na_s^+/\{Ca_s^{+2}+Mg_s^{+2}) / 2\}^{0.5}$
A = Uncultivated soil.
B = Cultivated soil.

Table 3: Classification of Soils Depending on Salinity and Sodium Adsorbtion Ratio (Ryne *et al*., 2003).

Soil	EC (ds m-1)	SAR $(meq./L)^{0.5}$
Natural	< 4	< 15
Saline	≥ 4	< 15
Alkaline	< 4	≥ 15
Saline – Alkaline	≥ 4	≥ 15

Table 4: Chemical Characteristics of the Water Samples.

Water Character	Sample No.			
	1	2	3	4
pH	7.5	7.1	6.9	7.1
EC (ds m^{-1})	4.650	4.780	4.430	0.842
Na^+ (ppm)	235	256	207	18
Ca^{+2} (ppm)	500	470	420	105
Mg^{+2} (ppm)	105	120	143	26
S.A.R. $(meq/L)^{0.5}$	2.491	2.721	2.226	0.408
NO_3^- (ppm)	560	760	620	86
Cl^- (ppm)	1020	925	950	102
SO_4^{-2} (ppm)	301	260	230	125
HCO_3^- (ppm)	155	164	142	95
$Cl^- + 1/2\ SO_4^{-2}$ (meq/L)	31.83	28.805	29.195	4.170

3.3 Sodium Adsorption Ratio (SAR):

From (Table 2), it is obvious that SAR values for soils studied are ranged between (0.805-2.552) $(\text{meq./L})^{0.5}$ indicating that all soils are natural and do not suffer from the problem of the increase in dissolved sodium ions (Table 3). All cultivated soils indicated higher SAR comparing with the uncultivated ones. This is due to the accumulation of extra sodium salts as a result of irrigation by valley's water. Moreover, there was a relative increase in SAR value in site No. (2) in comparison with the other sites. This is probably due to the relative increase of SAR value for the Valley's water in this site (Table 4).

3.4 Organic Matter:

Soil organic matter represent remnants of plants and microorganisms in different stages of decomposition and the diversity of its components. Despite the presence of organic matter in the soil with relatively small quantities, it has a major impact on soil structure, food stock, retain moisture, and biological activities.

The organic matter ammounts in the soils of different sites are ranged between 18.3 to 36.0 (gm kg^{-1}). These form good ratios in agricultural soils and are good for seed germination as the organic matter mmounts in arable soils in temperate heat regions is usually more than 30-40 (gm kg^{-1}), while soils in arid and semi-arid areas are containing overall less than 10 (gm kg^{-1}) organic matter (Ryne *et al*., 2003).

The results showed as well that the organic matter values in the cultivated soils are higher compared to the shoulders of the Valley as a result of the presence of some plant residues in the cultivated ones (Table 2).

3.5 Evaluation of Aldanfeeli Water for Irrigation Purposes:

Table (4) shows some chemical properties of water samples taken from the four sites under consideration. Beside being affected with large amounts of salts as the electrical conductivities are very high (EC > 2.250 ds m^{-1}) (Richards, 1969), the results indicated that Aldanfeeli Valley water is bad for agricultural purposes as the total concentration of both chloride and half sulphate ions in the three sites (1, 2, and 3) were (31.83, 28.805 and 29.195) meq./l respectively. These values are much higher than the concentrations suggested by (Doneen, 1954) for the classification of water by salinity regardless of the permeability of soils (table No. 5). Whereas, the Tigris River water in site (4) is good for agricultural purposes as the total concentration of both chloride and half sulphate ions was only (4.170) meq./l. This value is less than (7), especially the permeability of soils in this region is high due to soils' loamy texture.

Table 5: Classification of Irrigation Water by Salinity Regardless of Soils Permeabilities (Doneen, 1954).

Water Quality	$(Cl^{-} + 1/2\ SO_4^{-2})$ Concentration in water (meq. / L.)		
	Low permeability	Medium permeability	High permeability
Good	< 3	< 5	< 7
Medium	3 – 5	5 – 10	7 – 15
Bad	> 5	> 10	> 15

3.6 Trace Elements:

Table (6) and figures (2-6) indicate concentrations of heavy elements in soils and irrigation water samples under study, so the following points can be illustrated:

1. Concentrations of all trace elements in the cultivated soils (1B, 2B, and 3B) are higher than their counterparts in non-cultivated ones (1A, 2A, and 3A). This was due to accumulation of these elements in the cultivated soils as a result of their irrigation with Aldanfeeli Valleys' wastewaters.
2. Concentrations of all elements in the soils are higher than those in the water samples of the same sites as a result of their continuous accumulation over time.

3. Cultivated soils in site (2) showed a significant increase in the concentrations of all elements compared with the rest sites. This is because this site is located near the industrial zone, where industrial wastes are put directly into the Valley; whereas, site No. (4) showed very low levels of heavy metals as the water used for irrigation was coming directly from the Tigris River before its confluence with the valley.
4. Cadmium concentrations in the cultivated soils at the second and the third sites were (8.23 and 6.88) p.p.m. respectively. These concentrations exceeded cadmium critical limit of (5 µg g^{-1}) (Table 1). This was because of the element high concentrations in the original soils of both sites (7.32 and 6.40) p.p.m. respectively; and due to the high levels of this element in irrigation waters (7.1 and 5.3) p.p.m. respectively in sites II and III.
5. Concentrations of the lead in the second and the third sites of the cultivated soils were (114.25 and 91.06) p.p.m. respectively. These concentrations exceeded lead standard limit of (50 µg g^{-1}) (Table 1). These were probably because the two sites are located near the main streets where vehicles exhaust are containing high proportions of this element.
6. Iron in all sites indicated high concentrations maybe due to its abundance in the Earth's crust and multiplicity confiscation compared to other components.

Table 6: Concentration of Heavy Metals in Soils and Irrigation Water Samples.

Sample No.	Zn Ppm		Cd ppm		Pb ppm		Cu ppm		Fe ppm	
	Water	Soil	Water	Soil	Water	Soil	Water	Soil	Water	Soil
1A	2.1	18.24	2.2	2.70	2.3	20.24	1.3	4.26	1.8	115.48
1B		20.52		2.84		20.10		6.23		120.05
2A	10.2	16.46	7.1	7.32	15.8	44.00	3.5	8.32	12.3	112.88
2B		28.72		8.23		114.25		9.51		175.25
3A	7.1	21.40	5.3	6.40	8.5	46.22	2.0	5.94	7.1	115.52
3B		22.34		6.88		91.06		6.84		125.23
4B	0.07	6.32	0.01	0.84	0.14	7.04	0.05	2.30	0.08	78.25

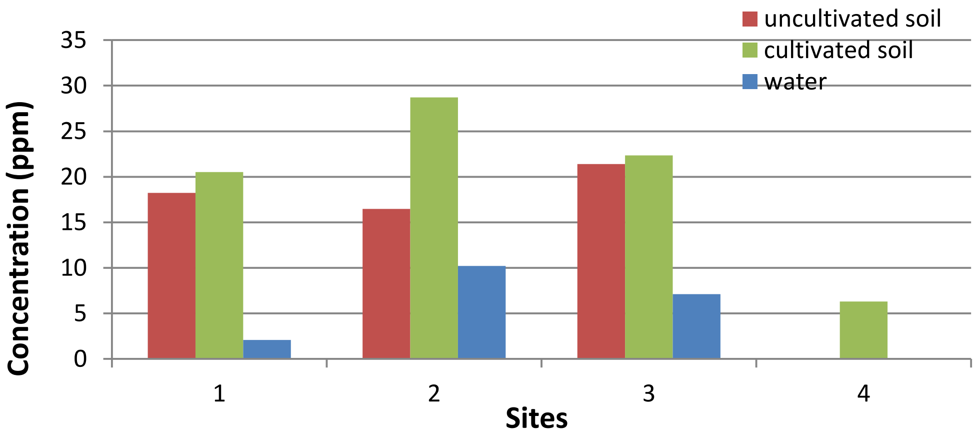

Figure 2: Concentrations of Zn in Soil and Water Samples.

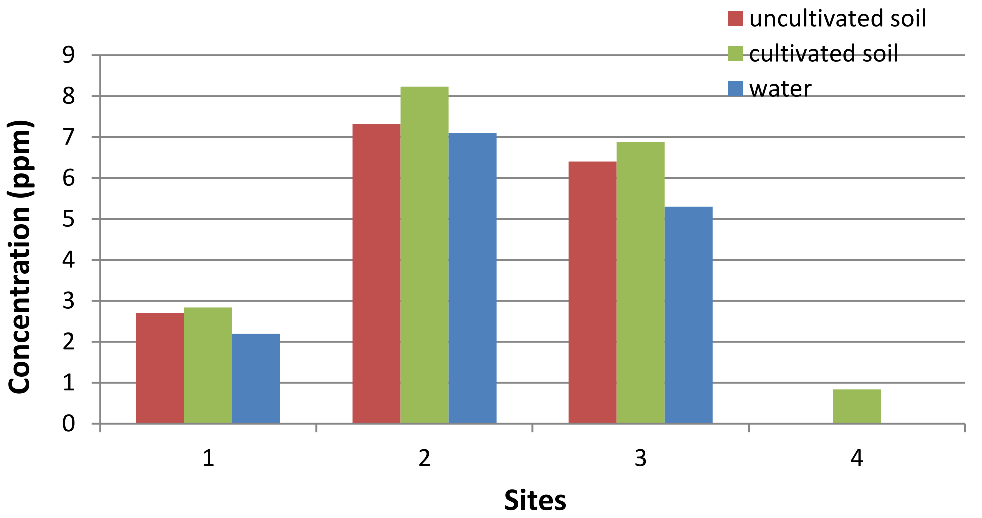

Figure 3: Concentrations of Cd in Soil and Water Samples.

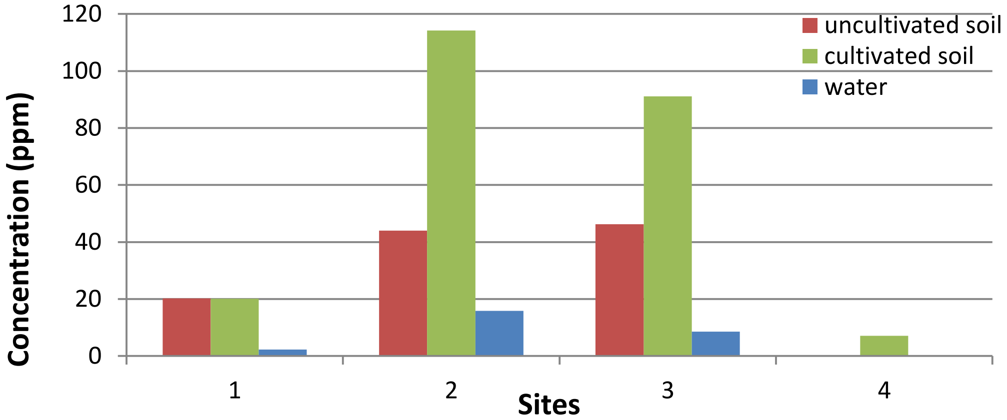

Figure 4: Concentrations of Pb in Soil and Water Samples.

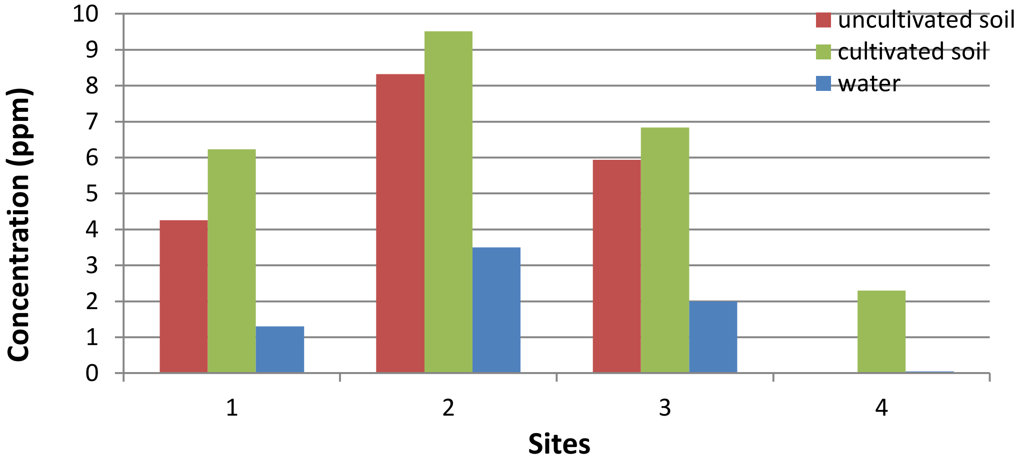

Figure 5: Concentrations of Cu in Soil and Water Samples.

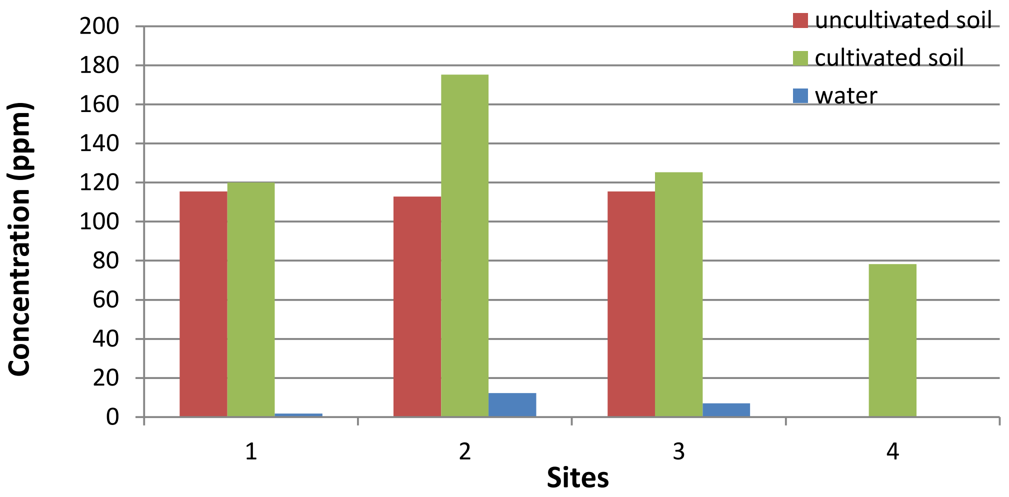

Figure 6: Concentrations of Fe in Soil and Water Samples.

4. CONCLUSIONS:

Due to the presence of many heavy metals including (Zn, Cd, Pb, Cu, Fe) in Aldanfeeli Valley wastewater; therefore, it is recommended not to use this water for the irrigation purposes, especially as large amounts of some of these elements are getting accumulated in the irrigated soils. It is worth mentioning that the contamination of soils with these elements could form a significant risk to human health through infection of kidney, lung, heart, liver, brain, bones, ability to breath and many other problems (Bowen *et al.*, 1969; Al-Omer, 2000; Kabata-Pendias and Mukherjee, 2007; Mirsal, 2008; Shereen, 2010; Al-Taie, 2012)..

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تأثير استخدام مياه وادي الدانفيلي على تلوث الترب بالمعادن الثقيلة

نايف بكر احمد

كلية علوم البيئة وتقاناتها / جامعة الموصل

المستخلص

تضمنت الدراسة الحالية جمع عينات من المياه والتربة من ثلاثة مواقع زراعية رئيسة على وادي الدانفيلي في مدينة الموصل (شمال العراق) ، حيث شملت عينات التربة نموذجين من كل موقع احدهما للتربة المزروعة والتي كانت تسقى بمياه وادي الدانفيلي غير المعالجة ، اما العينة الثانية فكانت للتربة غير المزروعة والمجاورة للوادي . وقد تم اختيار موقع رابع في نهاية وادي الدانفيلي لغرض المقارنة حيث ان التربة المزروعة كانت تسقى مباشرة من نهر دجلة قبل التقائه مع مجرى الوادي .

استهدفت الدراسة الحالية إلى تقدير تراكيز المعادن الثقيلة (الزنك ، الكادميوم ، الرصاص ، النحاس ، والحديد) في عينات المياه والترب ، وكذلك تحديد بعض الخصائص الكيميائية والفيزيائية للتربة، وهي: التوصيل الكهربائي ، درجة الحموضة ، المادة العضوية ، كربونات الكالسيوم ، تراكيز الايونات الموجبة والسالبة ، نسجة التربة ، والوزن النوعي .

اظهرت النتائج بانه على الرغم من حقيقة كون مياه وادي الدانفيلي تعتبر سيئة للأغراض الزراعية وذلك اعتمادا على ملوحتها ومجموع تراكيز أيونات الكلوريد ونصف الكبريتات ، الا ان النتائج أشارت الى أن جميع الترب قيد الدراسة لا تعاني من مشاكل الملوحة والقلوية . وفيما يتعلق بتراكيز العناصر الثقيلة (الزنك ، الكادميوم ، الرصاص ، النحاس ، والحديد) ، فقد كانت معدلات تراكيزها في الترب المزروعة (23.86 ، 5.98 ، 75.14 ، 7.53 ، 140.18) جزء لكل مليون جزء على التوالي ، أعلى من نظيراتها في الترب غير المزروعة والتي كانت (18.70 ، 5.47 ، 36.82 ، 6.17 ، 114.63) جزء لكل مليون جزء على التوالي. وقد اظهرت جميع عينات الترب وخصوصا المزروعة منها تراكيزاً أعلى للعناصر اعلاه مقارنة مع نظيراتها في عينات المياه المستخدمة للسقي ، حيث كانت معدلاتها في المياه (6.47 ، 4.87 ، 8.87 ، 2.27 ، 7.07) جزء لكل مليون جزء على التوالي. واظهر عنصر الحديد في جميع المواقع تركيزاً أعلى بالمقارنة مع بقية العناصر حيث كانت معدلاتها للمواقع المختلفة (140.18 و 114.63) جزء لكل مليون جزء في الترب المزروعة وغير المزروعة على التوالي. وكانت تراكيز الرصاص في الموقعين الثاني والثالث للترب المزروعة (114.25 و 91.06) جزء لكل مليون جزء على التوالي حيث تجاوزت الحد القياسي له والبالغ (50) جزء لكل مليون جزء ، بينما تجاوزت تراكيز الكادميوم لكلا الموقعين (8.23 و 6.88) جزء لكل مليون جزء على التوالي الحد الحرج له والبالغ (5) جزء لكل مليون جزء .

الكلمات المفتاحية: مياه، وادي الدانفيلي، تلوث، العناصر الثقيلة، الزنك، الكادميوم، الرصاص، النحاس، الحديد.