Soil Contamination by Heavy Metals in Floodplain of Qweik River, Aleppo, Syria

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Abstract:

The Fe, Cd, Cu, Mn, and Zn heavy metals in 48 samples from the soil of the floodplain at the midstream of the Qweik River, south of Aleppo City, near Al-ISS village have been investigated by using atomic absorption spectrophotometer.

The results showing that; the range of Fe between (2.1- 147.2 ppm), below the high limit of the soil and the relative high abundance of Fe in the first two stations closed to the river channel and enriched with organic matter enrichment.

The Cd concentration in the studied samples with a wide range (1.1- 9.2 ppm), higher than the standards in the soil and that may due to irrigation by sewage wastewater during long period of time.

The Cu concentration between (1.8-14.2 ppm) which is less than standards and the relative high concentration in the first two stations may associated with enrichment of the soil with organic matters. Also, Mn concentration between (0.1- 68.2 ppm) and Zn between (0.3- 8.6ppm), which are both below the standard limits of the soil contents. The wide range of these two elements may related to the high concentration of organic material in the first two stations.

Introduction:

Qweik river originated from Turkey and flow through Aleppo city (the second largest city of Syria) from the north to south, and because of the extraction of the water in the river became dry since 1970s. The sewage wastewater and industrial wastewater of the city flow in the channel of the river, and this water polluted by heavy metals. The wastewater mixed with natural water of Euphrates river by artificial channel extend from Al-Asad lake to Qweik river in Sandarat Campus, North Aleppo, the channel flow capacity is about $3m^3$/sec. the purpose of this project to enhance the water quality of Qweik river and dilute the concentrations of heavy metal pollutants (figure 1).

The major industries of the area deal with weaving and textile, tannery, cement and construction material, batteries and liquid gas, and chemicals. In practice, Qweik River contains a domestic-industrial, treated-untreated mix wastewater.

Some industrial units within the municipal boundaries also discharge untreated wastewater to the sewer system. This industrial wastewater contains specific metals and metalloids and other toxic elements, which hardly undergo treatment at the wastewater treatment plant because of its design limitations to treat domestic wastewater only.

Consequent to the discharge of wastewater from Aleppo to the Qweik River, there are possibilities of soil contamination in areas under wastewater irrigation. The concentrations of some metal ions in wastewater from the Qweik River have been found to be several folds above the maximum recommended levels in irrigation water. For instance, chromium (Cr) in the wastewater samples has been found to be as high as 0.85 mg/L (GOLD, 2005 in (ICARDA-IWMI, 2006), a value that is nearly 8 times greater than the maximum recommended concentration of 0.1 mg/L in irrigation water (FAO, 1985). The Cr contribution to wastewater is associated with tanneries. Even after the operation of the wastewater treatment plant in Aleppo, the possibilities of soil and crop contamination in wastewater irrigated areas cannot be eliminated for the reasons:

(1) many chemicals pass through the post-treatment effluent because the treatment plant has been designed to treat domestic wastewater, and (2) only about half of the wastewater generated is subject to treatment and the rest is diverted to the river in untreated form

The present study aims to:

1- Investigation of the Fe, Cd, Cu, Mn, and Zn heavy metals in the soil in floodplain of midstream of river south Aleppo near Al-Iss village (figure 1).
2- Evaluation of the results and compare it with the international standard limits and the Syrian Standardization Commission, 2003.

There is no information available on typical background values for metal ion concentrations in Syrian soils (Möller et al., 2005 in ICARDA-IWMI, 2006).

The environmental implications of wastewater irrigation in terms of soil and water pollution have rarely been studied in Syria soils. Further more, there are many studies about the contamination of heavy metals in many places such as:

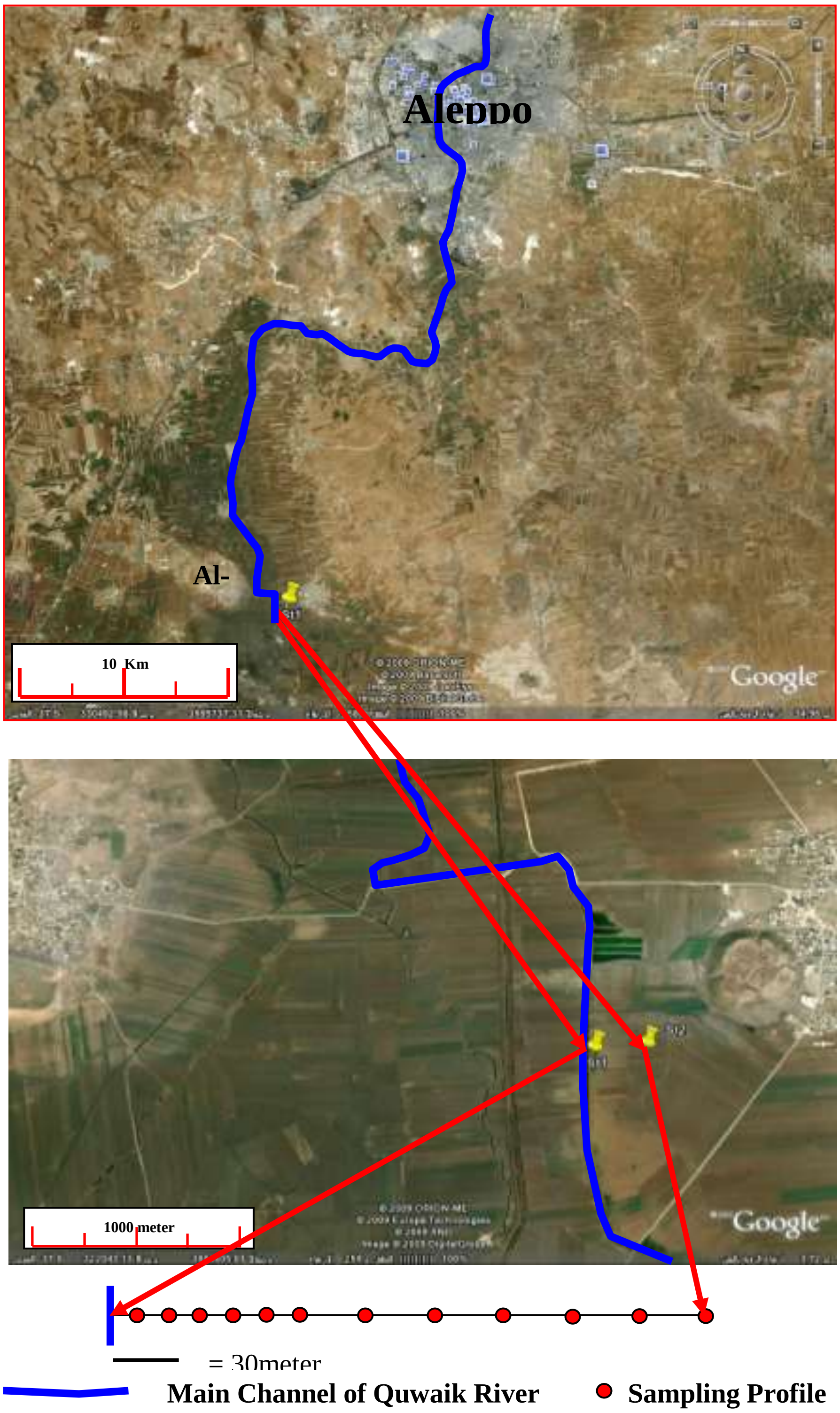

Figure 1: Location map of Qweik River showing the studied area and sampling profiles

De Mique et al., in (Kabata-Pendias and Pendias, 2001) based on the investigations of pollution in Oslo (Norway) and Madrid (Spain), have distinguished so-called "urban" pollutants: Ba, Cd, Pb, Sb, Ti, Zn, and Cu. in Warsaw (Poland), the relative increase is noticed for Li, Ni, Zn, Cr, Pb, Ba, Sr, and Fe, a moderate increase in Pb, Cd, and Cu, but not in Zn, was noticed in soils.

Darwish et al., 2008, studied the preliminary contamination hazard assessment of the land resources in central Bekka plain of Lebanon, they found that the range of heavy metal concentration remain within the multifunctional land use for all metals except Ni and Cr.

Also, (Margesin, and Schinner, 2005) point out that the most heavy metals are of geological origin, but contamination with them may be due to industrial, mining, agricultural, waste handling or other activity. Often a mixture of such metals occurs. The most common contaminants are As, Cd, Cr, Cu, Co, Pb, Hg, Ni, and Zn.

Slagle, et. a., 2004, assessed the trace element content of three major soil series in Major Land Resource Area of the Appalachian region of the USA by two extraction techniques. They were described and sampled, bulk density, texture, pH, cation exchange capacity (CEC), base saturation, and total carbon were determined for each described horizon. For the A, B, and C horizons of each soil series, concentrations of ten heavy metals (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Se, Zn) were determined by ICPAES after microwave digestion by USEPA Method 3051 and an HF method. They found that there is a difference in concentrations of heavy metals between the two used method.

Fox, et al., 2009, studied the Micro-Scale Distribution of Trace Elements in a High Boron Soil by using the microprobe x-ray fluorescence (μ-XRF) and Fourier transformed infrared (μ-FTIR) spectroscopy, and concluded that the collect information on the spatial distribution of elements in intact soil aggregates on a micron scale.

Al Zoubi, et al. 2008, studied the effect of sewage sludge on heavy metals accumulated in soil and indicated no effect of these metal on the studied plants except Cd.

Hejcman et. al. 2009 formed a change in trace elements concentrations as a result of fertilized soil for a period of 65 year, with in depth 0-10cm and 10-20cm from top soil.

Sampling and Analysis:

The soil in the study area is considered as a Terra Rossa, which is common in the Mediterranean region (Foster et al., 2004). The study location was between Universal Transverse Mercator UTM coordinates 322778.8, 3983981-323030.4, 3983978 at the midstream of Qweik River (figure 1). The sampling sites were 12 and extended from the eastern side of the river to a length of 270 m. The distance between the first 6 sites was 15 m, which was increased to 30 m in the remaining 6 sites (figures 2 and 3). The soil samples were collected from each site at depths of 0-10, 10-20, 20-50, 50-80 cm. Therefore, the total collective samples were 48 (12 sampling sites × 4 sampling depths).

The concentrations of Fe, Cd, Cu, Mn, and Zn trace elements were determined by using Atomic Adsorption Spectrophotometer in laboratories of ICARDA.

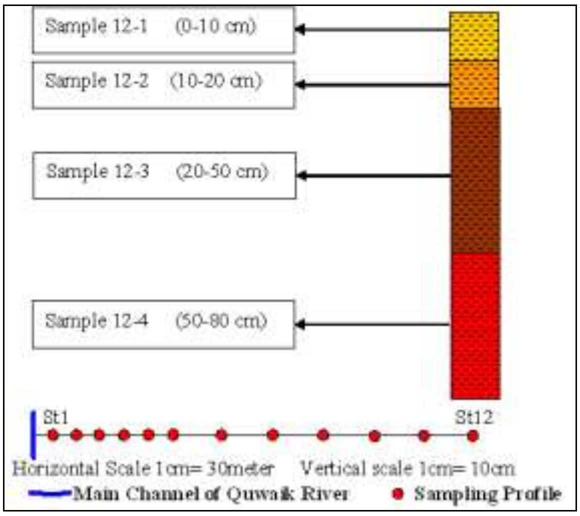

Figure 2: Sketch of the stations of soil profiles and representative samples of each profile.

Results and Discussion:

The previous studies in many locations through out the world indicated that the pollution by heavy metal take place as a result of contamination by the different type of wastewaters from industries and domestic uses. The following heavy metals are the most contaminant elements by waste sewage water, the study of these elements used to compare the results within the maximum standard limits of the concentration for agriculture purposes.

48 samples were analyzed for the purpose of heavy metal concentrations and the results listed in (table 1).

Figure 3: Field collection of samples by using hand auger

Table 1: Represent the concentrations of Fe, Cd, Cu, Mn and Zn (ppm), heavy metals in the soil samples of Qweik river flood plain

Field	Depth	Fe	Cd	Cu	Mn	Zn
no.	cm	ppm				
1	0-10	147.9	7.1	14.2	48.0	8.6
	10-20	76.4	5.5	4.9	17.6	6.3
	20-50	34.3	2.6	3.2	5.5	4.9
	50-80	27.9	5.3	2.3	6.9	1.6
2	0-10	68.9	5.9	9.1	49.7	8.5
	10-20	33.2	2.8	4.6	21.2	4.4
	20-50	19.9	3.5	2.1	5.1	1.5
	50-80	18.9	3.6	2.1	6.7	0.7
3	0-10	12.3	3.9	4.3	33.3	5.0
	10-20	35.7	2.7	3.1	13.7	2.8
	20-50	31.2	6.2	2.9	6.1	1.5
	50-80	16.9	9.2	2.6	12.5	0.6
4	0-10	22.1	2.2	3.1	20.0	3.3
	10-20	28.0	4.5	2.8	15.7	1.8
	20-50	20.5	1.9	2.9	14.4	0.6
	50-80	25.1	2.3	2.6	17.0	0.5
5	0-10	29.3	1.9	2.8	18.0	2.6
	10-20	19.6	2.5	3.2	21.1	1.8
	20-50	21.5	2.9	3.0	23.8	1.2
	50-80	23.2	5.1	2.7	28.8	0.6
6	0-10	22.3	4.9	2.8	17.8	2.1
	10-20	12.0	3.8	2.7	23.5	1.2
	20-50	18.8	4.3	2.4	25.6	0.6
	50-80	6.8	2.9	2.0	22.0	0.6
7	0-10	31.2	6.5	3.0	23.7	2.1
	10-20	23.4	2.7	2.9	29.9	1.6
	20-50	34.5	3.0	2.4	22.6	1.4
	50-80	13.6	5.1	1.8	22.1	0.3
8	0-10	26.5	4.6	2.9	33.1	2.3
	10-20	17.5	3.5	2.5	32.4	1.6
	20-50	25.6	1.8	2.6	27.7	0.6
	50-80	21.2	5.6	2.5	35.2	0.5
9	0-10	34.4	4.7	3.1	68.2	3.1
	10-20	38.8	5.0	2.6	41.5	1.4
	20-50	13.8	4.0	2.6	35.8	0.5
	50-80	15.3	3.0	2.3	25.5	0.7
10	0-10	2.1	3.8	2.3	42.3	2.1
	10-20	14.8	2.1	2.5	40.4	1.9
	20-50	12.5	2.9	2.2	21.9	0.3
	50-80	14.0	6.1	2.4	18.0	0.4
11	0-10	5.9	3.0	2.2	36.3	1.9
	10-20	16.7	3.2	2.5	40.0	2.1
	20-50	17.6	1.1	2.5	40.2	1.3
	50-80	16.2	2.0	2.5	17.1	0.6
12	0-10	21.5	3.9	2.7	49.3	1.7
	10-20	32.6	3.5	2.6	38.5	1.3
	20-50	35.5	2.0	2.6	28.7	0.7
	50-80	20.7	2.1	2.2	26.9	0.4

Iron (Fe):

In soils, Fe is believed to occur mainly in the forms of oxides and hydroxides as small particles or associated with the surfaces of other minerals, Iron concentrations in most soils ranged between 0.5-5%. However, in soil horizons rich in organic matter, Fe appears to be mainly in a chelated form. Certain fractions of Fe in soils reveal magnetic properties. The increasing of magnetic Fe to regular Fe in a soil, as compared to mother rock, indicates the impact of industrial pollution.

Both mineral and organic compounds of Fe are easily transformed in soils, and organic matter appears to have a significant influence on the formation of Fe oxides. These oxides may be amorphous, semicrystalline, or crystalline, even under the same conditions (Kabata-Pendias and Pendias, 2001).

The range of Fe concentrations in the studied samples between 2.1- 147.2 ppm, it is also noted that the concentration is high in the 1st two stations and that may due to association with organic matters, figure 4.

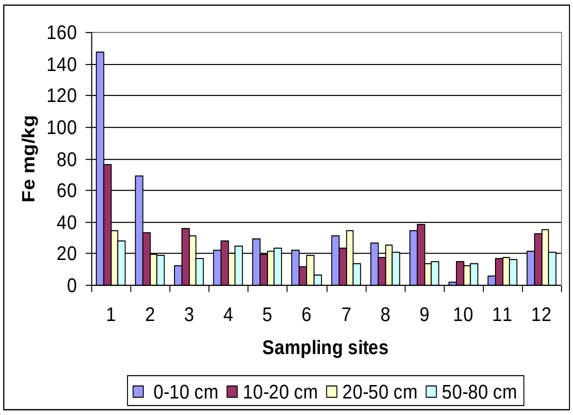

Figure 4: The horizontal and vertical Variation of Fe in the Soil of Selected horizons of the studied stations.

Cadmium (Cd):

There is growing environmental concern about Cd as being one of the most ecotoxic metals that exhibit highly adverse effects on soil biological activity, plant metabolism, and the health of humans and the animal kingdom. The abundance of Cd in magmatic and sedimentary rocks does not exceed around 0.3 ppm (Kabata-Pendias, and Pendias, 2001), and this metal is likely to be concentrated in argillaceous and shale deposits. Cd is strongly associated with Zn in its geochemistry, and also exhibits a higher mobility than Zn in acid environments. Cd compounds are known to be isotypic with corresponding compounds of such cations as Zn^{+2} , Co^{+2}, Ni^{+2}, Fe^{+2}, Mg^{+2}, and, in some cases, of Ca^{+2}.

During weathering, Cd goes readily into solution and, although known to occur as Cd^{+2}.

Cd adsorbed on clay mineral and organic matter, also Cd mobile in acidic soil and rocks. In soil developed under humid condition Cd accumulated down soil, while accumulation of Cd in top soil related to contamination effect.

Sewage sludge and phosphate fertilizers known as importance source of Cd (Kabata-Pendias and Pendias, 2001). Also Kabata-Pendias and Pendias, 2001, defined the allowable concentration of Cd in agricultural soil (table-2).

Al Zoubi, et al., 2008, point out that Cd increase in soil concentration by increasing sludge applications and it's the most hazardous contaminant in the food chain, and increased in some plants such as Maize cropping by 163% versus control.

Table-2: Maximum Allowable Concentrations of Heavy metals in Agricultural Soils Proposed in the Directives in Various Countries (ppm), (modified after Kabata-Pendias and Pendias, 2001, Lombi, et. al., 1998, and Bannick, et. al., 1998).

Element	Austria 1977	Poland 1993	Germany 1992	Russia 1986	U.K. 1987	EU 1986	U.S. 1993	Syria 2002*
Cd	5	1-3	1.5	-	3-15	1-3	20	20
Cu	100	30-70	60		50	50-140	750	1000
Zn	300	100-300	200	110	130	150-300	1400	3000

Notes:
1-Mn has not been considered to be a polluting metal in soils, and the maximum limit for its concentration for agricultural purposes in soil is 1500ppm.
2-*Syrian tolerable limits of Syrian Standardization Commission, 2002, (Al Zoubi, et al., 2008)

In the soil profiles of present study the concentration of Cd varies horizontally and vertically with wide range (1.1-9.2 ppm), and more than the tolerance limit compared by the standards in (table 2). Figure 5, showing the horizontal and vertical variations of Cd in the studied samples, the variation may related to the different degree of leaching of this element, and the high enrichment of Cd in the soil may related to irrigation by sewage wastewater, during long period of time.

Copper (Cu):

Cu in the Earth's crust is most abundant in mafic and intermediate rocks and has a tendency to be excluded from carbonate rocks. Cu forms several minerals of which the common primary minerals are simple and complex sulfides. These minerals are quite easily soluble in weathering processes and release Cu ions, especially in acid environments. Therefore, Cu is considered among the more mobile of the heavy metals in hypergenic processes. The Cu ions can also readily precipitate with various anions such as sulfide, carbonate, and hydroxide.

The mean levels for Cu vary from 13 to 24 ppm, being highest for kastanozems and chernozems and lowest for podzols and histosols (Kabata-Pendias, and Pendias, 2001).

The common characteristic of Cu distribution in soil profiles is its accumulation in the top horizons, and reflects the bioaccumulation of the metal and also recent anthropogenic sources of the element.

However, the Cu ions are held very tightly on both inorganic and organic exchange sites, also, soil minerals are capable of absorbing Cu ions from solution and that depending on the surface charge and sorbent. Contamination of soil by Cu resulted from utilization of Cu Containing material such as fertilizers, sprays, and agricultural or municipal wastes as well as from industrial emissions.

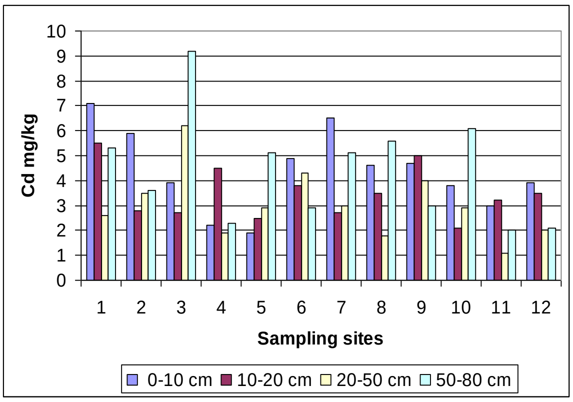

Figure 5: The horizontal and vertical Variation of Cd in the Soil of Selected horizons of the studied stations.

Makino, et al., 2000, studied the influence of soil drying under field conditions on exchangeable abundance of Mn, Co, and Cu contents and he concluded a difference in the concentration of these elements under different condition (table-2).

In the soil profiles of present study the concentration of Cu varies horizontally and vertically with wide range (1.8-14.2 ppm), and less than the tolerance limit compared by the standards in (table-2). It noted that the relative high concentration in the top soil in the 1st two station which is closed to the river channel, that may due to the high concentration of organic bioaccumulation materials, and the high effect of wastewater irrigation, figure 6.

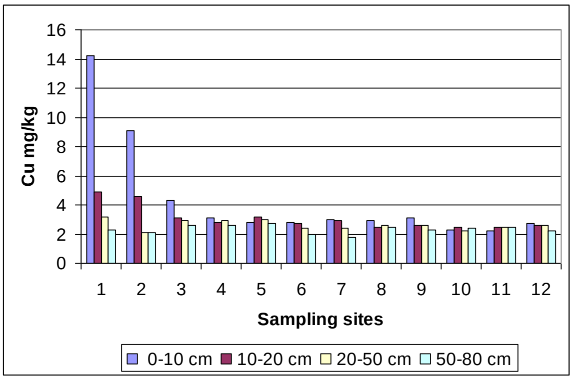

Figure 6: The horizontal and vertical Variation of Cu in the Soil of Selected horizons of the studied stations.

Manganese (Mn):

Mn is one of the most abundant heavy metals in the lithosphere, and its common range in rocks is 350 to 2000 ppm, (Kabata-Pendias, and Pendias, 2001).

During weathering, Mn compounds are oxidized under atmospheric conditions and the released Mn oxides are reprecipitated and readily concentrated in the form of secondary Mn minerals. The behavior of Mn in surfacial environment is very complex and is governed by different environmental factors, of which Eh-pH conditions are most important.

The Mn concentrations in soils are reported to accumulate Fe and several heavy metals such as Co, Ni, Cu, Zn, Pb, Ba, Ti.

All Mn compounds are very important soil constituents because this element is essential in plant nutrition and controls the behavior of several other micronutrients.

Mn has not been considered to be a polluting metal in soils, yet (Hemkes et al., 1980) reported the increase of Mn from 242 to 555 ppm (DW) in sludge-amended soil in 5 years. Maximum Allowable Concentrations value for Mn in agricultural soils is estimated at 1500 ppm. When Mn has accumulated in topsoil due to Mn application over a long period of time, toxic effects in some plants might be observed (Kabata-Pendias, and Pendias, 2001).

The concentration of Mn in the studied samples ranged from 0.1-68.2 ppm, which is below the standard limit (table 2), figure 7.

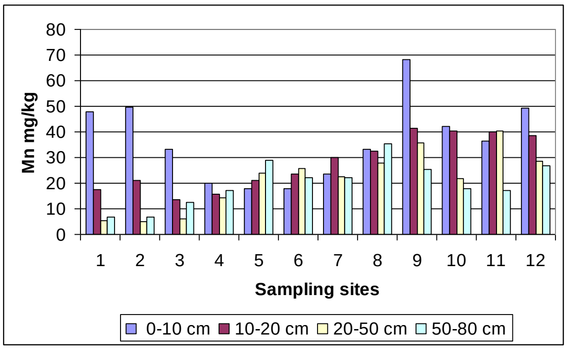

Figure 7: The horizontal and vertical Variation of Mn in the Soil of Selected horizons of the studied stations.

Zinc (Zn):

The Zn concentration in argillaceous sediments and shales is enhanced, ranging from 80 to 120 ppm; while in sandstones and carboniferous rocks, concentrations of this metal range from 10 to 30 ppm. Mean total Zn contents in surface soils ranged from 17 to 125 ppm (Kabata-Pendias, and Pendias, 2001).

Zn occurs chiefly as single sulfides (ZnS) in soil, when weathered give Zn^{+2}, so organic soil is non to capable of bonding Zn in stable form and Zn accumulate in organic rich soils.

The source of Zn as a contaminated material related to nonferric metal industry and then to agricultural practice. Soil contamination with Zn has already brought Zn to an extremely high accumulation in topsoils in certain areas (Kabata-Kabata-Pendias, and Pendias, 2001) (table-1).

In the soil profiles of present study the concentration of Zn varies horizontally and vertically with range (0.3-8.6 ppm), and less than the tolerance limit compared by the standards in (table-2).

It noted that the relative high concentration in the top soil in the 1st two station which is closed to the river channel, and that associated with high concentrations of organic matter , figure 8.

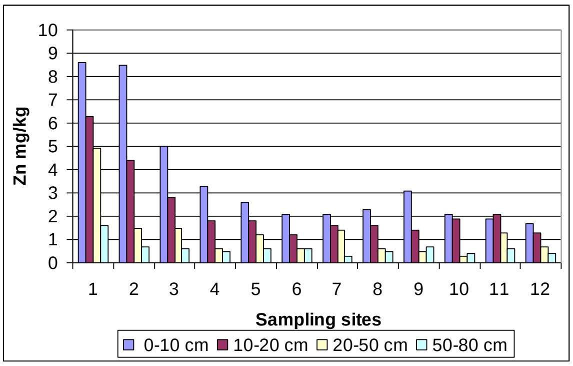

Figure 8: The horizontal and vertical Variation of Zn in the Soil of Selected horizons of the studied stations.

Summery and conclusions:

It noted that the relative high concentration of Fe, Cu and Zn in the top soil in the 1st two station which is closed to the river channel, and that associated with high concentrations of organic matter.

The concentration of Cd varies horizontally and vertically more than the tolerance limit compared by the standards. the variation may related to the different degree of leaching of this element, and the high enrichment of Cd in the soil may related to irrigation by sewage wastewater, during long period of time. The concentration of Mn is below the standard limit.

It is recommend to carry on analyses for other heavy metals such as Ni, Cr, Co, Pb, V, and Ti in the soil and plants, which is important to recognize the degree of pollution and contamination of the soil.

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تلوث تربة السهل الفيضي لنهر القويق بالعناصر الثقيلة، حلب، سوريا

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الملخص:

تراكيز عناصر الحديد، الكادميوم، النحاس، المنغنيز، والزنك، في ٤٨ نموذج من تربة السهل الفيضي لنهر القويق جنوب مدينة حلب وبالقرب من قرية العيس تم إيجادها بواسطة جهاز الامتصاص الذري الطيفي.

النتائج بينت بان عنصر الحديد تراوح بين (2.1– 147.2 ppm)، وهي اقل من حدود المواصفات العالمية وزيادة التركيز النسبي في أول محطتين يرتبط بزيادة تركيز المواد العضوية في هاتين المحطتين.

تركيز الكادميوم يمتد لمدى واسع (1.1– 9.2 ppm)، وهي اكثر من التراكيز الطبيعية للمواصفات القياسية للتربة، وذلك يعود الى السقي بالمياه الثقيلة الملوثة والناتجة من مدينة حلب خلال فترة زمنية طويلة مما ادى الى زيادة تركيز هذا العنصر في بعض انطقة التربة.

تركيز عنصر النحاس تراوح بين (1.8–14.2 ppm) وهو اقل من حدود المواصفات القياسية والزيادة النسبية له في اول محطتين ربما تعود الى ارتباطه كون التربة غنية بالمواد العضوية لقربها من القناة الرئيسية للنهر.

كذلك تركيز عنصر المنغنيز يتراوح بين (0.1– 68.2 ppm) والزنك يتراوح بين (0.3– 8.6ppm)، وهذه التراكيز اقل من الحد الاعلى لتراكيزهما في الترب الطبيعية والمدى الواسع لهذين العنصرين ربما يعود الى ارتباطهما مع المحتوى العضوي للتربة.