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A STUDY OF CONTAMINATION OF THE NORTHERN JORDAN VALLEY AGRICULTURAL FIELDS BY VARIOUS METAL IONS USING REGRESSION ANALYSIS.

By
Abu-Rukah, Y.
Dept. of Earth and Environmental Sciences, Yarmouk University, Irbid, Jordan
e-mail: yaburukah@yu.edu.jo
Hani. M. Samawi
Dept. of Statistics – Yarmouk University, Irbid, Jordan.
e-mail: hsamawi@yu.edu.jo

دراسة تلوث الأراضي الزراعية في غور الأردن بالمعادن الثقيلة باستخدام تحليل الأنحدار

يوسف أبو رقعة
قسم علوم الأرض والبيئة - جامعة اليرموك - الأردن
و
هاني سماوي
قسم الأحصاء - جامعة اليرموك - الأردن

أتمت التحاليل الجيوكيميائية لعينات التربة على أعماق ١٠ و ٢٠ و ٣٠ و ٤٠سم والتي تم جمعها من سبعة مواقع مختلفة في غور الأردن الشمالي، ولقد تم إستعمال ثمانية عشر متغيراً كيميائياً منهم AL, K, Na, Fe, Mg, Zn, Co, Ti, Pb, Si, Mn, بالإضافة إلى المتغيرات الأخرى pH, Ec, TDS.

ولقد وجد بعد دراسة النتائج أن معظم المواقع أظهرت زيادة في التراكيز خاصة على الأعماق الأولى، أسباب هذه الزيادة قد يكون مصدره المياه المستخدمة في الري، الأسمدة، المبيدات أو التركيب الجيولوجي للمنطقة.

Key word : Agricultural Fields, Metal ions, Regression analysis, Northern Jordan Valley.

ABSTRACT

Geochemical analysis were performed in lower subsurface soil samples of 10,20,30 and 40cm depth, collected from seven regions in the northern Jordan valley. Eighteen descripters (variables) for each sample were used. Among them were metal ions concentrations, such as Pb, Ti, Co, Zn, Mg, Fe, Na, K, Al, Cu, Si, and Mn. Other variables were pH, EC, and TDS. The soils in the study area are found to be alkaline since the pH value ranging between 9.2 – 9.5. Location 6 shows the highest TDS value, that's 1219.2 ppm. All the locations show high concentration of Pb, ranges between 50 (loc.1) to 150 ppm (loc.6). Zn values shows high concentration almost in all the locations, 100 (loc.1) to 300 ppm (loc.5 and 7). The Cd concentration very high in locations, 1,2,3 and 4 with ranges between 4 to 6.9 ppm. Ti concentration ranges between 3700 (loc.5 and 7) to 12300 ppm (loc.1).The sources of this increase, may be attributed to the water used in irrigation, fertilizers and the different types of pesticides, as indicated by the chemical and regression analysis.

INTRODUCTION

Soils are considered as a major sink for contaminants, especially heavy metals, and play an important role in environmental cycling to fix many species of heavy metals, Jaradat (1996).

Jordan Valley is a strip of 535 Km^2, located west of Jordan and divided into northern Jordan valley and southern Jordan Valley. Out of this, total rain fed annual cultivation is 110 Km^2 and irrigated annual cropping is 320 Km^2 (1). In recent decades there has been a radical evolution in agronomic practices in many regions of the world associated with attempts to increase agricultural productivity. Jordan valley could be considered as one of these regions where irrigated croplands have been the traditional agriculture of the area. However of late sixties intensive crops have been established producing more than two harvests per year. In general, Jordan is a small country with a limited agricultural land and water resources. Despite of this fact, this part of the country can be considered as one of the most important areas of the agricultural production. The farmers in this area rely heavily on different types of chemicals in their cultivation in order to increase land productivity. The agricultural production in the study area mainly consists of vegetables and fruits and mostly depends on the irrigation water from King Talal dam, King Abdulla Canal, Yarmouk River and Ziglab dam.

The prevailing situation of the area and introduction of green house technology, with more than two harvests per year increases pollution with heavy metal and organic compounds such as pesticides, insecticides, as well as other types of organic pollution. The use of fertilizers varies from one area to another but in general, very high quantities of inorganic fertilizers are added to crop to improve production. Fertilization practice is to apply up to 700 Kg N / ha / year for various agriculture activities. Moreover, because of the high temperature and humid conditions induced by irrigation, crops are subjected to several plagues which can endanger productivity and necessitate the user of several pesticides.

Forstner (1980[(2)]), Forstner and Wittman (1983)[3], and Ratha and Sahu (1993)[4] suggested that heavy metals concentrations in soils are strongly dependent on the grain size of the soils. Alloway (1990)[5] considered soils as a sink for anthropogenic heavy metals. Modak et al (6), Arakel and Haugjun (7)[7], Ratha and Sahu (1993)[4], Chakrapani and Subramaniam (1993)[8] Henberg and Bruemmer (1993)[9] and Cambeir (1994)[10] studied the behaviour and distribution of heavy metals in soils and in river basins. Coudela (1991)[11] used statistical methods, such as Mulitvariate analysis to find the correlation between physical variables and chemical variables, and stated that, the agricultural activation along the years have produced an important determination of soil and water. Salman and Abu-Rukah (1999)[12] determined the extent of pollution in the soil in northern Jordan from industries and waste treatment plants and found correlation and similarities between different samples at different variables.

Abu-Rukah (1998)[1] concluded in his study that the main sources of soil pollution in northern Jordan are pesticides, insecticides, fertilizers and contamination from local industries (olive oil mills), waste water treatment plants, highways and fuel industries. The main soil series distinguished in the study area by Abdul Hadi and Baddwi (1978)[13] are:

Series 31, which is the major one in the region, almost characterized by reddish soils with good porosity and permeability, and silt or clay textures. The grains are well developed and formed on the limestone substratum with a limited amount of chert. The soils of this series are found in low areas in which annual precipitation is less than 300 mm.

Series 9R, Rocky land with exposed bed rock covering of limestone of more than 15% associated with isolated patches of shallow or even deep soils.

The soil temperature regime for the study area of subsurface soil is hypothermic (22C°). The annual temperature at 50 cm depth, is more than 22C°. The soil moisture regime is ustic moisture regime and ustic – aridic transitional moisture regime, Abu-Ruka (1998)[1].

OBJECTIVE

The following objectives are intended to be achieved in the present study:

1. The study will include the determination of the various metal ions concentration in the soils of the agricultural fields.

2. The study the relationship between the concentration of the various metals and irrigation water, fertilizers, and pesticides.

3. The determination of major ions (Ca^{+2}, Mg^{+2}, Na^{+}, K^{+}, HCO^{-}, Cl^{-}, SO_4^{-2}) addition to heavy metals, NO_3, NH_4^{+}, and PO_4^{-3} in the water samples.

4. To apply the statistical technique (Multiple regression

analysis) to connect between the various metals and irrigation water, fertilizers, and pesticides in the agricultural fields in Jordan Valley.

APPLIED METHOD

Seven subsurface soil samples at 10 cm - 40 cm depth were collected from agricultural lands, and a total of twenty-eight samples analyzed, fig (9) the subsurface soil samples, 1, 2, 6 were collected from fruit yard fields, 3, 4 and 5 from vegetable fields and sample 7 from banana field. Besides the soil samples, seven water samples from the water used in irrigation from each location were collected and analyzed. The total soil samples analyzed were twenty eight. Seven water samples from each location were collected and analyzed. The concentration of metal ions in soil was measured by PY-Unicam SP atomic absorption (AA) Spectrophotometer. Soil samples (0.2g) was digested with 25% HCl and 2ml of the solution was further digested with 25% HNO_3. From this solution 2ml was taken and digested with 40% HF. 5ml Aliquot was displaced in water path for two hours and 50ml of H_3BO_3 was added. This solution was diluted with 40ml of distilled water and the AA analysis was performed. Electrical conductivity (EC) was measured for the soil samples which were washed by double distilled water. The measurements were performed with a digital conductivity meter PT1 – 58 serial No. 12588. The pH of the solution of the same samples was measured using pH meter PT1 – 55 serial No. 12564.

Water samples were collected. Measurements of pH and electric conductivity (EC) for water samples were conducted in situ by using portable pH and EC meters. Water samples were filtered using 0.45 μm membrane filter paper and then subjected to analysis. The determination of potassium, sodium, magnesium and clacium in the collected water samples was done by direct aspiration of these samples into atomic absorption (PYE UNICAM, SPQ, Phillips, atomic absorption spectrophotometer). SPECRONIC 20000 spectrophotometer used for the determination of nitrate, ammonia and sulphate. The titration methods were used for the determination of chloride by using potassium chromate (K2CrO4) as indicator and silver nitrate (AgNO3) as titration solution. Bicrabonate determined by titrating the samples with 0.02 NH2SO4 using methyl orange as indicator. The total dissolved solids (TDS) were determined by conductivity measurements. In this regards the calculation is carried out by using the equation TDS (mg/l)= EC (μS/cm) x 0.64, (EC is the electric conductivity).

To study the relationship between the concentration of various elements and the irrigation water, fertilizers and pesticides, regression analysis was used Weisberg (1985)[14].

The different types of fertilizers and pesticide used in the studied agricultural fields with the composition, source of irrigation, and the water class based on Na% and SAR are given in table 1.

RESULTS AND DISCUSSION

The concentration of the various metals in the collected soil samples from the agricultural fields in the study area were measured in clay fraction (<2μm). Clay fraction considered as a major carriers for both natural and anthropogenic compounds. Many researchers used metals concentrations in the clay fraction for the assessment of pollution in the soils. The acidity and alkalinity of soils is derined by their concentration H^+ and/or OH^- ions where pH is the negative logarithm of H^+. pH values of the collected subsurface soil samples at the different depth in the study area range from 9.2 - 9.5, (Table 2). This shows that, the concentration is exceeding the normal range. Since the pH is higher than 7.5, the soil in the study area is considered to be alkaline. The TDS concentration in the analyzed subsurface soil samples range between 2.66 – 12.19. Location 6 shows higher concentration in TDS. This increase may be attributed to the King Abdullah dam water used for irrigation, and to the moniak $(NH_4)_2SO_4$ fertilizer which contain 21% nitrogen as well as to the Afugan pesticide type that contains the active component known as Pyrazomynous as 30% of its total concent. The Afugan pesticide also has Diethyla, methyl, ethoxy carbon and monophosphate.

Pb concent clearly shows increase in the concentration in all the locations, which exceeds the normal limit in table 4. The concentrations range from 50 ppm (loc.1) to 150 ppm (loc.6). Cd concentration ranges from 4.0 ppm to 6.9 ppm in locations 1, 2, 3 and 4. While no concentration in locations 5, 6 and 7, (Table 2). The concentration of Cu, Cr, Co, Zn, and Ca (the range from 40 – 100 ppm, 40 – 230 ppm, 40 – 100 ppm, 100 – 300 ppm, and 126000 – 243000 ppm respectively) exceeds the permissible limits in all the locations as shown in (Table 4). Ti concentration range from 3100 pm – 12300 ppm locations 1, 2, 3, 6, and 7 shows higher concentration which exceeds the permissible limits given in (Table 4); 4600 ppm.

The conclusion that could be drawn from Table 1, Table 2 and Fig.2, which show the elements, the normal concentration in the soils and their range in the collected and analysed subsurface soil samples. The values given in table 4 based on Mason and Moore study (1982).[16] Almost all the locations show high concentration in the various metal ions in the soil of the study area which exceeds the permissible level stated in Mason Moore (1982).[16] The source of this increase in the various metal ion concentration could be due to water used in irrigation, such as King Abdullah Canal King Talal dam, Yarmouk river and Ziglab dam.

The results of the study are analyzed water samples from the different sources of irrigation are given in (Table 3). The increase of major ion concentration in the water samples attributed to the increasing of anthropogenic effect from agricultural sources, also the natural sources have their contribution. Sodium and chloride concentration in the analyzed water samples related to different natural sources besides the anthropogenic one. The exposed evaporatesand the brakish water deposites as well as the leaching of salts from salty soils in part of the study area also the Dead Sea all contributes in the increasing of sodium and chloride concentration. The impacts of the wate water North Ghors on the Jordan River water which is used in the fields irrigation is also another factor contributing in the chloride concentration increase. The increase in the pottasium concentration in the analyzed water samples is probably due to leaching of pottasium contents from clay of Ghor Kabid, since this contain K_2O comparing with MgO and Na_2O. The presence of the brackish and hot water springs in the area is clearly explaining the increase of HCO_3 value. The nitrate concentration increases should be due to the decay of plants. The anthropogenic contribution to the increase in the concentration of nitrate and ammonia appears in the forms of animal manures, waste water, fertilizer and pesticides. The increase usage of nitroge fertilization and manures in the adjacent areas as well as the effects of man and lifestock's waste attributes also to the increase in the NO_3 and NH_4. From the quality classification of water used for irrigation in the study area, based on Sodium percentage calculated from the equation defined in Todd (1986):[17]

$$\% Na = [(Na + K) 100] / (Ca + Mg + Na + K)]$$

And the equation:

$$SAR = Na/\sqrt{(Ca + Mg/2)}$$

And its relation to the Electric Conductivity (EC). The results show that the irrigation water used in location 1, 2, 3, 4, 6, 7 is permissible, while that of location 5 (Ziglab dam) is doubtful. This clearly indicates that the water used in irrigation in the study area is one of the source of increase in metal ion concentration in the subsurface soil.

Most of the fields, which used King Talal dam and Ziglab dam water show an increase in various chemical concentrations. Those, which use the Yarmouk River have the least concentrations (Table 1b). Also the fertilizers used contribute to the pollution of the subsurface soils, which contain various percentages of Phosphate, Pottasium and Nitrogen. Pesticides are also another caue of subsurface soil pollution. Seven different types of pesticides are used in agriculture to protect crops from various diseases. They contain different active components, which contribute to the increase of pollution in the subsurface soil of the study area.

To confirm our conclusion regression analysis was performed to study the rleationship between the various metal ion concentrations and after descriptors, such as source of irrigation water, fertilizers, and pesticides. The results of this analysis are shown in Table (5).[3] The coefficient of determination (R^2) is also used to explain the variation of the different variable concentrations with regards to the different sources of pollution. For Exapmple 12% of the variation in the Pb concentration could be due to fertilizer Urea which contain 46% Nitrogen (N). Also 99.4% of the EC concentration variation can be explained, as being due to the source of irrigation water from King Talal canal and the use of Amonic (NH_4) SO_4 fertilizer containing 36% K, 6% P and 12% N. The use of pesticide Pyrozone which contain Zinc ethylen and Diyathogarbmite and Seymezal with 88% viscous sulphur content in the increase in EC. Similarly 99.2% of TDS variation in concentration is due to the King Talal dam water used in irrigation, the amonic fertilizer $(NH_4)_2SO_4$ and pesticide Pyrozone and Seymezal. About 95.7% of the variation in the Fe concentration in the study area subsurface soils could be due to Ziglab dam water used in irrigation and urea fertilizer with 46% N, and Amonic fertilizer with 21%N. Also the pesticide Ronatak contains sypermetharium as active component, and Trimaltax forte pesticide that contains 20% mancozelo, 21% Cu sulphate, 6% Pyussian blue and adjuvants and inert 52.2%. All these have contributed to increasing the concentration of Fe to subsurface soils. For other metal ion concentrations and disoriplants relationship with the possible source of pollution (see Table 5).

Conclusions:

The important conclusions could be drawn from the present study are:

1. The soils are alkaline.
2. Location 6 shows the highest TDS, which exceeds the normal limit.
3. The Pb and Zn values high in all the locations.
4. Cd value high in locations 1, 2, 3, and 4.
5. Ti concentration is high in locations 5 and 7.

The sources for this increases attributed to the irrigation water, fertilizers, pesticides, and natural factors such as geological formations in the area.

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Table 1 : Shows the different types of fertilizers, pesticides and water used in the study area.

A) Fertilizers		Composition		
		K%	P%	N%
F1	Fertilizer 888	8	8	9
F2	Amonic $(NH_4)_2SO_4$	-	-	21
F3	Yoria $Co(NH_2)_2$	-	-	46
F4	DAP	-	46	21
F5	Amgalon	36	6	12
F6	EDTA	10	-	-

B) Pesticide		Composition
Pest1	Ronatak	Sypermetharim
Pest2	Randup	Isopropylamine salt of N- Phosphonomatly 1. glycine equivalent to glyphosphate
Pest3	Afugan	Diethyla, Methyl, Arthoxylarboni, Dyrazolo, pyrimid, Thonophosphate, the active component is Pyrazomnyas.
Pest4	Trimiltox forte	Mancozeb, Cu sulphate, Pyussian blue, Adjvtant and inert.
Pest5	Pemiltine	Curzata, Mancozab, Balonce, materials.
Pest6	Pyrozne	Zinc Athylen, Dayathyograbmito
Pest7	Seymezal	Viscous Sulfer.

C) Source of irrigation water		Water class based on Na% and SAR
W1	King Talal dam	Permissible
W2	King Abdulla Canal	Permissible
W3	Ziglab dam	Doubtful
W4	Yarmouk river	Permissible

Table 2 : Chemical data for the soil samples in the study area

Sample	Depth	pH	Ec µs/cm	Si ppm	Al ppm	Mg ppm	Ti ppm	Fe ppm	Pb ppm
1	1	9.20	1175	476100	91000	19300	11300	60000	50
1	2	9.17	1093	465000	95000	19200	12300	62000	50
1	3	9.25	1205	459000	100000	18700	11100	64000	70
1	4	9.24	1132	443000	95000	17200	12000	61000	70
2	1	9.16	616	334000	60400	16200	6600	37000	120
2	2	9.46	641	321000	61000	19400	7000	39000	70
2	3	9.45	687	319000	57000	16000	5700	35000	70
2	4	9.51	681	327000	59000	16300	7600	38000	70
3	1	9.17	1173	385000	64000	13600	6600	38000	110
3	2	9.30	1139	375000	67000	14600	6700	39000	96
3	3	9.22	1130	391000	70000	13700	7400	40000	90
3	4	9.24	1113	351700	70000	12500	7000	39000	80
4	1	9.17	416	300000	48000	15400	4200	27000	70
4	2	9.33	473	278000	44000	14900	4000	26000	90
4	3	9.39	424	273000	47000	15500	4100	28000	40
4	4	9.56	519	274000	48000	15000	4000	28000	80
5	1	9.22	1132	280000	52000	11700	4300	29000	70
5	2	9.36	1085	294000	51000	12000	4100	29000	110
5	3	9.28	1110	278000	48000	10800	3700	28000	90
5	4	9.17	1117	286000	50000	11400	4100	28000	70
6	1	9.15	1849	385000	73000	17200	6300	40000	150
6	2	9.18	1905	394000	75000	17300	6900	41000	80
6	3	9.34	1874	378000	78000	19200	6800	46000	50
6	4	9.43	1880	390000	83000	19800	6400	47000	80
7	1	9.23	718	370000	70000	21400	6300	38000	70
7	2	9.30	741	359000	68000	20700	7200	38000	50
7	3	9.30	690	382000	64000	21100	3700	35000	90
7	4	9.34	753	377000	74000	19300	9700	47000	80

Mn ppm	Na ppm	Cu ppm	Cd ppm	Cr ppm	Co ppm	TSD ppm	K ppm	Zn ppm	Ca ppm
1200	8300	90	5.7	170	80	752.0	8800	160	131900
1200	7300	80	4.0	170	100	699.5	8600	100	131000
1100	6200	60	6.9	170	90	771.2	7700	100	126400
1100	6200	80	6.9	170	80	724.5	7700	100	121000
870	5000	80	6.9	170	80	394.2	9600	230	202400
900	4600	100	6.9	170	70	410.2	5600	200	218000
760	5300	90	6.9	170	40	439.7	7000	200	224000
900	5600	90	6.9	230	50	435.8	5500	200	208000
900	4700	80	6.9	140	80	750.7	4900	200	122500
800	5500	80	6.9	190	50	729.0	6200	200	169000
800	5300	100	6.9	190	50	723.2	4700	200	170100
800	5000	100	6.9	160	50	712.3	22300	200	171000
500	5000	49	6.9	140	50	266.2	41000	200	228000
500	4500	50	6.9	170	50	302.7	8900	200	234000
500	5000	75	0.0	220	50	271.4	5100	200	243000
500	4500	80	0.0	410	50	332.4	6000	200	233500
500	3900	40	0.0	220	50	724.5	4200	200	227000
500	5000	80	0.0	200	30	694.4	4700	200	236000
500	4100	90	0.0	230	50	710.4	8000	300	236000
500	4700	70	0.0	220	50	714.9	9100	200	233300
800	4500	70	0.0	140	60	1183.4	10900	170	137000
800	5300	70	0.0	140	70	1219.2	7300	200	135000
900	6200	60	0.0	170	80	1141.8	7700	200	154000
800	5590	50	0.0	180	70	1203.2	13500	160	149000
800	6100	90	0.0	140	60	459.5	16200	300	159000
800	5300	90	0.0	110	50	474.2	6900	200	162400
800	7500	100	0.0	150	60	441.6	11500	200	149000
1000	6400	100	0.0	180	80	481.9	7700	100	126000

Table 3 : Results for the analyzed water used as source of irrigation in the study area

Area	pH	Ec µs/cm	TDS mg/L	Na mg/L	K mg/L	Ca mg/L	Mg mg/L	TH mg/L	HCO_3^- mg/L	Cl^- mg/L
A1	8.7	950	60.8	82	7	32	31.9	210	262	110.0
A2	8.4	914	58.5	82	7	32	31.8	220	260	108.5
A3	8.5	940	60.2	86	7	32	31.4	200	280	107.5
A4	8.6	934	60.0	84	7	37	31.4	240	280	106.5
A5	8.2	234	149.0	204	38	68	51.4	460	400	390.0
A6	8.4	930	59.5	82	7	37	31.1	220	260	112.5
A7	8.6	930	59.5	83	8	37	31.2	210	260	112.5

Cont. table 3 ……

SO_4^{-2} mg/L	NO_3^- mg/L	PO_4^{-3} mg/L	NH_4^{-2} mg/L	Mn mg/L	Pb mg/L	Al mg/L	Zn mg/L	Fe mg/L	Cd mg/L
22.7	24.8	0.121	0.68	0.03	0.07	0.25	0.022	0.17	0.016
40.8	24.1	0.110	1.134	0.013	0.05	0.24	0.007	0.15	0.012
50.0	28.8	0.170	0.368	0.009	0.00	0.13	0.004	0.03	0.006
64.0	308.0	0.140	0.75	0.004	0.03	0.11	0.002	0.07	0.005
34.0	100.3	2.400	7.72	0.274	0.04	0.64	0.008	0.53	0.010
18.9	28.9	0.114	1.20	0.005	0.00	0.03	0.002	0.04	0.000
18.8	26.6	0.078	1.20	0.006	0.00	0.12	0.001	0.06	0.004

Table 4 : Normal and range concentration of the various metal ions included in the present study.

No	.Metal Ions	Normal concentration (ppm)	Range concentration (ppm)	Locations shows higher concentrations exceeds the permissible limits
1-	Si	273000	273000 - 476100	1,2,3,5,6,&7
2-	Al	80000	44000 - 100000	1
3-	Mg	15000	10800 - 19800	1,2,6,&7
4-	Ti	4600	3100 - 12300	1,2,3,6,&7
5-	Fe	47200		1
6-	Pb	20	40 - 150	All locations
7-	Mn	850	500 - 1200	1,2,3,&4
8-	Na	9600	3900 - 8300	-
9-	Cu	45	40 - 100	All locations
10-	Cr	90	110 - 230	All locations
11-	Co	19	40 - 100	All locations
12-	K	96600	4200 - 22300	-
13-	Zn	95	100 - 300	All locations
14-	Ca	22100	126000 - 243000	All locations

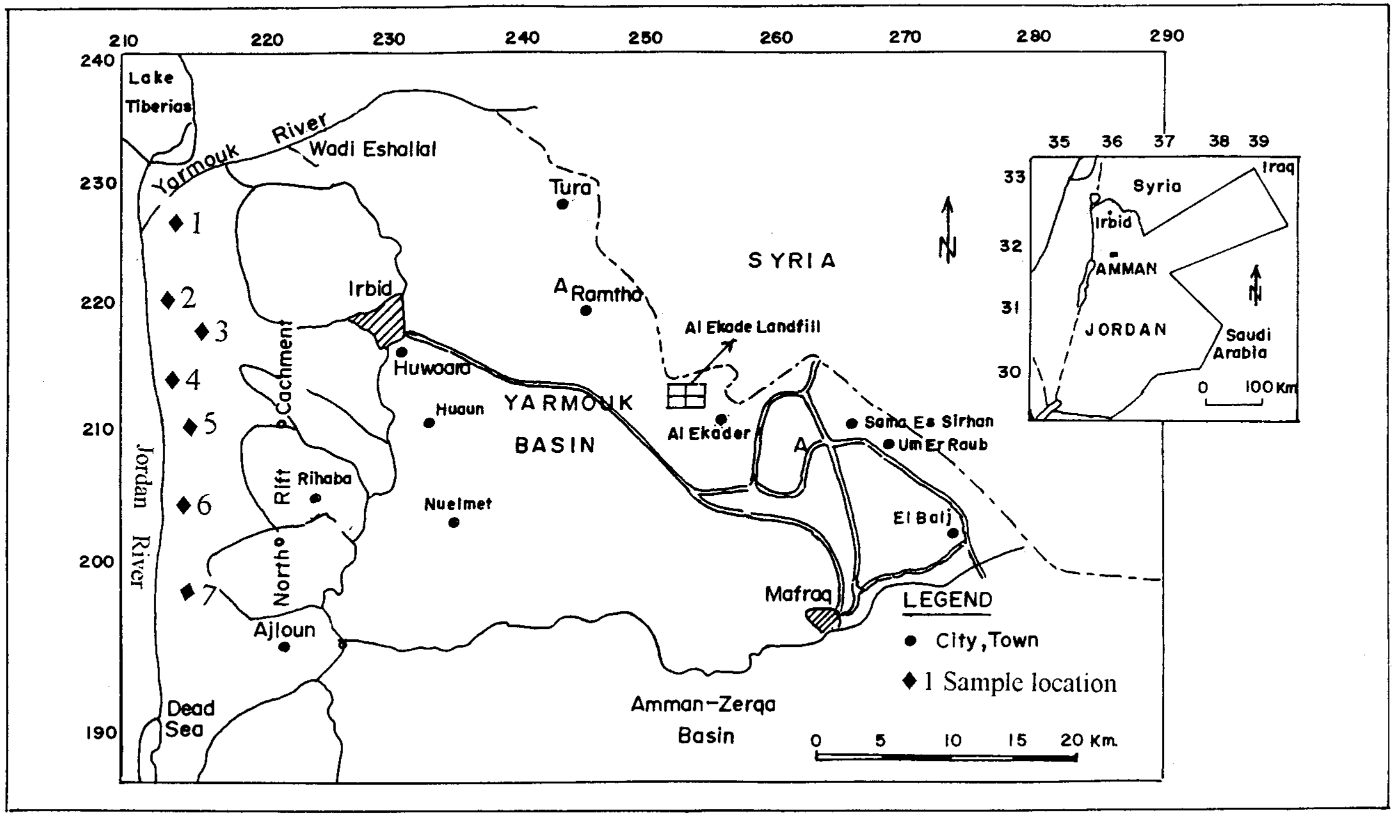

Fig. 1 : Location map of the study area