SALINITY AND DISTRIBUTION OF SOME HEAVY METALS IN THE SOIL OF AL-NASIRIYAH AREA, SOUTH OF IRAQ

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ABSTRACT

During the period from the first of May to December 2011, 53 boreholes were drilled in the Al-Nasiriyah area at 15m depth each. 53 soil samples were collected from the interval (0-50) cm. and 52 soil samples collected from the interval (50-100) cm. All samples were analyzed to determine the concentration of the heavy metals (Pb, Zn, Cr, Ni, Co, Cu) in addition to TDS and SO_3 . The results show that the soil salinity ranges from moderately saline to extremely saline and the analysis of the heavy metals indicated that soil of the study area is relatively free from pollution for the time being. Prediction maps showed that Ni, Cu and Cr have slightly higher values in bottom layer soil than in the top soil layer, while Co and Pb have the same values in the two layers. The minelogical composition of the soil was determined by analyzing (50) samples by XRD and the results shows that quartz is the most abundant mineral followed by calcite, feldspar, halite, and gypsum. Montmorillonite is the most abundant among the clay minerals, followed by palygorskite, illite, and kaolinite. Grain size analysis results show that the clay fraction is a dominant content in the soil of the area followed by sand and silt fractions.

دراسة الملوحة وتوزيع بعض العناصر الثقيلة في ترب منطقة الناصرية، جنوب العراق ثائر جرجيس بني

المستخلص

خلال الفترة الممتدة من الأول من آيار ولغاية كانون الأول من عام 2011 تم حفر 53 بئر في محافظة الناصرية وبعمق 15 متر من سطح الأرض. تم جمع 53 نموذج تربة تمثل التربة السطحية وذلك من العمق الممتد من 90 – 50 سم وجمع 52 نموذج تربة تمثل التربة السفلية للمسافات الممتدة من 50 – 100 سم من سطح الأرض، جميع هذه النماذج حللت لبيان تراكيز العناصر الثقيلة (Pb, Zn, Cr, Ni, Co, Cu) في التربة بالإضافة الى تحليل الكبريتات (SO3) وكمية الأملاح المذابة في التربة (TDS). بينت النتائج ان معدل ملوحة التربة يتراوح من متوسط الملوحة الى عالي الملوحة وان نتائج تحليل تراكيز العناصر الثقيلة تشير بان تربة منطقة الدراسة خالية من التلوث في التراكيز قليلة نسبيا في التربة تظهر مرتسمات الخرائط الافتراضية ان عناصر الذيكل والنحاس والكروم لها زيادة في التراكيز قليلة نسبيا في التربة وبيان المحتوى المعدني للتربة في منطقة الدراسة تم تحليل 50 نموذج بواسطة جهاز حيود الأشعة السينية وبينت النتائج ان معدن الكوارتز هو المعدن الغالب يلية معدن الكالسايت والفلاسيت والجبس أما نتائج تحليل المعادن الطينية فقد أظهرت ان معدن المونتموريلونايت هو المعدن الغالب يليه معدن الباليغورسكايت ثم الإيلايت والكاؤلين. أظهرت نتائج التحليل الحجمي لحبيبات التربة ان نسيج تربة منطقة الدراسة يغلب علية الحجم الطيني ثم الرملي بنسبة أقل ثم الغرين.

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INTRODUCTION

Regional geochemical and environmental reconnaissance survey, using soil as sampling media, was conducted in Al-Nasiriyah Sheet NH-38-3, scale 1/250000, during summer, and winter seasons of 2011. Fifty three drill boreholes, at depth (15) m were executed, and the location of these boreholes was determined by Global Position System (GPS) (Fig.1).

The study area is located within Al-Nasiriyah Governorate; south of Iraq. Two main cities are located within the study area, Al-Nasiriyah and Samawa, both of which represent Governorate's center, beside many small towns and villages. Euphrates River drains the study area between Samawa and Al-Nasiriyah cities, with NW – SE direction. Although Tigris River is not within the study area, its tributaries, Al-Gharraf and Shatt Al-Shattra (to the south) cross the map area from eastern side with N – S direction. The central part of the study area, the area between Shatt Al-Gharraf and Euphrates River and Shatt Al-Diwaniya, represents an abandoned area having desert features due to lack of surface water. The study area is limited, by the following coordinates (Fig.1): $(45^{\circ}~00-46^{\circ}~30)$ E and $(31^{\circ}~00-32^{\circ}~00)$ N

The study area is part of the Mesopotamian Plain and small sector of the Southern Desert plateau in the extreme western part of the area. The exposed geological formations, range in age from Middle Eocene, represented by the Dammam Formation up to Lower Miocene, represented by the Ghar Formation, in addition to the Quaternary deposits, which mainly covers the Mesopotamian plain, while the Pre-Quaternary deposits are exposed only in the desert plateau. The Quaternary sediments were classified according to their genesis as fluvial, lacustrine, aeolian, polygenetic anthropogenic deposits and gypcrete (Fig.2) Yacoub *et al.* (1985).

The aim of this study is to determine the geochemical and environmental conditions of the soils by preparing prediction maps for top and bottom soils of Al-Nasiriyah area by using geostatistical program, and to determine the physical properties of the soil.

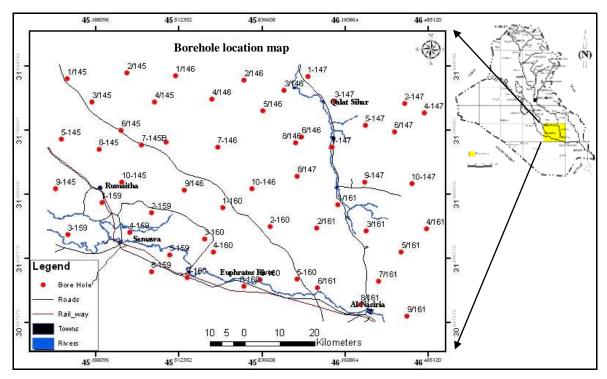


Fig.1: Location map of the study area and the drilled boreholes

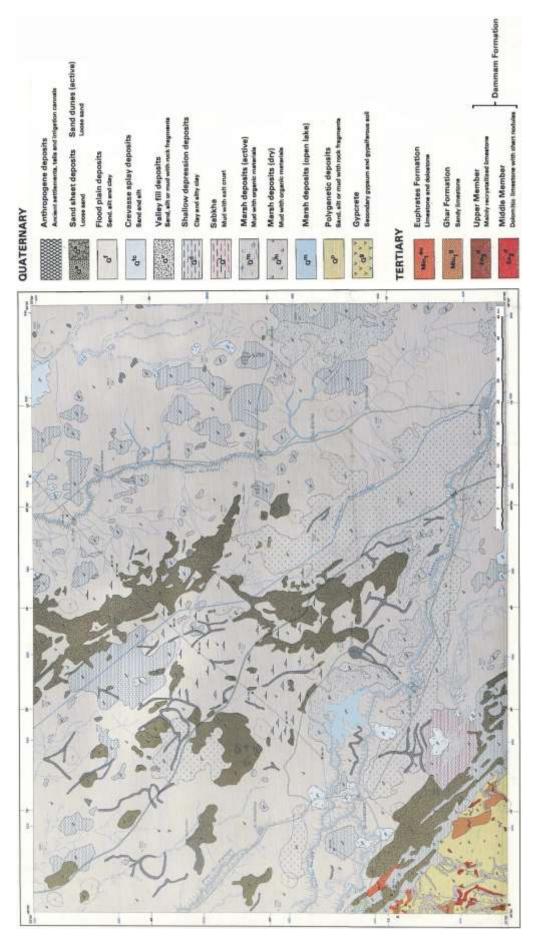


Fig.2: Geological map of Al-Nasiriyah area (Deikran and Mahdi, 1993)

PREVIOUS WORK

Many studies were carried out concerning the geology, geomorphology, ecology and geoenvironment conditions. The Mesopotamia Plain was included in many regional studies, such as hydrogeology (Parsons, 1957) and soil condition (Buringh, 1960). The later gave some information on Iraqi soils; particularly the fluvial system of the Tigris and Euphrates Rivers.

- Al-Rawi et al., (1976) reported the mechanical, chemical and mineralogical characteristics of some soil and alluvial sediments in the lower Mesopotamian plain.
- A more comprehensive geological study on the deposits of the lower Mesopotamian plain was carried out by the joint research group of the Geological Survey of Iraq and University of Paris (Yacoub *et al.*, 1980). During the field reconnaissance and laboratory study, they recognized six modern sedimentary environments; alluvial cone, delta fans, fluviatile channel, lake marsh, sabkha and estuarine.
- The final report of the geological survey of Mesopotamian Plain was compiled by the geological survey group (Yacoub *et al.*, 1985). They divided the Mesopotamia Plain into several sedimentary units depending on their genesis.
- Hanna and Al-Bassam (1983) reported and surveyed the Pb pollution in Baghdad by analyzing palm leaves and soil samples.
- Al-Bassam et al. (1985) gave the concentration of some heavy metals in Iraqi soils. Their results have shown that Pb contents are within the reported average for soil, except where pollution occurs either from natural or industrial sources.
- The distribution of some chemical elements in the sediments of Mesopotamia Plain have been studied by Hanna and Al-Hilali (1986) by analyzing 720 soil samples for Cr, Ni, Zn, Pb, Cu, and V, in addition to nitrates to determine background levels for each element and to follow up any future pollution. The results showed that the distribution of the heavy metals in the studied soils indicates that the Mesopotamia Plain (at that time) was free from pollution, except Pb in some local areas.
- Deikran and Mahdi (1993) reported about the geology of Al-Nasiriyah Quadrangle, sheet NH-38-3, at scale of 1/250000, and described the geology, structure, hydrogeology and economic geology of the area.
- Al-Bassam and Al-Mukhtar (2007) studied the heavy minerals in the + 63 μ m fraction of the Euphrates River sediments in various river sectors and discussed the source of enrichment of some heavy metals.
- Al-Khateeb et al. (2013) studied in details Al-Nasiriyah Sheet scale 1: 250 000 as a part of Mesopotamia Project, by drilling a total of 53 full core boreholes, beside 432 pits with depth 2 2.5 m. The study included geochemical and environmental surveys, hydrological and hydrochemical study, heavy minerals analysis, environment of deposition and sedimentation.
- Al-Bassam and Yousif (2013) reported on the geochemical distribution and background values of some minor and trace elements in Iraqi soils and recent sediments.

MATERIALS AND METHODS

From the drilled boreholes in the study area, 53 soil samples were collected from a depth of (0-50) cm, and 52 soil samples were collected from the depth interval (50-100) cm. All dry samples were preserved in polyethylene bags, while wet samples were preserved after sun drying, following GEOSURV Work Procedure No. 13 on Geochemical Survey (Benni, 2011). The samples were analyzed to determine the mineral composition of soil in the study area by X-ray diffraction analysis, and analyzing the trace elements (Pb, Zn, Cr, Ni, Co, Cu) and SO3,

beside TDS and grain size analysis, to determine the chemical and physical properties of the soil. Analytical accuracy was controlled by analyzing several standards, and by comparison with laboratory prepared soil standards following GEOSURV Work Procedure No.21 on Chemical Laboratories (Al-Janaby *et al.*, 1993).

RESULTS AND DISCUSSION

Grain Size Analysis

To determine the texture of Al-Nasiriyah soil, a sum of (1028) soil samples, collected from the drilled boreholes, have been analyzed to determine the percentage of sand, silt, and clay fractions. The results obtained from the grain size analysis show that the clay fraction is dominant in the soil of the area followed by sand and silt fractions, as illustrated in (Fig.3). Buday (1980) pointed out that the soils south of Baghdad are dominated by silt and clay.

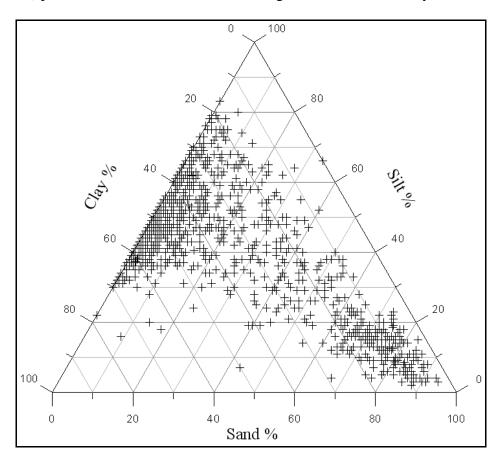


Fig.3: Distribution of sand, silt, and clay fractions in Al-Nasiriyah soil samples

Soil Salinity

Saline soils normally contain calcium and magnesium chlorides and sulfates. These compounds cause the white crust, which forms on the soil surface and the salt streaks along the furrows. The compounds which cause saline soils are very soluble in water; therefore, leaching is usually quite effective in reclaiming these soils (Fipps, 1994). Salt-affected soils develop from a wide range of factors including: soil type, field slope and drainage, irrigation system type and management, fertilizers, and other soil and water management practices. To detect soil salinity in the studied area; (47) soil samples were analyzed for sulfate (SO3) and Total Dissolved Salts (TDS), (Table 1). These selective samples were collected from the boreholes drilled in the area; represent the whole 1 m depth interval of the top soil.

Table 1: Simple descriptive statistics of SO₃, and TDS (%) concentrations

Variable	Valid N	Mean	Median	Min	Max	Std.Dev
SO3 %	47	1.5	0.72	0.16	9.7	2.1
TDS %	47	4.8	3.2	1.0	19.1	4.3

■ Total Dissolved Salts (TDS)

It is usually expressed in milligrams of salt per liter (mg/l) of water (also reported as ppm). Soil salinity may be expressed as TDS which can be calculated based on EC measurement as

TDS, in mg
$$L^{-1} = 640 \times EC$$
 (in umhos cm⁻¹ or dS m⁻¹)

The concentration of TDS in the study area ranges from (1-19.1) %, (Table 1); these values, when converted to EC, ranges from (15.6-298) dS/m. Therefore, and according to Dierickx (1997), the soil type is strongly saline to extremely saline, (Table 2). Geochemical distribution of TDS is homogenous, and show two zones of enrichment; the main one is located in the southeastern part of the area towards the marsh land. The other zone is located in the western part of the area close to the margins of the Southern Desert, (Fig.5). This zone is apparently influenced by the presence of evaporitic outcrops and Abu-Jir Fault Zone saline springs.

Table 2: Classification of soil salinity based on EC (Dierickx, 1997)

Classification	EC (dS/m)		
Non-saline	0 - 2		
Slightly saline	2 - 4		
saline	4 - 8		
Strongly saline	8 – 16		
extremely saline	> 16		

■ Sulfate (SO₃)

Under arid and semi-arid conditions, sulfate is retained for the most part in the soil and often separated as spots and nests of gypsum and may even form a marked horizon (Goldschmidt, 1954). The mean concentration of sulfate (SO3) in the studied soil samples is (1.5) % ranging from (0.16 - 9.7) %, (Table 1). This average is found to be slightly higher than that given by Shehata and Mahmood (1984) for soils of the Southern Desert; (SO₃ = 1.03%), but less than that given by Hanna and Al-Hillali (1986) for soils of Mesopotamia Plain ($SO_3 = 2.0 \%$), and much less than that given by Al-Bassam et al., (1981) for Hit – Nasiriyah saline soils in the vicinity of the Euphrates Fault Zone ($SO_3 = 10.6\%$). The geochemical distribution of SO3 copy the same geochemical pattern as that of TDS in the area, and show two zones of enrichment; the main one is located in the southeastern part (Fig.4). The increase in SO₃ content is toward the east direction to the marsh area which is a discharge area; it receives the sediments from Fan-Sheet Runoff unit, which is dominant in evaporitic components (Hanna and Al-Hillali, 1986). The other zone is located in the western part of the study area, close to the margins of Western and Southern Deserts as illustrated in (Fig.4), this zone is influenced by the presence of evaporitic outcrops (gypsiferous and anhydritic beds of Miocene age), in addition to water seepages of Hit – Abu Jir-Euphrates Fault Zone. The sulfate ion is a major contributor to salinity in many of the irrigation waters of the Mesopotamia. However, toxicity is rarely a problem, except at very high concentrations where high sulfate may interfere with uptake of other nutrients. In addition, the high sulfate content in the soil has a negative effect on many industies (e.g. brick industry).

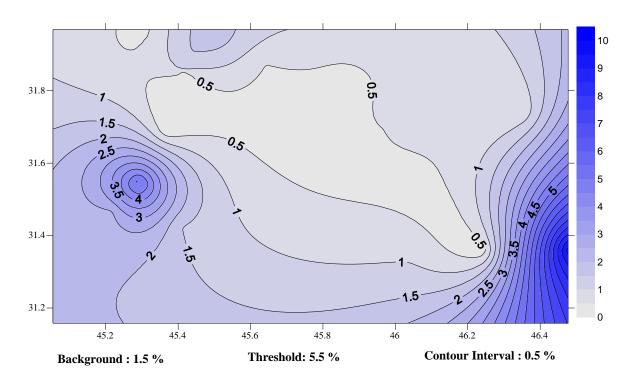


Fig.4: Regional Geochemical Distribution of SO3 (%) in Al-Nasiriyah area

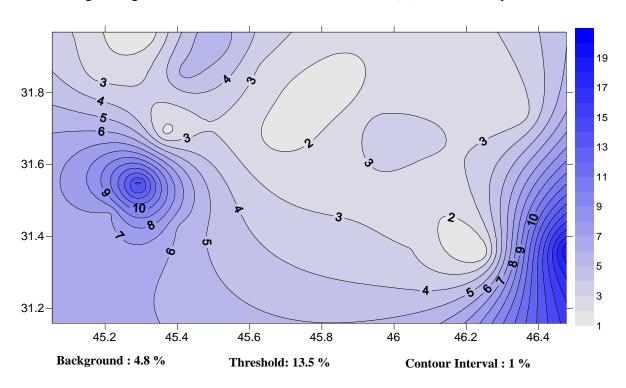


Fig.5: Regional Geochemical Distribution of TDS (%) in Al-Nasiriyah area

Mineralogical Analysis

The mineral composition of soil in the study area was investigated by X-ray diffraction analysis. A (50) soil samples were selected randomly from the top and bottom layer soil, which represent the whole 1m depth interval. The results show that the soil is mainly

composed of common mineral phases, among which are non-clay minerals where quartz is the most abundant mineral, followed by calcite, feldspar, halite, and gypsum. For clay minerals; the most abundant is montmorillonite followed by palygorskite, illite, and kaolinite. The sources for these natural phases in the soil sediments, include igneous and sedimentary complexes in Turkey and Syria, Injana and Dibdibba formations inside Iraq, as well as the clastics derived from northeast Iraq by the Tigris River and its tributaries, which show their influence in the Mesopotamian part of the river basin, (Al-Bassam and Al-Mukhtar, 2007). Low-grade metamorphic rocks and sedimentary rocks contain to a large extent, phyllosilicate minerals (excluding carbonates and quartz) which are very close in mineral character to that of clay minerals (Velde and Meunier, 2008).

REGIONAL DISTRIBUTION OF ELEMENTS IN TOP AND BOTTOM SOIL

The results of analysis of selective elements of the top and bottom soil samples can be represented by different methods; color maps produced by using geostatistical kriging methods was implemented in this study to compare the top and bottom soil samples and to follow the trace elements distribution. The color surface maps of the different elements show clear regional patterns, despite the low sample density. The patterns allow detection of the most important geochemical processes and geochemical distribution patterns which reflect geological controls and high or low homogeneity of metal content in the study area.

Distribution of Ni

Nickel content in the topsoil of Al-Nasiriyah area ranges from (96 – 241) ppm, with a mean of (166) ppm and median of (165) ppm. In the bottom soil samples it ranges from (105) ppm to (260) ppm, with a mean of (171) ppm, and median of (179) ppm (Table 3). The distribution of Ni in top and bottom soil is illustrated in Figure (6). There is a general similarity between the distribution of Ni in the top and bottom soil, with slight enrichment of Ni content in bottom than top soil, due to easy mobilization of this element during leaching as well as the strong ability of soil organic matter to absorb Ni and precipitates sulfides. Ni distribution in soil profiles is related either to organic matter or to amorphous oxides and clay fractions, depending on soil types. The highest Ni contents are always in clay and loamy soils (Pendias and Pendias, 2001). Al-Bassam and Yousif (2013) reported that the mean concentration of Ni in the flood plain of Mesopotamia terrain is (99) ppm, by analyzing 2131 of top soil samples, and they pointed out that the significantly elevated background values of Ni in the Mesopotamia samples demonstrates the influence of source rocks composition of the Zagros igneous complexes as a major factor. In the study area, the homogeneously higher or lower metal values mark the changes in backgrounds, from mainly low values in the west side to the higher values in the east (Fig.6), due to the influence on nickel content by the sediments influx of the Euphrates River (west) and the Tigris River (east) in the Mesopotamia plain sedimentary basin.

Distribution of Zn

Zinc content in top soil of Al-Nasiriyah area ranges from (44 - 92) ppm, with a mean of (67.3) ppm and median of (67) ppm. In the bottom soil samples Zn ranges from (25 - 83) ppm, with a mean of (63.3) ppm, and median of (66) ppm, (Table 3). In the Mesopotamia soil, the concentration of Zn ranges from (20 - 117) ppm, with a mean of (56) ppm. Mica and illite are the main hosts of Zn in these sediments according to Al-Bassam and Yousif (2013).

47

2

37

28.5

30

6.2

52

94

197

133.7

137

21.2

42

2

33

23.4

27

8.9

Element(ppm) Ni Zn Co Cr Pb Cu O - 50 cm (Top Soil) No. of Samples 53 53 48 48 53 43 44 21 19 50 96 6 Range 92 35 175 241 62 34 Max. 166 67.3 28 30.2 126.4 25.6 Mean 28 Median 165 67 30 124 27 Std.Dev. 27.5 10.9 3.3 23.4 6.6 6.8

- 100 cm (Bottom Soil)

52

22

44

28.1

28

3.9

47

25

83

63.3

66

11.8

52

105

260

171

179

32.5

Table 3: Descriptive statistics of selective heavy metals for soil samples at depth (0-50 and 50-100 cm) in Al-Nasiriyah area

The Zn balance in surface soils of different ecosystems shows that the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass (Pendias and Pendias, 2001). The distribution of zinc in top and bottom soil is illustrated in Figure (7). There are general differences between the distribution of Zn in the top and bottom soil, with slight enrichment of Zn content in the top relative to the bottom soil. In general the enrichment of this metal in the study area is located in west and east sides on both top and bottom soil. This may be due to the influence of Hit – Abu Jir-Euphrates Fault Zone in the west side and the influence of marshland in the east side of the area.

Distribution of Co

No. of Samples

Mean

Median

Std.Dev.

Range

Min.

Max.

Cobalt content in topsoil of Al-Nasiriyah area ranges from (21 - 35) ppm, with a mean of (28) ppm equal to a median of (28) ppm. In the bottom, soil samples it ranges from (22 – 44) ppm, with a mean of (28.1) ppm, equal to a median of (28) ppm, (Table 3). Benni in Al-Khateeb et al. (2013) pointed out that concentration of cobalt in soils of Al-Nasiriyah area ranges from (11-39) ppm with a mean of (27.5) pm. Cobalt interacts with all metals that are associated geochemically with Fe. However the most significant relationship has been observed between Co and Mn or Fe in the soil and between Co and Fe in the plant; the uptake by plants is a function of the mobile Co content of soil and of the Co concentration in solution (Pendias and Pendias, 2001). The distribution of cobalt in top and bottom soil is illustrated in Fig. (8). There is a general similarity between the distribution of Co in the top and bottom soil, with slight enrichment of Co content in bottom relative to top soil, probably due to easy mobilization of this element during leaching. There is slightly high concentration of this element in the west side of the area more than the east side, which could be due to the influence of the heavy minerals content in the sediments of the Euphrates River, which were derived partly from igneous and sedimentary complexes of Turkey and Syria (Al-Bassam and Al-Mukhtar, 2007).

Distribution of Cu

Copper content in top soil of Al-Nasiriyah area ranges from (19-62) ppm, with a mean (30.2) ppm and a median of (30) ppm. In the bottom soil samples Cu ranges from (2-37) ppm, with a mean of (28.5) ppm, close to median (28) ppm, (Table 3). These values are close to the reported values of Cu in different parts of Iraqi soils, and are within the reported average of the world. Hanna and Al-Hilali (1986) mentioned that the content of copper is highest in the flood plain unit compared to other units in the area.

The distribution of Cu in top and bottom soil is illustrated in Fig. (9). There is no significant difference in content of Cu between bottom layer and top layer in the study area (Fig.9). According to Aubert and Pinta (1977) the total content of copper in the soils of arid and semiarid regions is generally higher than it is in soils of other regions. Copper concentration depends on the parent rocks, humus, organic matter and clay content of the soil.

Distribution of Cr

Chromium content in top soil of Al-Nasiriyah area ranges from (50 - 175) ppm, with a mean of (126.4) ppm and median of (124) ppm. In the bottom soil samples it ranges from (94 - 197) ppm, with a mean of (133.7) ppm, close to median (137) ppm (Table 3). In the Mesopotamia samples, the range is (4 - 2000) ppm (mean 282 ppm) (Al-Bassam and Yousif, 2013). The distribution of Cr in top and bottom soil in the area is illustrated in Fig. (10). There is an enrichment of this metal in the eastern and northern parts in the top soil samples in the study area. This enrichment is probably due to the clastics derived from NE Iraq by the Tigris River and its tributaries, which show their influence in the Mesopotamian part of the river basin (Al-Bassam and Al-Mukhtar, 2007). In general, the Cr content of surface soil is known to increase due to pollution from various sources of which the main ones are several industrial wastes e.g., electroplating sludge, Cr pigment and tannery wastes, manufacturing wastes, and municipal sewage sludge (Pendias and Pendias, 2001). None of these pollution sources exist in the study area.

Distribution of Pb

The accumulation of Pb in surface soils is of great significance because this metal is known to greatly affect the biological activity of soils (Hughes $et\ al.$, 1980). Lead content in topsoil of Al-Nasiriyah area ranges from (6-34) ppm, with a mean of (25.6) ppm and median of (27) ppm. In the bottom soil samples the range is from (2-33) ppm, with a mean of (23.4) ppm, close to median (27) ppm (Table 3). These values are higher than the values reported by Al-Bassam and Yousif (2013) for the Mesopotamia soils, which range in concentration from (1-46) ppm with a mean (6.8) ppm, and higher than values reported by Hanna and Al-Hilali (1986) in the sediments of Mesopotamian Plain, with concentration ranges (2-80) ppm with a mean (9) ppm. The distribution of Pb in top and bottom soil in the area is illustrated in Fig. (11). The concentration of Pb in top soil shows higher values, especially in the southern part of the area, probably indicating various pollution sources near some towns, villages and main roads, which are exposed to various pollution sources, such as automobile exhaust, and industrial processes.

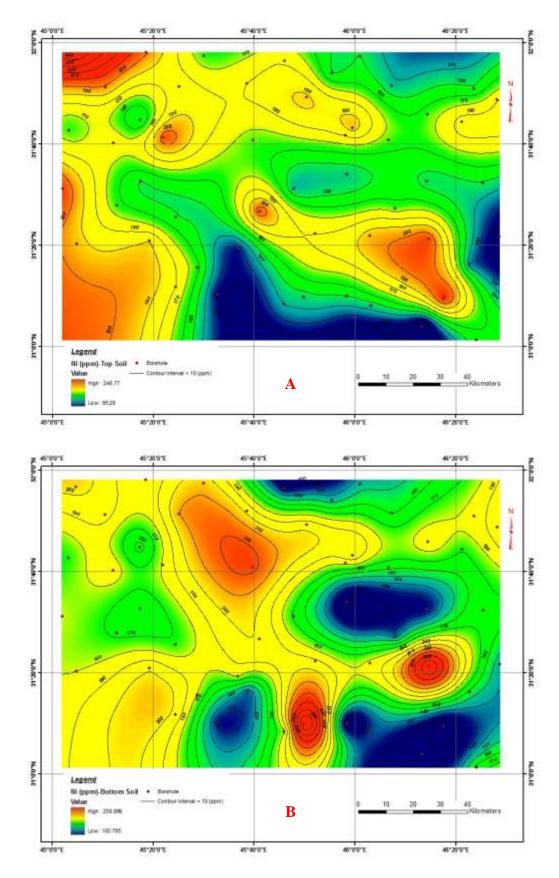


Fig.6: Prediction map of the distribution of Ni (ppm) in **A**) top soil and, **B**) bottom soil in Al-Nasiriyah area

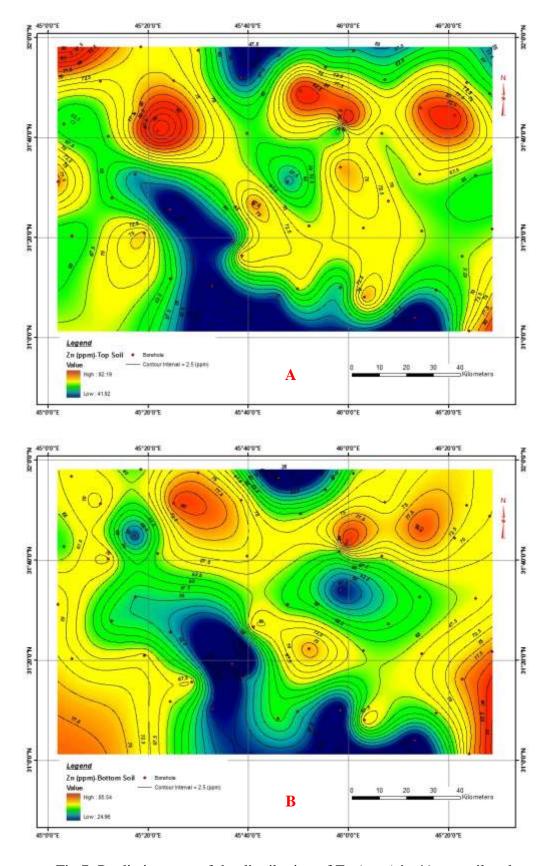


Fig.7: Prediction map of the distribution of Zn (ppm) in **A**) top soil and, **B**) bottom soil in Al-Nasiriyah area

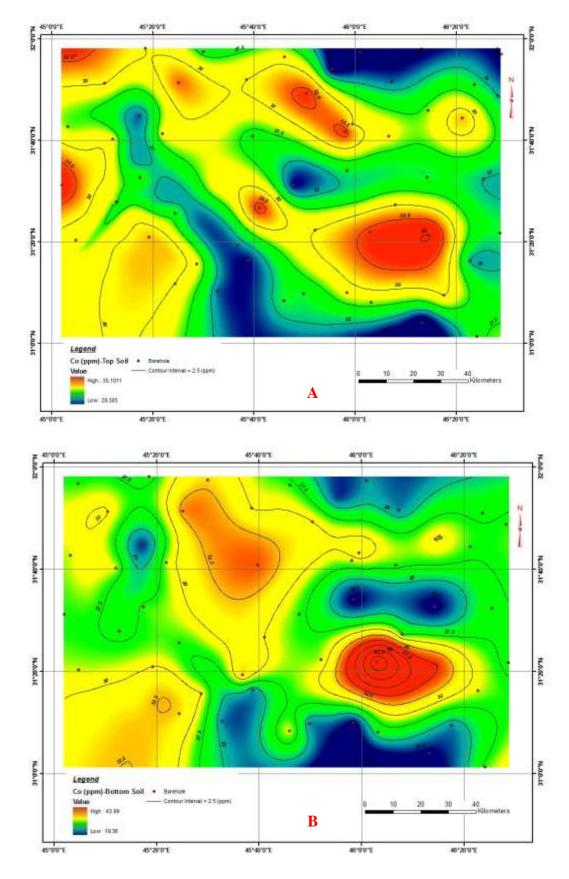


Fig.8: Prediction map of the distribution of Co (ppm) in **A**) top soil and, **B**) bottom soil in Al-Nasiriyah area

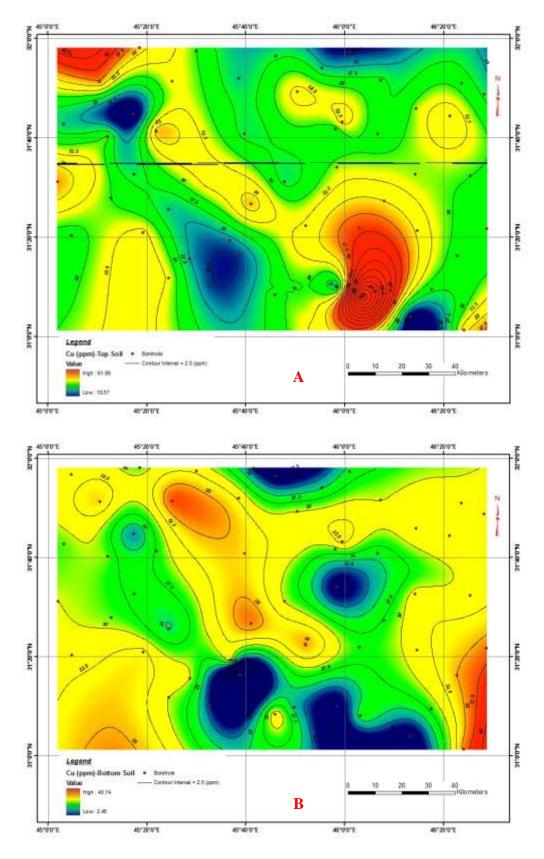


Fig.9: Prediction map of the distribution of Cu (ppm) in **A**) top soil and, **B**) bottom soil in Al-Nasiriyah area

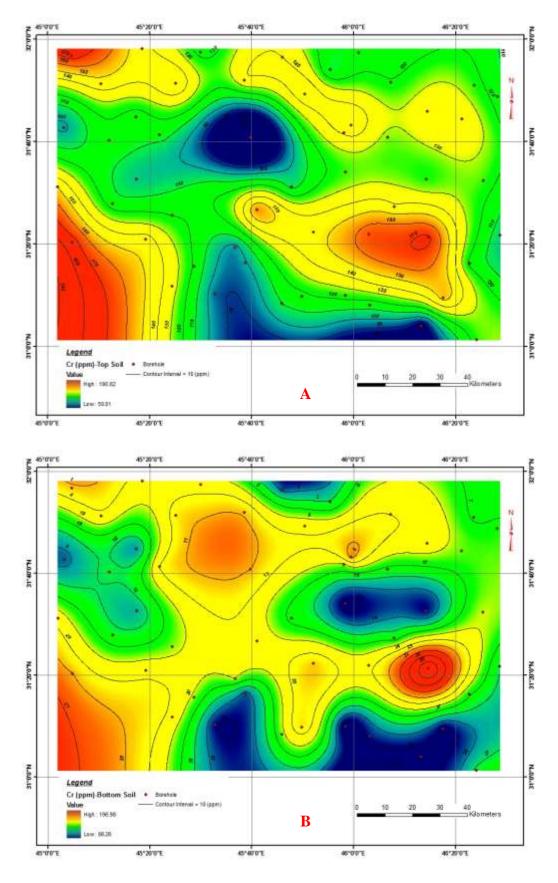


Fig.10: Prediction map of the distribution of Cr (ppm) in A) top soil and, B) bottom soil in Al-Nasiriyah area

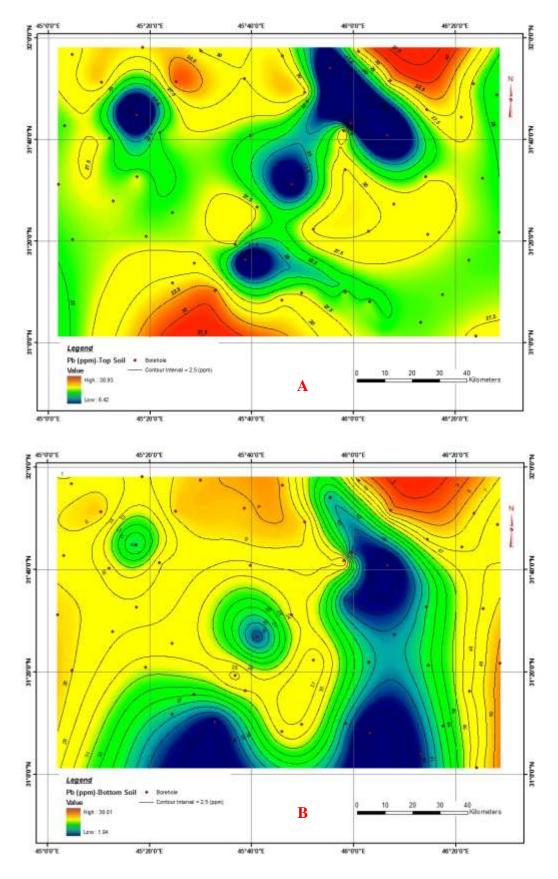


Fig.11: Prediction map of the distribution of Pb (ppm) in **A**) top soil and, **B**) bottom soil in Al-Nasiriyah area

CONCLUSIONS

Background levels for all analyzed elements (Ni, Zn, Pb, Cu, CO, and Cr) have been determined for Al-Nasiriyah soil. The data obtained from this work indicate that the soils of the study area are relatively free from pollution for the time being, except Pb, which is relatively higher than those previously reported for the Mesopotamia soils.

According to analytical results of TDS%, and SO₃%, the soil salinity ranges from strongly saline to extremely saline especially in the eastern part of the study area due to the influence of marshlands.

The analytical results of XRD of 50 soil samples show that among the non-clay minerals, quartz is the most abundant, followed by calcite, feldspar, halite, and gypsum. For clay minerals, the most abundant is montmorillonite followed by palygorskite, illite, and kaolonite.

Prediction maps of the analyzed elements show the concentration of nickel and chromium slightly higher in bottom soils (mean, 171 and 133.7 ppm respectively) than in top soil (mean, 166 and 126.4 ppm respectively), while cobalt has the same values (mean 28 ppm) in both top and bottom soil. The concentrations of those elements depend on their content in the parent rocks. The mean concentration of zinc, copper, and lead are almost the same in top and bottom soil in Al-Nasiriyah area.

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