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Evaluation of Heavy Metal Accumulation in Sawa Lake Sediments, Southern Iraq using Magnetic Study

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Abstract

Heavy metal contamination comprises a great concern in the environment. A magnetic study combined with heavy metal analyses was performed in the Sawa Lake in Al-Muthanna governorate (southern Iraq). Concentrations of selected heavy metals (Cr, Fe, Ni, As and Pb) have been measured and magnetic susceptibility (χ) of sediment samples collected from the lake bottom was calculated.

The results confirmed that a cement plant, which is located less than two kilometers away from the lake has no contamination levels on the lake's sediments. No enhancement in the magnetic susceptibility was observed. X-ray florescence (XRF) was performed for heavy metal analyses.

Spatial variations of χ with the mean value of 4.58 x 10^{-8} m^3kg^{-1} and results of other magnetic parameters suggest the magnetic carriers are a predominantly hard magnetic phase like hematite and the existence of small super-paramagnetic proportions. XRF analyses show average concentrations of (Cr, Fe, Ni) and very low for (As, Pb) which is typical for relatively clean areas. Magnetic susceptibility was insignificantly correlated with heavy metals due to low concentrations of both magnetic signals and heavy metal contents. This study has shed some light on the importance of applying the χ measurements techniques to monitor and assess lakes sediment pollution.

Keywords: Magnetic susceptibility, Sawa Lake, heavy metals, lake sediments

تقييم تراكم العناصر الثقيلة في رواسب بحيرة ساوه في جنوب العراق باستخدام دراسة مغناطيسية

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الخلاصة

يشكل التلوث بالعناصر الثقيلة مصدر قلق كبير في البيئة. أجريت دراسة مغناطيسية مشتركة مع تحاليل العناصر الثقيلة في بحيرة ساوه في محافظة المثنى (جنوب العراق). تم قياس تراكيز بعض العناصر الثقيلة (Pb ،As ،Ni ،Fe ،Cr) وتم حساب الحساسية المغناطيسية (χ) لعينات الرواسب جمعت من قاع البحيرة.
اظهرت النتائج أن معمل الأسمنت والذي يقع على بعد أقل من 2 كيلومتر من البحيرة بانه ليس له تأثير تلوث على رواسب البحيرة، حيث لم يلاحظ أي ارتفاع في قيم الحساسية المغناطيسية. تم إستخدام تحاليل الأشعة السينية (XRF) لتحاليل المعادن الثقيلة.

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الاختلافات المكانية للقيمة الحساسية المغناطيسية اظهرت قيمة وسطية بحدود ($4.58 \times 10^{-8}\ m^3kg^{-1}$) ونتائج المعاملات المغناطيسية الأخرى تشير إلى أن المواد الحاملة للمغناطيسية هي في الغالب معادن ذات مغناطيسية متوسطة مثل معدن الهيماتيت ووجود نسب قليلة من معادن عالية المغناطيسية.

اظهرت نتائج تحاليل XRF تراكيز متوسطة لعناصر (Ni ،Fe ،Cr) وتراكيز منخفضة جداً لعناصر (Pb ،As) وهذه التراكيز تعتبر نموذجية للمناطق الخالية من التلوث نسبياً. العلاقة بين الحساسية المغناطيسية وتراكيز العناصر الثقيلة ضعيفة بسبب القيم المنخفضة للحساسية المغناطيسية والتراكيز القليلة للعناصر الثقيلة. ألقت هذه الدراسة بعض الضوء على أهمية تطبيق قياس الحساسية المغناطيسية لمراقبة وتقييم تلوث البحيرات بالرواسب.

Introduction

Sawa Lake is a type of Endorheic basin [1] located in Al-Muthana governorate, southern desert of Iraq. It is unique because it is a closed basin without surface water available to feed it and is considered as a very important water resource to the neighbouring areas. The tectonic activity played an important factor in generating the lake's depression [2].

The results of hydrochemical composition show that the water supplied from the lake foot through a fault system balances the amount of water that is evaporated [3]. However, water intermixing due to the presence of local faults makes it difficult to distinguish the main aquifer contributing to the lake [1].

In the last twenty years, magnetic measurements have become popular because they are fast, economic and non-destructive measurements. Therefore, they have been used in assessing the environment to identify potential pollution from different sources, for example, a new sampling method had been used to detect particulate pollutants using magnetic measurements [4].

Values of magnetic susceptibility in a sample are controlled by three parameters; concentration of magnetic minerals, grain size, and the type of the ferro(i)magnetic mineral. Many environmental studies have been done on lake sediments using the magnetic method [5,6]. Many researchers tried to investigate magnetic susceptibility and its correlation with heavy metals [7-9].

Road side pollution was monitored using magnetic susceptibility and found its high values represents polluted areas caused by traffic frequency, roadside topography and other factors [10]. Air quality in China was monitored by detecting contaminants using magnetic measurements; an economic sampling method was designed which provides a suitable tool for evaluating distribution of air quality [4]. Environmental changes estimation due to industrial activities was studied; differences between magnetic properties and heavy metal concentrations in the Yangtze River watershed (China) suggest that the high concentration of ferrimagnetic mineral point out the heavy metal pollution [11].

The mineral magnetic behaviour of sediments from Lake Towuti (Indonesia) was investigated using rock magnetic analysis, X-ray diffraction and scanning electron microscopy analysis was also performed on a sediment core and the results demonstrate three different zones of magnetic properties related to differing levels of iron oxide dissolution and magnetite precipitation [12].

Sawa Lake water is oversaturated with calcium, magnesium and carbonates ions [13].

The aim of this study is to report magnetic and geochemical information of Sawa lake sediments. The lake lies in an industrial area (e.g. cement plants) and could be affected by fly ash or other pollution sources. Geochemical studies have been done on water chemistry and sediments but no magnetic study have been done yet [e.g. 1,3], a detailed magnetic study will be achieved for the first time on Sawa Lake sediments in southern Iraq.

Materials and Methods

A. Study Area

Sawa Lake is located in Al-Muthanna governorate, about 22 km south west of Samawa city (31°18'48.80"N, 45°0'25.25"E) and to the western branch of Euphrates (Figure-1). The lake is about 4.74 km in length, 1.75 km wide and maximum 5.5 m deep, it is surrounded by a salt edge which is higher than the lake water by 2.8 m and sea water by 18.5 m [1].

Figure-1 Google map of Iraq showing the location of Sawa Lake in Al-Muthanna province, southern Iraq.

The lake's water is originating from the topographically higher Western Desert areas, which is feeding the Sawa Lake through joints, cracks, and karst that are exist in the area. These could also provide pathway for groundwater penetration to the lake basin. High salinity water is dominated the lake and the equilibrium between evaporation and the pressure gradients in the source aquifers led to the stability of water level [14]. The lake sediments are mainly consisting of gypsum (87%), clay minerals (5.5%), quartz (4.5%) and halite (3%) [15]. The vicinity of the lake is covered by recent alluvial sediments that vary in thickness between 1 to 10 m. It is underlying by recent salts deposit. The climate of the study area is dry, with hot summer and cool winter seasons and medium humidity, the wind direction is a North-West with a speed of 4.1 m/s [16]. It was expected that the Sawa Lake sediments will be contaminated due to the accumulation of heavy metals emitted from Al Muthanna cement plant (source of contamination) which lies around 2 km west to the lake, it was operated since 1984 with annual production amount of about 1959000 tons.

B. Geological settings

The lithostratigraphy of the study area comprises the Rus, Dammam, and Euphrates formations as well as some Quaternary deposits [17,18]. The Rus Formation (early Eocene) is composed of anhydrites exchange with marl, shale, limestone and dolomite [19]. Dammam Formation (middle-late Eocene) is composed of limestone and porous (often), fissured and locally karstified dolomite [17]. Euphrates Formation (early Miocene) consists of limestone, clay, marl at the bottom and shelly and marly limestone at the top, interfingering with Gar Formation. [20]. Quaternary deposits (Holocene and Pleistocene) are sediments composed of inland sebkha, gypcrete and salt deposits [21]. Sawa Lake lies within the Euphrates Formation; it is a closed basin and has no flow, the seasonal fluctuations of water level are one to three meters, Sawa Lake is underlying by the underground aquifers within carbonate successions such as Umm Errdhuma, Dammam and Euphrates formations [16].

C. Sediment sampling

Fifty sediment samples (Figure-2) were collected from the upper few centimetres of the lake bottom at different distances from the sub-bottom springs using stainless steel trowel.

The samples were homogenized and air-dried at room temperature and then sieved using a mesh-size of 2 mm and stored later in the geological laboratory of Al-Muthanna University. The samples were packed and transported to the magnetic laboratory at Tübingen University in Germany, in which detailed magnetic analyses were performed.

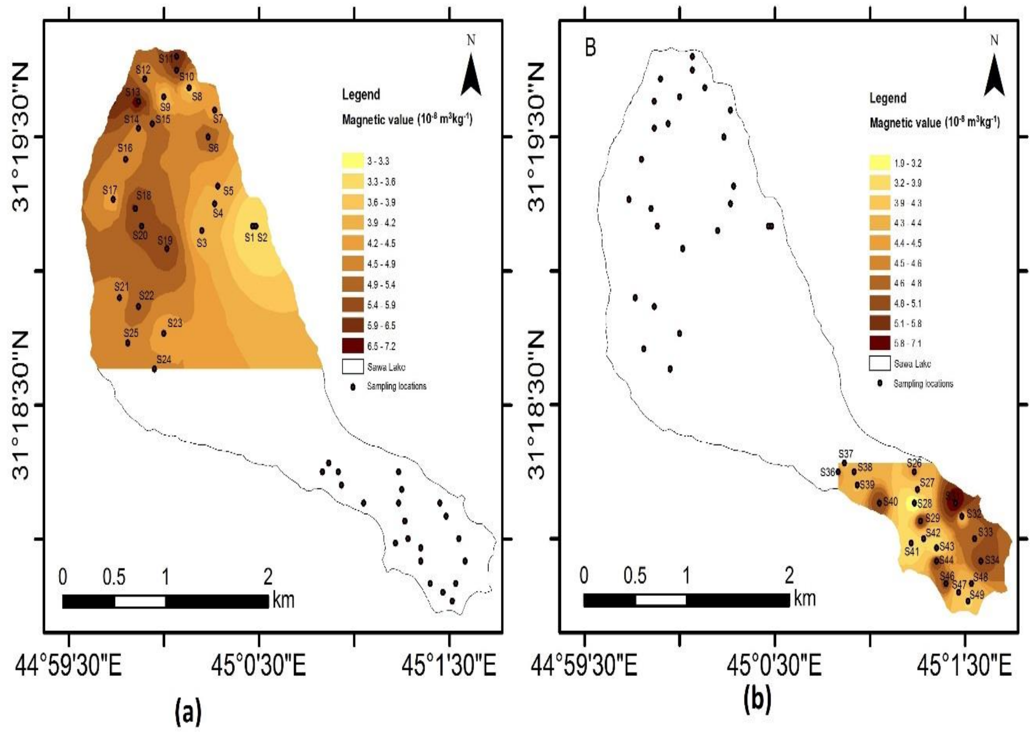

Figure 2-(a,b) Zoom view of sampling locations in the Sawa Lake, Southern Iraq, showing contour map of mass-specific magnetic susceptibility (χ in 10-8 m3kg-1) values of the samples (using GIS software)

D. Sample analysis

Magnetic investigations were carried out in the magnetic laboratory at the Department of Geosciences, Tübingen University. The samples were gently grinded to disaggregate the grains and were packed into non-magnetic lidded plastic containers (10 cm^3) and then weighed for magnetic measurements. Magnetic susceptibility was measured using a KLY-3 Kappabridge AGICO instrument. For frequency-dependent susceptibility (χ_{fd}%) a MFK1-FA Kappabridge AGICO instruments were used at frequencies of 976 Hz (F1) and 15616 Hz (F2) in a peak field of 200 A/m.

Anhysteretic remanent magnetization (ARM) intensity was measured in a 2G Enterprises superconducting magnetometer (2G-755R), a DC bias field of 40 µT and an alternating field of 100 mT was used to impart the ARM.

Isothermal remanent magnetization (IRM) intensity was measured by using a Molspin spinner magnetometer after imparting the IRM by a MMPM9 pulse magnetizer. The IRM acquired at 1000 mT was considered as the saturation IRM (SIRM), and a backfield IRM in a reverse field of 300 mT (IRM-300) was used to calculate the S-ratio according to the equation of Bloemendal [22].

Thermomagnetic runs of magnetic susceptibility (κ-T curves) were obtained using the Kappabridge KLY3 equipped with a furnace and a CS-3 heating unit (maximum temperature 700°C).

Some pilot samples were selected for heavy metal analysis (because mainly it is magnetic study and not geochemical study otherwise it is better to analyse all the samples); the samples were grinded and then contents of Cr, Fe, Ni, As and Pb were measured by X-ray fluorescence (XRF) using an Ametek Spectro Xepos model Xepos 03 STD Gas at Department of Geology, Baghdad University, Iraq. Laser-beam diffraction with a Malvern Mastersizer 2000 (at Departments of Geosciences, University of Tübingen, Germany) was used to determine the bulk grain size distribution (after removing the organic matter and carbonate dissolution), the instrument is sensitive for particle diameters between 20 nm to 2 mm. Later statistical analysis was carried out to quantify the results (i.e. correlation coefficient using Excel software).

Results and Discussion

A. Magnetic Properties

Statistical results of mass specific magnetic susceptibility and other magnetic properties are shown in Table-1.

Table 1-Statistical results of magnetic properties of sediment samples from Sawa Lake.

	χ (10^{-8} m^3kg^{-1})	χ_{fd} (%)	χ_{ARM} (10^{-8} m^3kg^{-1})	SIRM (10^{-5} Am^2kg^{-1})	S-ratio
Min	1.95	1.02	1.58	30.77	0.94
Max	7.24	3.39	51.67	95.21	0.99
Mean±SD	4.58±1.11	2.10±0.51	27.77±11.54	63.05±13.09	0.96±0.02
Median	4.45	2.10	26.21	61.54	0.96
Skewness	0.28	0.20	0.45	0.28	0.63
kurtosis	0.43	-0.11	-0.14	0.35	-0.67

Due to the fact that sediments contamination enhances the magnetic concentration of the signals, a magnetic susceptibility was performed to assess whether there is a contamination of Sawa Lake sediments (and the possible source of contamination) or not.

Magnetic susceptibility varies from 1.95×10^{-8} m^3kg^{-1} to 7.24×10^{-8} m^3kg^{-1} (Table-1) and its spatial distribution is shown in Figure-2. Magnetic grain size-dependent values of ARM/SIRM ratio versus mass-specific magnetic susceptibility for all sediment samples are displayed in Figure-3. As shown in Figure-3 negative correlation between χ and ARM/SIRM ratio indicates that smaller grains (having higher ARM/SIRM values) possess low χ, which means that coarser fraction (probably with detrital origin) carries the χ-signal. However, it doesn't relate to pollution.

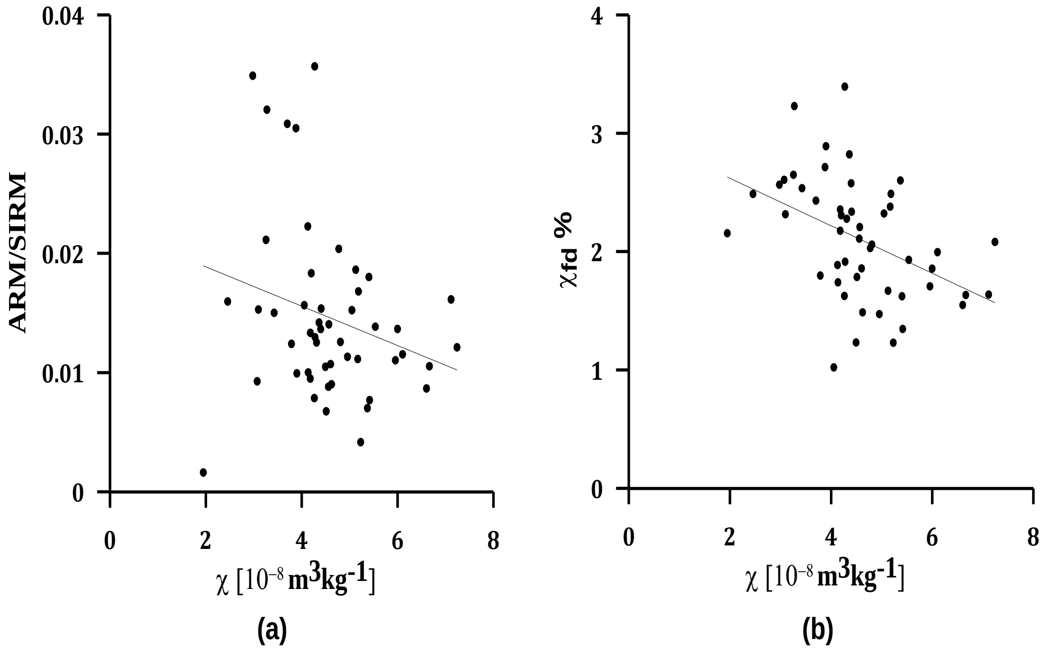

Figure 3-(a) Grain size-dependent values of ARM/SIRM versus χ; (b) ARM/SIRM versus χ_{fd}% mass-specific magnetic susceptibility for all sediment samples from the studied lake.

The negative relationship between heavy metals contents of (Cr, Fe, Ni, As and Pb) and ARM/SIRM ratio which claims also that the smaller grains having low HM contents (Figure-4).

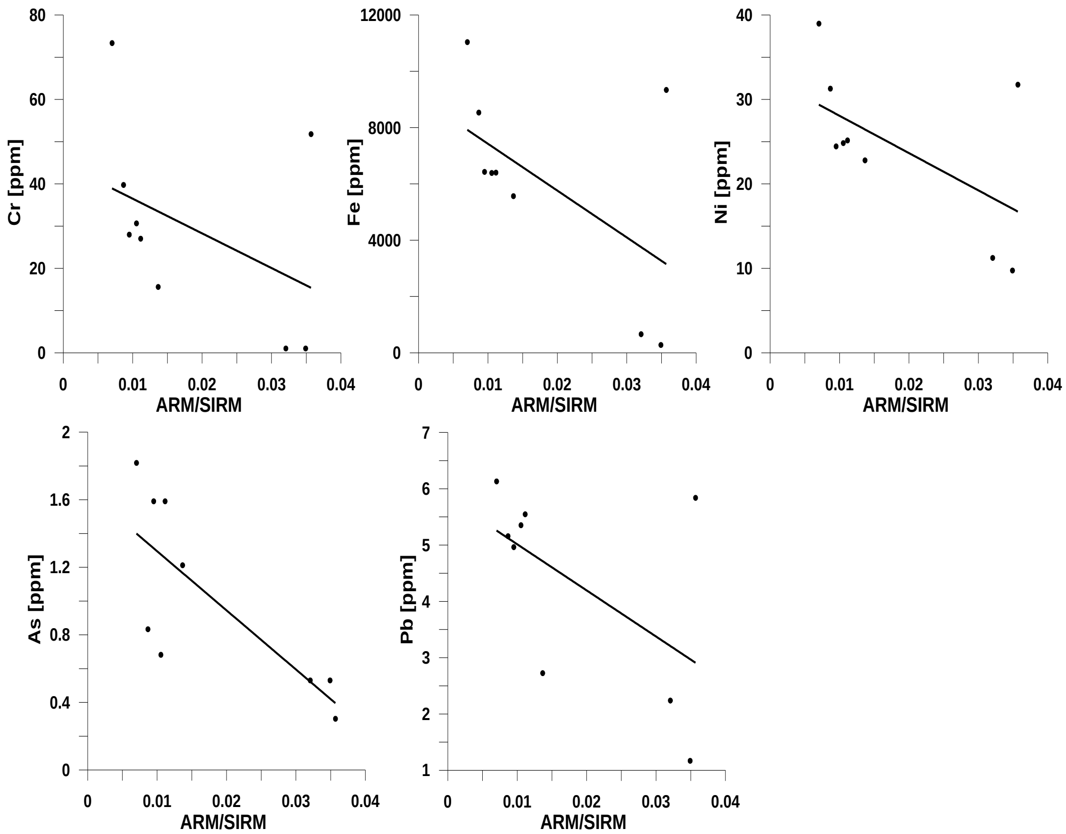

Figure-4 Heavy metal contents (Cr, Fe, Ni, As and Pb) versus ARM/SIRM ratio for selected samples.

The S-ratios provides a measure of the amounts of hard remanence to soft remanence [23], for most of the samples S-ratio is above 0.9 which indicates the high contribution of antiferromagnetic minerals which could be hard hematite (Figure-5).

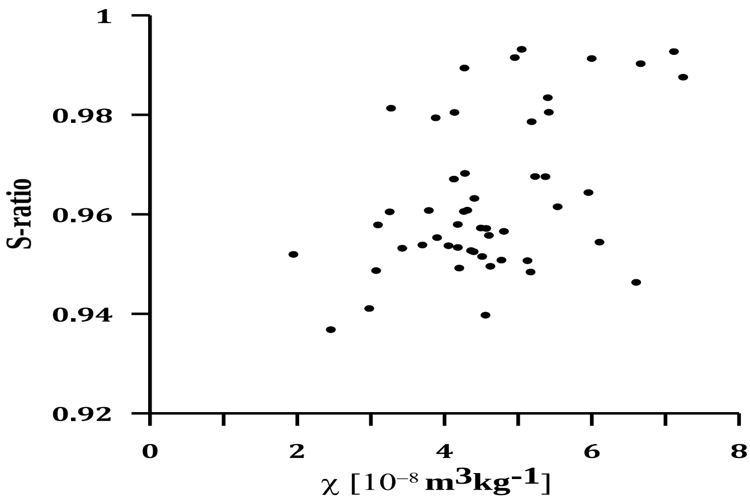

Figure 5-S-ratio versus mass-specific magnetic susceptibility for the studied samples.

Frequency-dependent magnetic susceptibility (χ_{fd}%) is sensitive to ultrafine grained super-paramagnetic (SP) particles and thus can provide information on the relative contribution of SP magnetite grains in the sediments [24]. Table-1 shows low values of χ_{fd}% which is below 3.4% (mean 2.1%) indicating an absence of nm-sized SP fraction of strongly magnetic particles. However, such grain size distribution is often observed in polluted areas, where most of the anthropogenic particles are of larger than SP magnetic grain sizes.

Measurements of high-temperature dependent magnetic susceptibility can be used to identify the type of magnetic minerals based on their Curie temperature. Thermomagnetic analyses of representative samples show that the magnetite is produced during heating, while the values of initial magnetic susceptibility at lower temperature in the heating curves are very low (or even negative e.g. diamagnetic), although the Curie temperature is around 580 ◦C, therefore no original magnetite existing in the selected samples but low magnetic minerals which could be paramagnetic or diamagnetic minerals (Figure-6).

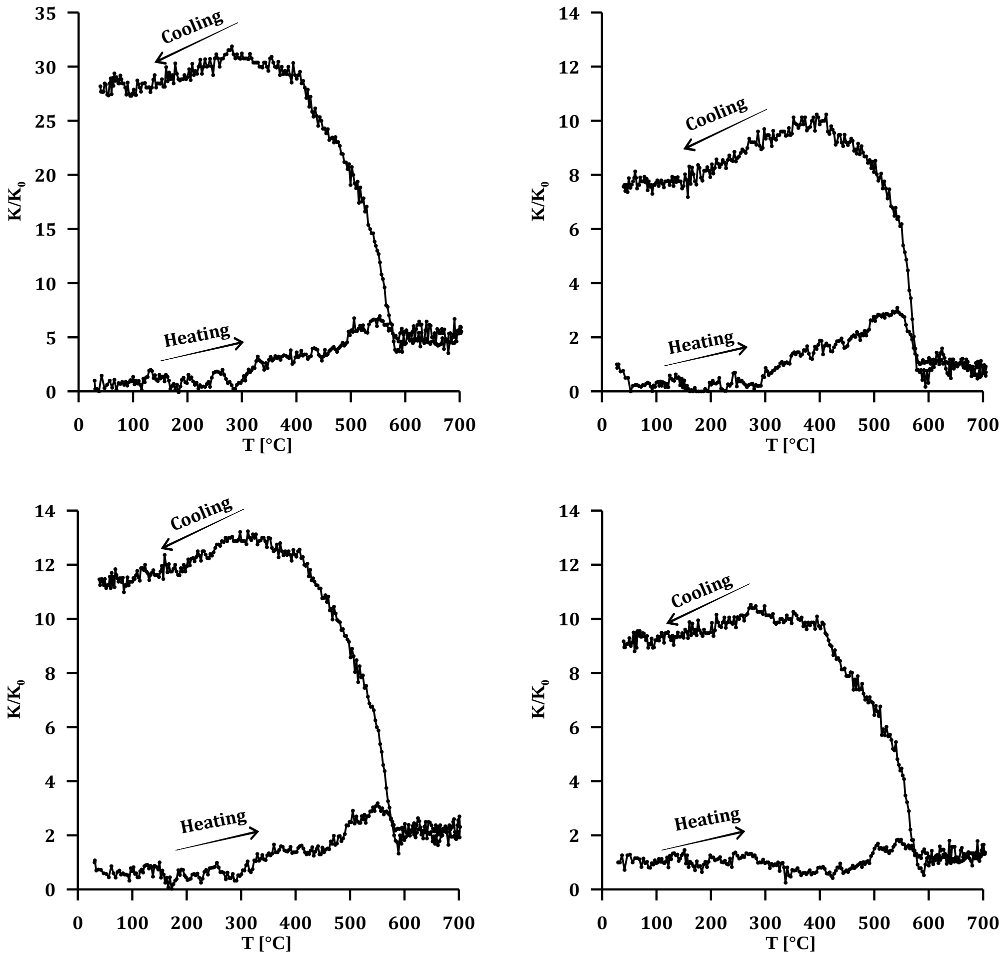

Figure 6-Temperature-dependence of normalized magnetic susceptibility (κ-T) curves of selected study samples.

To further analyse the magnetic constituents, the isothermal remanent magnetization (IRM) acquisition curves of selected samples has been used with different mass-specific susceptibility values χ (Figure-7). As shown in Figure-7 IRM values strongly increase for applied magnetic fields less than 300 mT, but they did not saturate even at the field of 1 T. This may indicate the presence of hard magnetic phase like hematite as magnetite saturates at 1 T.

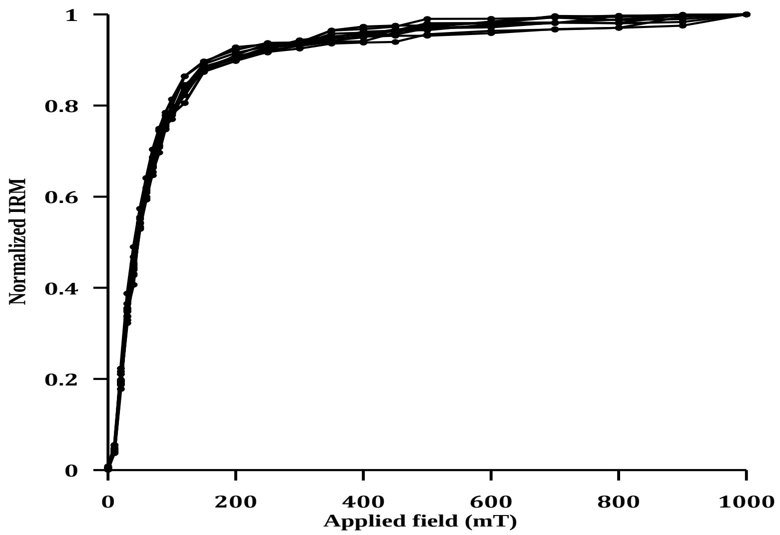

Figure-7 Isothermal remanent magnetization (IRM) acquisition curves of selected samples with different mass-specific susceptibility values χ.

Anthropogenic contaminated soils by fly ashes demonstrate enhanced magnetic susceptibility which could be correlated with various heavy metals such as (Pb, Cr, Ni, As and Zn) [25]. The major soil variety in the study area is represented by gypsum masses as the main mineral within the rock formation mixed with silty or sandy claystone in addition to quartz, clay minerals, iron oxide and organic matter as insoluble residues [26]. These soils are characterized by quite low magnetic susceptibility; within presented data, the enhancement of magnetic susceptibility was not observed in any sample, therefore, one cannot claim the effects of anthropogenic pollution in this case of study.

B. Grain Size Analyses

Distributions of bulk particle size of samples with different mass specific magnetic susceptibility values are shown in Figure-8. The overall grain size distribution of the bulk sediment samples determined by laser-beam diffraction. The observed bi-modal pattern of the physical grain size distribution shows the dominance of 20-30microns fraction and significantly lower content of coarser 200microns fraction.

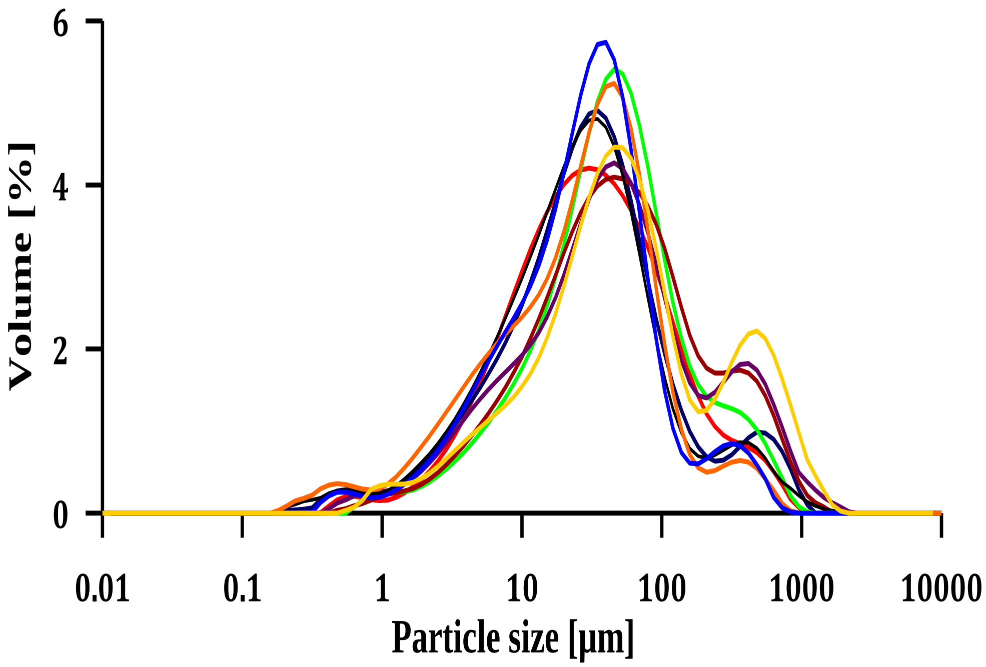

Figure 8-Grain-size distributions of selected samples with different mass-specific susceptibility values χ.

C. Heavy Metal Contents

Iron oxides are always accompanying heavy metals which caused by combustion and magnetic particles are good adsorbents and carriers of heavy metals, therefore the magnetic properties may be an effective indicator of heavy metal pollutants [27].

Table-2 displays the results of heavy metal (Cr, Fe, Ni, As and Pb) and magnetic susceptibility of these samples. It also shows that the sediment samples taken from the upper part of the lake bottom contain high mean concentrations of Cr (29.8 $mgkg^{-1}$), Fe (6069 $mgkg^{-1}$), Ni (24.47 $mgkg^{-1}$), As (1.01 $mgkg^{-1}$) and Pb (4.35 $mgkg^{-1}$), and the mean χ of geochemically measured samples is 4.94× 10^{-8} m^3kg^{-1}.

Table 2-Cr, Fe, Ni, Cu, Zn, As and Pb concentrations in selected sediment samples and their magnetic susceptibility (χ) and the correlation coefficient (Number of samples= 9) between heavy metals and χ.

Sample identification	Cr	Fe	Ni	As	Pb	χ
		($mgkg^{-1}$)				(10^{-8} m^3kg^{-1})
S1	1.03	661	11.24	0.53	2.24	3.27
S2	1.03	278	9.74	0.53	1.17	2.98
S5	51.79	9337	31.75	0.30	5.84	4.27
S10	15.60	5564	22.79	1.21	2.73	6.00
S15	39.75	8533	31.28	0.83	5.16	6.60
S20	30.65	6388	24.83	0.68	5.35	6.66
S22	27.03	6400	25.15	1.59	5.55	5.17
S23	27.98	6427	24.44	1.59	4.96	4.18
S25	73.35	11037	38.98	1.82	6.13	5.37
Mean	29.80	6069	24.47	1.01	4.35	4.94
R-squared	0.2	0.4	0.4	0.07	0.3	

Low correlation between χ and heavy metals as shown in Figure-9, which could be due to low magnetic signal (lack of anthropogenic ferromagnetic particles) and natural origin of investigated elements). This is also confirmed in Table-2.

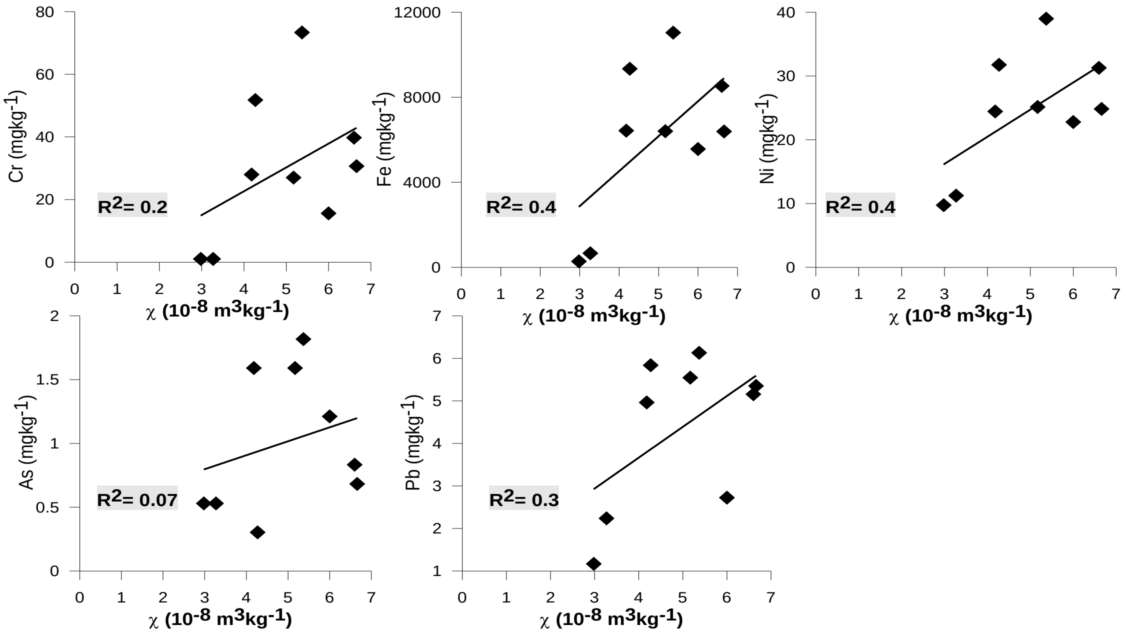

Figure-9 Heavy metal contents (Cr, Fe, Ni, As and Pb) versus magnetic susceptibility for selected samples.

Conclusions

A Magnetic and geochemical study on fifty sediment samples collected from the bottom of Sawa Lake in southern Iraq were carried out. The lake is located in an industrial area and flies ashes emitted from cement plant (located ~2 km west of the lake). Results of the studied sediment samples show that the antiferromagnetic iron oxides (probably hard hematite) are abundant without any contents of soft ferrimagnetic iron oxides (magnetite). Magnetic susceptibility values <10 x 10^{-8} m^3kg^{-1} is typical for paramagnetic minerals. In addition, only a small fraction of super-paramagnetic grains was detected in the samples. The macroscopic grain size distribution shows the dominance of 20-30microns fraction and significantly lower content of coarser 200microns fraction in the sediments. Magnetic susceptibility shows a weak correlation with heavy metal contents which could be due to the low magnetic signals in the sediments.

From the results of magnetic and heavy metals, it has been concluded that there are no anthropogenic effects on lake sediments.

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