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Clay mineralogy and heavy metal geochemistry of the Tigris River sediments in selected area of northern Iraq

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ABSTRACT

Thirteen samples of sediment were collected from the Tigris River between Hammam Al-Aleel and Fat'ha area, northern Iraq to determine the texture of these sediments, clay mineral assemblages and concentrations of some heavy metals. The grain size analysis of the samples revealed that the silt fraction is the most dominant type in the studied samples, and the size decreases down-stream in accordance with the river's morphology and gradient. The clay fraction was examined by employing XRD to recognize the clay mineral types. It was found that montimorillonite is the most dominant mineral, in addition to illite, palygoriskite, kaolinite and chlorite. The heavy metal elements were determined by Atomic Adsorption Spectrum (AAS) instrument and they included Zinc (Zn), Copper (Cu), Cobalt (Co), Cadmium (Cd) and Lead (Pb) in the clay fraction. However, due to human activities like fertilization of soil and industrial water, such elements as Pb (163 ppm), Zn (121 ppm), Co (33 ppm) were higher than the normal concentration, while the concentration of Cu (42 ppm) was lower than the normal.

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دراسة المعادن الطينية وبعض العناصر الفلزية الثقيلة في رواسب نهر دجلة في منطقة مختارة شمال العراق

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الملخص

تم جمع ثلاث عشرة عينة من الرواسب الحديثة من نهر دجلة بين حمام العليل ومنطقة الفتحة شمال العراق. أظهر تحليل الحجمي الحبيبي أن نسبة الغرين هي السائدة في المتوسط في العينات المدروسة بالإضافة إلى أن الحجم الحبيبي يتناقص إلى أسفل النهر متوافقا مع مورفولوجيا وانحدار النهر. تم فحص جزء الطين بواسطة XRD للتعرف على نوع المعادن الطينية ووجد أن المونتيمورلينايت هو السائد، بالإضافة الى معادن الإيلايت والباليغورسكيت والكاولينيت والكلوريت. تم فحص تراكيز العناصر الثقيلة المتمثلة بالزنك (Zn) والنحاس (Cu) والكوبالت (Co) والكادميوم (Cd) والرصاص (pb) في جزء الطين باستخدام جهاز طيف الامتزاز الذري (AAS). كانت تراكيز الفلزات الثقيلة في النماذج المدروسة هو Pb (163ppm)، Zn (١٢١ ppm)، Co (33 ppm) وكانت تراكيز هذه العناصر عالية مقارنة مع التركيز القياسي بينما كان تركيز Cu (٤٢ ppm) أقل من التركيز القياسية وجد ان تراكيز عناصر وهذا قد يكون بسبب الأنشطة البشرية مثل تسميد التربة والمياه الصناعية.

Introduction

The environmental pollution is mostly produced from human activities, which cause much sickness, and deaths occur due to pollution of the aquatic environment and precipitation with heavy metal elements, such as Pb, Zn, Cu, Co and Cd [1]. Metals in river deposited (soils and sediments) can be originated from lithogenic result from erosion and sedimentation of metal – bearing geological formations upstream. In addition to the anthropogenic source that is human activity increases metal concentrations in water river and subsequently in floodplain deposits [2]. Anthropogenic influences and degrades surface waters quality [3].

These metals are more dangerous than organic poisons because organics change over time, whereas metal elements are stable and occasionally form dangerous organic compounds. Therefore, it is very important to recognize them and define their concentration. The pollution by heavy metals may happen naturally or because of human activity, such as the remains of industrial, irrigation, fertilization or heavy waters. The recent sediment of rive may be derived from older rock (igneous, metamorphic or sedimentary) which outcropped on the surface of earth by weathering and erosion. Also, the soil forms additional source [4]. The composition of sediment is primary controlled by the source rock composition in addition to the weathering, transport and diagenetic process to minor extent [5].

The studied samples from sediments of the Tigris River are collected from the area between Hammam Al-Aleel and Fat'ha carriage in the south (Fig.1). The purposes of the study are to determine the pollution of these sediments by heavy metal elements (Pb, Zn, Cu, Co and Cd), study grain size properties and identify the clay minerals in fine fraction.

2. GEOLOGICAL SETTING

The study area is located in low folded zone in the north part and unfolded zone in the south part (Fig.1). Tigris River is parallel to some of anticlines in the area and is affected by subsurface anticlines, such as the Ajal, Tikrit, affecting the south part of study area [6]. The outcrop formations in the area are Euphrates and Jeribie formations exposed in the core of Makhul anticline with 55m thickness, composed of limestone and evaporites. In addition, Fat'ha formation (Middle Miocene) is exposed on the both sides of Tigris River from Hammam Al-Aleel to Fat'ha carriage. It is formed of alternative evaporating facies entering with limestone and marl with fine clastic [7]. It is represented by many cycles of deposition of evaporates, limestones, and marl and marly lagoonal environment. Injna Formation (Upper Miocene) is outcropped in many locations and formed of alternatives of sandstone, siltstone, clay stone [8] and contains thin lenses of secondary gypsum.

It is deposited in fluvial continental environment with thick clastic sediment succession. Muqdadiya Formation (Pliocene) is exposed on east sides of Tigris River and on both Hemrin Anticlines. In addition, it is formed of pebbly sandston, gravel, siltstone and claystone [6]. It is deposited in continental environment. The quaternary deposits (Pleistocene) form terraces on both sides of the Tigris River in addition to floodplain and extend to a wide distance on the east and west sides of the river. The quaternary deposits are clastic and rich in gypsiferous material [6], formed of mixture of gravel, sand and clay in horizontal layer of lenses with many levels of terraces of different elevation on both sides of river. The maximum elevation of oldest terraces is about 35m above the level of the river in the present time.

3. MATERIALS AND METHODS

The Tigris River sediments were uncrystalized and were collected from a section (along with the downstream) of the Tigris riverbank's natural outcrop. Sampling was done in various places along with the river course to represent the spatial variation of the sediment. Thirteen samples were collected in October 2022 at a minimum flow. Sampling stations were geo-referenced using the global positioning system (GPS) (Fig.1).

All samples represented the deposit of new top-layer materials. Samples were carefully selected to avoid pollution resulting from human activity, such agricultural fields, quarries, and levees. Taking about 2 kg of weight and keeping it in a plastic bag, the samples were left to dry in the original plastic bag at room temperature. Some aggregates were formed during drying a porcelain mortar and pestle was used to disaggregate samples, dividing them into two parts and taking one part for sieve analysis to separate very fine particles, silt, and clay (0.0630–0.0004 mm). Then, 100 gm from each sample was subjected to wet sieve analysis, and the grains passing through the sieve (more than 0.0620 mm) were pipette analyzed according to Stock's law. 10 ml of distilled water and 0.05 M of hexametaphosphate $(NaPO_3)_6$ were used prior analysis to avoid the flocculation of particles. The weight percentage was calculated for each size particle class. Grain size analysis was carried out at the University of Tikrit, applied Geology department, sedimentology and optical mineralogy labs. X-Ray Diffractometers (XRD) analysis was performed at the XRD Lab of the Ministry of Sciences and Technology. For clay mineral analysis, five samples (4, 8, 9, 10, and 12) with a higher clay percentage were chosen and analyzed with three different treatments (Ethylene glycol, Heating 350, heating 550) to separate polytype of clay minerals qualitatively. Heavy metals (Pb, Zn, Cu, Co, and Cd) in clay fraction were determined by using atomic absorption spectrometer technique. Digestion clay fraction by the HNO3 acid methods was used. The analysis was performed at Tikrit University, College of Engineering, Chemical Engineering Department.

4. RESULTS AND DISCUSSION

4.1Grain size analysis

Grain size analysis was carried out by utilizing dry and wet methods to determine the percentage of sand, silt, and clay fraction for the analyzed samples (see Table 1). The results showed the coarse grains at the north part and their decrease down the river. The upper Zab River brought more fine grains of silt and clay, increasing the percentage of their sizes. The predominant size in average among the samples was silt fraction with (42%), clay (29%), while the less one was sand with (28%). The study area was characterized by the prevalence of the fine size particles class from sediment, which represented the most chemical active part. Elements were dispersed in the aqueous phase and might be transformed into physical and biological materials, such as sediments (especially fine fraction) and organic matter. Elements could be removed from the water column by scavenging and/or absorption onto suspended particles or organic matter and could subsequently accumulate in bottom sediments. Thus, sediments act as sinks and potential sources of contaminants in the varying environment deposited. Metals deposited (soils and sediments) can be originated from lithogenic result from erosion and sedimentation of metal – bearing geological formations upstream. In addition, anthropogenic source that is human activity increases metals concentration in water river and subsequently in floodplain deposit [2].

4.2 Clay Mineral

Clay minerals, the principal products of weathering and soil formation, are formed due to water-rock interaction processes [1]. The mineralogical study for river sediment is important to understand the origin of sediment downstream [10]. From the XRD analysis, the following clay minerals were identified, as shown in (Fig.2). Smectite (montmorillonite) was recognized with reflection (001) about (d = 14A°), when treated with EG (Ethylene Glycol), (001) became (d = 17A°) and when heated to 550 C°, (001) became (d = 10A°). This mineral was derived from rock rich with Mg^{+2}, Fe^{+2} and Ca^{+2} or from the destroy of mica minerals. Also, the feldspar is considered a source of smectite. The climate condition and the alkaline environment are favored to form this mineral as authiginic minerals [11];[12]. Chlorite was recognized by basal reflections (d = 14A°) for level (001), (7.3 A°) for level (002), and not affected by EG treating and heating [13];[14]. Chlorite is a common mineral in the soil, especially under the acidic condition [11]. It is derived from metamorphic, granitic and sedimentary clastic rock, emerging in the basin of Tigris River. Shale is considered one of its main sources [12]. Kaolinite mineral was distinguished by a basal reflection (d=7.2 A°) for level (001) and was not affected by the treatment with ethylene glycol, but when heated to 550 ° C, it lost crystallization properties and was damaged [13]. Kaolinite is mostly derived from igneous rock rich in feldspar and older clastic sedimentary rocks. The presence of Kaolinite gives evidence of chemical weathering [15]. Kaolinite is also formed in acidic and wet climate condition [11], [16]. Illite mineral was recognized by basal reflection (d = 10 A°) for level (001), and was not affected by EG and heating treatment [13]. Illite is formed from rocks rich in Al and K and from granitic [11], [17]. Illite is a common mineral in the sediment of Tigris River, which is derived from shale and clastic rock at the upper river basin. Palygorskite is fibrous mineral diagnosed by the base reflection of level (001) shown at (d = 10.5 A°) and decreased to (d = 10A°) by heating [14]. The mineral is formed chemically in lagoon environment or from other clay minerals in lake and swamp [15]. The Palygorskite is also formed in arid condition [17].

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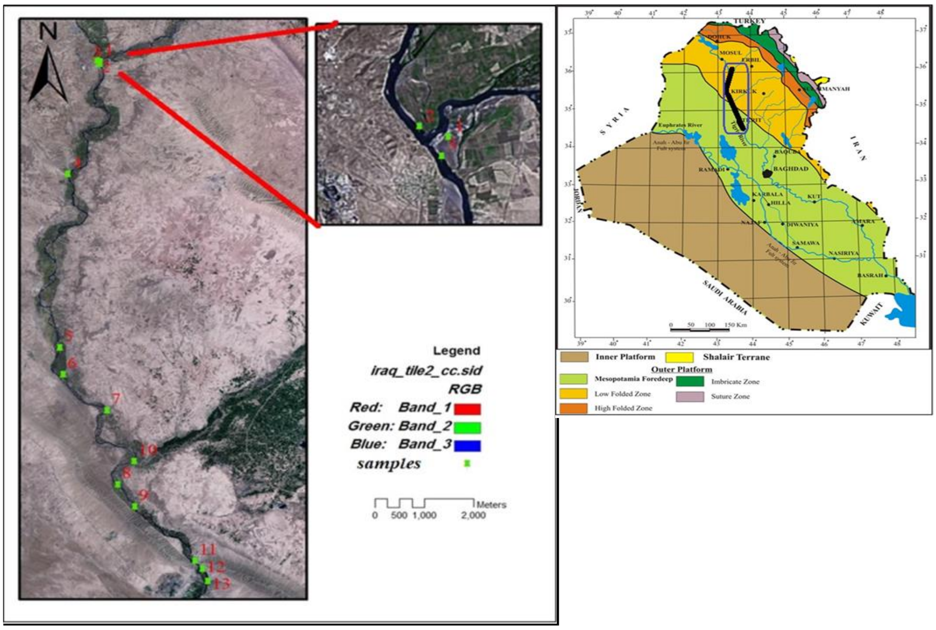

Fig. 1: Location map study area and samples site and Tectonic map of Iraq (after [9]).

Table 1: The grain size analysis of the studied samples.

Samples No.	location description	Sand %	Silt %	Clay %
1	Sifina village south upper Zab east side	55	32	13
2	Sifina village west side	72	12	15
3	Inlet of upper Zab above meeting with Tigris	16	57	27
4	Inlet of upper Zab below meeting with Tigris	19	32	50
5	Inlet of upper Zab below meeting with Tigris east side	29	46	24
6	Sidera village of near of water station east side	22	60	13
7	Subeh Village	51	29	17
8	Masahk village	3	49	46
9	Masahk bridge	9	51	40
10	River Terrace before Lower Zab	17	20	61
11	North Biji city	22	64	14
12	North power station	9	60	30
13	Albujwary village	41	36	23
Average		28	42	29

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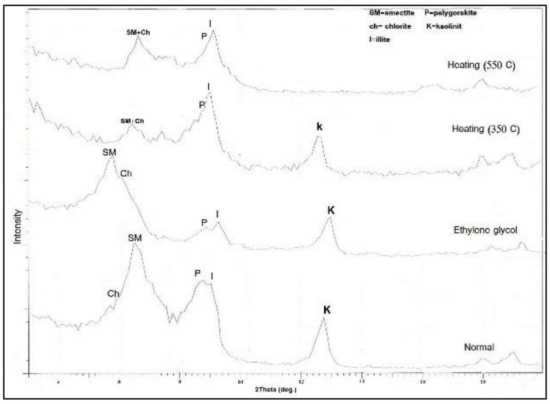

Fig. 2: X-Ray diffractometer chart for clay size in studied samples, representative samples (No-8).

4.3 Heavy elements

Metals in soils and sediments (deposits) can originate from lithogenic and anthropogenic sources, and their availability for uptake in biota is hypothesized to depend on both origin and local sediment conditions [2]. The following heavy metals were studied in the clay fraction of the studied samples (Table 2). Zinc has concentration 70 (ppm) at the earth crust, is increased in argillaceous soil, adsorbed in clay mineral and is present in sulfide and galena minerals [18]. Also, zinc increases in alluvial and organic soil and adsorbed on most clay minerals [19]. Pollution by zinc happens mostly because of minerals and industrial activity [20]. The concentration of Zn in the present study was in the range (173-85) with an average 121 (ppm) (see Table 2 and Fig.3), which is more than in the word standard, especially in the north of the study area and the heavy agriculture at Upper Zab River basin and the source rock in the river basin. Pollution by zinc may also be due to rich organic soil [20] where the zinc adsorbed on surface of clays rich in organics. The Zinc species is less soluble than other metals in water [21].

The copper concentration in the earth's crust is between 75-25 (ppm) with average 55 (ppm). The Cu in the soil is related to source rock and soil formation condition [20]. The transformation of Cu depends on pH as well as adsorption to organic matter and clay minerals [22] or resulted from sulfide complex analyzed during chemical weathering, especially in acidic environment [23]. The concentration of Cu in the present study was in range 31-56 (ppm) with an average 42 (ppm) (see Table 2 and Fig.3), which is within the normal average. Cadmium is present in igneous and sedimentary rocks, which most affect the Cd content in soil [20]. Cadmium is present with apatite mineral in igneous rock and is present in Ca-feldspar [24]. During the process of weathering, cadmium is adsorbed on clay mineral surface [20]. In addition, cadmium is found with Pb and Ga ore and is adsorbed on clay or organic material in reduction condition [22], [23], indicating that the low pH helps in dissolving and adsorption of Cd with clays and organic materials [25]. Phosphate fertilization has Cd cadmium concentration up to 83 ppm. It is sometimes associated with Fe and Mn oxides [20]. In the present study samples, the concentration of Co was lower than the lower detection limit of the instrument (<5 ppm) (Table 2). The concentrations of Cd and Co in the soil depend on the nature of the source rocks, where they have the highest concentrations in the ultrabasic rocks (about 200 ppm) and the lowest concentrations in acid rocks[26]. Cobalt is found in the sediments of the Tigris between 24 - 44 (ppm) with an average 32 (ppm) (see Table 2 and Fig.3), which is higher than international standard in the soil and shale. This may be due to the richness of the source rock, especially at north of Iraq where the outcrop of basic rock. The presence of the Pb is related to galena mineral or in the form of $PbSO_4$. Also, it is originated with mica, plagioclase, amphibole, pyroxene and garnet [18]. In [20], Pb in soil is of primary and secondary origin (from the decomposition of uranium and thorium). The concentration of Pb is mostly in upper layers of soil rich in organic materials [26] and forming stable sulphides [25]. Pb is deposited in reduction condition as sulphides, increasing its concentration in soil. It is dissolved at oxic condition, reducing its concentration in sediments [18]. In addition, Pb concentration increases in phosphate and organic fertilizers [20]. The lead concentration in the present study was between 24 - 26 (ppm) with an average (163) ppm. These concentrations are higher than the standard (see Table 2 and Fig.3), especially in the middle part of the study area, because of Baiji pumping station which works by gas, the heavy use of organic and phosphate fertilizers by farmers in addition to pollution by industrial area to the north of Biji city.

Table (2) Concentration of heavy metals (in ppm) in clay size of the studied samples.

Samples	**Pb**	**Zn**	**Cu**	**Co**	**Cd**
1	58	143	48	44	<5
2	43	99	40	39	<5
3	71	161	54	33	<5
4	45	132	41	32	<5
5	400	113	56	40	<5
6	281	160	50	29	<5
7	34	102	31	24	<5
8	32	92	32	29	<5
9	50	173	42	33	<5
10	35	97	39	38	<5
11	26	85	35	31	<5
12	38	128	38	28	<5
13	30	88	36	27	<5
Average	163	121	42	33	<5

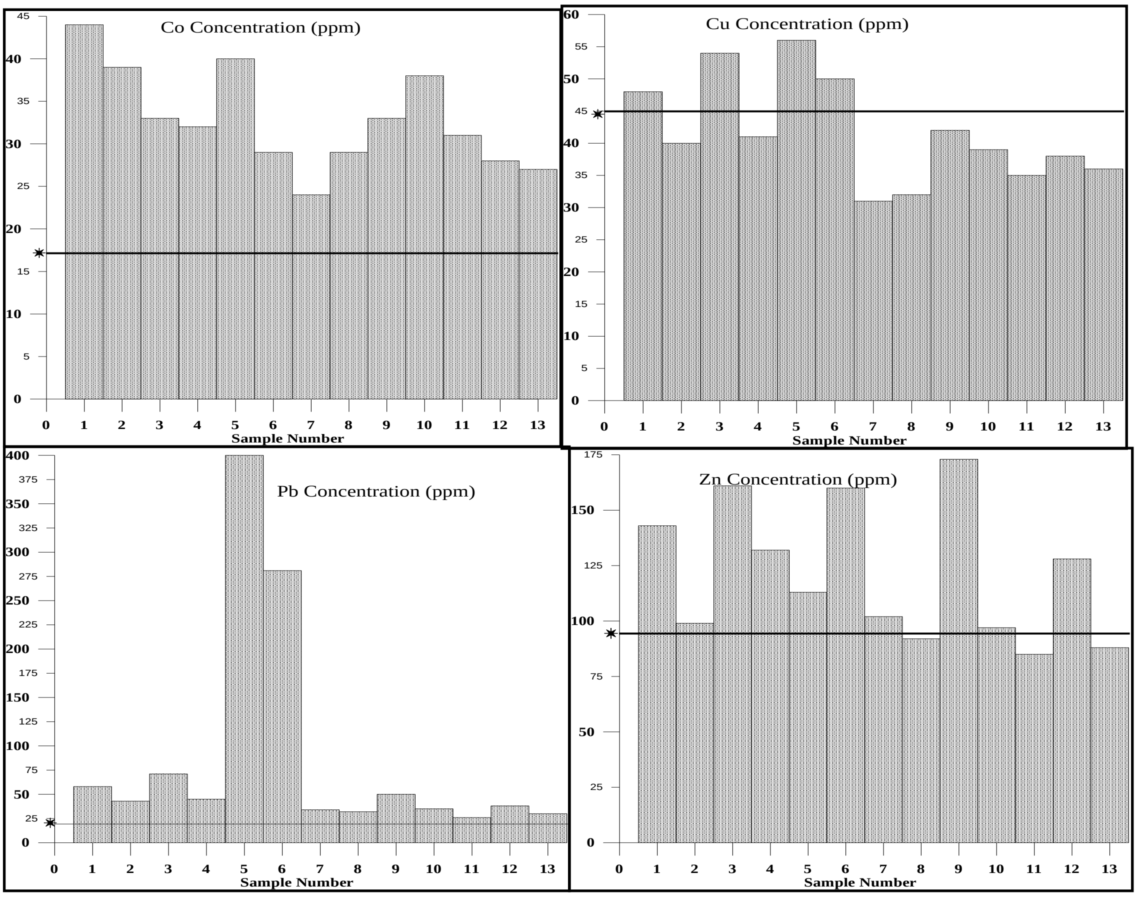

Fig. 3: Distribution of heavy metals in studied samples. *Average in shale[27].

5. CONCLUSIONS

1- The grain size analysis indicated that it decreases gradually downstream from north part of study area to the south.

2- Clay minerals identified in the present study samples are chlorite, montmorrilonite, illite, palygorskite, and kaolinite, originated from different source of rock in north Iraq.

3- The concentrations of heavy metals Pb, Zn, Cu, Co are mostly higher than the international standard, whereas Cu is lower than the international standard. The pollution and contamination by the elements of Pb, Zn, Co may be due to the heavy use of the different type of fertilization and the presence of industrials and water-pumping station on the river, which may increase the concentration and contamination by these elements.

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