



# SPATIAL VARIATION IN THE CONTENT AND DISTRIBUTION OF IRON OXIDES IN SEDIMENTS OF THE GHARAF RIVER IN IRAQ

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## Abstract

A study of the spatial distribution of iron oxides in the deposits of the Al-Gharaf river was conducted in some soils of Wasit and Thi Qar governorates due to the effect of six regulators of the Al-Gharaf river and its role in the quantitative and qualitative distribution, where the sampling areas were identified in front and rear each of the regulator, on the banks of the Al-Gharraf river channel, Within the area confined between the origin of the regulator and the channels which fed by the regulator. Soil samples were taken during spring season 2019, where 12 pedons distributed along the bank of the canal were digged in the middle of the variability in water levels between the highest and lowest levels of water and the depth of the digging is determined by the level of the water table. After bringing the samples, they were prepared for examination, and the necessary analyzes were performed on them. The results showed an increase in the total iron oxide values in soil of the front of the regulator compared to the soil at rear of the regulator in all locations and for both depths. The values of amorphous iron oxides were lower than that of Crystalline Free Iron Oxides in all the soils of the study. There was no clear and specific distribution of the values of amorphous iron oxides, either in the horizontal or the vertical plane, in the soils of the study. The values of crystalline iron oxides increased at both the surface and subsurface depths in soils of the front of the regulator compared to the soil of the rear of the regulator in all study locations. The vertical distribution of active iron values within the surface and sub-surface depths was the opposite of the distribution of the values of crystallized iron oxides. The values of active iron increased within the subsurface layers compared to the surface layers at all location. As the role of the regulators appears through their direct influence on the process of distributing iron oxides forms through sorting them according to their sizes, in addition to the role of the regulators in controlling the variability in water levels, which is reflected on its effect on the iron oxide content with the depth.

**Key words:** iron oxides, sediments, Gharaf River

## Introduction

The Al-Gharraf River is one of the most important branches of the Tigris River in Iraq, which branches from the Tigris River at the Kut Dam in Wasit Governorate, heading south, its length is about 168 km from its branch point from the Tigris River to Al-Badaa regulator. There are six of regulators distributed along the Al-Gharraf River, in order to controlling the distribution of water.

The majority of rivers in nature, which humans did not interfere with, are considered balanced, especially with regard to carrying sediments and water, but this balance changes greatly when rivers are controlled by building dams, as the process of controlling the flow system leads to a change in the hydrological, environmental, and geomorphological conditions of the canal and river stream (Li.D *et al.*, 2014) The

construction of dams in rivers reduces the velocity of the flow of water stream in the canal, which causes to increase the sedimentation of portable sediments towards the dam, as sediments deposited on both sides of the canal banks leads to a decrease in flow because of the narrowing of the cross section of the channel before it reaches the dam, also the accumulated sediments at the bottom of the channel have a role in the change in the terrain of the channels and all of this lead to changes in geomorphological conditions (Rhoads and Csiki, 2014).

Free iron is defined as iron that coated or adsorbed on surfaces of soil particles, and includes iron oxides and other iron forms in the soil, but not as part of the crystal net of other minerals present (Fan *et al.*, 2016). Iron oxides are found in the soil in various forms They may be in the form of coats surrounding the surfaces of clay

minerals, or in the form of complex organic compounds when they bind to the organic matter, or they may be in the form of solo particles as the size of clay particles (Greenland *et al.*, 1968). As for amorphous iron oxides, they are small size particles, their diameters about 50 - 100 angstrom, almost spherical in shape, and having a high surface area of up to 330 m<sup>2</sup> g<sup>-1</sup> (Schwertmann and Taylor, 1977) They may not have regular shapes, as they are weakly crystalline for mation, and are found in the soil either as the form of coats surrounding the metals granules, Or they are separate (Ulery, 2011) and they have few percentages in the soil and are inversely proportional to the degree of soil development (Rasheed, 2005). They are characterized by having more ability than crystalline oxides in adsorption of elements, due to the large specific surface (Essington, 2004). Crystallized iron oxides are considered to be particles with a high surface area, because of their small size, with a diameter of about 30-100 angstrom, so they affect various soil properties, and have a chemical effect on the iron cycle, which are compounds that spread in most environments (Anschutz and Penn, 2005). It differs from amorphous iron oxides, in that they are compounds of uniform crystalline forms, the surfaces of which do not possess porous voids, and predominate in developed soils, (Trived and Axe, 2001). As for the active iron, it is the ratio between the iron extracted with a solution of oxalate (Fe<sub>o</sub>) to the percentage of iron that was extracted with dithionite (Fe<sub>d</sub>), and this ratio shows the amount of its contribution to the crystallization of iron oxides and it may be used as an important criterion in clarifying the distribution of iron oxides types and their relationship to effective factors of the soil, as well as showing the relationship of iron oxides to the evolutionary state of the soils. The present study aims to know the spatial distribution of iron oxide types and the extent of influence of the regulators of the Al-Gharaf river in the quantitative and qualitative distribution of iron oxide types in the deposits of the Al-Gharaf river.

### Materials and methods

Sampling sites were chosen along the Al-Gharaf river soils that extend from the beginning of Al-Gharaf regulator in the Tigris River in the front of the Kut Dam, in Wasit Governorate and along the river in the south to rear of the AlBadaa regulator, in the Al-Shatrah district in Dhi Qar Governorate. Where the sites for digging of pedons were determined at each of the six regulators, along the Al-Gharraf River, which control the distribution of water ration for the lands that are irrigated from it, where the locatios for digging the pedons were set at the front and rear of each regulator, according to the presence of the sediments in the area and the sampling sites was

determined in the middle of the distance Trapped between the highest and lowest levels of river water during the previous years, and the depth of digging is determined by the level of water table.

### Laboratory procedures

Total free iron oxides were estimated by using the CBD method followed by Mehra and Jackson (1960), where the iron in soil was extracted in the form of free oxides, and then the iron was measured by using an atomic absorption device (AAS) along a wavelength of 882 nm. The amorphous free iron oxides in soil samples were estimated after being extracted with a solution of acid ammonium oxalate, after adjusting its acidity at pH = 3, and according to the method followed by Schwertmann (1964), then the iron was measured in the extract using the atomic absorption device (AAS), Then the values were converted to free amorphous iron oxides. As for the Crystallized iron oxides, their ratio was calculated by finding the difference between the value of the total oxides and the value of the amorphous oxides according to the following relationship.

$$Fe_a = Fe_t - Fe_o$$

The proportions of the active iron were found from the following relationship:

$$\text{Active iron ratio} = \frac{\text{Amorphous iron}}{\text{Total free iron}} \times 10^{-2}$$

## Results and discussion

### Total free iron oxides

It is clear from table 1 of the total free iron oxide values in the soil. The values were in the range 0.736 - 0.399 g.kg<sup>-1</sup> in the soil horizons of the study pedons, as it appears through the results the decrease of the free iron oxides content in the study soils, as they are newly transported deposits, and the abundance of iron oxides depends on the conditions that lead to soil development, Bortoluzzi *et al.*, (2015), this may indicate the weak activity of the chemical weathering process in those soils, where the lowest value appeared in the first Pedon soil (P1) of the horizon (C3) at the soil of the rear of the regulator, whereas the highest value in soil of the fifth Pedon (P5) in the horizon (C1) was at soil of the front of the regulator, as it is clear from the results, There are differences in the values of iron oxides in the vertical and horizontal direction between the front and rear of the regulator and it is clear from table 2 when taking the values of total free iron oxides on two depths, surface depth and sub- surface depth, that their values have increased in soil of the front of the regulator compared to

in soil of the rear of the regulator and in the all locations and for both depths, The reason for this is due to the high content of clay particles at the front of the regulator table 1, as there is a relationship between the fine part of the soil particles and the content of free iron oxides in the soil and this is consistent with Bzeni (1999) and Enya *et al.*, (2011) They have found that iron oxides increased

exponentially with the decrease in the size of the soil particles, and the highest recorded values were in the particles of the clay separator, and it was inferred that both free iron oxides and particles of clay separator contribute in the movement, and supported that AL-Rawi (2006). Where he found Significant relation between the values of free iron oxides and the total amount of clay in the soil?

**Table 1:** The content of some soil properties.

Location	Pedon No.	horizons	OM g.kg <sup>-1</sup>	Clay g.kg <sup>-1</sup>	Iron oxides (g. kg <sup>-1</sup> )			Active Iron
					Total free	Amorphous	Crystallized	
Front of Regulator (F)	P1	A	5.7	478.0	0.563	0.208	0.354	0.588
		C1	8.5	260.1	0.588	0.217	0.371	0.586
		C2	3.3	311.1	0.528	0.165	0.363	0.456
		C3	4.1	220.8	0.542	0.211	0.331	0.638
		C4	7.0	497.5	0.550	0.211	0.339	0.621
	P2	A	3.0	242.1	0.556	0.136	0.420	0.323
		C1	3.8	253.4	0.555	0.099	0.456	0.218
		C2	9.1	497.6	0.631	0.127	0.504	0.251
		C3	0.8	201.1	0.531	0.177	0.354	0.501
	P3	A	4.4	479.0	0.589	0.103	0.486	0.211
		C1	7.7	211.1	0.528	0.122	0.406	0.299
		C2	5.0	371.3	0.560	0.178	0.382	0.465
		C3	0.7	221.0	0.556	0.183	0.373	0.489
	P4	A	7.5	280.2	0.528	0.149	0.380	0.392
		C1	7.7	346.9	0.540	0.152	0.388	0.392
		C2	4.3	361.2	0.555	0.151	0.404	0.375
		C3	3.1	298.8	0.469	0.126	0.343	0.368
	P5	A	16.9	325.5	0.712	0.236	0.476	0.497
		C1	8.4	357.5	0.736	0.175	0.561	0.313
		C2	10.5	300.0	0.673	0.180	0.493	0.364
		C3	8.4	336.9	0.619	0.175	0.444	0.395
	P6	A	9.0	341.0	0.534	0.181	0.354	0.510
		C1	13.0	456.7	0.640	0.155	0.485	0.319
		C2	6.7	401.2	0.556	0.171	0.384	0.446
Rear of Regulator (R)	P1	A	4.7	180.5	0.488	0.151	0.337	0.449
		C1	1.6	81.6	0.539	0.275	0.263	1.043
		C2	2.3	280.7	0.594	0.182	0.412	0.442
		C3	2.0	100.2	0.399	0.126	0.274	0.461
	P2	A	1.7	181.5	0.538	0.142	0.396	0.358
		C1	5.7	201.2	0.579	0.189	0.390	0.486
		C2	3.3	118.7	0.439	0.150	0.289	0.519
	P3	A	4.3	280.7	0.531	0.132	0.399	0.331
		C1	5.7	217.5	0.474	0.145	0.329	0.442
	P4	A	5.1	221.5	0.437	0.128	0.309	0.413
		C1	6.4	278.0	0.472	0.204	0.268	0.763
	P5	A	4.7	251.3	0.567	0.153	0.414	0.370
		C1	5.7	280.0	0.568	0.179	0.389	0.460
	P6	A	2.3	120.9	0.484	0.160	0.324	0.494
		C1	7.0	299.1	0.524	0.183	0.342	0.534
		C2	4.7	220.8	0.488	0.164	0.324	0.507

In addition to the sedimentation conditions of the particles of the transported materials and their precipitation environments, they have important role to the variation in the distribution of iron oxides, as the percentage of particles of free iron oxides correlated with the ratio of the fine part of clay particles, and it is known that the percentage of the fine part of clay particles it higher in soil of the front of the regulator compared to in soil of the rear of the regulator, Which resulted increase in the values of free iron oxides in the soil of the front of the regulator. In addition to that the organic matter has an important role in increase the percentage of free iron oxides in the soil, where the AL-Rawi (2006) is found a significant correlation between the content of the organic material and the free iron oxides in the soil. Where the results of Table 1 showed an increase in the organic matter content in soil of the front of the regulator compared to in soil of the rear of the regulator, which affected the increase in the free iron oxide content in those soils. Whereas Rasheed (2005) clear up that both the moisture content and the organic matter have a role in increase the total free iron oxides in the soil, therefore the high content of the organic material at the front of the regulator, which accompanied the moisture content in that soil for a longer period, is due to the higher capability of these soils to retaining With water because this soil with a high content of clay particles and organic matter, which affected the increase in the values of free iron oxides in soil of the front of the regulator.

It is clear from table 1 that the values of iron oxides were increasing with depth and then decrease in the soil of all study pedons both at the regulator's front or at its rear, and this may be due to the effect of variability in water levels due to the closing and opening of the regulator's gates during the control process, which helped to oscillate the ground water within Soil pedons during this stage, This is reflected in the increase in iron oxide content due to the succession of oxidation and reduction processes, which increases the accumulation of iron ion, especially in the horizons where the variability is rapid and this is congruous with Essa (1990), where he found during his study of the

**Table 2:** Values of Total Free Iron Oxides, (g.kg<sup>-1</sup>) on two depths, surface and subsurface depths.

Pedon No.	Total free iron oxides (g.kg <sup>-1</sup> )			
	Front of Regulator		Rear of Regulator	
	Surface layers	Subsurface layers	Surface layers	Subsurface layers
P1	0.560	0.546	0.540	0.399
P2	0.555	0.580	0.551	0.485
P3	0.558	0.558	0.531	0.474
P4	0.538	0.511	0.436	0.472
P5	0.724	0.645	0.567	0.567
P6	0.569	0.583	0.497	0.500

patterns of variability of the ground water and their relationship to the oxidation and crystallization process of iron ion, The horizons for rapid variability of ground water had a higher iron oxide content than submerged horizons. Al-Hasseini (2005) found when studying the characteristics of some Hammar marsh dried soils in Iraq, the highest value of total iron was recorded in the horizons near the edge of the marsh, and this was attributed to the effect of variability of ground water in the process of oxidation and reduction and thus high total iron values.

### Amorphous iron oxides

It is evident from the values of table 1 that the values of amorphous iron oxides were between 0.099 - 0.275 g.kg<sup>-1</sup>, as the lowest value was found in the soil of the second pedon (P2) in the horizon (C1) at the soil of the front of the regulator, while the highest value was in the soil of the first pedon (P1) in the horizon (C1), at soil of the rear of the regulator, as it was also appeared that the values of amorphous iron oxides were less than the values of the crystallized iron oxides recorded in all study soils, this may be due to the activity of the process of transformation of iron into the most crystallized form in the soil, as the crystallization process increases with time (Schwertman and Leutz) 1966) This is an indication of the nature of the prevailing environmental conditions, whether in the source region or in its sedimentation areas, which helped to activate some of the pedogenic processes that led to increase the crystallization, such as the effect of the climate factor on the transformation process, where high temperatures and the length of the drought period in the location of study soils, that led to Increase the rates of transformation of those oxides in the most crystallized direction, and these results are consistent with many studies conducted on Iraqi soil (Al-Fatlawii, 2016 and Majeed, 2017) or, the reason may be due to the high content of crystalline oxides in the source soils in the northern regions of Iraq, as they are well-developed soils that have long time formed, leading to the transformation

of iron oxides into more developed formulas, and these results are consistent with what was found by Bzeni (1999).

The results of table 3, which represents the values of amorphous iron oxides, for two depths (surface and subsurface depths), showed that there is no specific and clear distribution of the values of amorphous iron oxides on the horizontal or vertical level in pedons of the soils of the study, as the values rose in the surface horizons of the soil of the front regulator compared to soil of the rear regulator, except for soils of the pedons P2 and P3 and this behavior is similar to the distribution behavior of total free iron oxides in those soils, and is consistent with (Mawlood and Essa, 2019) they showed that the behavior of the Crystalline and amorphous iron oxides was similar to the behavior of the distribution of total free iron oxides, both horizontally and vertically, while the values of amorphous iron oxides in the subsurface horizons were lower in soils of the front of the regulator compared to in soil of the rear of the regulator, except for the Pedon P1 and P3. According to our belief, the variation in the distribution of amorphous iron oxide values in the surface horizons of the study soils, can be attributed to the variation in the distribution of both the organic matter content and the clay particles between the front of the regulator and the rear of the regulator, which was reflected on amorphous iron oxide distribution. As the organic matter inhibits the crystallization of these oxides, while its distribution corresponds to the distribution of the particles of the clay in the soil (Bzeni, 1999), where Al-daini (2012) found that the values of amorphous iron oxides have increased with increasing the content of organic matter in the soil, and he was showed that the reasons for this are due to the influence of the content of the organic matter on the reduction of iron and thus discouraging the crystallization process. Also, the effect of the difference in the distribution of the moisture content of the soil between soil of the front of the regulator and soil of the rear of the regulator, as a result of the process of

**Table 3:** Values of amorphous iron oxides (g.kg<sup>-1</sup>) on two depths, surface and subsurface depths.

Pedon No.	Amorphous iron oxides (g.kg <sup>-1</sup> )			
	Front of Regulator		Rear of Regulator	
	Surface layers	Subsurface layers	Surface layers	Subsurface layers
P1	0.199	0.211	0.188	0.126
P2	0.124	0.152	0.157	0.163
P3	0.112	0.179	0.132	0.145
P4	0.150	0.138	0.127	0.204
P5	0.206	0.177	0.153	0.179
P6	0.172	0.165	0.167	0.170

controlling of the water level during the process of managing for the regulators through the process of the distribution the water shares, Which allows to make the moisture content for a longer period in soils of the front of the regulator compared to in soil of the rear of the regulator, as well as the characteristics of soil of the front of the regulator, which are distinguished by its fine texture, and its high content of organic matter, which contributed to maintain the moisture content of the soils for a longer period compared to the soils of the rear of the regulator and that Reflected on the increased of the content of amorphous iron oxides in those soils. As for the opposite case in the subsurface horizons, The difference may be attributed to the increase in the amount of amorphous iron oxides due to its presence in as connected form with the particles, and it may be has size as much as the silt and sand particles (Font, 1992), which were sorted as size nearly of the sizes of those particles at the soil of the rear of the regulator.

#### Crystallized iron oxides

The results of table 1 show that the values of crystalline iron oxides in the soil under study were between 0.263 - 0.561 g. kg<sup>-1</sup> and that the lowest value was within the soil of the first Pedon (P1) and horizon (C1) at the rear of the regulator, while the highest value was in the soil of the fifth Pedon (P5) in the horizon C1 the front of the regulator.

Through the results of table 4, the increase in the rates of crystalline iron oxides at the surface and subsurface depths has been observed, in soil of the front of the regulator compared to that of the soil at the rear of the regulator and in the all pedons, The reason for this may be due to the sorting process caused by the regulator to increase the deposition of crystalline iron oxides in the front of the regulator higher than its rear of the regulator, as they are has the same size of the clay particles, which confirms the high correlation between these oxides and the content of the clay particles, where the results showed

**Table 4:** Values of iron oxides crystallized (g.kg<sup>-1</sup>) on two depths, surface and subsurface depths.

Crystallized iron oxides (g.kg <sup>-1</sup> )				
Pedon No.	Front of Regulator		Rear of Regulator	
	Surface layers	Subsurface layers	Surface layers	Subsurface layers
P1	0.359	0.335	0.337	0.274
P2	0.432	0.429	0.394	0.322
P3	0.446	0.379	0.399	0.329
P4	0.386	0.373	0.309	0.268
P5	0.518	0.468	0.414	0.389
P6	0.397	0.384	0.330	0.329

The current study has a high content of clay particles in soil of the front of the regulator table 1. Also, its movement is associated with the movement of the clay particles (AL-Rawi, 2006) and (Al-Daini, 2012).

The results of table 4 showed an increase in the values of crystalline iron oxides in the surface depths of the soil compared to their value at the subsurface depths, and in the all pedons, whether in soil of the front of the regulator or in soils of the rear of the regulator because of these difference between the moisture content and the process of drought which the surface horizons expose. Due to the high temperatures and evaporation rates, which led to the further crystallization of those oxides in the surface layers of the soil, This is consistent with what Al-Mashhadani (2011) found, where she found that the heat and drought conditions to which the soil is exposed are sufficient to crystallize the iron oxides. Also, Jarallah (2007) showed, that the crystallized iron oxides have increased in the soil he has studied, due to the exposure of the soil surface to evaporation and dehydration due to higher temperatures compared to the subsurface horizons, which helped in the process of transformation of the amorphous iron oxides into oxides higher crystallization over time.

#### Active Iron

It is clear from table 1, that values of active iron in the soil of the study pedons horizons ranged between 0.211 - 1.043, where the lowest value was in the soil of the third Pedon (P3) in the horizon A of front of the regulator, while the highest value recorded in the soil of the first Pedon P1 in the horizon C1 in rear of the Regulator.

It was noticed through the results of table 5 that the vertical distribution of the values of active iron and within the surface and sub-surface depths was opposite to the distribution of the values of crystallized iron oxides, where the values of active iron increased in the subsurface horizons compared to the surface horizons and at all

**Table 5:** Active iron on two depths, surface and subsurface depths.

Active iron				
Pedon No.	Front of Regulator		Rear of Regulator	
	Surface layers	Subsurface layers	Surface layers	Subsurface layers
P1	0.554	0.629	0.546	0.460
P2	0.271	0.376	0.401	0.508
P3	0.255	0.473	0.331	0.441
P4	0.387	0.373	0.412	0.763
P5	0.405	0.468	0.370	0.460
P6	0.397	0.418	0.508	0.516

Locations, With the exception of Location P1 of the rear of the regulator and P4 of the front of the regulator, as this difference can be attributed to distribution to the difference in environmental conditions represented by the high temperature to which the surface horizons are exposed compared to the subsurface horizons, in addition to the difference in the moisture content between the two depths, where all these conditions helped to increase the crystallization of a some of amorphous iron oxides at the surface horizons, which affected the variance in the vertical distribution of the values of active iron oxides. This is consistent with what was reached by Abbas and Hassan (1987) as it was found that there is a difference in the distribution of the formulas in which iron is present when studying the ratio of effective iron oxides, due to the variability in the moisture content between the study locations, as well as the active iron will increase with the increase of amorphous iron, and the amorphous iron increases with the increase of the moisture content in the soil (Ogunsola *et al.*, 1989; Fink *et al.*, 2016).

From the results of table 5, it is clear that the horizontal variation in the values of the active iron did not take a specific pattern in the distribution, as the largest proportion of these values were found in soil of the rear of the regulator compared to in soil of the front of the regulator, especially in the surface horizons of the P1, P2, P3, P4, P6 pedons and in the subsurface horizons of the P2, P4, P6 pedons also, this is due to the deposition conditions, and the difference between the distribution of the crystallized and amorphous iron oxides ratios, especially since the active iron rates in these soils were low and affected by the variation of those conditions.

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