Combination Impact of Humic Acid and Main Soil Orders on Iron Availability Using Solubility Diagram and DRIS-chart

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Abstract

The current study investigated the impact of three humic acid concentrations on iron availability in four different types of soil in the Kurdistan Region of Iraq: Vertisols, Aridisols, Mollisols, and Inceptisols. Fe availability was assessed using two complementary methods: solubility diagrams and the Diagnosis Recommendation Integrated System (DRIS) chart. A pot experiment was carried out to examine the effects of three humic acid spraying quantities (0, 30, and 60 kg ha^{-1}) on Fe availability for sorghum plants throughout the summer sorghum growth season in 2014 (July 15, 2014, to October 1, 2014). The findings from both approaches showed that whereas Vertisols and Mollisols showed more Fe availability and more balanced Fe/N, Fe/P, and Fe/K, Aridisols and Inceptisols showed restricted Fe solubility and nutritional balance. Humic acid considerably increased sorghum grain output and Fe availability.

particularly at 30 kg ha^{-1}, which may be explained by chelation activities that promote iron mobility, but higher rates (60 kg ha^{-1}) did not consistently overcome chemical Fe limits. Fe was often available in the following order: Vertisols > Mollisols > Inceptisols > Aridisols. The results demonstrate that the primary factor affecting iron solubility in calcareous vegetable-growing soils in the Kurdistan Region of Iraq is solid-phase siderite ($FeCO_3$). DRIS diagnostics and solubility diagrams are helpful resources for comprehending Fe behavior and its management significance.

Keywords: Calcareous soil, DRIS chart, humic acid, iron, solubility diagram

Introduction

Iron (Fe) is an essential micronutrient for plant growth, it is required for respiration, photosynthesis, electron transport, the synthesis of chlorophyll, and other enzyme functions. (20). Iron is plentiful in the Earth's crust. Still, its availability is sometimes limited in calcareous soils due to their high pH and calcium carbonate content, which precipitates iron as insoluble ferric hydroxides and oxides (Fe^{3+} forms).(29, 37). Nevertheless, under certain reducing conditions, Fe^{3+} may transform into the more soluble ferrous form (Fe^{2+}) in the rhizosphere, becoming the dominant species available to plants. (15). The soil examined in this study from the Kurdistan Region of Iraq belonged to four soil orders: Inceptisols, Mollisols, Vertisols and Aridisols (16). Their pH is slightly alkaline and their calcium carbonate content ranges from 10 to 30% (13). Sorghum is one of the crops whose solubility and availability are limited by these soil properties, and it is vulnerable to iron shortages. Research indicates that humic acid may enhance the availability of iron in calcareous soils by chelating iron ions and boosting their mobility in the soil solution. (24). To gain a deeper understanding of the nutritional balance and Fe^{2+} availability in sorghum, two complementary methods are frequently employed. Numerous studies have examined the availability of iron in the region using solubility diagrams. Furthermore, the availability and equilibrium of macronutrients (N, P, K) have been investigated using the DRIS stands for Diagnosis Recommendation Integrated System. technique. The DRIS uses data from plant research, whereas the solubility diagram uses the amounts of soil chemicals. The goal of both methods is to comprehend the limitations on plant nutrient availability. (5, 13). Studies in the Iraqi and Kurdistan Region have reported low Fe availability in calcareous soils and its negative impact on crop nutrition and productivity, highlighting the need for improved nutrient management strategies (12, 30). Accordingly, the present research examines the impact of applying humic acid at three different levels (0, 30, and 60 kg ha^{-1}) on Fe^{2+} availability and the nutritional status of sorghum in the calcareous soils of the Kurdistan regions. This study aims to comprehend Fe^{2+} availability in order to evaluate soil fertility, optimize agricultural output, improve nutrient management, and boost sorghum production in the area's calcareous soils.

Materials and Methods

The Pot Experiment

A pot experiment was conducted during the summer 2014 sorghum growing season (15 July 2024 to 1 October 2024). Sorghum yield was used as an indication to examine the effects of three humic acid treatment levels (0, 30, and 60 kg ha-1) on iron availability at the Grdarasha Agricultural Farm, College of Agricultural Engineering Science, University of Salahaddin, Erbil. The range of the GPS measurements was 253 to 988 meters. The factorial experiment was set up using three replications of a completely randomized design (CRD). Twelve sample sites that reflected the predominant soil orders in the Erbil Governorate were selected: Three locations were chosen for each order of Inceptisols, Mollisols, Vertisols, and Aridisols. Mergasur, Choman, and Shaqlawa represented Inceptisols, Rawanduz, Koya, and Daraban represented Mollisols, Harir, Grdarasha, and Omermamek represented Vertisols, and Dibaga, Makhmur, and Qaraj represented Aridisols (Figure 1). Recent studies and standardized soil maps of Erbil, which provided the scientific foundation for the selection of sample sites, were used to categorize the soil orders at these locations. (25). One composite soil sample was taken from the top layer (0–30 cm) at each location using a stainless-steel auger. The samples were softly crushed, allowed to air dry, and then sieved using a 2 mm sieve in order to prepare them for additional chemical and physical analysis. Sixty days after the pot experiment was planted, soil was taken from each experimental unit for analysis. Plant samples were dried for 72 hours at 65° C, ground in a stainless steel mill, and stored in plastic containers prior to chemical analysis. The soil samples were concurrently air dried, filtered via a 2-mm screen, and stored in plastic bottles before being subjected to chemical analysis.

Physical and Chemical Characteristics of Soil

Numerous methods were used to evaluate the physical characteristics of the soil, such as actual density, dry density, field capacity, wilting point, particle size distribution, and soil texture prediction. The chemical properties (18) soluble potassium (K^{+}) and sodium (Na^{+}) were measured using the Corning 400 Flame photometer, and organic matter (OM) was found using the Walkley and Black wet dichromate oxidation method(34). Electrical conductivity (EC) of saturated paste extract was measured using an EC-Meter model (WTW82362 Weih, Geomany). Bicarbonate ($HCO3^{-}$) and carbonate ($CO32^{-}$) were measured titrimetrically using 0.01 N HCl, phenolphthalein, and methyl orange markers (6). The Mohr approach was used to quantify chloride (Cl^{-}), and 0.01 N EDTA-2Na was used to titrimetrically detect soluble calcium (Ca^{2+}) and magnesium (Mg^{2+}) (4). The cation exchange capacity (CEC), which gauges a soil's overall capacity to store exchangeable cations, indicates the amount of negative charge per unit mass of soil. (8), After soaking the soils with 1 M NaOAc at pH 8.2, it was assessed by washing them with ethanol. After substituting 1 M NH4OAc for exchangeable sodium, the sodium concentration was measured using a flame photometer. (4) The total calcium carbonate (CaCO3) was measured using the acid neutralization method (1 N HCl) (26). In contrast, active calcium carbonate (CaCO3) was determined using the modified Drouineau method.

Total nitrogen (N) was calculated using the Kjeldahl method(27). Available phosphorus (P) was obtained using 0.5 M NaHCO3 at pH 8.5 and measured spectrophotometrically using Olsen's method (22). A calibrated pH meter model (Metter-Toledo 8603 Schnerzenbach, Switzerland) standardized with pH 4.1 and 7.0 buffers was used to measure the hydrogen potential of soil pH. Readings were obtained after five minutes of stabilization (33).

Iron Solubility Diagram Experiment

To determine the solubility of iron, 108 soil samples were duplicated and incubated at room temperature. After transferring 2 g of air-dried soil to a 50 ml centrifuge tube with 20 ml of 0.01 M calcium chloride CaCl2 and shaking for 48 hours, the sample was centrifuged at 2500 rpm for 15 minutes, filtered through a 0.22µm filter, and then evaluated using a pH meter and atomic adsorption spectroscopy (AAS) to assess soluble Fe and pH using solubility diagram techniques akin to those described by (24) in research on Fe^{2+} solubility in calcareous soils. The solubility curve of Fe minerals was established using log-free Fe^{2+} ion activity vs hydrogen potential pH. Based on dispersed Ksp values for Fe minerals, it was expected that pH would regulate Fe^{2+} activity and that the phase of Fe minerals indicated in Table 1 would regulate Fe solubility in the calcareous soils.

Table 1: lists the phases, reactions, and Ksp of iron minerals that are utilized to create a ferrous solubility.

Minerals	Formula	Equation	Ksp
Iron Oxide	FeO	FeO+2H+-----Fe2++H2O Log Fe2+= 13.48-2pH	13.48
Iron Hydroxide	Fe(OH)2	Fe(OH)2+2H+-----Fe2++2H2O Log Fe2+= 12.9-2pH	12.9
Siderite	FeCO3	FeCO3+2H+-----Fe2++CO2(g)+H2O Log Fe2+= 7.92-2pH	7.92

DRIS chart

(5) developed the DRIS (Diagnosis and Recommendation Integrated System) system, which uses nutrient ratios to evaluate crop nutrient balance to analyze the link between iron (Fe) and nitrogen (N) and phosphorus (P) and potassium (K) in sorghum using nutrient ratios. Nutrient ratios were plotted on a DRIS chart (Figure 1). Points at the origin, or the center of the inner circle, show that the plant's nutrient content is balanced and are anticipated to increase plant yield. However, when the ratio of these nutrients falls between the two circles in Figure 1, the plant's nutrient concentrations are out of balance, which is predicted to reduce plant yield.

Nutrients that fall outside the wide circle on the DRIS chart are considered significantly unbalanced; these values are indicated by vertical arrows that show whether the ratio is too high or too low according to the recommended DRIS chart described in reference (11). For example, a balance between Fe and K in the plant is observed when the Fe/K ratio is from 0.050 to 0.037. However, if the ratio of Fe to K is greater than 0.050, it indicates an imbalance with high levels of Fe (denoted by the ↑ symbol), while a ratio of less than 0.037 indicates an imbalance due to low levels of Fe (denoted by the ↓ symbol).

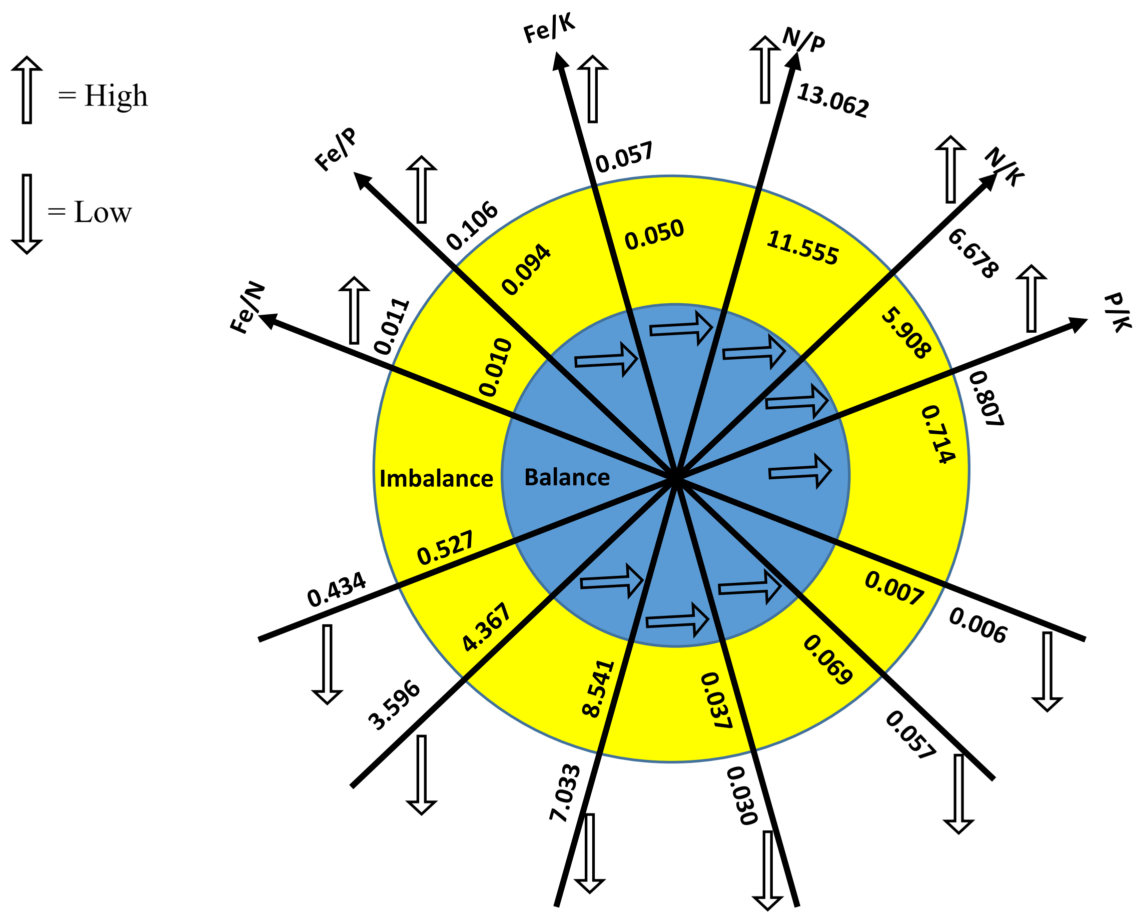

Fig. 1: Iron status Depending on Iron DRIS chart (28).

Results and Discussion

Specific properties of the soil

Table 2 displays several physical and chemical characteristics of the soils under study. The texture of the studied sites varied noticeably among the twelve locations of all orders. Clay, loam, silty clay loam, silty clay, and sandy loam were among the textures that were detected. This variation in texture is mainly related to the differences in parent material, topography and land use among the studied areas (2).

The range of the clay concentration was 223.20 to 538.30 mg kg^{-1}. Rawanduz (Mollisols) had the largest quantity, whereas Choman (Inceptisols) had the lowest. This phenomenon is probably due to the fact that mollisols are more advanced than other orders. The samples silt content varied from 190.70 to 448.20 mg kg^{-1}. Koya (Mollisols) had the largest quantity, while Dibaga (Aridisols) had the lowest. The concentration of sand ranged from 91.00 to 627.60 mg kg^{-1}. Dibaga (Aridisols) had the most, whereas Koya (Mollisols) had the least. The range of electrical conductivity in the soils under investigation was 0.40 to 6.20 dS m^{-1}. The Aridisols sample from Qaraj had the greatest value, whereas the Inceptisols sample from Shaqlawa had the lowest value. The samples were slightly to moderately alkaline, with pH values ranging from 7.30 to 8.10. Soil organic matter (SOM) values varied widely, ranging from 7.20 to 33.10 mg kg^{-1}. The Koya soil (Mollisols) had the greatest value, while the Omermamek soil (Vertisols) had the lowest. This might be due to the creation of organic materials and severely degraded plant remnants in the Koya area. The cation exchange capacity (CEC) ranged from 20.00 to 38.75 Cmole Kg^{-1}. The Inceptisols in Shaqlawa had the highest value, while the Aridisols at Dibaga had the lowest. The total $CaCO_3$ levels in the calcareous soils ranged from 14.00 to 42.50 percent. The Omermamek Vertisols had the greatest total $CaCO_3$ value, while the Mergasur Inceptisols had the lowest. Following the trend of total $CaCO_3$, active $CaCO_3$ varied from 5.41 to 16.04%, with the Mergasur Inceptisols having the lowest value and the Omermamek Vertisols having the highest.

Table 2: Selected Chemical and Physical Characteristics of the Soils Under Study

Code	Soil orders	Locations	Sand	Silt	Clay	Texture Name	O M mg kg^{-1}	Total $CaCO_3$ %	Active $CaCO_3$ %	EC dS m^{-1}	pH	CEC Cmol Kg^{-1}
			mg kg^{-1}									
S1	Inceptisols	Mergasur	236.00	273.20	490.80	clay	21.00	14.00	5.41	0.60	7.30	32.50
S2		Choman	566.00	210.70	223.30	Loam	13.70	15.00	5.78	0.50	7.60	30.00
S3		Shaqlawa	235.700	373.50	390.80	clay loam	7.20	18.00	6.9	0.40	7.30	38.75
S4	Mollisols	Rawanduz	160.700	301.00	538.30	Clay	13.10	21.00	8.02	0.41	7.40	32.50
S5		Koya	91.00	448.20	460.80	Silty Clay	33.10	29.00	11	2.20	7.40	28.75
S6		Daraban	153.50	423.20	423.30	Silty Clay	10.60	30.00	11.38	0.50	8.00	25.00
S7	Vertisols	Harir	116.00	353.20	530.80	clay	8.20	26.00	9.89	0.51	8.10	25.62
S8		Grdarasha	178.50	446.20	373.30	Silty Clay Loam	12.40	25.50	9.70	1.00	7.60	21.25
S9		Omermamek	141.00	385.70	473.30	Clay	7.20	42.50	16.04	0.53	7.80	20.62
S10	Aridisols	Dibaga	627.60	190.70	181.70	Sandy Loam	17.50	33.50	12.68	2.60	7.40	20.00
S11		Makhmur	325.10	383.20	291.70	clay loam	24.10	30.00	11.38	4.00	7.60	23.12
S12		Qaraj	424.20	308.20	267.60	Loam	21.00	22.50	8.58	6.20	7.80	25.37

Grain Yield Affected by Humic Acid Application Levels

The effects of varying applied humic acid levels (H1 = 0 kg ha^{-1}, H2 = 30 kg ha^{-1}, and H3 = 60 kg ha^{-1}) on grain production of various soil types are depicted in Figure (2). Depending on the soil order and locations, applying humic acid has different impacts on the yield. In the Inceptisols (Mergasur, Choman, and Shaqlawa), the highest grain yield was recorded under the H3 level at Choman (14 *Mg* ha^{-1}), while the lowest value occurred in Shaqlawa under H1 (4.5 *Mg* ha^{-1}). Overall, the application of humic acid slightly increases yield in Mergasur and Choman soils, whereas the response was less pronounced in Shaqlawa.

In the Mollisols (Rawanduz, Koya, and Daraban), the H2 level produced the highest yield in Koya (14 *Mg* ha^{-1}), while Daraban showed a reduction in yield at the same level. This inverse relationship in Daraban suggests that excessive humic acid might have led to nutrient imbalance or interference with soil microbial activity, as reported by (9, 32).

The Vertisols (Harir, Grdarasha, and Omermamik) exhibited their maximum yield (14 *Mg* ha^{-1}), under H2 in Omermamik soil, indicating that moderate humic acid rates enhanced nutrient uptake and plant growth. Similar positive responses to humic substances have been reported by (14), who found that humic acid application improved soil structure and increased yield.

In the Aridisols (Dibaga, Makhmur, and Qaraj), the highest grain yield was obtained from Qaraj under H3 (12 *Mg* ha^{-1}), while the lowest yield occurred in Makhmur under H1 (6.5 *Mg* ha^{-1}). The increase in yield with high humic acid levels in Qaraj soil may be due to improved soil water - holding capacity and enhanced nutrient availability as noted by (7). Overall, grain yield ranged from (4.5 to 14 *Mg* ha^{-1}), with the highest value observed in Mollisols and Vertisols and the lowest in Aridisols and Inceptisols. These differences reflect the variation in organic matter content, cation exchange capacity, and native fertility among soil orders. Grain yield was used as a response variable to classify nutrient balance conditions and support DRIS diagnosis under different humic acid levels.

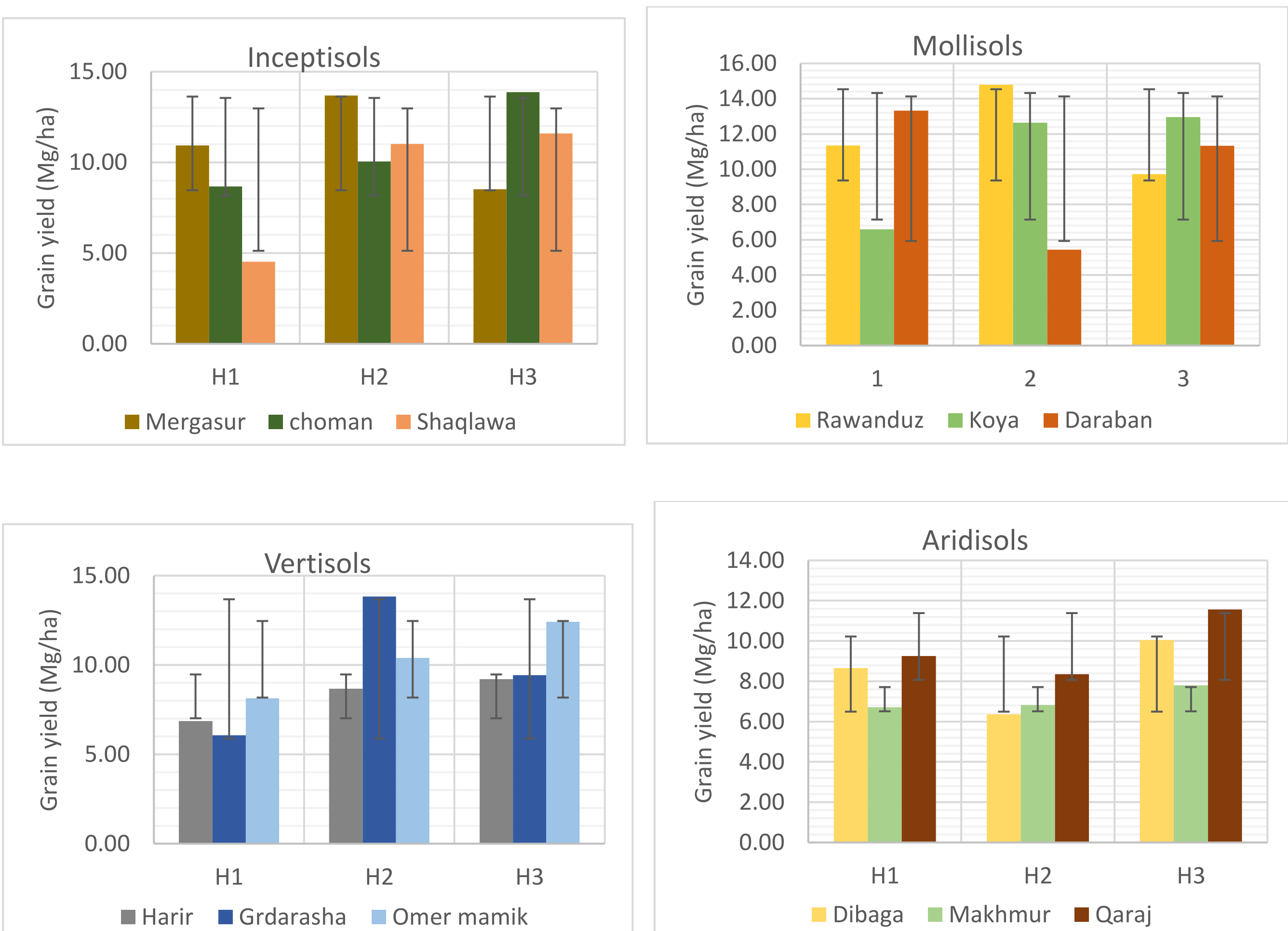

Fig. 2: Levels of humic acid compared with grain yield of sorghum

Impact of Various Humic Acid Levels on the (Fe) Balance in the Examined Soils

The effects of varying humic acid levels on the iron (Fe) balance in the soil orders under study are displayed in Table (3). The results demonstrated that there were substantial regional differences in humic acid levels and Fe nutritional relationships. Fe and other macronutrients (N, P, and K) were often frequently out of balance, especially when humic acid levels were high. A number of locations, including Mergasur (H1 and H3), Choman (H2), Shaqlawa (H3), and Makhmur (H1), showed imbalances (IB↑) for the Fe/N ratio, indicating that increasing humic acid changed Fe-N interactions by improving Fe solubility and absorption relative to N. Humic compounds have been shown to increase Fe availability and alter nutritional ratios in similar ways (1, 14, 23).

In terms of Fe/P ratios, a number of places, including Shaqlawa, Choman, Daraban, and Makhmur, had high imbalance status (HIB↑) under H3 level, suggesting that high humic acid levels raised Fe in relation to available P, maybe as a result of Fe-P complexes precipitating at higher Fe concentrations. This is consistent with the findings of (31), who noted that humic compounds have the ability to chelate iron and affect its equilibrium with phosphate in soil solution.

Overall, there were fewer imbalances in the Fe/K ratio, with balanced (B) status predominating in Mergasur, Rawanduz, and Daraban, and greater imbalance (HIB↑) occurring occasionally in Omermamek and Makhmur soils. Fe/N and Fe/P imbalances were more common under higher humic acid rates in Aridisols (Dibaga, Makhmur, and Qaraj), whereas Vertisols (Harir and Grdarasha) soil maintained more balanced Fe ratios. The data showed that the response of Fe balance to humic acid depended on soil order and native fertility. The sequence of Fe availability and balance was often Vertisols > Mollisols > Inceptisols > Aridisols. Because of their high organic matter and cation exchange capacity, which improve Fe complexation and mobility, Vertisols and Mollisols have higher Fe balance and solubility. (7, 32).

Table 3: Humic acid levels and their effects on the (Fe) balance in the soils under examination.

Locations	Humic Acid Levels kg ha^{-1}	Fe %	N %	P %	K %	Fe/N Ratio	Fe/N Status	Fe/P Ratio	Fe/P Status	Fe/K Ratio	Fe/K Status
Mergasur	H1	0.0158	1.42	0.23	0.34	0.0111	HIB↑	0.068	IB↑	0.047	B
	H2	0.0144	1.96	0.20	0.53	0.0073	B	0.073	B	0.027	HIB↑
	H3	0.0191	1.86	0.21	0.55	0.0103	IB↑	0.091	B	0.035	IB↑
Choman	H1	0.0129	1.61	0.19	0.44	0.0080	B	0.070	B	0.029	HIB↑
	H2	0.0123	2.05	0.13	0.47	0.0060	HIB↑	0.096	IB↑	0.026	HIB↑
	H3	0.0152	2.05	0.14	0.43	0.0074	B	0.108	HIB↑	0.036	IB↑
Shaqlawa	H1	0.0147	1.69	0.14	0.30	0.0087	B	0.108	HIB↑	0.050	B
	H2	0.0177	1.96	0.23	0.34	0.0090	B	0.076	B	0.052	IB↑
	H3	0.0170	1.66	0.16	0.32	0.0102	IB↑	0.109	HIB↑	0.054	IB↑

Rawanduz	H1	0.0169	2.11	0.18	0.46	0.0080	B	0.093	B	0.037	IB↑
	H2	0.0159	1.81	0.35	0.32	0.0088	B	0.046	HIB↑	0.050	B
	H3	0.0161	2.15	0.13	0.41	0.0075	B	0.123	HIB↑	0.039	B
Koya	H1	0.0067	1.62	0.15	0.32	0.0042	HIB↑	0.046	HIB↑	0.021	HIB↑
	H2	0.0162	1.81	0.31	0.25	0.0090	B	0.052	HIB↑	0.065	HIB↑
	H3	0.0140	1.81	0.14	0.27	0.0077	B	0.100	IB↑	0.053	IB↑
Daraban	H1	0.0137	1.52	0.14	0.36	0.0090	B	0.095	IB↑	0.038	B
	H2	0.0139	1.47	0.14	0.40	0.0094	B	0.100	IB↑	0.035	IB↑
	H3	0.0139	1.47	0.25	0.32	0.0094	B	0.057	HIB↑	0.043	B
Harir	H1	0.0133	2.06	0.33	0.50	0.0065	HIB↑	0.040	HIB↑	0.027	HIB↑
	H2	0.0139	1.81	0.12	0.51	0.0077	B	0.115	HIB↑	0.027	HIB↑
	H3	0.0125	1.27	0.14	0.41	0.00984	IB↑	0.091	B	0.031	IB↑
Grdarasha	H1	0.0142	1.66	0.17	0.31	0.0085	B	0.085	B	0.046	B
	H2	0.0175	2.16	0.15	0.42	0.0081	B	0.119	HIB↑	0.042	B
	H3	0.0155	1.52	0.17	0.24	0.0102	IB↑	0.091	B	0.066	HIB↑
Omermamek	H1	0.0147	1.56	0.17	0.42	0.0094	B	0.088	B	0.035	IB↑
	H2	0.0138	1.47	0.14	0.21	0.0094	B	0.101	IB↑	0.067	HIB↑
	H3	0.0154	1.42	0.26	0.42	0.0109	HIB↑	0.059	IB↑	0.037	B
Dibaga	H1	0.0167	2.06	0.20	0.27	0.0081	B	0.085	B	0.062	HIB↑
	H2	0.0164	1.61	0.14	0.33	0.0102	IB↑	0.114	HIB↑	0.050	B
	H3	0.0153	2.10	0.79	0.29	0.0073	B	0.019	HIB↑	0.053	IB↑
Makhmur	H1	0.0164	2.45	0.13	0.24	0.0067	HIB↑	0.130	HIB↑	0.070	HIB↑
	H2	0.0112	1.42	0.12	0.34	0.0079	B	0.091	B	0.033	IB↑
	H3	0.0146	1.76	0.17	0.32	0.0083	B	0.085	B	0.046	B
Qaraj	H1	0.0136	2.25	0.16	0.36	0.0061	HIB↑	0.086	B	0.038	B
	H2	0.0077	1.52	0.17	0.30	0.0051	HIB↑	0.045	HIB↑	0.026	HIB↑
	H3	0.0163	1.62	0.10	0.29	0.010	IB↑	0.158	HIB↑	0.057	HIB↑

Iron solubility diagram

The solubility diagram of iron in the calcareous soils under investigation was shown in Figure (3). the solubility diagram of Fe in the studied calcareous soils. The data points of soluble Fe for all humic acid levels (H1, H2, and H3) were located below the stability lines of iron hydroxide and iron oxide and close to the equilibrium line of siderite ($FeCO_3$). This pattern indicates that Fe^{2+} activity in the soil solution is low and mainly controlled by the formation of siderite, which is a poorly soluble Fe mineral. The predominance of these low solubility Fe forms explains the restricted Fe availability in soil, even though total Fe concentration remains high. This result agrees with (21), who reported that Fe solubility reaches a minimum in calcareous soils with pH ranging from 7.4 to 8.5.

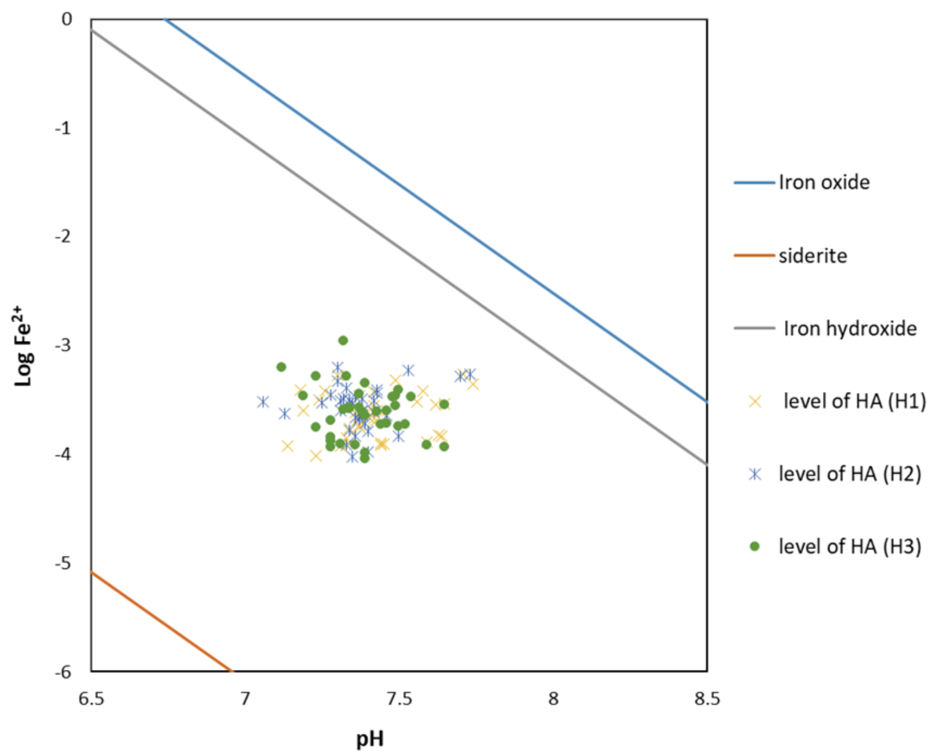

Fig. 3: Impact of humic acid concentrations (HA) on the soil iron availability and solubility diagram

There is a substantial correlation between these nutrition variables and the Fe solubility diagram. At pH 7.0–7.8, the majority of the points in the solubility data (Figure 3) fall around log Fe^{2+} values between –3.5 and –4, suggesting very low soluble iron concentrations. In this area, Fe becomes chemically inaccessible due to the predominance of Fe-oxide and $Fe(OH)_3$ phases (10, 19) Such low Fe solubility is predicted given the calcareous nature of the tested soils, as alkaline pH significantly reduces Fe^{2+} activity (17).

Comparison between the Solubility diagram and DRIS

The thermodynamic precipitation of Fe observed in the solubility diagram is consistent with DRIS analysis (Table 3), which shows that Fe/N, Fe/P, and Fe/K ratios fall into the balanced (B) or imbalanced-deficient (IB↑ to HIB↑) categories, suggesting poor Fe nutritional status in the plant tissues. It has been noted that integrating DRIS with geochemical solubility models improves the understanding of nutrient imbalances in various crops cultivated in calcareous environments (5, 35).

For instance, in Mergasur and Koya locations, Fe/N and Fe/P ratios displayed HIB↑ values, while Fe/K ratios were mostly balanced. A Similar pattern was observed in Harir, Qaraj, and Makhmur, where Fe deficiency symptoms were reflected by low Fe/N and Fe/P ratios. These findings indicate that soil Fe availability is chemically limited rather than nutrient-limited by total Fe content, as plants' absorption of Fe was limited even in the presence of humic acid treatments. Similar results have been reported by (3), who found that plant Fe absorption can be limited even when humic acid levels rise. This suggests that soil chemical speciation, rather than total Fe concentration, is the primary factor controlling Fe availability.

Furthermore, the congruence between the solubility diagram and the DRIS indices indicates a high link between soil Fe solubility and plant Fe status. In soils where the solubility diagram showed under saturation with respect to iron hydroxide and siderite stability dominance, the DRIS data simultaneously showed low Fe ratios, indicating Fe insufficiency in plants. In certain places, such as Grdarasha, Omermamek, and Dibaga, where the Fe/N and Fe/P ratios moved from HIB_3 to IB_3 or balanced, the injection of humic acid resulted in minor improvements in the Fe status. According to the findings from humic substances act as Fe chelates and biostimulants, (36), promoting iron availability to plants. This can be explained by the chelating and complexing effect of humic substances, which enhance Fe solubility and maintain Fe in more available forms for plant uptake.

In general, both the solubility diagram and the DRIS chart gave similar trends and conclusions regarding Fe behavior in the studied soils. The low solubility of Fe and the dominance of siderite as a stable phase explain the restricted Fe availability and the imbalanced Fe nutritional status observed in plants. Therefore, rather than insufficient Fe inputs, the primary cause of Fe insufficiency in these soils is chemical limitations on Fe solubility under high pH conditions. In order to diagnose Fe availability and comprehend Fe dynamics in calcareous soils, combining the solubility diagram and DRIS techniques proved to be a successful strategy.

Conclusion

Using an Fe solubility diagram and a DRIS chart, we examined the iron (Fe) availability for four soil orders (Inceptisols, Mollisols, Vertisols, and Aridisols) in the Kurdistan Region of Iraq. Because of differences in soil pH, total and active calcium carbonate concentration, organic matter, and cation exchange capacity, iron availability varied among the soil orders under study. The highest Fe availability and balanced Fe ratios were observed in Vertisols and Mollisols, whereas the lowest Fe availability occurred in Aridisols and Inceptisols, where high $CaCO_3$ contents and alkaline pH limited Fe solubility. Vertisols and Mollisols had the maximum Fe availability and balanced Fe ratios, whereas Aridisols and Inceptisols had the lowest Fe availability due to their high $CaCO_3$ concentrations and alkaline pH, which restricted Fe solubility. According to the current study's findings, the solid phase of the siderite Fe mineral primarily regulated the solubility of iron in these calcareous soils. The DRIS chart and solubility diagram both showed this pattern, which showed frequent Fe imbalances in plant tissues and poor Fe^{2+} activity in soils. Due to the chelating and complexing actions that increased Fe mobility and plant absorption, humic acid application boosted Fe availability and sorghum grain yield in a number of soils, especially at modest rates (30 kg ha^{-1}). Nevertheless, since chemical constraints under alkaline conditions remained to limit Fe absorption, larger humic acid levels (60 kg ha^{-1}) did not consistently enhance Fe availability. Although Aridisols and Inceptisols had a chronic Fe shortage, Vertisols and Mollisols generally maintained improved Fe status in both soil and plants. These results highlight that humic acid can partially enhance Fe availability, but Fe status in calcareous soils remains largely controlled by soil chemical properties, emphasizing the importance of combining solubility diagrams and DRIS charts to assess Fe nutrition in crops.

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