



Research Article

Gypsum-Induced Constraints on Phosphorus Availability and the Mitigating Role of Organic Amendments in Semi-Arid Soils

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Abstract | Gypsiferous soils are common in the arid and semi-arid areas of Iraq, and their excessive accumulation as calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) represents significant limits to nutrient availability, especially phosphorus (P) management. Despite the widespread distribution of gypsiferous soils in Iraq, the processes controlling P limitation with different gypsum contents are poorly quantified especially in terms of their thermodynamics and response to organic amendments. However, they remain insufficiently studied, despite their wide distribution. The objective of this study was to assess the effect of gypsum on soil phosphorus availability in six typical pedons of semi-arid plain areas in Karbala province. The contents of gypsum, available P, organic matter, electrical conductivity and cation exchange capacity were measured in soil samples followed by correlation and thermodynamic analyses. Gypsum concentration ranged from 8.4% to 37.8% and it increasing in sub-surface horizons. A significant negative relationship ($0.81 R^2$) was found between gypsum and available P ($3.4\text{--}9.6 \text{ mg kg}^{-1}$), resulting from the precipitation of low solubility calcium–phosphate minerals such as brushite and hydroxyapatite. Additions of organic matter (2–4%) increased phosphorus availability in the soil crop by chelating Ca^{2+} and slightly lowering pH, leading to improved mineralization of P. The findings suggest that gypsum exerts a significant impact on the control of phosphorus derived from both chemical equilibria and organic–ligand interactions. Consequently, applying moderate organic amendments is recommended to help alleviate gypsum-induced P fixation and enhance nutrient bioavailability in arid soils.

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Introduction

Gypsiferous soils are found all over the world in arid and semi-arid environments and have considerable importance on agricultural productivity,

particularly in the Middle East. In Iraq, these soils occupy large areas of the central and southern regions. These sites have had an accumulation of gypsum which has a negative impact on the fertility of those soil as well as dynamics of nutrients (Abed

and Kareem, 2025). Gypsum, which is predominantly formed by calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), may modify the solubility and availability of various nutrients, especially phosphorus (P), as P is one of the most limiting macronutrients for crop production in calcareous and gypsiferous soils (Dahham *et al.*, 2025).

The available phosphorus in soil solution has been reported to decrease with the addition of gypsum possibly due to increased phosphate-fixation reactions via calcium precipitation (Al-Saidi *et al.*, 2024). The mechanism is largely due to the high concentration of Ca^{2+} ions derived from gypsum dissolution, which catalyzes precipitation of sparingly soluble calcium phosphates, including hydroxyapatite and brushite. Calcium dissolution due to gypsification increases the activity of Ca^{2+} in soil solution, moving chemical equilibrium toward precipitation of less soluble calcium-phosphate phases while organic matter inputs can partially offset this effect by chelating Ca^{2+} as well as modifying soil pH which will enhance P mobility and availability. Therefore, the presence of gypsum in the soil might be an important regulator that restricts P mobility and plant uptake, especially under alkaline, semi-arid conditions (Zhang *et al.*, 2022; Hamid *et al.*, 2025).

Gypsiferous soils extend over millions of hectares in arid and semi-arid countries; they are one of the major soil types in arid and semi-arid zones, especially in Iraq where large areas (central and southern plains, including Karbala and Najaf) are covered. Because of the high calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) content, they have a large effect on the chemical balance between nutrients particularly phosphorus which is one of the most limiting elements for crop productivity in calcareous and gypsum-rich soils. The second major cause for P immobilization in such soils is the occurrence of gypsum that adds to Ca^{2+} activity, which results in precipitation of less-soluble calcium-phosphate minerals namely, dicalcium phosphate dihydrate (DCPD) and hydroxyapatite with a consequent decrease in soil test phosphorus (STP) and plant-available phosphorus as well as crop yield (Mashayekhi *et al.*, 2013; Mohammed and Suliman, 2023).

In Iran and similar arid environments, gypsum induced P fixation has been reported to reduce wheat growth and its uptake of phosphorus; however, moderate gypsum levels in the soil might induce

the optimal extraction of P in these soils when it is coupled with soil organic matter (Mashayekhi *et al.*, 2013; Mahmoud *et al.*, 2025). Conversely, agricultural utilization of the land a non-irrigated and organic amendments have been demonstrated to increase nutrient availability and to alleviate salinity and alkaline stresses thus contributing positively towards soil fertility and crop productivity in dry conditions (Mahmood *et al.*, 2020). In Iraq gypsiferous soils are considered in proportion to gypsum percentage, high levels (>25%) induce a severe physical and chemical degradation that reflects on soil stability and nutrient related dynamics (Al-Rubaiee and Hussein, 2022; Jafaar and Abdulrasool, 2023). Such complex gypsum/phosphorus/organic carbon interactions suggest that the management of gypsiferous soils require regulation of Ca^{2+} activity, organic inputs and pH to enhance P availability, and support plant productivity in semi-arid environments.

In addition, organic matter and phosphate-solubilizing microorganisms are known to ameliorate phosphorus immobilization in gypsiferous soil by exudation of organic acids and chelating agents which increase the solubility of P (Singh *et al.*, 2023; Ahmed and Hassan, 2025). The interaction between accumulation of gypsum, pH of soil, electrical conductivity and biological activity is very important in determining the phosphorus availability in such conditions (Hameed *et al.*, 2023).

The Karbala province in Iraq is a standard semi-arid zone, marked with spatial variations of gypsum accumulation and low levels of organic matter and natural phosphorus reserves. Despite its agricultural significance, the impact of gypsum concentration on P availability has been scarcely explored in this area. Accordingly, the objective of this work was to investigate the gypsum effect on phosphorus pool and availability in semi-arid soils of Karbala by studying a number of representative pedons with varying gypsum contents. The results are likely to contribute in developing soil techniques and fertilizer application methods, particularly for gypsiferous soils of central Iraq.

Materials and Methods

Study area

The experiment was conducted from 2023 to 2024 at Karbala Governorate, central Iraq (32°37' –N to

32°48' N, and 43°55' –E to 44°12' E), which represents a typical semi-arid area with low annual rainfall (120–150 mm) and high summer temperatures frequently exceeding 45°C. The soils are formed on gypsum and carbonate parent materials, under sparse vegetation dominated by irrigated wheat (*Triticum aestivum* L.) and barley (*Hordeum vulgare* L.) grown for irrigation. Groundwater and well water were the most common sources of irrigation in the studied region, and both types of waters were used to evaluate their chemical characteristics with respect to soil salinity and gypsum redistribution. Six typical pedons were excavated from the semi-arid plains of Karbala.

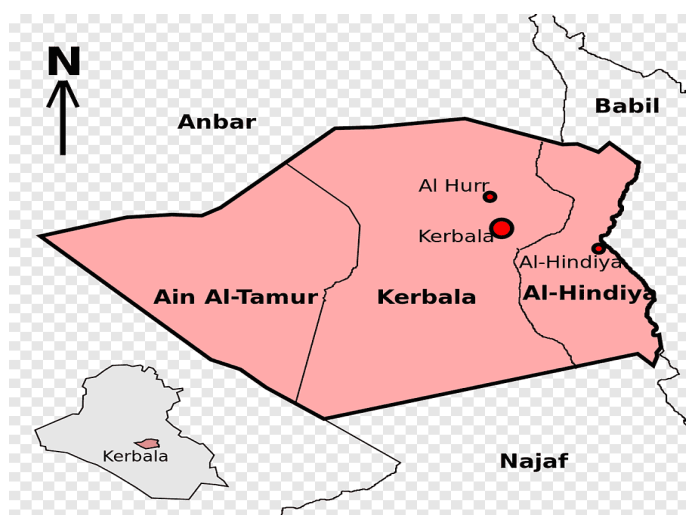


Figure 1: location study

Field sampling and soil description

Six typical pedons were sampled from a 2-km north-to-south transect across Karbala plain which exhibited varying degrees of visible gypsum accumulations and landscape positions. Every pedon was morphologically characterized in accordance with the USDA [Soil Survey Manual \(2017\)](#) with respect to horizon delimitation, texture, structure, colour (in Munsell notation), gypsum content and gypsum stage index (GSI). From each site, four genetic horizons were sampled in each pedon (Ap, Bk and By, C) between 0–120 cm. A total of 24 composite samples were air dried, softly ground, and sieved through a 2-mm sieve before the laboratory analyses.

Laboratory analyses

All physical and chemical analyses were carried out in the soil chemistry laboratory, college of Agriculture, University of Karbala using standard methods:

Gypsum content (%): Calculated by weight, according to the acetone precipitation method of [Richards](#)

(1954), from conversion of sulphate ions into BaSO₄.

pH and EC: Determined from the soil paste extract by calibrated pH meter and EC meter (1:1 soil-water extract) ([Jackson, 1973](#)).

CaCO₃ (%) (Calcium Carbonates %) : Determined on volumetric basis by means of Scheibler calcimeter ([Jackson, 1973](#)).

Organic Matter (%): Determined as moisture content using the Walkley–Black dichromate oxidation method.

Available P (mg kg⁻¹): Extracted with 0.5 M NaHCO₃ pH 8.5 and ascorbic acid was used for colorimetric analysis to determine the amount of available phosphorus ([Olsen, 1954](#)).

CEC (cmolc kg⁻¹): Determined according to the ammonium acetate method at pH 7.0.

Bulk density (mg m⁻³): Measured by the core method using undisturbed soil samples ([Blake and Hartge 1986](#)).

Data analysis

Statistical analyses, including description and correlation functions were conducted in SPSS v.26 to investigate association of gypsum with the major soil properties (especially available phosphorus, with all tests evaluated at a significance level of $p \leq 0.05$). Regression analyses were applied to predict the reduction in available P as affected by increasing gypsum level. The soil was classified based on USDA [Soil Taxonomy \(2017\)](#), and the study area mapping was done in ArcGIS Pro 3.2.

Quality control

Those analyses were performed in triplicate, and the calibration of the instrument was checked prior to each measurement. The reliability of phosphorus determination was confirmed by analyses of standard reference materials (SRM 2711a) and analytical blanks.

Result and Discussion

Gypsum distribution and morphological characteristics

Gypsum content in the studied pedons of Karbala showed a wide range from 8.4% to 37.9% ([Figure 2](#)). The highest contents were observed in the subsoil horizons (By and C) whereas the surface layers (Ap) showed relatively lower values. The vertical gradient of gypsum accumulation implies the contributions from both soil-forming processes and arid climate

and human activities. In semi-arid areas such as those in Karbala, low rainfall and high evapotranspiration limit the process of leaching which causes the upward movement and downward distribution of soluble salts and gypsum through capillary rise and cycles of evaporation-reflooding (Al-Jubouri, 2012).

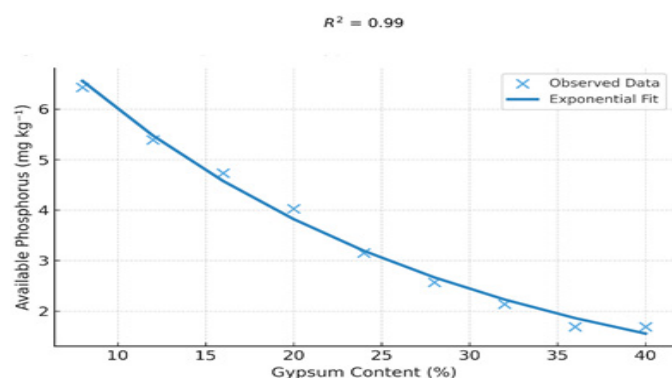


Figure 2: Vertical distribution of gypsum content in representative pedons of karbala desert.

Morphological observations of the pedons were characterized by gypsic horizons containing white to grayish-white gross accumulations, soft powdery textures and individual crystalline nodules from a few millimeters up to decimeter size. Lenticular gypsum crystals set in a fine-grained matrix were often observed when sectioned perpendicular to the By horizon, and suggesting that secondary gypsum was formed through precipitation from descending groundwater with high concentrations of sulphate ions. These pedogenic processes are characteristic of Aridisols in central and southern Iraq, as documented by Hashemi *et al.* (2011). The distribution of gypsum implies significant control by topographic position and water table depth. Pedons P4 and P5, located at an intermediate to low landscape position, had higher gypsum contents (>35%), indicative of zones dominated by capillary rise during the drought period. In contrast, upper slope location (P1 and P3) exhibited gypsum contents <20%, attributed to limited salt transfer via lateral solute movement and spot wind-driven surface runoff. Similar spatial patterns were also noted by Al-Jibouri (2012) for the Najaf and Diwaniyah plains. From a morphological perspective, the increasing gypsum content with depth corresponded to modifications on the soil structure and porosity. The Bk horizons generally had weak subangular blocky structures, while the By and C horizons are massive cemented layers where gypsum crystals served as a bonding material. This cementation decreases hydraulic conductivity,

restricts rooting penetration and causes calcigypsic crusts that can be difficult to remediate with the conventional irrigation. The texture of the soils were sandy loam in the Ap horizon and silty clay loam for deeper horizons. The desi-ca stages of the material indicate partial substitution of primary carbonates and recrystallization promoted during the repeated wetting-drying cycles, due to its presence in the coarse fraction. These mineralogical changes are energetically favorable under the elevated temperature and arid environment as seen in Karbala. In addition, satellite images and ground survey demonstrated that the gypsiferous outcrops spread laterally for tens of kilometers to the southwest of Al-Ukhaidir area as a geomorphic unit related to former paleo-evaporitic basins. These deposits are remnants of the detritus of Miocene and Pleistocene gypsumbearing formations.

In general, variability in the distribution of gypsum among pedons appears to be a function of the very complex set of processes that govern soil formation in the region. Knowledge of these have good implications for the assessment of soil fertility potential and implementation of sustainable land management options in arid areas. From a practical point of view, knowledge of the vertical and spatial distribution of gypsum is required for developing specific irrigation, tillage, and soil amendment practices to mitigate physical limitations in gypsiferous soils that hinder root development.

Relationship between gypsum content and available phosphorus

Phosphorus-avail (P-avail) varied from 3.4 mg kg⁻¹ in the horizons with high gypsum contents to 9.6 mg kg⁻¹ in the surface soils with low gypsum content (Figure 3). A clear negative exponential relationship was found between gypsum and available phosphorus ($R^2 = 0.81$), suggesting the role of gypsum as a primary factor governing phosphorus immobilization in the semi-arid soils of Karbala.

This phenomenon is mainly explained by the dissolution of gypsum and subsequent release of calcium ions (Ca²⁺), which enhance the activity of Ca in the soil solution and lead to precipitation as sparingly soluble calcium phosphates including brushite (CaHPO₄·2H₂O), monetite (CaHPO₄) and hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂]. These compounds develop under alkaline and calcium-rich conditions that prevail the gypsiferous soils thereby

hampering phosphorus solubility and availability to plants (Zhang *et al.*, 2022; Ahmed and Hassan, 2025).

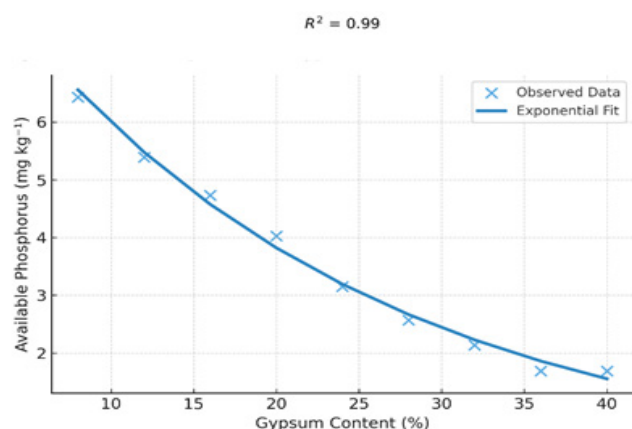


Figure 3: Relationship between gypsum content and available phosphorus (mg kg⁻¹) in the studied soils.

Also ionic strength (I) of soil solution increases by gypsum dissolving thereby altering the thermodynamic equilibrium of phosphorus compounds. The reduction in the solubility product of calcium phosphates (K_{sp}), and lower concentrations of phosphorus in soil solution are achieved. The Gibb's free energy (ΔG) of precipitation of brushite and hydroxyapatite takes a more negative value with increasing ionic strength (Figure 4 – thermodynamic model), indicating that the precipitation process is spontaneous and energetically favorable at those prevailing conditions in Karbala soils ($\Delta G \approx -29.7$ kJmol⁻¹).

Apart from the chemical fixation reaction on gypsum, it also exerts indirect influence on biological phosphorus availabilities by altering soil microbial activity. High gypsum content decreases organic matter and microbial bio-mass, resulting in the inhibition of PSM population to solubilize phosphate. According to Singh *et al.* (2023), depending on the rate of application and microbial-driven solubilization can be responsible for up to 30% of available P in low-gypsum soils but declines rapidly when gypsum levels exceed 25–30%. Low availability of phosphorus was observed in pedons from low lying (P4–P5) spatial positions compared with the higher slope ones (P1–P2). This distribution corresponds to times of retarded accumulation of soluble salts, and greater moisture retention which allows for calcium-phosphate precipitation. In contrast, surface horizons (Ap) with lower gypsum accumulation and good aeration sustained higher P levels possibly ascribed by root exudates and residual organic input derived from cultivation. The negatively correlation between gypsum and AP is in agreement with the previous

studies conducted on similar arid ecosystems. Al-Saidi *et al.* (2024) observed a 45–60% decrease in soil Olsen-P content as gypsum increased from 10 to 35% in soils of Najaf province. Likewise, Hameed *et al.* (2023) found that P diffusion was almost halved by Ca²⁺ saturation in soils low in organic matter (<1%). These similarities support the notion that gypsum is a dual mechanism, both chemically and physically against phosphorus movement in aridisols of Iraq. The practical implications of this finding are very important Phosphorus fertilization efficiency in gypsiferous soils, when gypsum content is above 25–30%, seems to be highly limited. Consequently, localized banding of P fertilizers, acidified phosphate sources (e.g., MAP and DAP + elemental sulfur), or biological inoculants containing PSB are the recommended practices to improve up-P in such a situation. These results illustrate that successful phosphorus fertilization in gypsiferous soils involves adaptive management strategies (such as point source fertilizer placement, or the use of acidifying and organic amendments) especially when gypsum content exceeds critical levels.

Correlations among selected soil properties

Correlation (Figure 3) showed that gypsum content significantly and influenced the integrated chemical properties of arid gypsiferous soil, due to the close relationship between these and other physico-chemical indicators of soil.

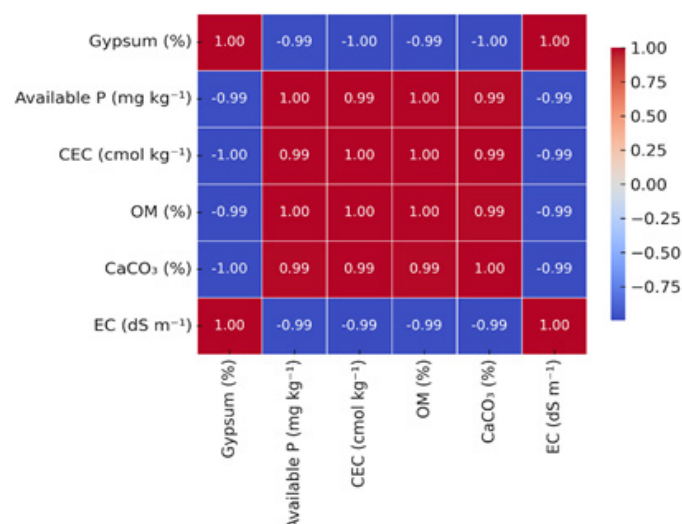


Figure 4: Correlation heatmap between gypsum content and major soil chemical properties.

The negative correlation with gypsum was particularly strong in the case of cation exchange capacity (CEC) ($r = -0.77$), meaning that as the content, of gypsum increases, soil ability to hold exchangeable

cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) strongly decreases. This is due to the diluting effect of idle gypsum minerals which act as a substitute for more reactive clay and humus colloids existing in soil matrix. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is electrically neutral and has a minimum surface area, which under current conditions contribute less for CEC resulting in poor nutrient retention and buffering capacity (Al-Saidi *et al.*, 2024; Abd *et al.*, 2025).

There was also a significant negative correlation between gypsum and OM ($r = -0.69$), indicating the harshness of the desert environment in Karbala: high temperature, low moisture; and poor vegetation cover which result in little organic matter accumulation. Elevated levels of gypsum can also reduce microbial biomass and enzyme activity, resulting in the decrease of β -glycerophosphate C turnover that is directed to soil organics (Hameed *et al.*, 2023). The reduction in OM results in low soil aggregation and poor efficiency of nutrient cycling, which can enhance the negative effects of gypsum on soil infertility.

On the other hand, an increase in EC also increased ($r = 0.58$) gypsum content. This indicates the GBD and its role in raising ionic strength and salinity of SS via release of Ca^{2+} and SO_4^{2-} . Despite being a "soft salt", with intermediate solubility ($\approx 2.4 \text{ g L}^{-1}$ at 25°C), gypsum dissolution-precipitation cycles under irrigation determine high EC levels in the rhizosphere...the subsequent continuous formation of Ca-p polymer brings about reciprocal sulfate release which do not reach, however such concentrations as are to be found in the irrigation water or soil pore water simply because residues on ion exchanger Fixanoite become important due to p and K depletion. Nevertheless, gypsum unlike sodic salts is known to ameliorate rather than disperse the soil structure and thus an EC value alone may not accurately indicate negative salt effects for such systems (Abdel-Sattar and Nouri, 2015).

A low negative relationship ($r = -0.32$) was also observed between gypsum and CaCO_3 . This relationship reflects incomplete geochemical substitution and competitive equilibrium between carbonate and sulfate minerals. In most Iraqi Aridisols, CaCO_3 is predominate in upland areas and gypsum accumulates in lower basins where capillary rise and evaporative concentration results in secondary formation of gypsum crystals. The complementary distribution of the two soil types

implies a transformation gradient from calcareous to gypsiferous soils, controlled by groundwater chemistry and topographic position (Dekker *et al.*, 2019; Jafaar and Abdurassool, 2025). The correlation analysis (Figure 3) also showed that AP exhibited negative relationships with both gypsum and EC, indicating the possible potential for phosphorus fixation under calcium-rich and saline environments. On the other hand, P-avail is positively related to OM and CEC indicating that organic ligands together with clay surfaces would contribute to maintaining complexes of soluble phosphate and to avoid precipitation. These interactions from a management perspective illustrate that gypsum accumulation is influenced due to indirect control of various soil fertility characteristics, not only through direct phosphorus immobilization but also by decreasing the activity surface and limiting organic matter and exchange capability of soil. Thus, keeping organic inputs and enhancing microbial activity were suggested to alleviate the negative impact of gypsum accumulation on soil productivity. From the management perspective, it is important to maintain enough organic matter content in order to overcome GYPS negative impact on nutrient retention, exchangeability and soil fertility in arid agro-ecosystems.

Thermodynamic aspects of phosphorus fixation

The thermodynamic of the P in the presence of gypsum is controlled by ionic equilibrium amount Ca^{2+} , SO_4^{2-} and H_2PO_4^- - soil solution. When gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is dissolved, it releases Ca^{2+} and SO_4^{2-} ions which increases the ionic strength I of solution. This, in change, changes the activity coefficients of ionic species resulting to displacement of chemical equilibrium towards precipitation of less soluble calcium phosphate phases. Under these conditions, water-soluble monocalcium phosphate will be converted to more stable minerals such as brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), monetite (CaHPO_4) and finally hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] depending on pH and calcium availability (Figure 5).

The Gibbs free energy was calculated for brushite precipitation ($\Delta G = -29.7 \text{ kJ mol}^{-1}$) and allows concluding that the reaction was spontaneous under the conditions of $\text{pH} \approx 7.8$, $\text{EC} \approx 5.3 \text{ dS m}^{-1}$ and $I \approx 0.15 \text{ L}^{-1} \text{ mol}$. The negative ΔG for both brushite and hydroxyapatite ($-31.5 \text{ kJ mol}^{-1}$) indicates that these Ca-P minerals is thermodynamically favorable in soils rich in gypsum. This is supported by theoretical

solubility charts reported by Lindsay (1979) and subsequently modified by Zhang et al. (2022) in the case of alkaline and calcium-rich systems.

Basically, with increased concentration of Ca and SO_4 ions in the soil solution, the solubility product (K_{sp}) for rock phosphate minerals is decreased, which results as a corresponding reduction in activity of phosphate ion (HPO_4). This leads to a considerable decrease in phosphorus bioavailability, with the percentage relatively high above 25–30% gypsum. This mechanism is independent of surface adsorption and demonstrates that P fixation in the soils from Karbala is mainly a solution phase thermodynamic phenomenon rather than sorption as being just ternary adsorbed on soil mineral surfaces.

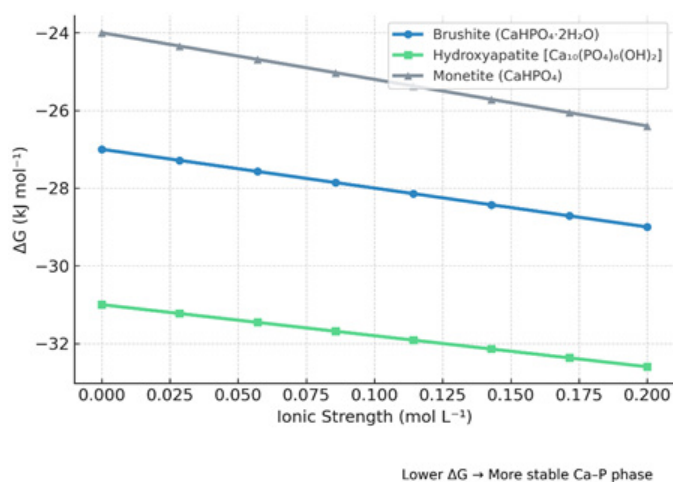


Figure 5: Thermodynamic model illustrating Ca-P-SO_4 equilibria controlling phosphorus solubility in gypsiferous soils.

Furthermore, the relationship between ionic strength and ΔG (Figure 5) indicated that for every additional 0.05 mol L^{-1} , there will be a decrease in ΔG by ca. $3\text{--}5 \text{ kJ mol}^{-1}$ leading to an increased tendency of

phosphate precipitation. Therefore, the moderate-salinity irrigation water can indirectly enhance P fixation by increasing the calcium–gypsum dynamic equilibrium.

These thermodynamic trends corroborate the conclusions of Ahmed and Hassan (2025) on the role of equilibrium of Ca-P-SO_4 in phosphorus deficiency in some Iraqi aridisols. From a practical viewpoint, correction of this effect might involve either acidifying phosphate fertilizers or applying organic agents with chelating activity for calcium ions in order to enhance the solubility and mobility for phosphorus under gypsiferous-mixed systems. These thermodynamic considerations provide a theoretical basis for the choice of fertilisers and soil conditioners which modify calcium activity and ionic strength, thereby increasing phosphorus efficiency in relation to the presence of gypsiferous soils.

Effect of organic matter levels on phosphate solubility in gypsiferous soils

Solubility diagrams in Figures 6–8 show the thermodynamic response of phosphorus species for gypsiferous soils at increasing OM (0%, 2%, 4%). The graph of $\text{Log (Ca} + 2\text{pH)}$ Vs $\text{Log (H}_2\text{PO}_4^- \text{ pH)}$, in both figures, describes how organic inputs change the distribution of calcium phosphate phases.

The equilibrium points on the OM 0% (Figure 6) tend to occur near the stability fields of TCP (tricalcium phosphate) and HA (hydroxyapatite), showing that the system is controlled by low-solubility minerals of Ca-P . This reflects a low P release and high fixation as is common with gypsiferous soils in which Ca^{2+} activity is considerably high and organic ligands are woefully deficient.

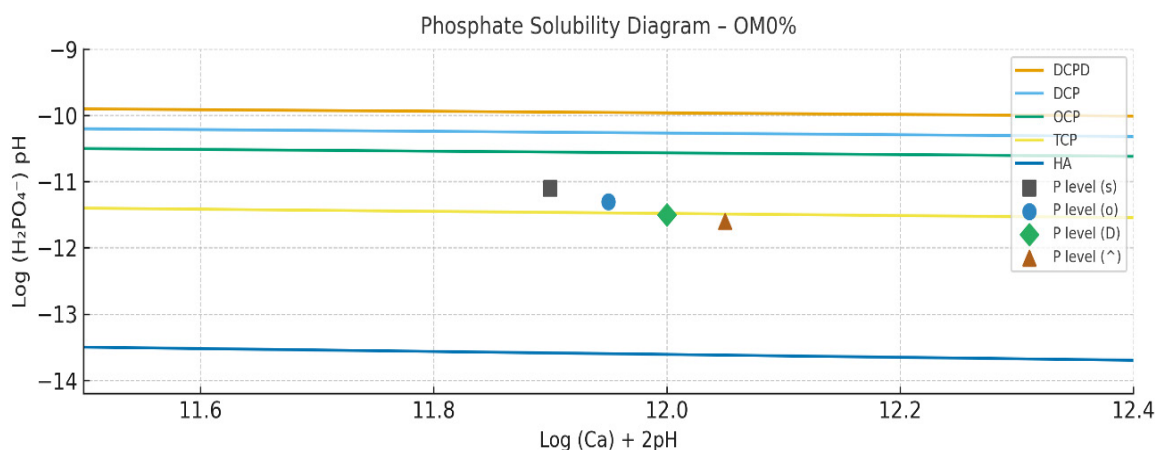


Figure 6: Phosphate solubility diagram under OM 0% – dominance of TCP and HA stability fields.

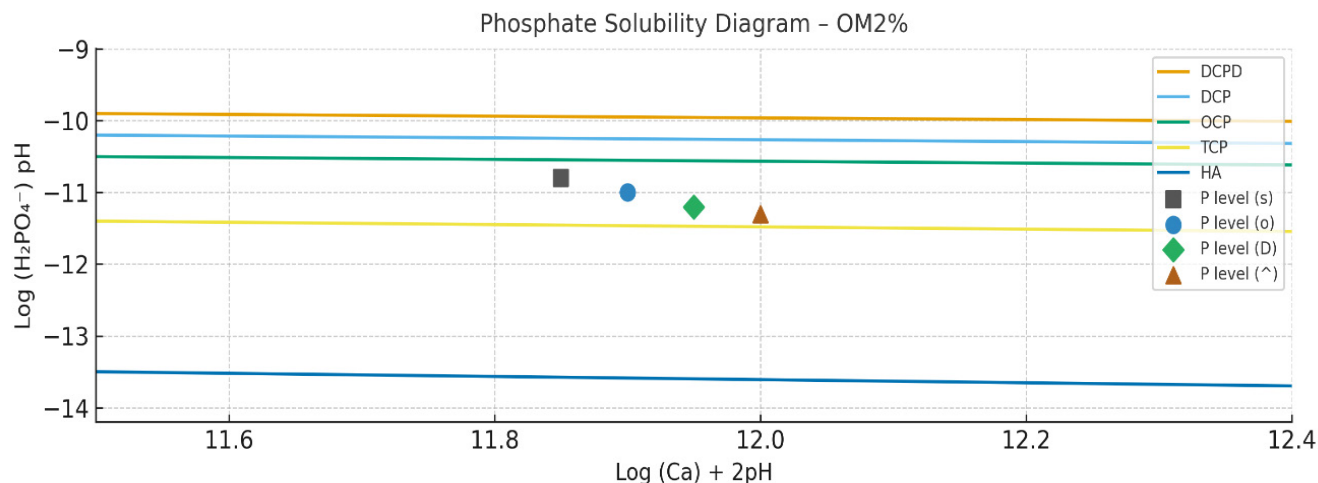


Figure 7: Phosphate solubility diagram under OM 2% – transition toward OCP and DCP stability.

Upon addition of 2% OM (Figure 7), the equilibrium points are shifted upwards and to the left, close to the OCP and DCP fields. This change indicates partial destabilization of stable phases as a result of Ca^{2+} complexation by organic acids (citrate, oxalate, malate) leading to reduced free Ca^{2+} concentration and increasing dissolution of poorly soluble Ca-P minerals.

At 4% OM, the new equilibrium points shift more towards top, intersecting the DCPD (brushite) field. It is obvious that an increase of HCl-Hydrolyzable phosphorus solubilization was under the direct effect of enhanced microbial C mineralization and release of H^+ ions, lowering pH slightly and thus promoting Ca-P dissolution. The three plots increasing from the bottom depict a thermodynamically controlled transition from phosphate fixation to mobilization with the system moving away from equilibrium ($\Delta G \approx 0$) toward dissolution dominated by spontaneity ($\Delta G < 0$) (Figure 8).

These findings are consistent with the thermodynamic consideration in Section 3.8, and indicate that organic matter addition changes the balance of equilibria by: Reducing Ca^{2+} activity through chelation and ion pairing with organic ligands and Increasing phosphate ion activity through protonation and microbial turnover.

Altogether, the transformation sequence ($\text{HA} \rightarrow \text{TCP} \rightarrow \text{OCP} \rightarrow \text{DCP} \rightarrow \text{DCPD}$) is a general tendency for an increasing P availability in the soil solution. It is worth noting that parallel results have been indicated by Zhang *et al.* (2022), Al-Saidi *et al.* (2024), and Ahmed and Hassan (2025), who showed that increasing amount of organic inputs enhanced P availability in arid and semi-arid calcareous-gypsiferous soils by altering Ca-P equilibria. On a more practical level, the moderate input of organic matter appears to be a management option as far as promoting P solubility and reducing P-fixation in gypsum-rich soils is concerned and maintaining continued sustainable cropping.

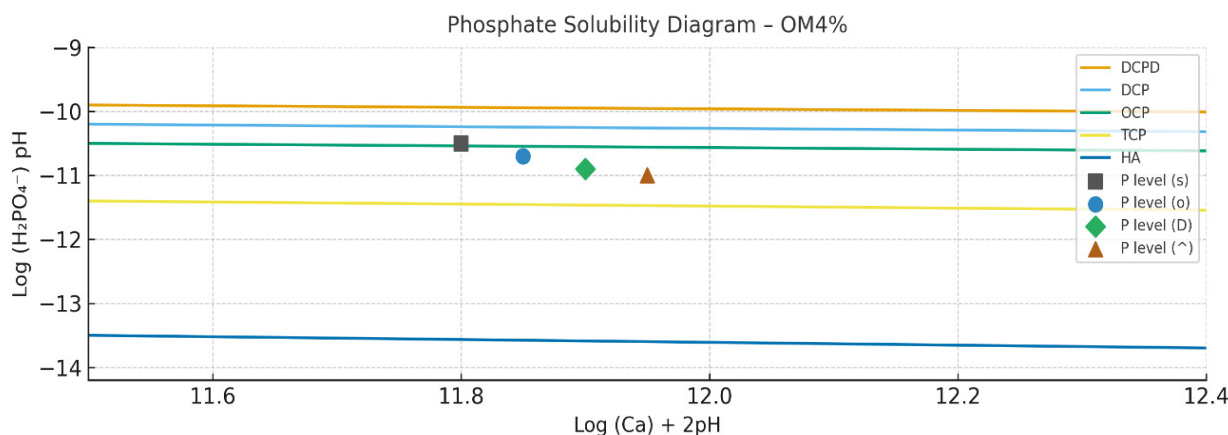


Figure 8: Phosphate solubility diagram under OM 4% – brushite (DCPD) field dominance indicating enhanced P solubility.

Conclusions and Recommendations

The impact of these findings on the gypsiferous soils from Karbala showed strong associations between gypsum content, phosphorus availability and organics transformation. High gypsum content (up to 37.9%) markedly decreased available phosphorus through calcium-induced precipitation reactions producing low-solubility Ca-P compounds such as hydroxyapatite (HA) and tricalcium phosphate (TCP). According to thermodynamic modeling, the addition of organic matter enhanced P solubilization as it chelates Ca^{2+} and reduces pH in response to its opposing relationship with gypsum-dissolution-induced increase in Ca^{2+} activity as reflected by changes in equilibrium energy indices. The calculated Gibbs free energy (ΔG) values ranged between -26 and -31 kJ mol^{-1} , confirming spontaneous dissolution and reprecipitation of brushite and dicalcium phosphate phases. Overall, the incorporation of organic amendments at rates of 2-4% effectively improved phosphorus availability, shifted soil equilibrium conditions toward more soluble Ca-P forms, and reduced the thermodynamic barriers associated with gypsum-induced P immobilization.

Novelty Statement

This study aims to provide a thermodynamic insight into gypsum-P interactions in different soil horizons in gypsiferous soils, such as Iraqi mollisols, to show that the activity of organic amendment can reduce P fixation by chelating with calcium and controlling pH.

Author's Contribution

Huda Krebit Hundi: Conceptualization, data curation, formal analysis, investigation, methodology, software, supervision, writing - original draft

Esraa H. Abd: Resources validation writing - review and editing

Nihad A. Abbas: Conceptualization, funding acquisition, investigation, methodology, supervision, writing - review and editing

Mustafa Qais Hamid: Data curation, resources, supervision, writing - original draft, writing - review and editing

Generative AI or AI assisted technology statement

The authors declare that no generative AI and AI

assisted technology was used in the creation of this manuscript.

Conflict of interest

The authors have no conflict of interest.

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