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Vivianite formation in organic-rich matrices

Sophie Banke

Propositions

Title: **Vivianite formation in organic-rich matrices**

PhD candidate: **Sophie Banke**

These propositions are regarded as opposable and defensible, and have been approved as such by the promotors Prof.dr.ir. M.C.M. van Loosdrecht, Dr. K. Reitzel Jensen, and external adviser Dr.ir. T.J.F. Prot.

1. Iron–organic complexation is generally blamed for anomalies in iron behaviour, but it is difficult to test because organic matter is still the dark matter of environmental systems. (*this thesis*)
2. Iron-carbonate interactions are often overlooked but play a pivotal role in iron cycling across matrices. (*this thesis*)
3. The identity of iron sulphides formed in digested sludge continues to evade clear characterization. (*this thesis*)
4. Currently, commercial-scale vivianite recovery is feasible only from wastewater sludge streams. (*this thesis*)
5. Environmental, sanitation, and agricultural sectors struggle to agree on phosphate management strategies because their objectives fundamentally diverge.
6. Advancing resource-recovery technologies is in vain if policy development does not keep pace with them.
7. If a tree were planted for every failed PhD experiment, the climate gains might end up greater than those produced by the PhD work itself—assuming the PhD produces any at all.
8. No 'perfect' PhD trajectory exists; success depends far more on secure funding, research autonomy, and mental health than on academic talent alone.
9. Iron–phosphate chemistry is more engaging and rewarding than magnesium– or calcium–phosphate chemistry.
10. A walk in the rain often drives more scientific progress than procrastinating in front of a screen.

Vivianite formation in organic-rich matrices

Sophie Monika BANKE

M.Sc.Sophie Banke

Vivianite formation in organic-rich matrices

197 pages

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„Und jedem Anfang wohnt ein Zauber inne, der uns beschützt und der uns hilft, zu leben.“
- Hermann Hesse

Translation

“Within every beginning dwells a magic that protects us and helps us to live.”

„When shit hits the fan, you gotta duck.“
- not Hermann Hesse

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SUMMARY

The global phosphorus challenge encompasses two interrelated issues. First, ensuring a sustainable supply of phosphorus, an element essential for all living organisms and a critical component of mineral fertilizers. Today, most phosphate rock is extracted from a concentrated set of regions, including Morocco, Russia, the United States, and China. This geographical imbalance creates supply vulnerabilities for countries with little or no mineable phosphate resources, such as those within the European Union, whose phosphorus security is increasingly exposed to geopolitical tensions. Second, the predominantly linear use of mined phosphorus results in its accumulation in landfills, long-term build-up in agricultural soils, and eventual runoff into aquatic systems. In these environments, phosphorus acts as a limiting nutrient, accelerating eutrophication and triggering excessive algal growth, hypoxia, and the degradation of aquatic ecosystems. To address both supply insecurity and environmental pressures, phosphorus recovery from secondary streams, specifically manure, wastewater treatment sludges, and lake sediments, which form the focus of this thesis, has emerged as a vital strategy.

Across all three matrices, manure, wastewater treatment sludge, and lake sediments, anaerobic conditions readily develop when oxygen supply is interrupted, as in digestion reactors or storage tanks. Under these conditions, and in the presence of sufficient iron, either dosed intentionally as a coagulant to control sulphur emissions and precipitate phosphorus or present naturally in lake sediments, the ferrous phosphate mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) can form. The high thermodynamic stability and paramagnetic properties of vivianite make it a particularly attractive target for phosphorus recovery, as it allows for the crystallization of phosphate into a single mineral phase that can subsequently be magnetically separated. Magnetic recovery has been repeatedly demonstrated at pilot scale in digested sludge, underscoring the value of investigating vivianite formation across multiple matrices to identify both barriers and cross-system synergies.

Previous work identified constraints on vivianite formation in pig manure when aiming to recrystallize the fine magnesium- and calcium-bound phosphate particles ($<150 \mu\text{m}$) into a single ferrous phosphate phase. Iron doses three times higher than those required to form vivianite in digested sludge were needed to efficiently form vivianite in pig manure. The initial working hypothesis attributed this effect to the distinct composition of manure organics relative to sludge, drawing on sediment studies that proposed that 25% of the iron equivalent to organic carbon must be dosed before vivianite formation. However, attributing the limitation solely to organics is challenging, given the heterogeneity of manure-derived organic matter and the difficulty of quantifying iron binding to organic versus phosphate ligands.

To address this gap, in Chapter 2 of this thesis, the phosphorus/dissolved organic carbon scale was introduced, expressing the mmol of dissolved phosphorus per mol of dissolved organic carbon, to quantify how different organic compounds influence iron-phosphorus binding. Using this scale, organic ligands including bipyridine, citrate, humate, alginate, acetate, and dissolved organic matter extracted from pig manure were ranked in terms of their capacity to dissolve vivianite or inhibit its formation. Experiments with individual ligands in ultrapure water, in the presence of phosphate and iron, enabled clear attribution of observed effects to vivianite formation or dissolution, and to specific molecular structures, strengthening scientific debates around the role of organics in vivianite stability. Citrate, commonly exuded by plant roots, inhibited vivianite formation to 100% and dissolved approximately 50% of vivianite, reinforcing the notion of vivianite as a potential slow-release fertilizer. Humate, representative of natural organic degradation products, dissolved about 10% of vivianite and inhibited its formation by 40%, which aligns with its expected behaviour in soils. In contrast, manure-derived dissolved organic matter neither inhibited vivianite formation nor dissolved substantial amounts, and mainly affected crystal morphology. These findings indicated that organic matter alone could not explain the inhibited vivianite formation observed in pig manure.

An alternative explanation for decreased vivianite formation in manure was required. Although vivianite-mediated phosphorus recovery had not been previously examined in manure, the recovery of calcium phosphates and struvite had been studied extensively. A key barrier to forming these phases in manure is competitive carbonate binding, a consequence of manure's inherently high alkalinity. In Chapter 3 of this thesis, it was demonstrated that in aged and digested manure samples, siderite (FeCO_3), a ferrous carbonate mineral, formed preferentially over vivianite. This behaviour was linked to a threshold concentration of dissolved inorganic carbon (DIC), above which carbonate outcompetes phosphate for ferrous iron. Lowering carbonate availability increased the fraction of phosphate precipitated as vivianite: this was more readily achieved in fresh manure with low DIC and, at the lab scale, by stripping carbonates and ammonium from digested manure using N_2 . Furthermore, siderite was detected in thermally hydrolyzed, digested sludge at approximately 3 g/L carbonate, highlighting that carbonate inhibition extends beyond manure and validating the matrix-comparative approach of this thesis.

In Chapter 4, the formation of vivianite in dredged lake sediment was explored as a potential means to enhance sediment reuse or recirculation as part of lake restoration. Although the lake water exhibited elevated dissolved phosphate concentrations of eutrophic lakes (~ 2 mg/L), vivianite precipitation following iron addition occurred only when Supplementary Information phosphate was dosed, indicating that under ambient conditions, iron preferentially bound competing anions such as carbonate and sulphide, and possibly organic ligands. Previous work had shown that vivianite forms only when phosphate is already adsorbed on iron oxyhydroxides prior to anaerobic incubation.

Together, these findings suggest that phosphate availability is low in sediments and that vivianite may form only where iron and phosphate co-occur locally. Quantification of vivianite in sediments was further complicated by Mössbauer spectroscopy failing to detect the naturally occurring vivianite, an otherwise reliable technique for manure and sludge. These analytical challenges underline the need for integrated spectroscopic, microscopic, and extraction-based approaches. Overall, the prospects for recovering vivianite from dredged sediments appear limited.

Finally, in Chapter 5, the formation of vivianite from iron sulphides was investigated. Iron sulphides typically form before vivianite, yet Fe–S speciation (FeS_x) remains difficult to resolve, particularly in the absence of crystalline sulphide phases such as pyrite (FeS_2). The controlled oxidation of iron sulphides, FeS_x , via microaeration at different oxidation-reduction potentials (ORP) in digested sludge was explored, with the aim of converting sulphides to elemental sulphur while leaving Fe(II) available for vivianite formation. However, the pyrite-like phase detected by Mössbauer spectroscopy persisted, and vivianite content decreased in aerated solids. Meanwhile, increases in dissolved sulphur and decreases in dissolved phosphorus indicated iron–phosphate interactions. Two hypotheses were proposed: (i) coupled iron–sulphide oxidation of a labile FeS_x phase with concurrent phosphate precipitation/adsorption onto oxidized iron, and (ii) decoupled oxidation in which elemental sulphur is oxidized while mixed-valence iron phases (e.g., green rust) oxidize and bind/adsorb phosphate. Although sulphide destruction could not be demonstrated conclusively, the observed decrease in soluble phosphate highlights a practical route to enhance phosphorus removal without increasing iron dosing and motivates further work on Fe–S speciation dynamics.

Across manure, lake sediments, and digested sludge, this thesis shows that the dominant constraints on vivianite formation are carbonate competition in high-alkalinity conditions, such as in manure and certain sludges; phosphate unavailability and analytical limitations in sediments; and iron sulphide formation in all three matrices. The carbonate barrier in a high alkalinity environment could be overcome, making vivianite recovery from pig manure technically feasible. In a broader perspective, current politics and economics in the agricultural, environmental, and sanitation sectors, as well as the lack of common phosphate management strategies, play a role in exploring vivianite-based phosphate recovery. This underscores that intersectoral collaboration, while increasingly emphasized, remains insufficient in practice and that only genuinely transdisciplinary efforts, such as those pursued in the ReCaP project, offer a realistic way forward in addressing the Global Phosphorus Challenge.

SAMENVATTING

De wereldwijde fosforproblematiek omvat twee nauw verbonden vraagstukken. Ten eerste, het waarborgen van een duurzame aanvoer van fosfor, een element dat essentieel is voor alle levende organismen en een cruciaal bestanddeel vormt van minerale meststoffen. Tegenwoordig wordt het merendeel van het fosfaaterts gewonnen in een beperkt aantal regio's, waaronder Marokko, Rusland, de Verenigde Staten en China. Deze geografische concentratie creëert leveringsrisico's voor landen met weinig tot geen winbare fosfaatvoorraden, zoals de lidstaten van de Europese Unie, waardoor de fosforzekerheid steeds gevoeliger wordt voor geopolitieke spanningen. Ten tweede leidt het overwegend lineaire gebruik van gewonnen fosfor tot accumulatie in stortplaatsen en landbouwbodems, en uiteindelijk uitspoeling naar aquatische systemen. In deze omgevingen fungeert fosfor als limiterend nutriënt dat eutrofiëring versnelt en overmatige algengroei, hypoxie en aantasting van aquatische ecosystemen veroorzaakt. Om zowel de leveringsonzekerheid als de milieudruk te verminderen, is fosforterugwinning uit secundaire stromen, specifiek mest, zuiveringsslib en waterbodems die de focus vormen van dit proefschrift, naar voren gekomen als een essentiële strategie.

In alle drie de matrices, mest, zuiveringsslib en waterbodems, ontwikkelen zich gemakkelijk anaerobe omstandigheden, zoals in vergistingsreactoren of opslagbassins. Onder dergelijke omstandigheden, en in de aanwezigheid van voldoende ijzer, hetzij doelbewust gedoseerd als coagulant om zwavelemissies te beheersen en fosfor te precipiteren, hetzij van nature aanwezig, kan het ferro-fosfaatmineraal vivianiet ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) worden gevormd. De hoge thermodynamische stabiliteit en paramagnetische eigenschappen van vivianiet maken het tot een bijzonder aantrekkelijk mineraal voor fosforterugwinning, omdat hiermee fosfaat kan worden gekristalliseerd in één minerale fase die vervolgens magnetisch kan worden gescheiden. Magnetische terugwinning is herhaaldelijk gedemonstreerd op pilotschaal in vergist slib, wat het belang onderstreept van onderzoek naar vivianietvorming in andere matrices om zowel belemmeringen als systeembrede synergieën te identificeren.

Eerder onderzoek identificeerde beperkingen voor vivianietvorming in varkensmest bij pogingen om de fijne magnesium- en calciumgebonden fosfaatdeeltjes ($<150 \mu\text{m}$) te herkristalliseren tot één ferro-fosfaatfase. IJzerdoseringen die driemaal hoger waren dan welke nodig zijn voor vivianietvorming in vergist zuiveringsslib bleken noodzakelijk om efficiënt vivianiet te vormen in varkensmest. De aanvankelijke hypothese ging uit van een onderscheidende samenstelling van organische stof in mest ten opzichte van slib, in lijn met sedimentstudies die suggereren dat circa 25% van het ijzer-equivalent aan organisch koolstof moet worden gebonden voordat vivianiet kan vormen.

Om een beter begrip te krijgen omtrent de rol van organisch materiaal en vivianietvorming in mest werd in Hoofdstuk 2 de P/DOC-schaal geïntroduceerd, die het aantal mmol opgelost fosfor per mol opgelost organisch koolstof uitdrukt, om te bepalen hoe verschillende organische verbindingen de ijzer-fosforbinding beïnvloeden. Met deze schaal werden organische liganden zoals bipyridine, citraat, humaat, alginaat, acetaat en opgeloste organische stof (DOM) uit varkensmest gerangschikt naar hun vermogen om vivianiet op te lossen of de vorming ervan te remmen. Experimenten met individuele liganden in ultrapuur water, in aanwezigheid van fosfaat en ijzer, maakten het mogelijk om de waargenomen effecten van individuele componenten toe te schrijven aan vivianietvorming of -oplossing, en aan specifieke moleculaire structuren. Citraat, wat veelvuldig wordt uitgescheiden door plantenwortels, remde de vorming van vivianiet volledig en loste circa 50% van het mineraal op, wat de geschiktheid van vivianiet als langzaam vrijkomende meststof onderbouwt. Humaat, representatief voor natuurlijke organische afbraakproducten, loste ongeveer 10% van het vivianiet op en remde de vorming met 40%, in overeenstemming met gedrag dat wordt verwacht in bodems. Daarentegen remde mest-afgeleid DOM de vivianietvorming niet en loste het slechts beperkte hoeveelheden op, en beïnvloedde het voornamelijk de kristalmorfologie. Deze bevindingen lieten zien dat organische stof op zichzelf de beperkte vivianietvorming in varkensmest niet verklaart.

Een alternatieve verklaring voor de verminderde vivianietvorming in mest was daarom nodig. Hoewel vivianietgerichte fosforterugwinning niet eerder in mest was onderzocht, is de terugwinning van calciumfosfaten en struviet wél uitgebreid bestudeerd. Een belangrijke belemmering voor de vorming van deze mineralen in mest is competitieve carbonaatbinding, een gevolg van de intrinsiek hoge alkaliniteit van mest. In Hoofdstuk 3 werd aangetoond dat in oude en vergiste mestmonsters sideriet (FeCO_3), een ferro-carbonaatmineraal, zich preferentieel vormt boven vivianiet. Dit gedrag bleek te worden bepaald door een drempelwaarde voor opgelost anorganisch koolstof (DIC), waarboven carbonaat het wint van fosfaat in de binding met ferro-ijzer. Het verlagen van de carbonaatbeschikbaarheid verhoogde het aandeel fosfaat dat als vivianiet precipiteerde: dit was gemakkelijker te bereiken in verse mest met lage DIC en op labschaal, door carbonaten en ammonium te strippen uit vergiste mest met N_2 . Daarnaast werd sideriet gedetecteerd in thermisch gehydrolyseerd, vergist slib bij circa 3 g/L carbonaat, wat aantoont dat carbonaatremming verder reikt dan mest en de matrixvergelijkende benadering van dit proefschrift bevestigt.

In Hoofdstuk 4 werd de vorming van vivianiet in opgebaggerd sediment onderzocht als mogelijke strategie om sedimentthergebruik of -circulatie te verbeteren in het kader van herstel van meren en plassen. Hoewel het meerwater verhoogde opgeloste fosfaatconcentraties vertoonde zoals typisch is voor eutrofe meren (~2 mg/L), trad vivianietprecipitatie na ijzerdosering alleen op wanneer aanvullend fosfaat werd toegevoegd. Dit

wijst erop dat onder natuurlijke omstandigheden ijzer vooral bindt aan concurrerende anionen zoals carbonaat en sulfide, en mogelijk organische liganden. Eerder werk had al aangetoond dat vivianiet slechts vormt wanneer fosfaat vooraf is geadsorbeerd aan ijzeroxhydroxiden vóór anaerobe incubatie. Samen suggereren deze bevindingen dat de beschikbaarheid van fosfaat laag is in sedimenten en dat vivianiet waarschijnlijk alleen vormt waar ijzer en fosfaat lokaal samen voorkomen. Kwantificatie van vivianiet in sediment werd verder bemoeilijkt doordat Mössbauer-spectroscopie het natuurlijk voorkomende vivianiet niet detecteerde, terwijl deze techniek in mest en slib wél betrouwbaar is. Deze analytische uitdagingen benadrukken de noodzaak van geïntegreerde spectroscopische, microscopische en extractiegebaseerde methoden. Al met al lijkt vivianiet-terugwinning uit gebaggerde sedimenten beperkt toepasbaar.

Tot slot werd in Hoofdstuk 5 de vorming van vivianiet uit ijzersulfiden onderzocht. Ijzersulfiden vormen zich doorgaans vóór vivianiet, maar de chemie van Fe en sulfide interacties (FeS_x) blijft moeilijk te karakteriseren, vooral in afwezigheid van kristallijne sulfidefasen zoals pyriet (FeS_2). De gecontroleerde oxidatie van ijzersulfiden, FeS_x , via micro-aëratie bij verschillende oxidatie-reductiepotentialen (ORP) in vergist slib werd onderzocht, met als doel de omzetting van sulfides in elementair zwavel, terwijl Fe(II) beschikbaar blijft voor vivianietvorming. De pyriet-achtige fase die door Mössbauer-spectroscopie werd gedetecteerd bleef echter aanwezig en het vivianietgehalte in beluchte vaste fracties nam af. De stijgende opgeloste zwavelconcentraties en dalende opgeloste fosfaatconcentraties duiden op interacties tussen ijzer en fosfaat. Twee hypothesen werden voorgesteld:

(i) gekoppelde oxidatie van een labiele FeS_x -fase met gelijktijdige fosfaatprecipitatie of -adsorptie aan geoxideerd ijzer; (ii) ontkoppelde oxidatie waarbij elementair zwavel wordt geoxideerd terwijl ijzer in gemengde oxidatietoestanden (bijv. green rust) oxideert en fosfaat bindt of adsorbeert. Hoewel vernietiging van sulfiden niet overtuigend kon worden aangetoond, wijst de waargenomen daling in oplosbaar fosfaat op een praktische route voor verbeterde fosforverwijdering zonder extra ijzerdosering, en vormt het een stimulans voor verder onderzoek naar Fe-S-speciatiedynamiek.

Dit proefschrift laat zien dat in mest, waterbodems en vergist slib dominante beperkingen voor vivianietvorming bestaan die specifiek gerelateerd zijn aan: carbonaatcompetitie in sterk alkalische matrices zoals mest en bepaalde slibsoorten; beperkte fosfaatbeschikbaarheid en analytische uitdagingen in sediment; en ijzersulfidevorming in alle drie onderzochte matrices. De carbonaatbarrière in sterk alkalische omgevingen kan worden overwonnen, waardoor vivianietterugwinning uit varkensmest technisch haalbaar blijkt. In bredere zin spelen de huidige politieke en economische contexten in de landbouw-, milieu- en sectorector, evenals het ontbreken van robuuste fosforbeheerstrategieën, een bepalende rol bij de verkenning van vivianietgebaseerde fosforterugwinning. Dit onderstreept dat intersectorale samenwerking, hoewel steeds benadrukt, in de praktijk

vaak tekortschiet, en dat alleen werkelijk transdisciplinaire inspanningen, zoals binnen het RecaP-project, realistische vooruitzichten bieden voor het aanpakken van de Global Phosphorus Challenge.

1

Introduction

1.1 THE GLOBAL PHOSPHORUS CHALLENGE

Phosphorus functions simultaneously as an essential nutrient, a critical raw material, an environmental pollutant, and historically a “light bearer.” Reconciling these roles remains a central challenge. As a nutrient, phosphorus is indispensable for skeletal development, nucleic acid synthesis, and cellular metabolism, and has long been recognized as a key component in agricultural fertilizers. Prior to industrialization, phosphorus consumed by humans and livestock was largely recycled back to agricultural land through manure [1]. Industrial development and the geographic separation of food production and population centers, however, created a growing dependence on mineral phosphorus fertilizers to sustain global food demand [1]. Because Europe lacks economically viable phosphate deposits, phosphorus has been designated a critical raw material [2]. Global supply is concentrated in a small number of countries, such as Morocco, Russia, the United States, Saudi Arabia, and China, which account for approximately 80% of global phosphate sales; consequently, around half of EU imports originate from Russia and Morocco [3]. The onset of the Russia–Ukraine conflict highlighted this vulnerability through a rapid spike in fertilizer prices [4], and the EU faced political pressure over the exemption of fertilizers from sanctions. Phosphate inequities are also evident in agricultural productivity: in many African regions, low crop yields correlate with chronically low phosphorus inputs [5], making low-income countries disproportionately sensitive to fertilizer price volatility [4]. These combined risks underscore the need to recover phosphorus from secondary sources to reduce dependence on global markets.

A range of secondary phosphorus streams exists globally, including manure (15–20 Mt P/year), mining and fertilizer industry wastes (6–12 Mt P/year), wastewater (3.7 Mt P/year), and food waste (1.2 Mt P/year) [6]. Although manure and sewage sludge are partially reused in agriculture, substantial phosphorus losses persist, with material ending up in landfills, accumulating as legacy P in soils (≈ 815 Mt P), or ultimately settling in sediments (>2.6 Mt P) [6]. These losses represent both a missed recycling opportunity and a major environmental concern: phosphorus entering aquatic systems accelerates eutrophication (Schindler, 2016), driving hypoxia, ecosystem degradation, and deterioration of freshwater quality. Thus, recovering phosphorus from secondary streams contributes simultaneously to pollution mitigation and to long-term food security.

Land application remains the most direct route for phosphorus recycling. In 2020, for example, Ireland and Spain applied approximately 90% of their sewage sludge to agricultural land. In contrary, it is forbidden in some countries such as the Netherlands, Switzerland, and Turkey where no agricultural use was reported [7]. Reductions in land application are largely attributed to the presence of heavy metals, organic micropollutants, and pathogens in sludge [8]. Furthermore, when land application serves primarily as waste disposal rather than nutrient management, the risk of phosphorus runoff increases.

As a result, targeted phosphorus recovery technologies are needed. Although significant advancements have been made in phosphorus recovery, particularly in wastewater treatment [9], recovered phosphorus products currently struggle to be cost-competitive [6]. In Switzerland, for instance, phosphorus recovered from sludge ash was produced at three times the market price of phosphoric acid, which was below 1100 USD/t at the time. Market uptake is further hindered by insufficient volume, quality assurance, including uncertainties surrounding contaminant levels, nutrient availability, and product standardization [10–12]. Consequently, policy intervention is required to create incentives for recycling. The revised Urban Wastewater Directive mandates phosphorus discharge limits and imposes recycling requirements that must be transposed into national legislation by 2028 [13], yet comprehensive regulatory frameworks exist in only a few countries [14]. In Germany, implementation is hindered by legal restrictions on the use of recovered phosphorus fertilizers [15] and by insufficient technological capacity [16]. Overall, phosphate recycling faces technological, knowledge-based, logistical, economic, societal, and regulatory barriers, requiring transdisciplinary approaches to address the fragmented nature of phosphorus streams, recovery pathways, and national policies [6].

One example of such an approach is the EU Horizon 2020 Marie Skłodowska-Curie Innovative Training Network “RecaP,” within which 15 Early Stage Researchers (ESRs), including the work presented in this thesis, examine phosphorus recycling from technological, agricultural, economic, and societal perspectives (Figure 1-1) [17]. When Hennig Brand first isolated elemental phosphorus from urine, he named it the “light bearer” due to its luminescence. While the RecaP project has not resolved the global phosphorus challenge, it has illuminated new pathways toward sustainable phosphorus management.

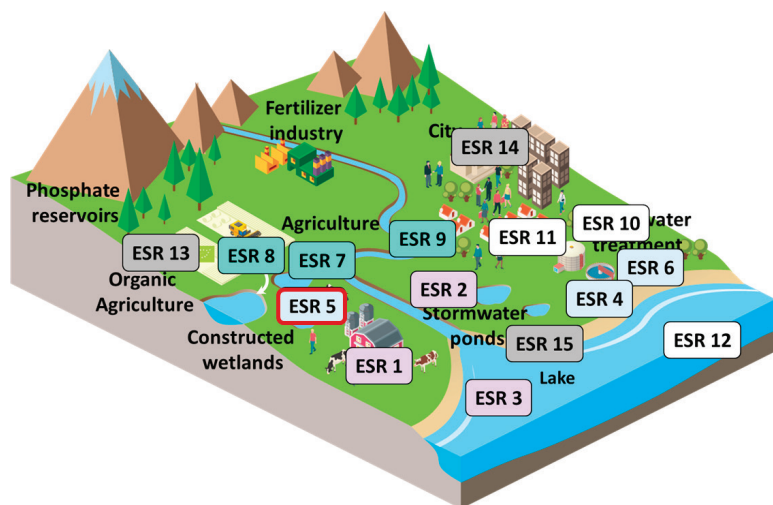


Figure 1-1 Scheme of the RecaP project with different Early Stage Researchers (ESR) research areas within the global phosphorus challenge, this thesis is highlighted as ESR 5.

1.2 PHOSPHATE RECOVERY FROM SECONDARY RESOURCES

Phosphorus management spans three main sectors, agriculture, sanitation, and the environment, each characterized by distinct matrices, speciation, and recovery opportunities [17]. This thesis focuses on three secondary phosphorus streams, one from each sector: pig manure (agriculture), digested municipal wastewater sludge (sanitation), and dredged lake sediment (environment). Understanding what these streams have in common and recognizing their differences can facilitate the transfer of phosphate recovery technologies between the systems. Table 1-1 summarizes the principal management objectives, typical concentration ranges, and leading recovery technologies across these streams.

Table 1-1 Streams of interest for phosphorus recovery discussed in this thesis, with general target of phosphorus management, phosphorus concentrations, and current phosphate related technologies.

	lake sediment	pig manure	digested sludge
target	lake restoration, eutrophication prevention [18]	reuse as fertilizer [19]	economic waste disposal, P recovery [7]
phosphorus concentration g/kg DW	1-6 [20,21]	19-46 [22-25]	22-40 [26,27]
current P (recovery) technology	PhosLock® [28], aeration [29], dredging and land application [30], biological interventions [31]	Pelleting [32], dissolution & reprecipitation* [33,34]; recrystallisation [24]*	leaching/high temperature treatment of ashes, struvite precipitation [35], Ravita [36]*, Vivimag [37]*

* not commercial yet

In aquatic systems, phosphorus (P) management typically prioritizes remediation—limiting internal P loading and preventing eutrophication—rather than material recovery. As such, phosphate recovery from sediments is uncommon, and overall recovery potential is relatively small compared to manures or sludges [28,38]. Remediation approaches often aim to immobilize phosphate, either by aeration to promote oxidizing conditions and the formation of Fe(III)-phosphate phases [29], or by applying lanthanum-containing clays (e.g., Phoslock®), which can provide more persistent sequestration at higher cost [28]. However, even when oxidized Fe phases prevail, anoxic periods can induce P release via reductive dissolution. Dredging offers an opportunity to remove P-rich sediments to prevent redissolution from happening, and potentially reuse them, for instance via land application [30,39]. Yet this practice is often constrained by the presence of heavy metals and other contaminants [40]. Moreover, P availability in sediments is uncertain [30], in part because phosphorus speciation is more diverse and evolves over longer timescales under variable redox and mineralization regimes than in manures or sludges [41]. These

features suggest that targeted recovery strategies—particularly those that address iron-bound phosphorus—could help reduce P pollution and enable reuse during dredging.

The efficient reuse of manure phosphorus could supply roughly 10–20% of the global phosphorus demand [42]. Yet P-rich manures accumulate in high-livestock regions (e.g., the Netherlands, Belgium, Denmark, northern Germany), exacerbating local nutrient imbalances [43]. As a consequence, land application limits and transportation requirements are increasingly applied [44,45]. Pig farms often lack sufficient land for nutrient-balanced spreading, making pre-treatment to reduce volume before transport necessary [19]. While pelleting and composting effectively remove water, they do not correct the low N:P fertilization ratio [19] or enable targeted P recovery. Precipitation-based recovery (e.g., struvite or calcium phosphate) is conceptually attractive [33]; however, in pig manure, most P resides in the solids [22]. This typically necessitates acidic dissolution followed by alkaline reprecipitation to isolate P, resulting in high chemical consumption [33,34]. Recently, recrystallization of P into defined mineral phases has gained traction as a lower-chemical alternative. For example, Schott et al. [24,46,47] utilized a up-flow anaerobic sludge blanket (UASB) reactor to form calcium phosphate granules, recovering approximately 58% of the total phosphorus in pig manure [24]. Recrystallization into ferrous phosphate vivianite, a phase directly relevant to iron phosphate binding under reducing conditions, is a novel approach which will be investigated in this thesis.

In the sanitation sector, phosphorus removal is mandated in several countries, as stipulated under the EU Urban Wastewater Directive, which utilizes either enhanced biological phosphorus removal (EBPR) or chemical precipitation with aluminum or iron salts [48]. Approximately 90% of influent P is retained in the sludge [9], which, in principle, could be applied to land. In practice, the agricultural use of sludge is restricted in some countries due to the presence of heavy metals, micropollutants, and pathogens [8], and like sediments and manures, sludge application rarely targets phosphorus (P) use to match crop needs. Despite growing interest, only ~61 P recovery facilities operate globally, concentrated in the USA, Japan, and the Netherlands, with a reported yield of ~420,000 t P yr⁻¹ [35], which is only 10% compared to the secondary phosphorus in wastewater globally. Aqueous phase recovery (e.g., Crystal Green by Ostara®, Nuresys, PhosphoGreen by Suez, Struvia by Veolia, and Phosphaq by Paques) precipitates struvite (magnesium ammonium phosphate) or calcium phosphate after EBPR, but typically accesses only the soluble P fraction, achieving ~10–30% of influent P recovery [49]. Sludge-based recovery can reach ~40–60% of influent P, but usually requires acid leaching and depollution (e.g., the Stuttgart process [50]), which increases chemical demand and process complexity [49]. Further, the Ravita process focuses on recovering phosphoric acid from metal phosphate sludge. Ash-based recovery after sludge incineration (e.g., Tetrphos by Remondis or planned full scales by EasyMining and SusPhos) can achieve ~80–90% of influent P with minimal contamination [49]. However, it entails high capital costs [49], requires mature

infrastructure [51], and irreversibly loses organic matter. As many WWTPs employ iron salts for chemical P removal, iron–phosphate interactions are intrinsic to sludge matrices [27]. Under anaerobic conditions, Fe(III) can be reduced to Fe(II), favouring the recrystallization of phosphate into vivianite [27]. Compared with acid dissolution/precipitation, recrystallization into vivianite offers the potential for lower chemical consumption and better integration into existing sludge treatment trains. Its paramagnetic properties enable magnetic separation (~60% recovery of influent P) [37]. These attributes motivate the exploration of vivianite-centred recovery as a complementary pathway within the sanitation sector.

Knowledge transfer across sediments, manures, and sludges bears relevance, when manure or sludge are applied to land, or when phosphorus mobilization in the different streams is studied and could be interesting for technological transfer. Most technological advances have been made in recovering phosphorus from wastewater streams, making the transfer of sludge technology to manure and sediments an interesting prospect

1.3 PHOSPHATE MINERALS

When evaluating phosphorus recovery technologies across different matrices, the mineral form in which phosphate is recovered is central. Key considerations include the thermodynamic likelihood of mineral formation, the expected purity, technical applicability, and potential end uses of the recovered product. The thermodynamic factor will be expressed through the equilibrium soluble phosphate concentration, $c(P)_{eq}$, derived from the solubility product. However, practical recovery is further influenced by kinetic factors and matrix composition, which can alter supersaturation, nucleation, and purity in real systems [52], making $c(P)_{eq}$ a benchmark value for this process. This section focuses on three phosphate minerals of technological relevance: struvite, calcium phosphate granules, and vivianite (Figure 1-2).



Figure 1-2 Three phosphate recovery minerals in focus: struvite (left [53]), calcium phosphate granules (middle [85]), and vivianite (right [65]).

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is currently the most established mineral product recovered from wastewater streams. It is typically precipitated from the aqueous phase, enabling high product purity, such as the 99% purity reported for Crystal Green® [53]. Because aqueous recovery after enhanced biological phosphorus removal typically captures only the soluble fraction, overall P recovery remains low. 10-30% of influent P (see Section 1.2). Struvite's slow-release fertilizing properties [54] make it suitable for a combined nitrogen–phosphorus application. Its technological maturity is reflected in multiple full-scale installations worldwide [35] and its legal recognition as an EU fertilizing product [6,55]. However, recovering struvite from more complex or impure matrices, such as manure, digested sludge, or sediments, is challenging. Thermodynamically, struvite has a relatively high equilibrium soluble phosphate concentration at pH 7, $c(\text{P})_{\text{eq}} = 6.0 \cdot 10^{-4} \text{ M}$ [56] as calculated by Visual MINTEQ, meaning it is disfavored in the presence of competing cations, particularly Ca^{2+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$. In consequence, formation of more stable or less soluble mineral phases is likely to co-occur with struvite precipitation, decreasing purity [57]. As a result, struvite formation is most effective in relatively clean, soluble P-rich streams, whereas its applicability in digested sludge, manure or sediments is more limited.

Despite advances in struvite technology, calcium phosphate (Ca-P) precipitation has recently gained attention as a recovery route [58]. Similarly to struvite, Ca-P recovery can achieve high purity but relatively low efficiency, because only the soluble fraction of P is accessed [49]. Calcium phosphate products, including amorphous calcium phosphate and hydroxyapatite, are already used in fertilizer manufacturing and can serve as both direct fertilizers and precursors for the fertilizer industry [58]. Thermodynamically, calcium phosphate is more stable than struvite, with a lower $c(\text{P})_{\text{eq}} = 1.2 \cdot 10^{-4} \text{ M}$ for amorphous $\text{Ca}_3(\text{PO}_4)_2$ [56]. This suggests that, under appropriate pH and Ca^{2+} concentrations, Ca-P precipitation can outcompete struvite formation. Beyond aqueous precipitation, recrystallization technologies offer opportunities to recover Ca-P from more complex matrices. UASB reactors have produced calcium phosphate granules from manure and blackwater [24,46,47,59]. A key limitation of Ca-P granulation is its variable mineralogy and relatively low purity, which is influenced by the co-precipitation of carbonates and organic matter, for example. This heterogeneity complicates product standardization and marketability.

The ferrous phosphate mineral vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) has recently emerged as a promising P-recovery product, particularly in iron-rich, anaerobic environments (section 1.2). From an agricultural perspective, the phosphate availability of vivianite is limited in neutral to alkaline soils, making it less effective as a direct P fertilizer [60]. It can, however, serve as an iron fertilizer [61]. Beyond fertilizers, new applications are being explored, including the splitting of vivianite into iron for recirculation and phosphate for fertilizer production, as well as its potential use as a precursor for lithium-iron-phosphate (LFP) battery cathodes [62], which could create new value chains. Thermodynamically, vivianite has one of the lowest equilibrium phosphate solubilities among the three minerals, with

$c(P)_{eq} = 2.5 \cdot 10^{-6}$ [63] making it poorly soluble and able to reduce soluble P concentrations significantly. In digested sludge where Fe^{2+} is abundant, vivianite is the dominant phosphate mineral, binding up to 70–90% of total phosphorus [64–66], and a purity of ~80% has been shown in a pilot study [37], optimization above 95% are also feasible (unpublished data). This indicates that Fe–P mineral formation is strongly favoured over competing phases such as struvite or calcium phosphate under neutral pH and reducing conditions. This could make vivianite an important phosphate recovery product beyond iron-coagulated wastewater sludge [27], including in iron-rich sediments [67] and in manure systems dosed with iron salts [68]. Nevertheless, phosphate has to outcompete sulphide, the thermodynamically preferred binding partner of ferrous iron [69], and other compounds in the matrix, such as carbonate [70] and organic matter [71,72], for iron binding. Ensuring the formation of vivianite over other iron(II) compounds is therefore required.

Struvite is the most mature recovery product, but it is primarily interesting in matrices where P is available in high concentration in the soluble phase and with little or no impurity to enable the marketability of a pure product. Calcium phosphate offers broader relevance to the fertilizer industry but crystallising calcium phosphate minerals and achieving a pure mineral phase for commercialisation is challenging. Vivianite combines thermodynamic favourability, magnetic separability, and relevance to iron-rich anaerobic systems, making it particularly attractive for the complex matrices targeted in this thesis—namely, manure, digested sludge, and sediments. Investigating the maximization of vivianite formation presents a valuable opportunity to assess this recovery route across these matrices.

1.4 MOTIVATION

Vivianite recovery and formation in anaerobic wastewater treatment sludges was pioneered by Wilfert (2018) [73] and further advanced by Prot (2021) [68]. Building on this work, vivianite formation was also investigated in other anaerobic matrices such as pig manure. When adding iron to manure, Prot and Schott observed that approximately three times more iron was required to form vivianite than in digested sludge [68]. This discrepancy indicates that, in manure, iron is bound by ligands other than phosphate. Identifying these competing iron sinks is essential to understanding why vivianite forms efficiently in digested sludge, but not in manure, and to evaluating whether lessons from one matrix may transfer to others, such as lake sediments. This motivates a broader investigation into barriers and enablers of vivianite formation across diverse anaerobic environments.

The first iron compound known to form before vivianite is iron sulphide, which is thermodynamically favoured [69]. In waterlogged sediments, vivianite is generally observed above a reactive Fe/S ratio of about 0.9 [74], while in digested sludge, the empirical threshold is around 1.0 [65]. More mature sediments may also contain crystalline sulphide minerals such as pyrite (FeS_2), mackinawite (Fe_{1+x}S), and greigite (Fe_3SO_4) [75]. Occasionally, pyrite has also been identified in digested sludge using XRD [76] or SEM–EDX [77]. Yet, determining the nature of the primary FeS_x phase that initially forms in digested sludge [65], manure [78], or lake sediments [79] remains challenging because the particles are too small or insufficiently crystalline for XRD detection [77,80] and often overlap with pyrite signals in Mössbauer spectra [27]. Although sulphide formation clearly competes with vivianite formation, the amount of sulphur in manure is too low to explain why three times more iron is required to form vivianite. Sulphide competition alone cannot account for the observed difference.

Since sulphides do not fully explain the increased iron demand in manure, other strong iron-binding ligands must be considered. Organic matter is one such candidate. In lake sediments, organic matter plays a dual role: it facilitates phosphate release under anaerobic conditions [74] but can also bind iron through iron–organic complexes [71]. Based on iron chemistry in soils [81] Kleeberg estimated that additional iron, equivalent to roughly 25% of the organic carbon, would be required for vivianite formation in lake sediments. However, demonstrating iron–organic complexation as the dominant sink is difficult because the relevant organic compounds are hard to isolate and identify in these heterogeneous matrices [82]. As a result, iron–organic binding can be hypothesized but is equally difficult to confirm or exclude.

In contrast to the diffuse role of organic carbon, inorganic carbon is a well-established competitor for mineral phosphate precipitation. High alkalinity and elevated carbonate concentrations in manure reduce struvite and calcium phosphate recovery by promoting carbonate formation [46,47,83]. Similar processes could interfere with vivianite formation, either by binding iron to carbonate such as the ferrous carbonate siderite (FeCO_3) or green rust ($[(\text{Fe}^{2+}_{1-x}\text{Fe}^{3+}_x(\text{OH})_2)^{x+} \cdot [(x/n)\text{A}^{n-} \cdot (m/n)\text{H}_2\text{O}]^{x-} \text{ with } \text{A}^{n-} = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{Cl}^-, \text{OH}^-]$ [70,84]. Thus, inorganic carbon represents another plausible barrier to vivianite formation that has not yet been systematically assessed.

This thesis, therefore, examines how organics, carbonates, sulphides, and phosphates compete for iron and how this competition governs vivianite formation across different anaerobic matrices (Figure 1-3). Understanding these interactions enables the identification of new opportunities for recovering vivianite from sediments, manures, and digested sludges.

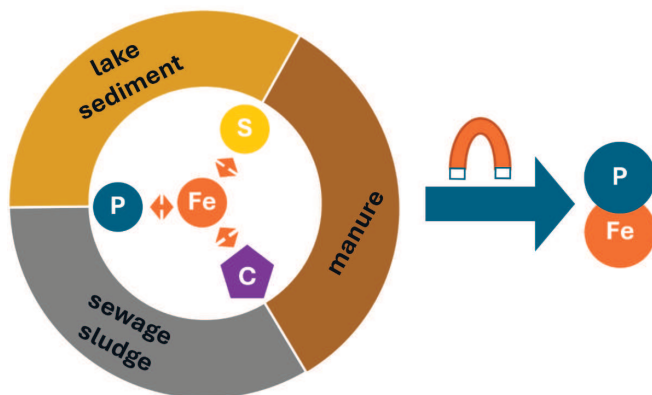


Figure 1-3 Fe-P, Fe-S and Fe-C interactions in three different matrices (left), the goal of improving Fe-P interaction using that knowledge and magnetically recovering vivianite (right).

1.5 THESIS OUTLINE

To investigate whether organic ligands significantly compete with phosphate for iron, **Chapter 2** examines the influence of a range of synthetic and natural organic compounds on vivianite formation and dissolution. A scale of iron-binding strength was established for these ligands and compared with dissolved organic matter extracted from pig manure. By analyzing both dissolution and formation processes, the chapter distinguishes the effect of iron–organic complexation from other mechanisms that influence vivianite formation in the presence of organics.

Building on this controlled assessment of organic interactions, **Chapter 3** turns to another class of iron-binding ligands: inorganic carbon. Here, the relevance of iron carbonate precipitation is evaluated in manures with varying alkalinities. Thresholds for carbonate concentrations were determined to identify when iron carbonates are likely to form rather than vivianite. These findings also reveal implications for wastewater sludges with high alkalinity. Finally, potential interventions to limit or redirect iron carbonate formation are explored, including adjustments to manure storage times and integrating phosphorus recovery with nitrogen, carbon, and energy recovery processes.

Chapter 4 investigates vivianite formation in dredged sediments—matrices where phosphate, sulphide, organic matter, and carbonate dynamics differ substantially from those in manure or sludge. Vivianite is naturally occurring in lake sediments, but concentrations are generally lower, requiring more sensitive analytical methods. Phosphorus in both the solid and dissolved phases are also generally lower, potentially influencing the competitive landscape among iron-binding ligands. The potential in stimulating vivianite formation using iron dosing for recovery from dredged sediments was evaluated. Further, methods detecting vivianite in these sediments were explored using complementary

analytical techniques, including Mössbauer spectroscopy, and sequential phosphorus extractions.

Finally, **Chapter 5** focuses on an active strategy to overcome competition from sulphides, a major iron sink identified in earlier chapters. This chapter tests whether iron sulphides can be selectively destabilized through oxidation–reduction potential (ORP)–dependent microaeration, thereby increasing the proportion of iron available to bind phosphate and, ideally, inducing vivianite formation. Low-temperature Mössbauer spectroscopy is used to characterize iron speciation in unprecedented detail and to better understand the effects of microaeration on iron mineral phases.

Together, these chapters address the four major competitors for iron—organics, carbonates, sulphides, and phosphate—across multiple matrices and environmental conditions, ultimately identifying constraints and opportunities for promoting vivianite formation and recovery.

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2

Different influences of organic ligands on vivianite formation and dissolution

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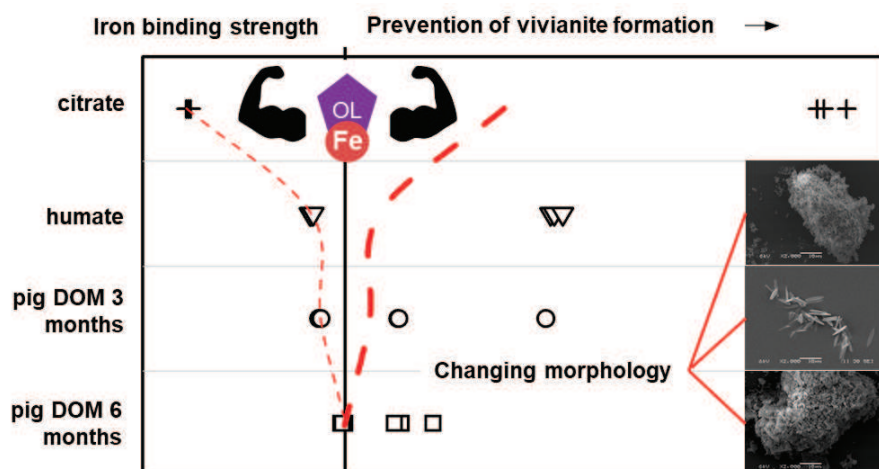
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ABSTRACT:

Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) has emerged as a promising mineral for phosphorus (P) recovery from digested sludge, and it may also contribute to phosphate management in lake sediments and manure, given the similar anaerobic conditions across these environments. However, organic ligands in these matrices have been proposed to complex with iron (Fe), thereby reducing the efficiency of vivianite formation. This study aims to elucidate the impact of organic ligands on vivianite formation, particularly focusing on their binding strength with iron and the subsequent effects on vivianite formation in pig manure. Organic ligands not only form complexes with iron but also influence the crystal growth process. We investigated how different organic ligands affect the formation and dissolution of vivianite, assuming that ligands with higher iron-binding strength would enhance phosphate solubilization. Our findings revealed that citrate nearly completely inhibited vivianite formation (up to 100%) and caused a 50% dissolution of existing vivianite, while humate hindered vivianite formation by 40% but only led to a 10% dissolution. Interestingly, pig-derived dissolved organic matter had minimal effects on the precipitation of iron and phosphorus but significantly altered the morphology of the resulting products, which varied depending on the age of the manure filtrate. While the iron binding strength of organic ligands does influence vivianite formation, it does not solely account for the reduced vivianite formation observed in complex matrices like manure. Therefore, a more nuanced assessment of the role of organic matter in vivianite formation is warranted.

Keywords: Iron complexation, manure organic matter, organic ligands, phosphorus recovery, vivianite

Graphical Abstract:



2.1 INTRODUCTION

Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) is a key mineral in phosphorus recovery from wastewater, binding up to 70-90% of the phosphorus present in anaerobic digesters [1]. Phosphate recovery as vivianite is advantageous due to its formation within a moderate pH range of 6-8 [2], its low solubility [3], its applicability as an iron fertilizer [4], and its potential use as a precursor for LiFePO_4 batteries [5]. Additionally, its paramagnetic properties enable a straightforward magnetic-based recovery process. Pilot-scale recovery of vivianite from digested municipal wastewater sludge has already been demonstrated [6]. While vivianite naturally occurs in lake sediments, its formation in these environments is less predictable than in digested sludge [7]. Manure may offer an alternative matrix for vivianite-mediated phosphate recovery, facilitating land application of the manure after phosphate removal in areas of high livestock production. The anaerobic conditions in manure should be conducive to vivianite formation, though prior research indicates that competing components in manure can interfere with iron availability [8].

Iron-organic interactions are central to various environmental processes. For instance, organic matter affects the weathering and reformation of iron oxides in soils, enhancing iron availability [9]. It also mobilizes iron (II) during river bank filtration [10], while small organic acids, such as citric and oxalic acids, dissolve iron oxides and release adsorbed phosphorus [11]. Lalonde et al. [12] reported that up to 20% of organic carbon in sediments is associated with iron phases. Building on this, Kleeberg et al. [13] estimated that approximately 25% of organic carbon in lake sediments binds to iron, thereby limiting the formation of vivianite.

Organic ligands have been hypothesized to impact vivianite formation [14,15]. Alginate and humate have been shown to limit vivianite formation at a concentration of around 1 g/L [16–19]. At high levels (10 g/L) acetate can also inhibit vivianite formation, though effects are minimal at concentrations below 5 g/L [18]. Vivianite dissolution by organic ligands has also been previously studied. For example, Yang et al. [20] and Gypser and Freese [21] observed that citrate partially dissolves vivianite at pH 6, while the effect of humate on vivianite dissolution was minimal under similar conditions [21]. Despite these findings, a systematic framework to correlate organic ligand concentrations with vivianite formation efficiency is lacking, and the influence of iron-binding strength has yet to be directly investigated.

During vivianite formation, organic ligands with high iron-binding strength should make iron unavailable for vivianite formation. However, inhibition could also arise if organic ligands bind to vivianite crystal nuclei, impeding further crystal growth [16,22]. Nevertheless, iron-organic binding strength should be the primary factor driving vivianite dissolution forward until the thermodynamic equilibrium is reached. Hence, the extent

of vivianite dissolution by an organic ligand should give insight into the degree of the iron-binding strength.

Previous studies have largely focused on the effects of organic ligands on either vivianite formation [16–19,22,23] or vivianite dissolution [20,21,24]. By addressing both formation and dissolution, which was not realized in previous research, we aim to elucidate how iron-complexing organic ligands influence vivianite formation and evaluate the role they could play in manure. Given the complexity of manure, we opted for a comparative approach, examining dissolved organic matter in manure alongside those in controlled systems relevant to vivianite formation. Our approach offers a novel perspective on the complex interactions between organic ligands and vivianite formation, with potentially surprising insights for phosphate recovery in manure systems.

2.2 MATERIALS & METHODS

2.2.1 Organic ligands

This study examines the effects of several organic compounds on vivianite formation and dissolution, selecting organics that are chemically relevant to vivianite:

- **Bipyridine** has been proposed as a potential extractant for quantifying vivianite due to its specific affinity for iron (II) bound within vivianite [25,26].
- **Citrate**, a small molecule exuded by plant roots, is frequently used to evaluate the bioavailability of phosphorus fertilizers [27].
- **Volatile fatty acids** are key transformation products arising during the anaerobic digestion of organic materials such as sludge and manure [28,29]. Acetate serves as a representative compound of this group.
- **Humate**, a stable degradation product of organic matter, forms in complex matrices like sewage sludge, manure, and sediments. Its structure includes functional groups that can effectively complex metal ions, including Fe [30].
- **Alginate** represents polysaccharides, the most abundant natural biopolymers, and is relevant in the context of food science and waste management [31].
- **Pig dissolved organic matter (DOM)**, derived from pig manure filtrate, was included to represent a real environmental matrix and provide a comparison against the more defined organic compounds. Given the biological activity in manure, which drives continuous organic matter degradation, pig DOM solutions aged for three and six months were tested.

Proteins were excluded based on prior findings from Li et al. [19], who observed negligible effects on vivianite formation using Bovine Serum Albumin. Similarly, amino acids like alanine and aspartic acid have minimal impact on phosphate precipitation with iron (III) [32], and their iron (II) complex formation constants are even lower [33].

Preparation of pig DOM and humate solutions involved centrifugation (Beckman Coulter, Avanti J-15R) of raw pig manure at 25,000 rpm for 10 minutes to address the poor settling properties of pig manure. The humate solution was processed similarly to allow for better comparability with the manure filtrate. Supernatants from these preparations were then filtered through 0.45 μm filters and dissolved organic carbon (DOC) served as the baseline for comparing the different organics. Setting the DOC concentration to a uniform level ensured consistent comparability among organic ligands, based on literature from sediment studies that estimate iron binding relative to organic carbon [13]. For each ligand, a stock solution with a DOC concentration of 730 mg/L was prepared (see Table A 2-4), followed by dilution to a target concentration of 330 mg/L. This concentration was selected because it is equivalent to a 1 g/L humate solution, a level used in the dissolution study by Gypser and Freese [21] and to balance solubility constraints, particularly for less soluble compounds like bipyridine and humate.

2.2.3 Dissolution and formation experiments

All experiments were carried out in triplicate in serum bottles in a glove box under a nitrogen atmosphere ($\text{O}_2 < 100$ ppm).

For the dissolution experiments, 50 mg of synthetic vivianite was mixed with 100 mL of organic solution. Vivianite for the dissolution experiment was synthesized at room temperature from solutions of 600 mM K_2HPO_4 (VWR Chemicals BDH) and 900 mM $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Sigma Aldrich). Solutions (50 mL) were mixed under anaerobic conditions in a glove box, and the precipitated solid was then washed three times with ultrapure water and dried in the glove box in the dark.

For the formation experiments, a phosphate solution was prepared by adding 5 mL of 40 mM K_2HPO_4 stock solution to 45 mL of the organic solution, and an iron solution was prepared by adding 5 mL of a 60 mM $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ stock solution to 45 mL ultrapure water. The iron and phosphate solutions were mixed together, aiming at a Fe/P ratio of 1.5 according to vivianite stoichiometry. The pH was measured by potentiometry and adjusted to pH 8 with 1 M NaOH or 1 M HCl for each sample. Negative controls were prepared for humate and pig DOM experiments containing only humate and pig DOM solutions. Formation and dissolution experiments were replicated without organics in ultrapure water.

The samples were agitated at 120 rpm at room temperature on a rotary platform shaker (Heidolph, Unimax 2010). Samples (1.5 mL for dissolution, and 1 mL for formation) were taken after 1 h, 4 h, 24 h, 48 h, and 168 h with subsequent filtering through 0.45 μm filters. At the end of the experiment, the pH was measured again. All samples were centrifuged (Beckman Coulter, Avanti J-15R) at 4750 rpm for 10 min to efficiently settle most of the solids that are formed when synthesizing vivianite in an aqueous matrix, washed twice with 50 mL of ultrapure water, and centrifuged at the same settings. The remaining solid particles were dried in the air at room temperature, and the yield was determined.

2.2.4 Analysis

Iron and phosphorus concentrations from vivianite formation and dissolution experiments were monitored with ICP-OES measurements (Perkin Elmer, Optima 5300 DV). The filtered samples were diluted and topped with 300 μL HNO_3 (69 %). The ICP-OES was equipped with an Autosampler, Perkin Elmer, type ESI-SC-4 DX fast, and the data were processed with the software Perkin Elmer WinLab32. The rinse and standard internal solutions were 2 % HNO_3 and 10 mg/L of Yttrium. The DOC (Shimadzu DOC-L) was measured for every ligand solution to normalize the results with the exact DOC in the samples.

Synthetic vivianite and solids were characterized by determining the Fe/P ratio by digestion in 69% nitric acid with subsequent ICP-OES analysis. Attenuated Total Reflectance Infrared ATR IR spectroscopy (Bruker Alpha II) was measured by tightly pressing 1-2 mg of solid on the crystal. The received spectra were converted to transmission, baseline corrected using the rubberband method (64 points) and normalized to the highest intensity. X-Ray Diffractometry (XRD) (Bruker D8 Advance diffractometer) was performed by depositing the powder on a Si510 wafer, measuring with Cu Ka radiation (Coupled $\theta - 2\theta$ scan $5^\circ - 80^\circ$, step size $0.020^\circ 2\theta$, counting time per step 2 s), and using Burker software DiffracSuite.EVA vs. 6 for data evaluation. SEM (Scanning Electron Microscopy) (JEOL JSM-6480LV) was prepared by coating the solids with a 10 nm layer of gold at 15 Pa and 25 mA to make the surface electrically conductive. SEM was executed at 6 kV accelerating voltage, 10 mm working distance, and using JEOL SEM Control User Interface.

2.3. RESULTS

2.3.1 Solution chemistry

Phosphate dissolved from vivianite in the presence of organic ligands

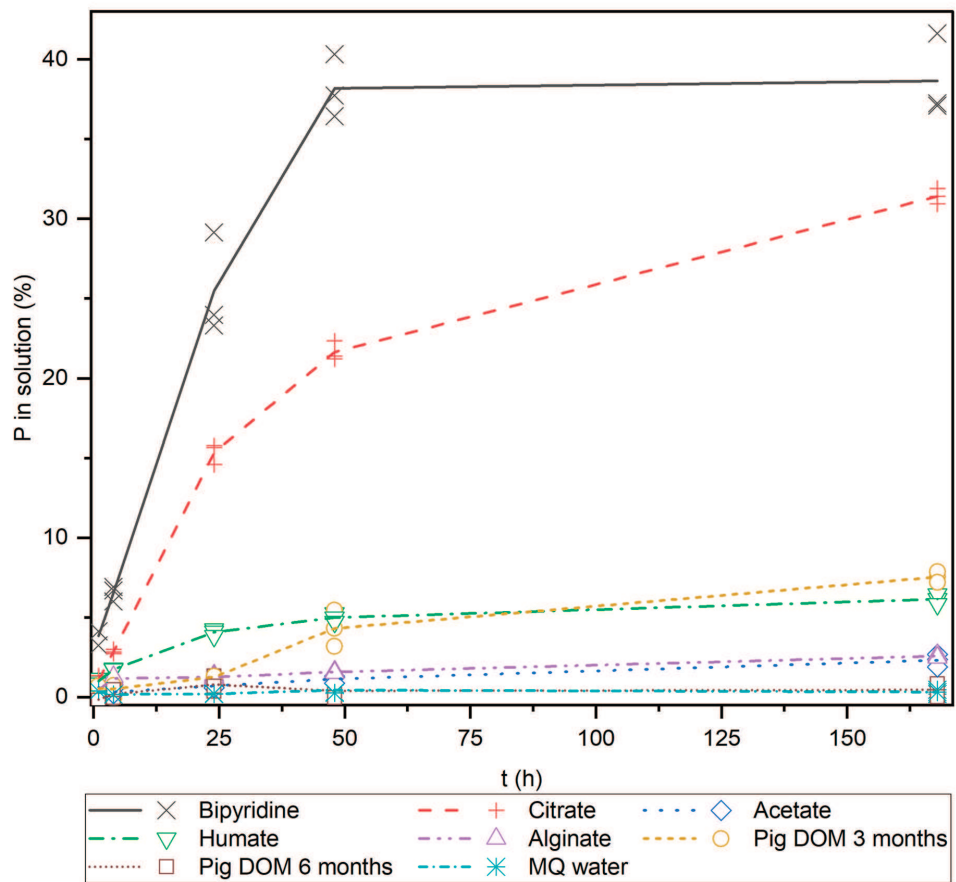


Figure 2-1: Phosphate dissolution from vivianite after addition of organic ligands (DOC 330 mg/L). Start concentration of vivianite was 60 mgP/L.

In the initial phase of this study, the evolution of phosphate concentrations in solution was monitored to assess vivianite dissolution in the presence of each organic ligand (Figure 2-1). The ligands could be grouped into three categories based on their effects:

- Bipyridine and citrate exhibited the most pronounced vivianite dissolution capacity. After one week, bipyridine and citrate dissolved 39% and 31% of the vivianite, respectively, based on solubilized phosphorus. Notably, equilibrium for citrate had not been

achieved even after one week, indicating continued dissolution potential (Figure A 2-2).

- Humate and three-month-old pig DOM induced moderate vivianite dissolution, with phosphorus release reaching up to 6% by the end of the experiment. Though both humate and 3-month-old pig DOM contributed to vivianite dissolution, their effects were minor compared to those of bipyridine and citrate.
- Acetate, alginate, 6-month-old pig DOM, and ultrapure water showed minimal impact on vivianite dissolution, with solubilized phosphorus concentrations remaining below 3% after 16 h. These ligands displayed negligible dissolution capabilities relative to the significant effects observed with bipyridine and citrate.

Phosphate left in the solution during vivianite formation in the presence of organic ligands

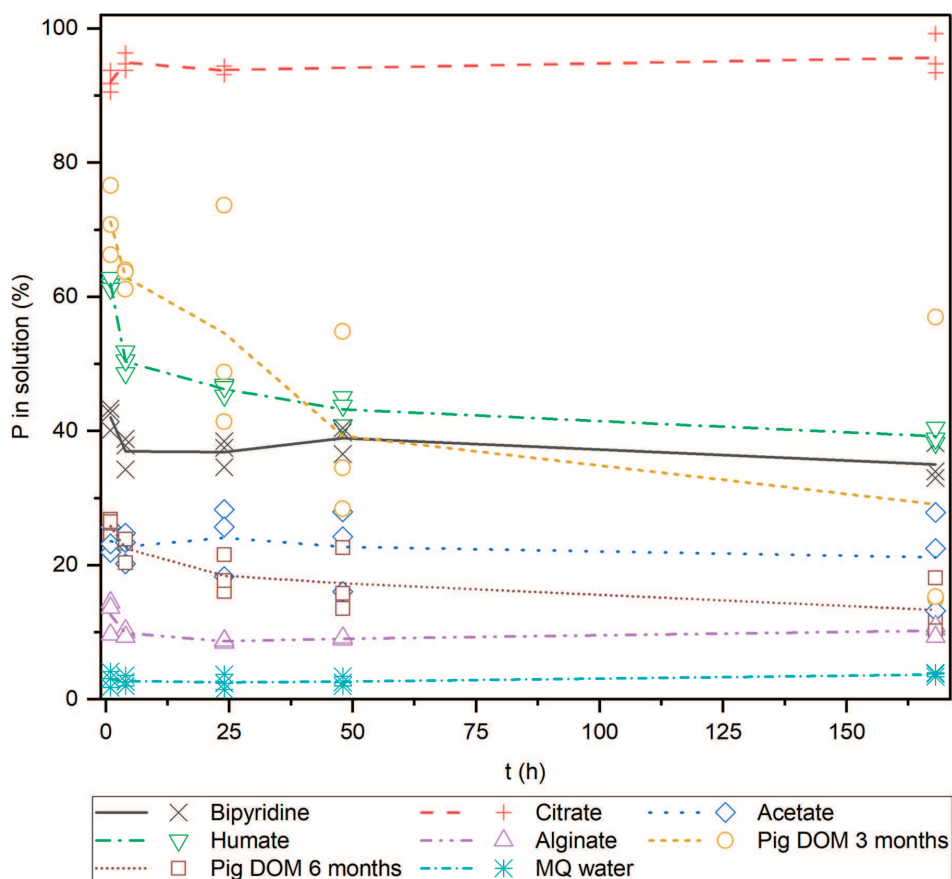


Figure 2-2: Influence of organic matter on vivianite formation, phosphate remaining in solution after start of crystallization experiment. Organic compounds were dosed at a DOC of 330 mg/L. Start concentration for phosphate was 60 mgP/L.

To assess the relationship between vivianite dissolution capacity and inhibition of vivianite formation by organic ligands, the phosphorus concentration in solution during vivianite formation was analyzed for each substance (Figure 2-2).

In the control with ultrapure water, where no organic ligands were present, nearly all phosphorus precipitated within the first hour, leaving about 4% in solution. In contrast, solutions containing organic ligands took longer to reach equilibrium, typically stabilizing after approximately 4 h. However, in both pig DOM solutions, phosphorus concentration continued to decrease significantly even beyond 48 hours. For humate, a slight decrease in phosphorus concentration was observed after 4 hours, with a gradual decline continuing up to 168 h.

Among the organic ligands, citrate displayed the strongest inhibitory effect on vivianite formation, retaining 96% of phosphorus in solution. Humate and bipyridine also substantially inhibited phosphorus precipitation, with 39% and 35% remaining in solution, respectively. In comparison, alginate, acetate, and the two pig DOM solutions demonstrated a milder inhibitory effect on phosphorus precipitation, with 10-20% of phosphorus retained in the solution.

2.3.2 Solid phase analysis

Precipitates were collected by centrifugation (Figure A 2-3) and subsequently analyzed using XRD, IR spectroscopy, and SEM patterns (Figure 2-3). XRD indicated the presence of vivianite in all recovered solids except for the precipitate from the 6-month-old pig DOM solution. This precipitate exhibited a high degree of amorphousness, as indicated by a broad hump centered around $20^\circ 2\theta$, which prevented clear identification by XRD.

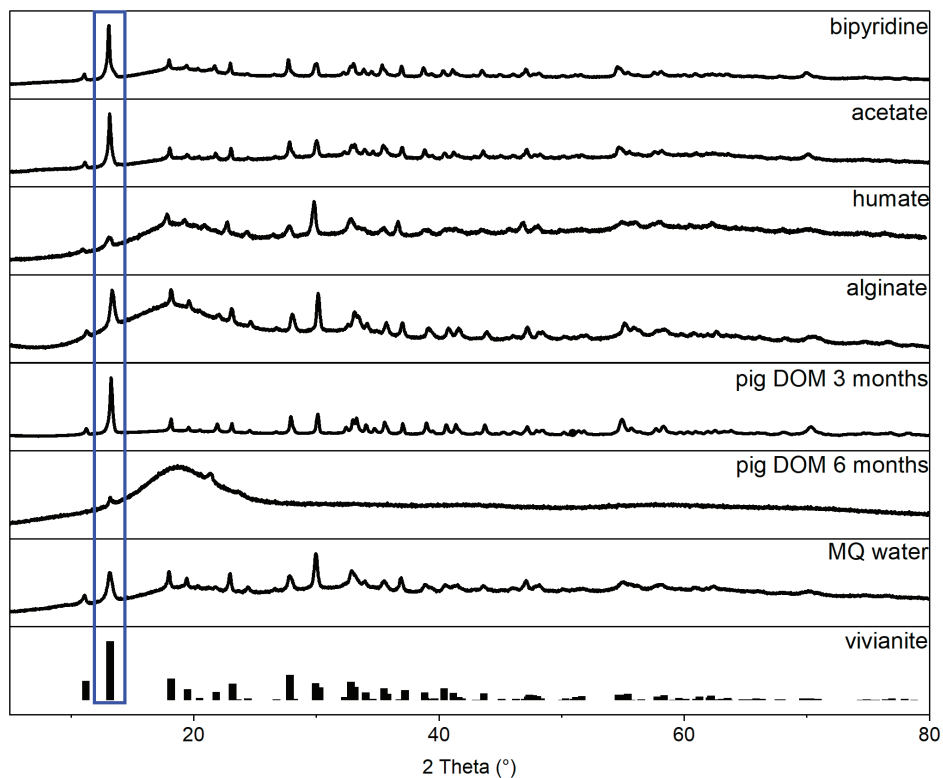


Figure 2-3: XRD patterns of vivianite formed in the solutions with different organic ligands, including a reference synthetic vivianite [34] (bottom). The blue box indicates the main reflex for vivianite.

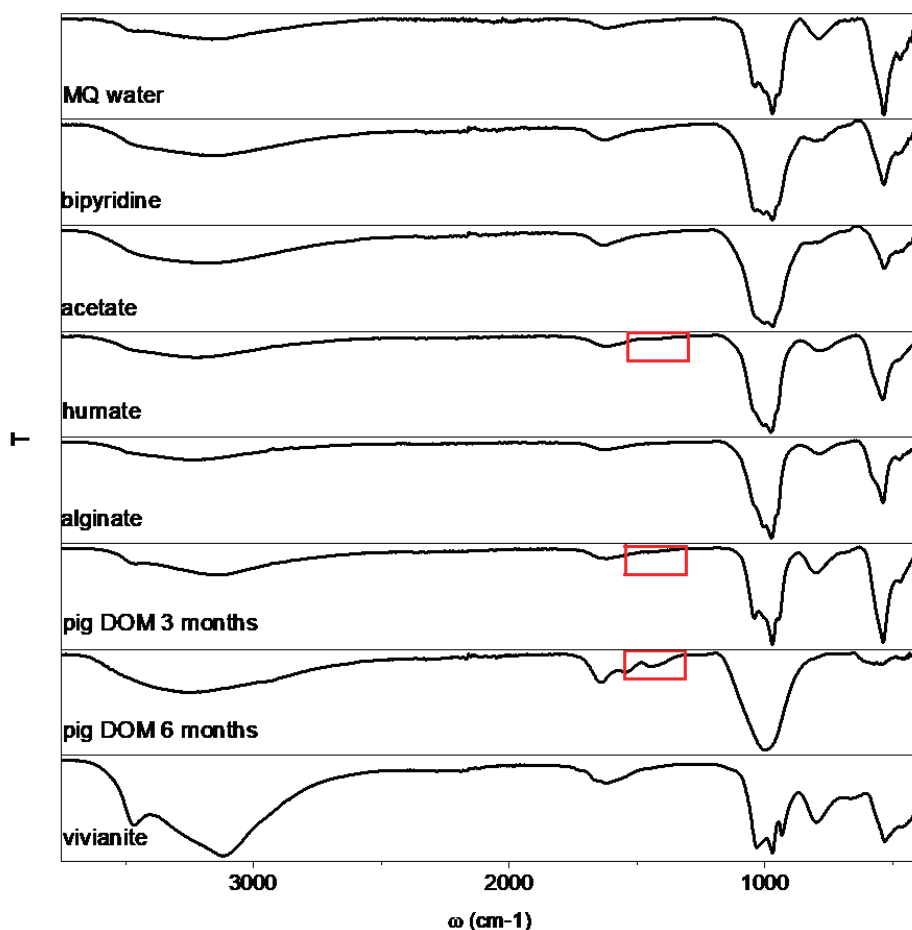


Figure 2-4: IR spectra of precipitates formed in ligand solutions after washing with ultrapure water with reference vivianite from the Ruff database [35]. Bands marked in red could stem from organic residue (Table A 2-3).

The IR spectra of all recovered precipitates, except for the 6-month pig DOM sample, displayed features consistent with the vivianite reference spectrum. Characteristic vivianite bands (Figure 2-4, Table A 2-3) include the hydroxyl stretching around 3200 cm^{-1} , HOH bending around 1600 cm^{-1} , P-O stretching bands near 1000 cm^{-1} , water librational vibrations around 800 cm^{-1} , and out-of-plane bends near 500 cm^{-1} [36]. Additional bands around 1440 cm^{-1} (highlighted in red in Figure 2-4) were noted in the spectra for humate and pig DOM precipitates. These bands correspond to organic carbon-related bonds, such as C-H scissoring, C=C breathing, and phenolic C-O stretching [37].

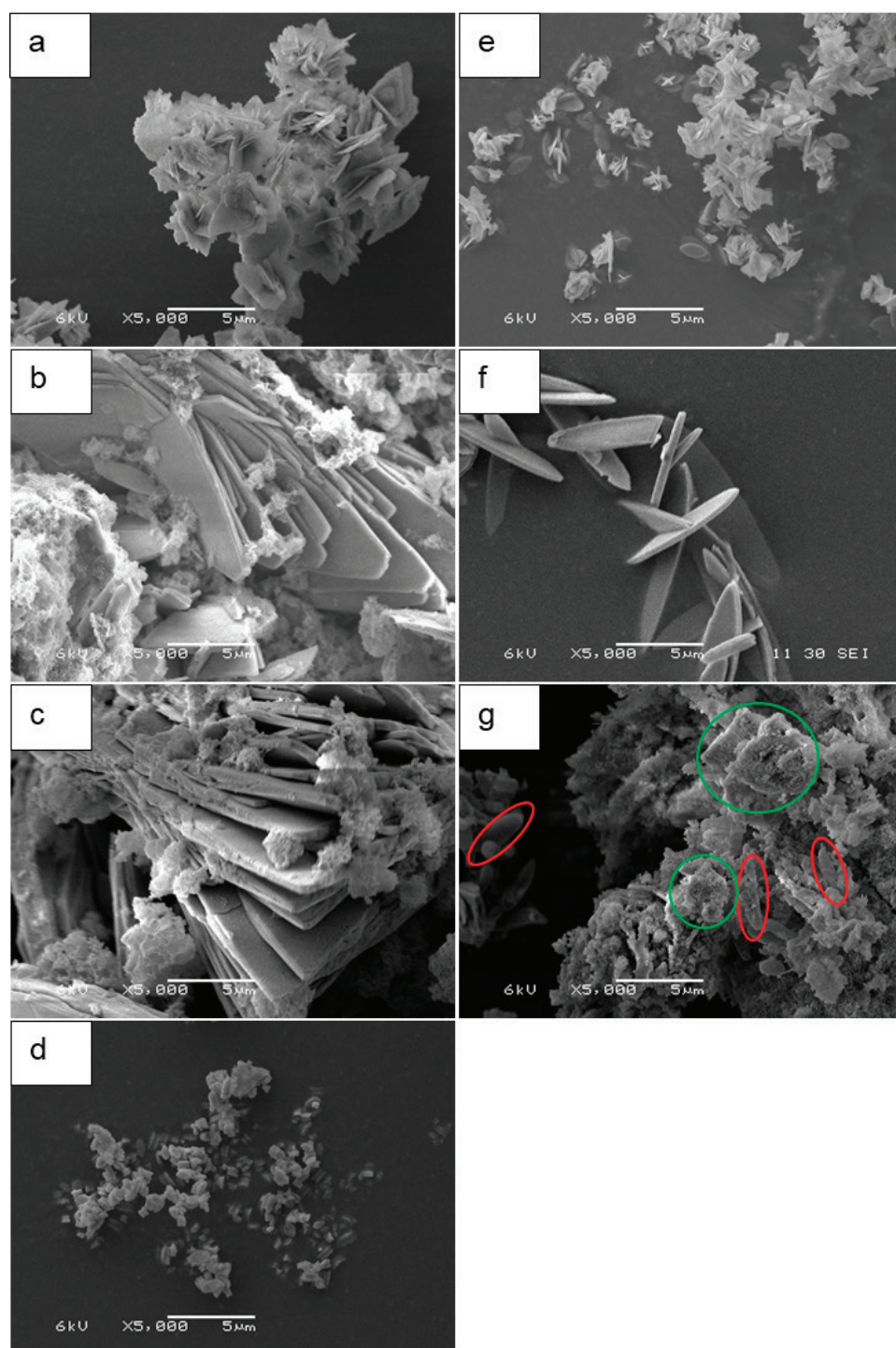


Figure 2-5: SEM images of precipitates formed in different organic solutions at 5000x magnification with (a) MQ water, (b) bipyridine, (c) acetate, (d) humate, (e) alginate, (f) pig DOM 3 months, (g) pig DOM 6 months.

The SEM images of precipitates formed from different ligand solutions are presented in Figure 2-5 at 5000x magnification to show the crystal structure and 2000x magnification in Figure A 2-6 to show precipitated flocks. In ultrapure water, vivianite predominantly forms small plate-like structures that assemble into flower-like clusters approximately 5 μm in diameter. When precipitated in bipyridine solution, two phases appear: one of small, rounded, porous aggregates, and another comprising elongated plates about 10 μm in length. Vivianite formed in an acetate solution shows a structure of larger, pointed, fan-shaped plates (over 10 μm) stacked in layers, with a secondary phase of small, rounded, porous formations interspersed.

In contrast, vivianite precipitated in humate, alginate, and 3-month-old pig DOM is composed of more isolated plates with rounded edges. For vivianite in alginate, small flower-like structures (1–2 μm) are observed, while the precipitate from humate shows accumulated, thicker plates less than 1 μm long. Plates formed in 3-month-old pig DOM are thin, roughly 10 μm in length, and occasionally assemble into flower-like formations. Meanwhile, vivianite precipitated in 6-month-old pig DOM yields a mix of thin, 2 μm long, vivianite-like plates (marked in red) and bigger flat plates (marked in green). Notably, only minimal precipitate was recovered from 6-month pig DOM samples following centrifugation, as shown in Figure A 2-3.

2.4 DISCUSSION

2.4.1 Comparison of Vivianite Dissolution and Formation potential of Organics based on DOC

Comparison of the ligand strengths

To evaluate the effectiveness of organic ligands in dissolving vivianite and inhibiting its formation, the molar phosphate concentration in solution was normalized against the molar DOC concentration (Table A 2-1). The amount of phosphate remaining in or released to the solution was used as an indicator for the extent of vivianite formation or dissolution. Phosphate was chosen as a proxy for vivianite processes because, in typical scenarios, all phosphate is associated with vivianite when not in solution, whereas iron can precipitate as something other than vivianite.

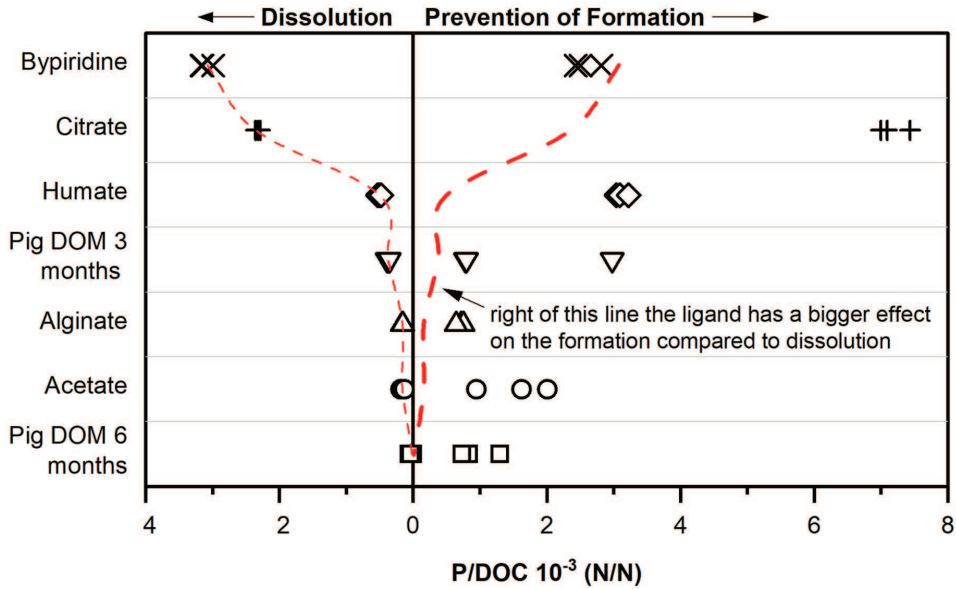


Figure 2-6: Comparison of the vivianite dissolution and vivianite formation inhibition capacity for 7 organic ligands. P in solution per DOC (N/N) of each organic solution after 168 h (Table A 2-1). Left part of the axis: Organics organized by their Vivianite dissolution strength. Right part of the axis: Respective Vivianite formation prevention strength with trendline pointing out Vivianite dissolution strength.

This is supported by the higher phosphorus-to-iron ratios observed in solution (Figure A 2-1) and the elevated Fe/P ratios in the recovered solids (Table A 2-3).

Figure 2-6 presents the normalized data, with vivianite dissolution shown on the left side of the x-axis and vivianite formation on the right. The organic ligands are arranged from strongest to weakest dissolution potential in descending order (indicated by a thin red line). This order is mirrored on the formation side of the graph, marked by a thick red line. If data points on the formation side fall to the right of the thick red line, this suggests that the ligand has a greater inhibitory effect on vivianite formation than its dissolution potential alone would predict.

The role of iron-binding strength

Vivianite dissolution in the presence of organic ligands is likely driven by the complexation of free iron in solution [11,21,24]. Given the low solubility of vivianite ($K_{sp} = 10^{-35.76}$ [3] (Equation 1)), the activity of dissolved iron and phosphate ions remains minimal at neutral pH:

$$K_{sp} = [\text{Fe}^{2+}]_{eq}^3 \cdot [\text{PO}_4^{3-}]_{eq}^2 \quad [\text{Equation 1}]$$

With $[Fe^{2+}]_{eq}$ and $[PO_4^{3-}]_{eq}$ the activity of iron and phosphate at equilibrium.

The addition of ligands induces vivianite dissolution by binding free iron in solution, thereby shifting the equilibrium toward further dissolution. The efficiency of a ligand in dissolving vivianite is generally related to its iron-binding strength, expressed by the complex formation constant

$$K_f = \frac{[Fe^{2+}_x OL_y]}{[Fe^{2+}]^x \cdot [OL]^y} \quad \text{[Equation 2]}$$

With $[Fe^{2+}]$ the iron concentration, $[OL]$ the concentration of the organic ligand and $[Fe^{2+}_x OL_y]$ the concentration of the iron-organic complex.

The ligand binding strength depends on the density and type of functional groups present [22]. Bipyridine, for instance, has a high affinity for iron (II) attributed to interactions between iron and the free electron pairs of the nitrogen [38]. Despite the high complex formation constant of bipyridine ($\log K_f = 17.5$ [39]), only 31% of iron could theoretically be complexed due to stoichiometric limitations, as each iron ion requires three bipyridine molecules for binding. However, bipyridine dissolved 38.5% of vivianite, possibly due to partially binding with fewer than three molecules.

Other ligands primarily bind iron through deprotonated carboxylic (COO⁻) and hydroxy (O⁻) groups. Citrate, with three carboxylic and one hydroxy group, has a strong affinity for iron, with a $\log K_f = 5.89$ for the $[Fe\text{-citrate}]^-$ complex [40]. Although citrate could theoretically complex all available iron, it dissolved only 31% of vivianite within the first week, suggesting equilibrium had not been reached (Figure A 2-2). Extended data indicates ongoing phosphorus release, aligning with findings by Gypser and Freese [21], who reported 80% phosphate release from vivianite over 8 weeks.

The iron-binding strength of acetate is low, with $\log K_f = 1.4$ for the $[Fe\text{-acetate}]^+$ complex [40], which explains its low potential to dissolve vivianite. Interestingly, some humate-metal interactions have been described to resemble acetate-type binding [41]. Nonetheless, humate dissolved more vivianite than acetate. However, humate is not only able to interact with iron through carboxylic groups but also via phenolate (ph-O⁻) and possibly sulfur or nitrogen-containing groups [30]. Yamamoto et al. [42] reported a $\log K_f = 5.8$ for iron-humate complexes at pH 5, which appears high since the iron citrate complex has a formation constant at a similar value, but citrate is dissolving significantly more vivianite. Gypser and Freese [21] similarly observed an 8% vivianite dissolution with humate at pH 6 and DOC of 546 mg/L, comparable to the 6% dissolution observed here. However, quantifying humate binding remains challenging due to its non-stoichiometric nature and dependence on origin.

In manure, iron is likely complexed by a mixture of polysaccharides, humate-like substances, and volatile fatty acids, with humate being the most potent among them. The capacity of 3-month-old pig DOM to dissolve vivianite likely reflects a humate-like composition of functional groups, while 6-month DOM, resembling alginate and acetate, showed minimal dissolution (Figure 2-1). The increased humate-like behavior in fresher manure is unexpected, as aging generally favors humate precursors and depletes biodegradable polysaccharides [43]. Further analysis of organic transformations during manure aging could clarify these shifts in functionality.

In summary, small ligands like citrate and bipyridine show high iron binding strength and effectively dissolve vivianite. While natural organic matter, such as humate, also binds iron, its binding strength is insufficient for significant vivianite dissolution via complexation. Similarly, manure-derived DOM exhibited limited complexing ability. These dissolution experiments suggest that organic ligands can induce vivianite dissolution and influence its formation; however, binding strength alone does not fully explain their impact on vivianite formation, as further discussed in the following section.

Table 2-1 Vivianite formation inhibition of acetate, humate and alginate in this study and literature with starting phosphate concentration, organic ligand (OL) concentration, Fe/P ratio and pH.

	inhibition %	P (mM)	OL (g/L)	Fe/P	pH	study
acetate	5	4	4.72	1.5	6	[18]
	10		9.44			
	25	2	0.82	1.5	8	this study
	4	10	0.1	1.5	7	[19]
humate	30	4	2.5	1.5	6	[18]
	70		3.5			
	30	5	1.8	1.5	6.5	[17]
	60		2.5	2		
	40	2	1	1.5	8	this study
alginate	12	10	0.8	1.5	7	[19]
	30	5	0.88	1.5	6.5	[17]
	25		1.77	2		
	12	10	0.8	1.8	8	[16]
	10	2	1.13	1.5	8	this study

Vivianite formation vs dissolution

For the organic ligands tested, aside from bipyridine, inhibition of vivianite formation appears more pronounced than their impact on vivianite dissolution. Previous studies have examined the role of ligands such as acetate, humate, and alginate in vivianite formation. When comparing findings, however, it is essential to consider not only the concentration

of these organic ligands but also variables including initial phosphate concentration, Fe/P ratio, and pH (Table 2-1).

The impact of acetate on vivianite has been shown to be minor [18], which aligns with its relatively weak iron-binding strength. In this study, however, the influence of acetate on vivianite formation was more pronounced, likely due to pH-induced iron oxidation effects. Under slightly alkaline conditions, iron(II) hydroxide precipitation is favored, and this phase readily oxidizes to iron(III) oxide [18,44]. Chen et al. also noted that acetate itself can enhance iron oxidation [18]. Iron oxide precipitates can still act as phosphate sinks through adsorption, which could have led to additional phosphate removal at pH 8 in this study in comparison to the results by Chen et al. at pH 6.

Similarly, humate displays a more substantial effect on vivianite formation than its iron-binding strength alone would suggest. In general, the inhibition of vivianite formation by humate intensifies with higher humate concentrations and lower phosphate levels (Table 2-1). In this study, 1 g/L humate and 2 mM phosphate concentrations were approximately half those used by Cui et al. [17] with 2.5 g/L humate and 4 mM phosphate. Yet, there seems to be a trend of around 40% inhibition in vivianite formation at 1 mmol phosphate per 0.5 g humate.

Alginate impeded vivianite formation by 10 % in this study which was slightly greater than would be expected based on its iron-binding strength. Zhang et al. [16] reported comparably low inhibition levels with 12 % inhibition at 0.8 g/L alginate, whereas Cui et al. [17] observed stronger inhibitory effects (30%) at 0.88 g/L. Cui et al. performed their experiments at a pH of 6.5, which might have increased the effect of alginate in their case. Nevertheless, the role of alginate in vivianite inhibition appears to be less critical than the one of humate [17].

Pig DOM also shows stronger vivianite formation inhibition than would be expected based on iron-binding strength. Vivianite formation in three-month-old pig DOM shows a response similar to humate, whereas formation in six-month-old pig DOM more closely resembles that with alginate. This indicates that the composition and aging of pig DOM may dynamically influence vivianite crystallization, potentially reflecting shifts in its organic profile with age.

In the next step, factors beyond iron-binding strength that impact vivianite formation are evaluated:

Iron-organic complexation occurs more rapidly than vivianite formation: Since vivianite formation is notably more efficient than vivianite formation, the process is unlikely to be thermodynamically driven. If iron-organic complexes form more quickly than

vivianite during its formation phase, this could lead to a supersaturation level insufficient for vivianite nucleation, thereby limiting its precipitation. Wei et al. observed that humate can reduce supersaturation through Mg^{2+} complexation in struvite crystallization [45]. Iron-organic complexation may offer a kinetic advantage over vivianite formation, as only one type of binding—between the functional group and iron—is necessary. In contrast, vivianite formation requires a more organized structure, with specific binding environments at two iron sites. Statistically, this organized arrangement is less probable than iron binding to the functional group of an organic ligand. Thus, this kinetic advantage alone could account for the discrepancy between the efficiencies of vivianite dissolution and formation.

Organic ligands binding to vivianite crystal nuclei: Li et al. [22] proposed that iron-humate binding might extend the Fe-O-P bond length within vivianite clusters. Coordination of an organic ligand to these clusters may destabilize them, thereby lowering the nucleation rate and size of vivianite crystals. Compared to precipitation in ultrapure water, vivianite formation in the presence of organic ligands was observed to be slower, supporting the hypothesis that organic-ligand interactions with crystal nuclei can impede nucleation. This reduction in nucleation rate due to organic binding to crystal nuclei could play a role in inhibiting vivianite formation.

Organics blocking crystal growth sites: Wei et al. [46] noted that humate blocked growth sites on struvite crystals, and Zhang et al. [16] suggested a similar role for alginate in vivianite inhibition. Since pig DOM contains polysaccharides, humate precursors, and various organic macromolecules, it is plausible that similar site-blocking effects could contribute to vivianite inhibition in this matrix. Such organic macromolecules may obstruct crystal growth sites, further hindering vivianite formation.

Evaluation of DOC as a base of comparison

In this study, the iron binding affinities of various organic compounds were investigated by examining the influence of dissolved organic carbon concentration on vivianite formation and dissolution. Using DOC as a normalization approach offers a practical advantage: since any organic substance in natural environments contains carbon, DOC analysis provides a feasible method for estimating iron binding across diverse systems. This approach aligns with the hypothesis proposed by Kleeberg et al. [13], which suggests that around 25% of iron in natural environments is bound to organic matter. However, our findings demonstrate variability in iron binding across different organic types. For instance, alginate limited vivianite formation by binding approximately 10% of iron, while pig DOM bound 10–20%, and humate displayed a higher binding potential, sequestering 40% of iron. These findings suggest that while Kleeberg's 25% assumption provides a rough approximation, individual organic compounds like humate may exhibit considerably higher iron binding capacities. This implies that sediment iron binding potential could be better

predicted by assessing humate content specifically, rather than assuming a uniform 25% binding capacity.

One limitation of normalization by DOC is its inability to account for the specific functional groups that influence iron binding strength, as binding affinities depend on more than just carbon content. While alternative quantification techniques could target these specific interactions, many were not feasible for this study. For example, pH titration can identify charged functional groups [45] but would overlook non-charged groups like nitrogen in bipyridine. Another approach, following the iron titration method of Gould and Genetelli [47], could capture all iron-binding components within each organic compound mixture, allowing a comprehensive comparison across organic solutions. Adjusting this method for systems containing iron, phosphate, and organics could, therefore, offer a more nuanced understanding of organic interactions with vivianite.

Ideally, the iron binding should be assessed in terms of stoichiometry; however, quantifying binding capacity in molar terms is challenging for some organics. While straightforward for small, defined compounds like bipyridine and citrate, it is less feasible for polymeric or complex mixtures like alginate, humate, and pig DOM. The latter contains macromolecules with variable structures, alongside biopolymers and smaller ligands, complicating efforts to standardize binding comparisons across organic types.

2.4.2 Precipitates vary in the presence of different organic ligands

The precipitates formed exhibit different characteristics, such as morphology and settleability after centrifugation (Figure 2-5, Figure A 2-3).

The crystal size of vivianite synthesized in acetate and bipyridine solutions appears to be larger than that of the vivianite formed in MQ water or in the presence of other organic ligands. This observation may be attributed to a reduction in supersaturation index (SI) caused by decreased soluble iron levels. Moreover, the secondary phase could be due to iron(III) oxide formation [18] as explained in section 2.4.1.

The morphology of vivianite precipitates varies when humate is present. For instance, Li et al. [19] documented flower-like structures with thin plates like those observed in MQ water, while Cui et al. [17] identified irregular shapes, and Chen et al. [18] observed compact, thick plates similar to those in this study. Considering humate iron binding seemed to depend on the type of humate, morphology may also be linked to humate type. Further, the concentration ratio of humate to phosphate appears critical, as demonstrated by Cui et al. [17].

At alginate concentrations above 400 mg/L with an initial phosphate concentration of 10 mM, Zhang et al. [16] observed morphological shifts in vivianite. In the present study,

however, alginate concentrations were approximately 1 g/L, with phosphate concentrations of 2 mM. Under these conditions, vivianite morphology largely resembled that in MQ water, albeit with smaller crystals. Organic adsorption on crystal surfaces could have contributed to smaller particle size and worse settling properties [16] (Figure A 2-3).

The elongated plate morphology of vivianite precipitated in three-month-aged pig DOM is similar to that observed in vivianite formed with manganese and magnesium under high salinity conditions [48]. While ICP analysis did not detect elevated magnesium in the precipitates, high salinity levels in pig DOM were evident. Organic adsorption onto the crystals may further influence morphological characteristics.

In contrast, vivianite formed in six-month-old pig DOM was less crystalline, as evidenced by the lack of clear XRD peaks, though a reflex within the characteristic vivianite region ($14^\circ 2\theta$) was present. SEM imaging revealed mixed phases, with some elongated plates resembling those in three-month pig DOM (circled in red), suggesting limited vivianite formation. The other precipitates observed could stem from organic matter as indicated by IR measurements and iron oxide formation. Elevated pH and volatile fatty acids, similar to the acetate solution conditions, could have contributed to iron oxide precipitation. One reason for decreased vivianite formation in 6-month-old pig DOM could be the prolonged induction time for vivianite crystallization, as proposed by Schott et al. [49] to explain the poor crystallinity of calcium phosphate in pig manure. During pig manure aging, compounds that extend the induction phase of vivianite crystallization could be formed.

The following factors influence the characteristics of vivianite crystals:

- **Saturation Index:** For optimal crystal growth, the SI of the solution must fall within the narrow meta-stable zone of vivianite [50]. If the SI is excessively high, precipitation occurs quickly, producing smaller, less crystalline solids. Conversely, if SI is too low, precipitation is unlikely. Iron-complexing ligands can reduce SI, helping to reach the meta-stable zone and thereby promoting larger, well-formed crystals.
- **Organic Adsorption on Vivianite:** Organic compounds can attach to the growth sites of vivianite, affecting crystal shape and size, as discussed in Section 2.4.1. During crystal growth, flat plates are stacked, forming step-like structures. Organic adsorption at these steps alters the energy required for further growth, potentially favoring rounded rather than plate-like shapes [51]. Adsorption can also block growth sites, leading to smaller crystals [22]. Additionally, adsorbed organics alter the surface charge of crystals; if the surface charge increases, repulsive forces between particles also increase, resulting in poorer settleability [46].
- **Interfering Ions:** Pig DOM and humate solutions contain various ions, such as Mg, K, and Ca, which may interfere with vivianite crystallization. These ions can block growth sites on crystals or be incorporated in the structure itself [48].

2.4.3 Outlook

We investigated the influence of iron binding strength on vivianite formation due to challenges in promoting efficient vivianite crystallization in manure. Previous studies have attributed limited vivianite formation to organic interference across various environments, including lake sediments [13], digested sludge [19], hydrothermal sludge [23], and urine [14]. This prompted us to explore a similar hypothesis for manure. However, our results suggest that dissolved organic matter in manure does not complex iron as extensively as anticipated. This led us to conclude that organics are sometimes overly attributed with influencing vivianite formation, and that studying organic effects within a complex matrix like manure is significantly more challenging than in controlled, clean conditions.

Through this work, we also gained insights into the behavior of specific organic ligands. Citrate, for example, often serves as an indicator of bioavailability [27]. In our study, a sustained release of phosphorus from vivianite was observed in presence of citrate, which aligns with previous research by Yang et al. [20] suggesting the potential of vivianite as a slow-release fertilizer. This finding may particularly renew interest in vivianite as a source of iron fertilizer in agricultural applications.

In lake sediments, where more recalcitrant organic compounds like humates are prevalent, iron binding is likely dominated by humates. Sediments also typically contain lower phosphate levels compared to digested sludge. Higher humate levels and lower phosphate levels could reduce vivianite formation since iron would be more likely to be bound by humate. Testing this hypothesis through a focused study on the composition and iron complexation behavior of lake sediment organic matter could provide valuable insights.

Our experiments indicate that the concentration of iron-complexing ligands in pig DOM is not high enough to significantly reduce iron and phosphorus precipitation from the solution. However, the morphology of precipitates formed in pig manure filtrate is substantially altered, suggesting that the influence of manure components on crystal formation may be both organic and inorganic. Further research into the specific organic and inorganic components in manure and their roles in crystallization processes would help clarify these interactions and optimize vivianite formation in complex matrices.

To mitigate the influence of organic ligands on vivianite formation, potential strategies should be explored. The carboxyl groups in compounds such as citrate and humate play a significant role in the binding of iron, increasing the affinity of these ligands for the metal. In matrices with high concentrations of such ligands, an effective approach could involve their separation prior to iron dosing using functionality-based resin adsorption. Alternatively, monitoring temporal changes in the iron-affinity of a given matrix – such as

manure in this study - could help to identify optimal conditions for vivianite precipitation. This, in turn, would enhance the efficiency of the process.

2.5 CONCLUSION

This study investigated the influence of the iron-binding strength of organic ligands in manure compared to other organic ligands known to affect vivianite chemistry. By normalizing the impact of different organics on their DOC concentrations, ligands of varying complexity were compared to their ability to dissolve or inhibit vivianite formation. Citrate strongly inhibited vivianite formation due to its high iron-binding affinity, while humate demonstrated the potential to kinetically outcompete vivianite formation. In contrast, pig DOM primarily affected the morphology and recoverability of precipitates but not due to the binding strength of the organics. These findings suggest that although iron-organic complexation can hinder vivianite formation, it is not always the primary mechanism behind reduced vivianite crystallization in complex matrices.

Acknowledgment

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SUPPLEMENTARY INFORMATION.

Table A 2-1 Vivianite Dissolution and Formation potential expressed in P/DOC 10-3 (N/N), with pH for each triplicate of each organic solution.

	Dissolution						Formation					
	DOC mM	pH	P/DOC 10-3 (N/N)	pH	P/DOC 10-3 (N/N)	pH	DOC mM	pH	P/DOC 10-3 (N/N)	pH	P/DOC 10-3 (N/N)	pH
Bypyridine	27.7	7.9	2.99	7.9	3.17	7.8	27.1	8.8	2.43	8.6	2.82	7.9
Citrate	27.0	8.3	2.29	8.4	2.36	8.4	26.7	8.4	7.00	8.4	7.09	7.6
Acetate	29.4	7.8	0.18	7.6	0.16	7.6	27.7	9.5	2.01	7.7	0.95	9.7
Humate	24.5	7.4	0.50	7.4	0.52	7.4	25.1	7.3	3.05	7.4	3.10	7.5
Alginate	32.6	7.2	0.16	7.7	0.16	7.6	29.0	6.9	0.72	6.9	0.75	6.1
Pig DOM 3 months	40.6	8.9	0.37	8.8	0.39	8.9	38.2	8.9	0.78	8.9	2.98	8.9
Pig DOM 6 months ultrapure	28.2	8.3	0.06	8.1	0.00	8.2	27.8	8.6	0.84	8.6	0.73	8.5
		7.1		7.2		7.3		6.6		5.8		6.3

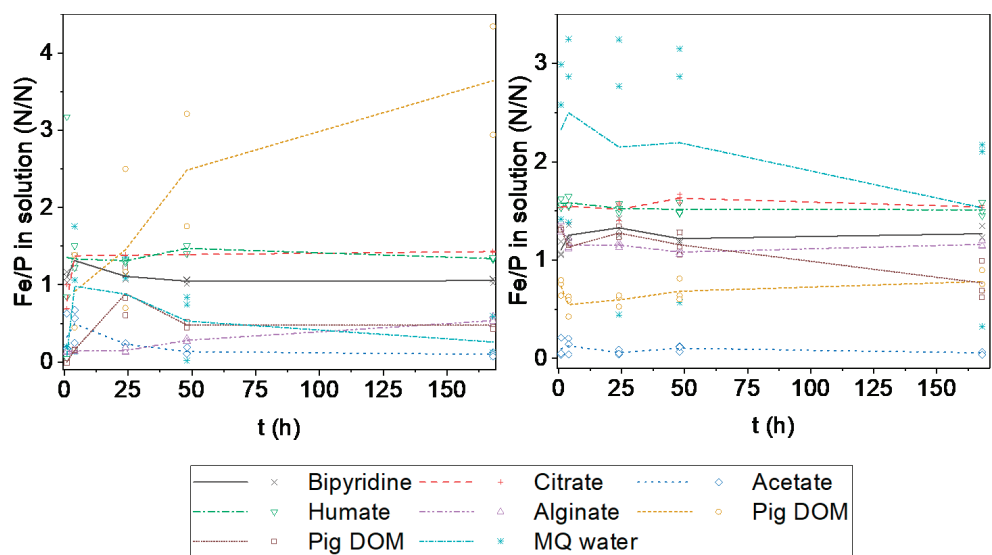


Figure A 2-1 Fe/P in solution during vivianite dissolution (a) and formation (b). If all the Fe and P that are not bound in vivianite were in solution, the ratio of Fe/P would be 1.5 according to starting concentrations and vivianite stoichiometry of 1.5. For some ligands, more P than Fe was in solution, $\text{Fe/P} < 1.5$. This means there is some extra Fe precipitated but not in the form of vivianite. Discrepancies could be explained by minor oxygen leakages and precipitation of Fe(III).

Table A 2-2 Fe/P ratio for one of the precipitates obtained after centrifugation of each organic solution. Ideally, Fe/P in vivianite is 1.5. Higher ratios indicate additional Fe precipitation which could be explained by minor oxygen leakages and precipitation of Fe(III).

Organic	Fe/P
Bipyridine	1.7
Acetate	1.8
Alginate	1.6
Humate	1.6
Pig DOM 3 months	1.8
Pig DOM 6 months	1.7
ultrapure	1.5

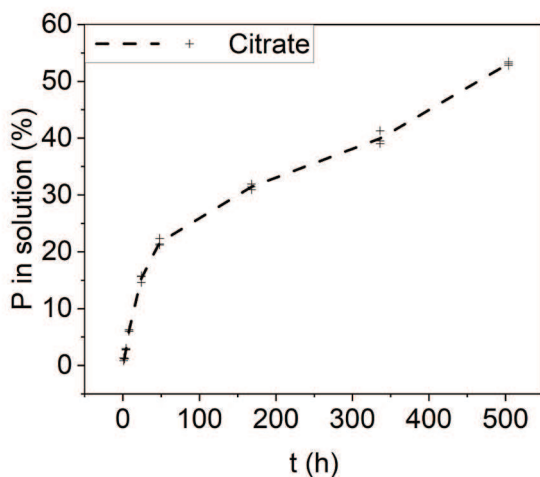


Figure A 2-2: P dissolved in citrate solution at DOC 330 mg/L until 504 h, line points out the average of citrate to guide the eye.

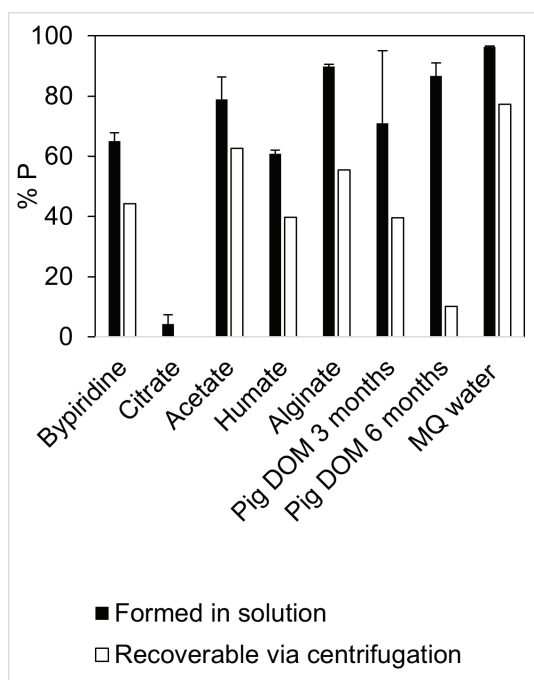


Figure A 2-3 Yield of precipitate before centrifugation (@ 4750 rpm, 10 min) based on the amount of precipitated P and after centrifugation based on the mass of vivianite (The error of recoverable via centrifugation was not established because triplicate precipitates were previously unified). About 80 % of the precipitated P could be recovered via centrifugation in ultrapure water and acetate. In bipyridine and humate solutions, roughly 65-70 % of the initial precipitate could be recovered. The yield of recoverable P in alginate and 3 months pig DOM is lower, around 55-60 %. Very little precipitate recovery was observed in 6 months pig DOM (11 % of the initial precipitate).

Table A 2-3 Attributions for vivianite in IR spectra from synthetic vivianite used in dissolution experiment and the vivianites formed during formation experiment according to Šijakova-Ivanova (2018).

Synthetic for dissolution	ultrapure	Bipyridine	Acetate	Humate	Alginate	Pig DOM	Vivianite Attribution
3465	3465	3477		3492	3467	3459	Hydroxyl stretching
3094	3160	3150	3190	3216	3146	3137	
1605	1597	1624	1633	1621	1617	1622	Water HOH (bending)
1036	1041	1040			1040	1040	PO (stretching)
966	1009	1005	1003	1005			
937	970	970	970	976	968	970	Water liberational
802	789	791	795	789	785	799	
530	536	532	532	538	532	536	Outplane bends
458	470	479	464	475	475	471	
666	715	691	684			686	Other
				1437		1457	

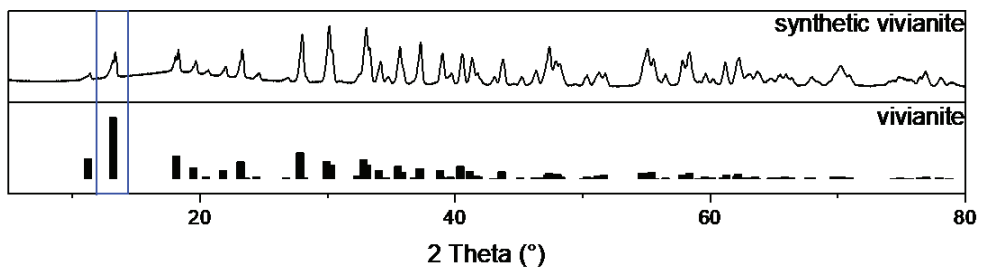


Figure A 2-4 XRD patterns of synthetic vivianite used in vivianite dissolution experiments with reference synthetic vivianite [26] (bottom). The blue box indicates the main reflex for vivianite.

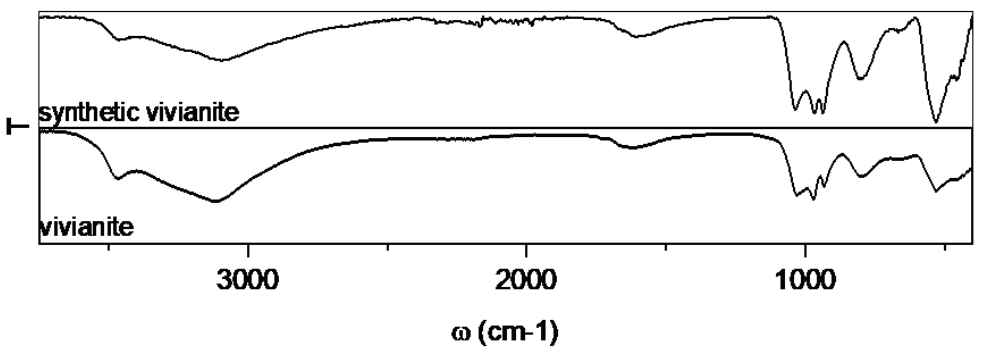


Figure A 2-5 IR spectra of synthetic vivianite used during dissolution experiment after washing with ultrapure water with reference vivianite from the Ruff database [27]. Bands marked in blue can be attributed to vivianite (Table A 2-3).

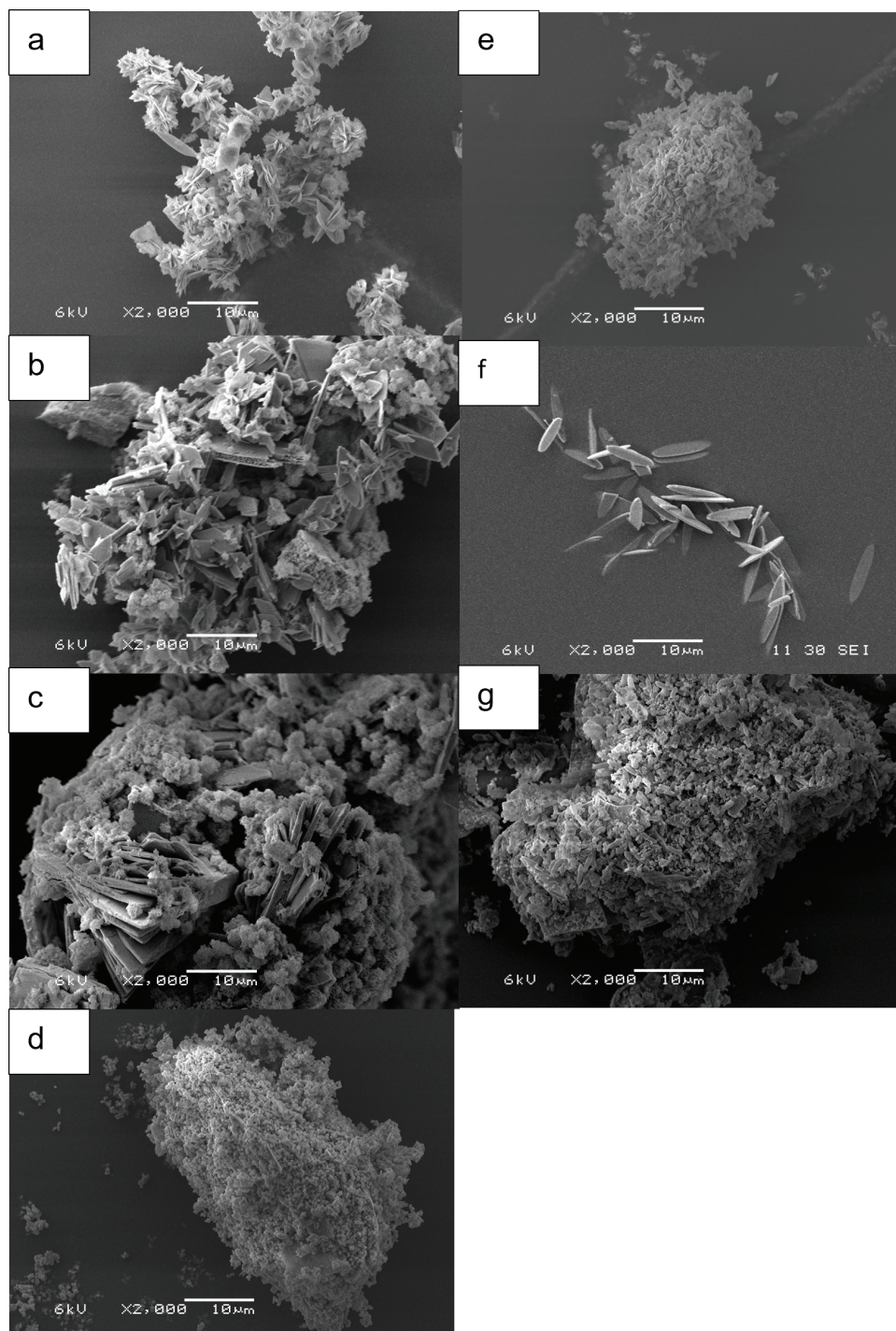


Figure A 2-6 SEM images of precipitates formed in different organic solutions with (a) MQ water, (b) bipyridine, (c) acetate, (d) humate, (e) alginate, (f) pig DOM 3 months, (g) pig DOM 6 months at 2000x magnification to show precipitated flocks.

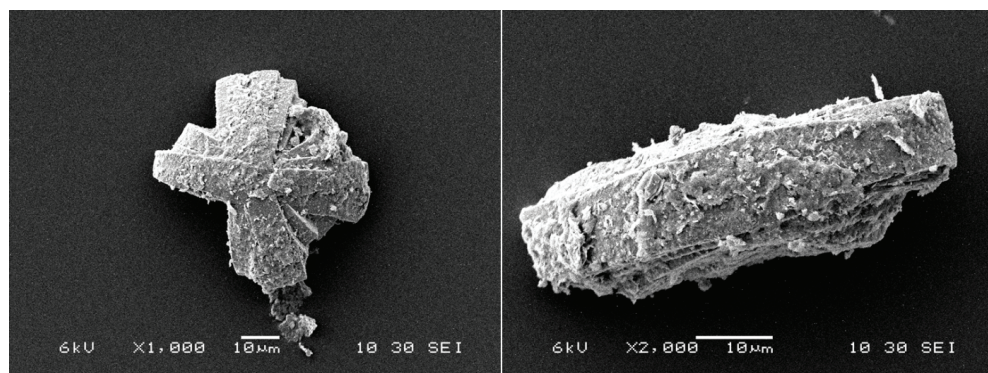


Figure A 2-7 SEM images of synthetic vivianite used during vivianite dissolution experiments.

Table A 2-4 Organics, with supplier, and weight concentration c in dissolution and formation experiment.

Organic	Supplier	c (g/L)
Trisodium Citrate	Alfa Aesar	2.61
2,2'-Bipyridine	Thermo Fisher Scientific	0.95
Acetic acid	VWR Chemicals BDH	1.83
Humic acid	Sigma-Aldrich	2.19
Sodium alginate	Sigma-Aldrich	2.52
Pig manure	pig fattener (4400 animals) Marum, the Netherlands, sampled January 2023, stored at 4 °C, used April 2023	

3

Phosphorus recovery from pig manure: elucidating the competition between vivianite and siderite formation

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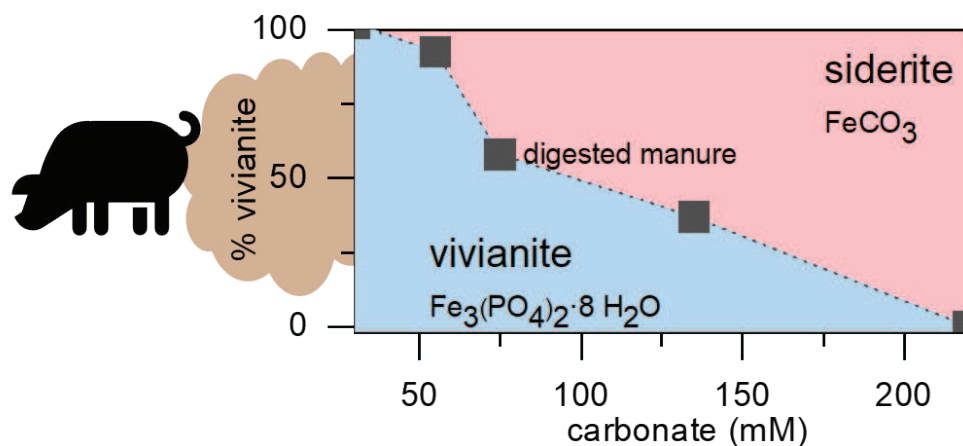
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ABSTRACT

Phosphorus runoff from agricultural land is a major driver of eutrophication, with manure serving as a significant source of phosphorus input. In regions such as the Netherlands, high livestock densities and limited land availability pose challenges for manure management, particularly in pig farming. Recovering phosphorus from manure and redistributing it to phosphorus-deficient areas offers a sustainable solution. This study explores phosphate recovery via vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) precipitation—a method previously demonstrated in municipal wastewater treatment plant sludge—and evaluates its applicability to pig manure. Vivianite formation was investigated in fresh, 4-month-aged, and digested pig manure, as well as in Thermal Hydrolysis Plant (THP) derived digested sewage sludge. A key finding is that high dissolved inorganic carbon (DIC) concentrations inhibit vivianite formation by promoting siderite (FeCO_3) precipitation. In digested manure, a DIC threshold of approximately 3 g/L HCO_3^- was identified, below which vivianite formation is favored. THP sludge, characterized by elevated DIC, exhibited similar inhibitory effects. More generally, vivianite was shown to form without significant competition with siderite if the DIC concentration is < 2.5 times Fe concentration. Experimental results were compared with thermodynamic predictions using Visual MINTEQ and experiments in ultrapure water, revealing discrepancies which may be attributed to the ionic composition in environmental matrices. Strategies such as combining ammonia and DIC stripping or targeting fresh manure were shown to enhance vivianite formation. These findings can be used to propose the integration of vivianite-based phosphorus recovery into broader resource recovery frameworks, including biomethane production, ammonium recovery, and carbon capture.

Graphical Abstract



3.1 INTRODUCTION

Phosphate fertilizers play a critical role in modern agriculture, with a substantial portion of phosphate input in European soils originating from manure application [1,2]. However, manure-based phosphorus (P) is often applied in excess, leading to runoff into surrounding water bodies. This runoff accelerates eutrophication, resulting in algal blooms and hypoxic conditions that threaten aquatic ecosystems, where phosphate is frequently the limiting nutrient [3,4]. Elevated phosphate concentrations are particularly prevalent in regions with intensive agricultural activity, such as the Netherlands, Belgium, Denmark, and northwestern Germany [1,2]. Regulatory restrictions on manure spreading in areas like the Netherlands have led to the export of surplus manure, which incurs additional costs and results in the loss of valuable organic matter [5,6].

To address this issue, phosphate recovery from manure and its reutilization as a secondary resource in phosphate-based industries has been proposed [7]. In manure, phosphorus predominantly exists as magnesium ammonium phosphate (struvite) and calcium phosphates, typically in particulate forms smaller than 150 μm in both cattle and pig manure [8,9]. Especially in the Netherlands, pig farmers are challenged by the high livestock density in pig farming and the increased amount of land necessary to dispose of the manure [10]. This intensification makes pig manure a particularly suitable target for nutrient recovery technologies, which could enable the redistribution of phosphorus from regions with surplus to those with a deficit. Commonly employed manure treatment methods include composting and solid-liquid separation followed by pelleting. However, due to the typically low nitrogen-to-phosphorus (N/P) ratio and high transportation costs, physical treatment alone is often insufficient to address nutrient imbalances and environmental concerns [11]. In recent years, thermochemical conversion technologies such as pyrolysis and hydrothermal carbonization have gained attention for their ability to mitigate odor, reduce greenhouse gas emissions, and eliminate pathogens, while simultaneously lowering the risk of water and soil contamination [11,12]. Despite these benefits, the resulting biochar and hydrochar exhibit considerable heterogeneity in elemental composition and phosphorus speciation [13], which complicates their direct use to make phosphorus-based products. Targeted phosphorus recovery from these materials often necessitates additional chemical extraction steps. In contrast, precipitation-based approaches—such as the formation of struvite or calcium phosphate—enable the recovery of phosphorus in a more defined mineral phase, offering a more controlled and efficient pathway for nutrient recycling [11]. Current precipitation techniques often involve acidification followed by reprecipitation with alkaline salts, a process that entails substantial chemical consumption [7,14,15]. A promising alternative lies in transforming these phosphorus precipitates into a single mineral phase—vivianite ($\text{Fe(II)}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$)—through iron dosing. Vivianite, a paramagnetic iron phosphate mineral, is known to form under anaerobic conditions and has been successfully recovered magnetically at pilot scale from

sewage sludge digesters [16–18]. Its thermodynamic stability within pH 6–8 [19] renders it a potentially favorable sink for phosphate, offering a recovery method that circumvents the need for heavy acidification and reprecipitation.

Initial proof-of-principle experiments demonstrated that vivianite indeed forms in pig manure at laboratory scale, with most phosphate recovered at a Fe/P molar ratio of 4.5 [20]. This is considerably higher than the optimal Fe/P ratio of 1.6–1.9 reported for sewage sludge, which is itself only slightly above the theoretical stoichiometric ratio of 1.5. The need for elevated iron dosing in manure not only increases chemical costs but also leaves behind iron-rich residues that may limit the agronomic value of the treated manure [21]. The underlying cause of this inefficiency remains unclear, necessitating further investigation into iron interactions within manure. Sulfide has been identified as a thermodynamically favored competitor for iron binding over phosphate [22], but sulfur content alone does not fully account for the high iron requirements observed. Insights from sediment studies suggest that organic matter may sequester iron, potentially limiting its availability for vivianite formation [23,24]. However, recent findings indicate that dissolved organic matter in manure does not bind iron strongly enough to impede vivianite precipitation [25]. Given that neither sulfide precipitation nor organic complexation fully explains the observed inefficiency in vivianite formation, additional factors must be considered. Thermodynamic modeling in this study indicates that under elevated levels of dissolved inorganic carbon (DIC), the formation of ferrous carbonate (siderite) is thermodynamically favored, potentially outcompeting vivianite precipitation. While the influence of DIC on struvite and calcium phosphate formation has been previously explored [26–28], its role in the competition between siderite and vivianite in manure systems has not yet been addressed.

In this study, DIC is used to describe carbonate chemistry relevant to mineral precipitation. However, DIC is closely related to alkalinity, a parameter more commonly used in agricultural contexts. Under the near-neutral pH conditions typical of manure and sludge, alkalinity is primarily governed by bicarbonate (HCO_3^-), the dominant DIC species. Therefore, DIC serves as a chemically precise proxy for alkalinity in this context. This work investigates the impact of DIC on vivianite formation across manure matrices with varying DIC concentrations and proposes mitigation strategies to enhance phosphate recovery, including DIC stripping and targeting low-DIC substrates.

3.2 MATERIAL & METHODS

3.2.1 Pig manure preparation and characteristics

Fresh pig manure was collected in September 2023 from the Tijs farm located in Hoge Hexel, the Netherlands (3900 feeder pigs with straw bedding). The experiment with fresh manure was conducted shortly after collection. To simulate manure aging under controlled conditions, fresh manure was stored in a jerry can equipped with a gas exhaust system at ambient laboratory temperature (23 °C) for a period of four months. Notice that, in the Netherlands, approximately 30% of manure was stored in pits as of 2020, with the remainder managed through systems such as solid-liquid separation or deep litter bedding [29]. On Dutch pig farms, manure was typically retained in storage pits for durations ranging from six months to one year [30]. Given that ambient outdoor temperatures in the Netherlands are generally lower than laboratory conditions, the elevated temperature during laboratory storage may partially compensate for the shorter retention time. Consequently, this setup approximates the partial anaerobic digestion that occurs during pit storage, albeit under more controlled and accelerated conditions. In addition, mono-digested manure from the same source, collected at the same time, was used in a separate set of experiments conducted in May 2024. The digester temperature was 38 °C with a retention time of 40 days [31]. The composition of these three manure types—fresh, 4-month-aged, and digested—is summarized in Table 3-1.

Table 3-1 Total elements of microwave-digested and soluble fraction of 0.45 µm filtered fresh, 4-month-aged, and digested manure.

c (g/kg dried)	Fresh manure	4-month-aged manure	Digested manure
total elements (N=3)			
Mg	20 ± 1	16 ± 2	26 ± 1
P	18 ± 1	14 ± 2	30 ± 1
Fe	1.9 ± 0.2	1.4 ± 0.2	18 ± 1
S	14 ± 1	11 ± 2	23 ± 1
Ca	29 ± 2	26 ± 5	41 ± 1
TS (g/kg)	123 ± 1	132 ± 2	55 ± 1
VS (g/kg)	98 ± 1	101 ± 2	35 ± 1
mg/L			
soluble fraction (N=3)			
Mg	570 ± 20	352 ± 4	30 ± 1
P	7.9 ± 0.3	11.9 ± 0.4	17 ± 1
Fe	-	-	22 ± 1
S	540 ± 20	540 ± 80	112 ± 1
Ca	290 ± 30	61 ± 2	12.6 ± 0.5
K ⁺	5550 ± 40	6140 ± 40	5510 ± 80
Na ⁺	1770 ± 50	1910 ± 50	1610 ± 90
Cl ⁻	3580 (N=1)	3650 ± 40	2730 ± 40

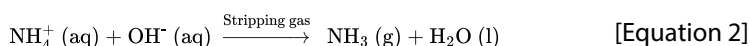
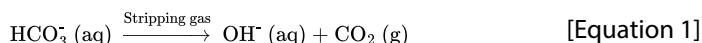
Table 3-1 Total elements of microwave-digested and soluble fraction of 0.45 μm filtered fresh, 4-month-aged, and digested manure. (*continued*)

c (g/kg dried)	Fresh manure	4-month-aged manure	Digested manure
NH_4^+	7040 (N=1)	7220 $\pm$ 40	7530 $\pm$ 30
HCO_3^-	6700 (N=1)	19500 (N=1)	23000 $\pm$ 2000
pH	7	7.7	8.7

Stripping digested manure

Unlike fresh and aged manure, digested manure can contain a more heterogeneous mixture of feedstocks [32] and is often supplemented with additives, such as iron salts (Table 3-2), to suppress hydrogen sulfide emissions [33]. Despite this complexity, digested manure offers operational advantages for phosphorus recovery, including lower solids content and wider adoption of anaerobic digestion for biogas production [34]. Integrating vivianite-based phosphate recovery into existing digestion infrastructure presents a promising pathway for circularity.

To enhance vivianite formation and minimize excessive iron dosing, DIC was removed from digested manure via gas stripping (Figure A 3-1). This process involved purging 1.5 L of digested manure in a 5 L bottle with nitrogen gas under continuous magnetic stirring (Heidolph), while collecting the stripped CO_2 in a 0.1 M NaOH solution. This method facilitates the combined removal of ammonia and CO_2 without using a base to increase the pH (for ammonia stripping), or an acid (for CO_2 stripping) (Equations 1 and 2). Overall, the pH increased during the process, implying that the protonation of DIC cost more protons than the deprotonation of ammonium (Figure A 3-1).



Samples (200 mL + 5 mL for analysis) were collected after 0 h, 24 h, 48 h, 96 h, and 168 h of stripping. As CO_2 removal increased the pH, samples were acidified to pH 8 using 2 M HCl (Titrand) to optimize conditions for vivianite formation [19], with the resulting DIC concentrations ranging from 30 mM to 220 mM.

3.2.2 Iron dosing experiments

In fresh, 4-month-aged, and digested manure

To investigate the prevalence of struvite, vivianite, and siderite under varying concentrations of dissolved inorganic carbon (DIC), a series of iron dosing experiments were conducted using three distinct manure matrices: fresh manure, 4-month-aged manure, and stripped digested manure. Iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) from a 10.7 M stock solution was introduced in the manure, first at a stoichiometric Fe/S molar ratio of 1 to fa-

cilitate sulfur binding, and then at a Fe/P ratio of 1.5 to promote vivianite formation. Iron addition was performed gradually with intermittent stirring to mitigate foam formation resulting from gas release. All treatments were conducted in triplicate, alongside control samples without iron addition. The experimental vessels were sealed, connected to a gas exhaust system, and incubated at room temperature on a rotary platform shaker (Heidolph Unimax 2010) operating at 100 rpm for a duration of up to two weeks. Sampling (5 mL per time point) was performed at regular intervals to monitor soluble elements, ammonium, and DIC concentrations. By monitoring the soluble phase, dissolution and precipitation processes can be tracked, inferring information on phase transformation in the solid phase. Since the experiments on the different manure types were performed sequentially, the sampling times were readjusted for each experiment. The soluble phase did not change much after 48 h in the fresh manure experiment, which was executed first. Therefore, the 4-month-aged experiment was terminated after 384 h, and after 48 h for digested manure, the latter reflecting a more practical timeframe for applied settings. The complete overview of experimental volumes and sampling time points is provided in Table 3-2. At the final sampling point, 50 mL were withdrawn from each bottle for solids analysis to determine the different mineral phases in the sample and quantify the amount of vivianite and siderite.

Table 3-2 Iron dosing experiments in different manure, with manure volume, batch type, iron dose added to the manure, and soluble phase sampling points.

	V (L)	batch type	Fe added (g/L)	soluble phase sampling times (h) (for ICP)
fresh	0.5	triplicate with blank	7.9	1, 2, 3.5, 6, 24 [*] , 48 [^] , 168 [^] , 336 [^] , and 504 [*] h
4-month-aged	0.5	triplicate with blank	6.8	1, 6 [^] , 24 [*] , 48 [^] , 192 [^] , and 384 [*] h
stripped		0, 24, 48, 96, 168 h		
digested	0.2	stripped	5.6	1, 4, 24, and 48 h

*sampling points include NH_4^+ , ^sampling points include DIC

In ultrapure water

To isolate the role of DIC without the complexity of manure matrices, additional experiments on vivianite formation were conducted in ultrapure water. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6 \text{H}_2\text{O}$) from the water authority Aa & Maas in the Netherlands (via Aquaminerals) was used as phosphorus feedstock. In a glovebox ($\text{DO} < 0.1 \%$), NaHCO_3 was added at different DIC concentrations (3, 30, and 300 mM) to 100 mL serum bottles containing struvite (5 mM of P), and the pH was adjusted to 8 (Table A 3-1). Iron was added from the 10.7 M $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ stock solution at a stoichiometric Fe/P ratio of 1.5 (7.5 mM Fe). The ultrapure system used 10-fold lower concentrations of both struvite and iron compared to the manure experiments, in order to limit pH shifts in a system with limited buffering capacity. Therefore, the struvite-to-DIC ratios in the 3 and 30 mM DIC experiments were comparable to those in fresh and aged manure, respectively. The bottles were shaken at

room temperature at 100 rpm for two weeks. Aliquots (1.5 mL) were collected at 0.5 h, 1.5 h, 3.5 h, 6 h, 24 h, 48 h, 168 h, and 336 h for analysis.

3.2.3 Characterization

For soluble phase analysis, samples were centrifuged at 4750 rpm for 10 minutes (Beckman Coulter, Avanti J-15R), and the supernatant was filtered through 0.45 μm syringe filters (Millipore). Elemental concentrations were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Thermo Scientific iCAP Pro, with yttrium standard). Ammonium was quantified using ion chromatography (Metrohm Compact IC Flex 88), and DIC was determined via total organic carbon analysis (TOC-L CPH, Shimadzu) [27,28].

Manure total elemental composition was assessed via microwave digestion of 2 mL wet samples in 69% HNO_3 using a sludge and solids protocol (180 $^{\circ}\text{C}$ for 15 minutes) (Milestone Ethos Easy) [27,28], followed by ICP-OES analysis.

For solid phase analysis, the final samples (50 mL) were centrifuged at 4750 rpm for 10 minutes and imported into a glovebox with N_2 atmosphere (25 $^{\circ}\text{C}$). The supernatant was decanted inside the glovebox, the solids were spread out in petri dishes, and dried under an aluminum cover with small holes for aeration to minimize light exposure of the samples. Characterization included the following:

- Scanning Electron Microscopy (SEM; JEOL JSM-6480LV) coupled with Energy Dispersive X-ray Spectroscopy (EDX; Oxford Instruments x-act SDD Energy Dispersive X-ray spectrometer) to investigate morphology and elemental distribution [35,36]. Small pieces of the dried manure were stuck on the SEM-EDX holder in the glovebox, but air-exposed when mounting the samples in the apparatus. Samples were then gold-coated (10 nm) under vacuum (15 Pa, 25 mA), and measurements were taken at 12 kV with a 10 mm working distance. Data acquisition and analysis were performed using JEOL and Aztec software.
- X-Ray Diffraction (XRD; PBruker D8 Advance diffractometer), to investigate crystalline phases as previously done on digested sludge [35], was performed on samples ground in the glovebox, and sent for measurement in parafilm-sealed tubes, but air-exposed during analysis. Powders were mounted on Si510 wafers, scanned with Cu K α radiation (5 $^{\circ}$ –80 $^{\circ}$ 2 θ , 0.008 $^{\circ}$ step size, 2 s/step), and analyzed using Bruker DifraccSuite EVA software.
- Mössbauer Spectroscopy, to speciate and quantify iron phases as has previously been established for digested sludge samples [35,37,38]. Measurements were performed at 295 K, with conventional constant acceleration or sinusoidal velocity spectrometer, using a $^{57}\text{Co}(\text{Rh})$ radioactive with a $\alpha\text{-Fe}$ as calibration reference. Samples were ground and sealed in the glovebox before exporting them outside for measurements. For the 4-month-aged manure, additional measurements were conducted at 4 K due to

unclear vivianite signals at room temperature. At this temperature, magnetic ordering permits more definitive phase identification due to sextet formation [39]. Spectra were analyzed using MossWinn 4.0 [40].

The phosphate fraction bound to the iron in vivianite detected with Mössbauer Spectroscopy was estimated using Equation 3:

$$\% P \text{ vivianite} = \frac{(\% Fe \text{ vivianite A} + \% Fe \text{ vivianite B}) \bullet \text{total Fe}}{1.5 \bullet \text{total P}} \bullet 100 \% \quad [\text{Equation 3}]$$

With % Fe vivianite A and B as determined by Mössbauer spectroscopy, total Fe and P, the total molar concentration of the element determined at the end of the experiment, and the factor 1.5 reflects the molar Fe/P ratio typical of stoichiometric vivianite. The error on this value was calculated using Gaussian error propagation and assuming an error of 3 % on total elemental concentrations based on the error margins in Table 3-1.

3.2.4 MINTEQ calculations

Visual MINTEQ was used to simulate how vivianite precipitation in fresh, 4-month-aged, and stripped digested manure is affected by varying DIC and NH_4^+ concentrations. Model inputs were based on measured elemental compositions (Table 3-1) and ion chromatography results for Na^+ , Cl^- , and K^+ . DIC and NH_4^+ concentrations could only be measured in the liquid phase. However, XRD indicated the presence of these ions to also be present in the solid phase, as calcite and struvite respectively (Figure 3-2). Hence, the input for CO_3^{2-} was the sum of DIC and the equimolar concentration of total calcium assuming most calcium was bound in calcite, and the input for NH_4^+ was the sum of soluble NH_4^+ and the equimolar concentration of total phosphorus assuming most phosphorus was bound as struvite. For HS^- total sulfur was input assuming most sulfur to be present as sulfide in the anaerobic conditions of the manures (section 3.1). Simulations were conducted at the final pH of each experiment, using the Specific Ion Interaction Theory (SIT) modeling [41], with details provided in Table 3-3.

Table 3-3 Input values for MINTEQ calculations based on the SIT ionic activity model, with varying DIC and ammonium values. List of possible solids: $\text{Ca}_3(\text{PO}_4)_2$ (am2), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (s), Mackinawite, Vivianite, Struvite, Siderite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (s), Calcite, Magnesite, $\text{Fe}(\text{OH})_2$ (am).

		c (mM)					
		digested manure					
component	fresh	4-month-aged manure	30 mM DIC	55 mM DIC	75 mM DIC	135 mM DIC	220 mM DIC
CO_3^{2-}	200	410	90	115	135	195	280
NH_4^+	460	460	50	100	200	345	430
Fe^{2+}	140	120	135	120	115	115	115
PO_4^{3-}	70	60	80	70	60	50	55
HS^-	55	45	55	50	40	35	40

Table 3-3 Input values for MINTEQ calculations based on the SIT ionic activity model, with varying DIC and ammonium values. List of possible solids: $\text{Ca}_3(\text{PO}_4)_2$ (am2), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (s), Mackinawite, Vivianite, Struvite, Siderite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (s), Calcite, Magnesite, $\text{Fe}(\text{OH})_2$ (am). (continued)

	c (mM)						
Ca^{2+}	90	90	120	75	70	60	60
Mg^{2+}	100	90	85	75	65	55	55
K^+	140	155	140	140	140	140	140
Na^+	75	80	70	70	70	70	70
Cl^-	200	200	290	290	290	290	290
pH	7.0	7.5	7.1	7.3	7.6	7.6	7.9

3.3 RESULTS & DISCUSSION

3.3.1 Vivianite vs siderite formation in manure

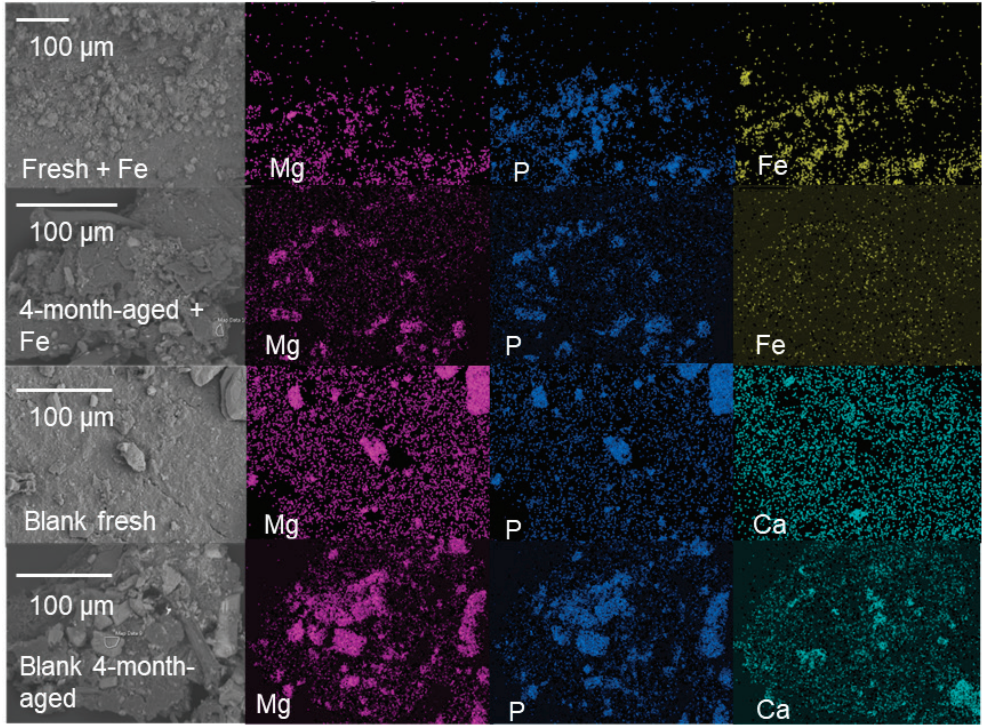


Figure 3-1 Electron microscopy images of iron-dosed fresh manure and 4-month-aged manure, as well as respective blanks. The EDX maps of Mg, Ca, Fe, and P highlight the presence of phosphate as vivianite in the iron-dosed fresh manure, and as struvite in the others.

The presence of phosphate in fresh and 4-month-aged manure with and without iron addition was studied by SEM-EDX analysis (Figure 3-1). Elemental mapping revealed a

predominant co-localization of magnesium and phosphorus in the blank manures, suggesting that magnesium-bound phosphorus is the dominant P species in both fresh and 4-month-aged manures. The morphology of these phosphorus-rich regions, characterized by well-defined, box-like structures, is consistent with struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystals (Shaddel, 2019). This interpretation was corroborated by X-ray diffraction (XRD) data (Figure 3-2), which confirmed the presence of struvite and showed the presence of calcite in the blank samples. A notable feature in the XRD patterns is the broad hump with the struvite peak at approximately $20^\circ 2\theta$, suggesting potential structural disorder in struvite, or the presence of poorly crystalline or ultrafine particles. Most of the phosphorus is likely present as struvite. Based on the elemental composition of the manures (Table 3-1), there is enough magnesium to bind all the phosphate in struvite (struvite Mg:P = 1). Nevertheless, the presence of calcium phosphate is not uncommon in manure [42] and a small amount of the phosphate could be bound to calcium in this manure, since SEM-EDX imaging revealed a few particles in fresh manure where calcium and phosphorus signals overlapped.

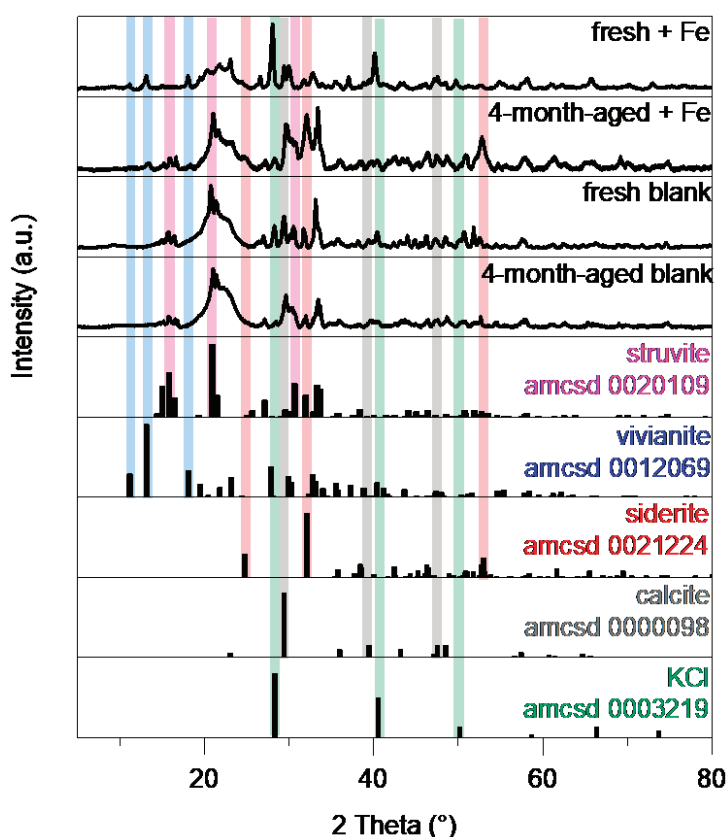


Figure 3-2 Baseline corrected XRD patterns of blank and iron amended fresh and 4-month-aged manures with the identified crystal phases [70].

Upon iron addition, the iron precipitated in both fresh and 4-month-aged manure, with a quicker precipitation in the latter (Figure A 3-2). Moreover, the DIC decreased in both manures, with a bigger decrease for the 4-month-aged manure. In the fresh manure, roughly 80% of the magnesium was released into the solution within 24 h, indicating the dissolution of struvite (Figure A 3-2). The pH dropped from 7.0 to 6.8 in the fresh manure and 7.7 to 7.2 in the 4-month-aged manure over the course of the experiment. The SEM-EDX analysis of the solids shows a co-localization of iron and phosphorus elemental maps in the fresh manure. The iron and phosphorus maps are congruent with round shapes approximately 10-20 μm in diameter, indicating vivianite. In the 4-month-old manure, the predominant magnesium and phosphorus co-localization was observed, as in the blank manures, indicating struvite. The iron distribution in this sample appeared more diffuse, with a reduction in high-density agglomerates that would indicate mineral formation. XRD patterns revealed the disappearance of struvite reflexes in fresh manure, with new peaks appearing, corresponding to vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). Moreover, reflexes that are likely attributed to KCl are more intense in this sample, which could be related to the sample containing more liquid before it started drying. Both K^+ and Cl^- concentrations are high in the liquid phase of the manure and are deposited during the manure drying process. In contrast to the fresh manure, the 4-month manure retained some struvite and calcite but also exhibited weaker vivianite signals. Notably, an additional crystalline phase corresponding to siderite (FeCO_3) emerged in the 4-month-aged manure.

Table 3-4 Distribution of Fe species according to Mössbauer analysis at 295 K measurements of fresh manure and 295 K and 4 K measurements of 4-month-aged manure, with isomer shift (IS), quadrupole splitting (QS), magnetic field (B), line width (LW), and related Fe spectral contribution percentage (% Fe). The last column shows the estimated percentage of P in vivianite based on vivianite quantification from Mössbauer analysis. Errors: IS, QS, LW ± 0.01 mm/s; B ± 1 T; % Fe ± 3 %.

	T	Fe species	IS (mm/s)	QS (mm/s)	B (T)	LW (mm/s)	% Fe	% P in vivianite
Fresh manure	295 K	vivianite A	1.14	2.37	-	0.35*	23	97
		vivianite B	1.22	2.91	-	0.35*	41	
		Fe(III)/ Is Fe (II)	0.47	0.59	-	0.55	36	
4-month-aged manure	295 K	vivianite A	1.16	2.41	-	0.32*	19	49
		vivianite B	1.19	2.81	-	0.32*	13	
		siderite	1.23	1.85	-	0.31	37	
		Fe(III)/ Is Fe (II)	0.38	0.68	-	0.51	31	41
		vivianite A	1.56	1.86	28	0.62*	13	
		vivianite B	1.51	2.21	16	0.62*	14	
4-month-aged manure	4 K	Fe(III) vivianite A	0.54	-0.36	43	1.30*	9	
		Fe(III) vivianite B	0.57^	-0.49	49	1.30*	15	
		low spin Fe (II)	0.43	1.58	-	1.19^	26	
		siderite	1.43	-	17	1.16 ^	26	

*fixed same line width for vivianite A and B contributions, ^fixed parameters

The Mössbauer spectroscopy analysis, presented in Figure 3-3 and Table 3-4, further elucidated the nature of iron speciation in Fe-dosed fresh and 4-month-aged manures. For both manures, vivianite was identified at 295 K by the presence of two distinct doublets representing the two unique Fe(II) environments within the vivianite structure with one iron atom in site A and two iron atoms in site B per unit cell [43]. These doublets can be identified as vivianite with isomer shifts (IS) of 1.16 and 1.20, and quadrupole shifts (QS) of 2.45 and 2.91 in the literature [44]. In fresh manure, the Mössbauer fitting suggests that 64 % of the total iron was present as vivianite. Based on Equation 3, this would account for 97 ± 6 % of the total phosphorus. The remaining 36% of iron was attributed to either Fe(III) (such as oxidized vivianite [37] species or low-spin Fe(II), possibly arising from iron sulfides. Given that most phosphate would be bound in vivianite based on the Fe (II) vivianite A and B contributions alone, and that iron sulfides are thermodynamically favored under reducing conditions [22], this portion of the iron is likely present as an iron sulfide phase, in agreement with previous studies [45]. Moreover, studies on digested sludge assumed the stoichiometry of Fe/S to be 1 [35] which is a typical stoichiometry of iron sulfide phases [46]. The calculations of the percentage of iron bound to sulfur based on this stoichiometric ratio and the measured elemental composition of manure, the sulfur concentration would account for 37 % of the total iron, consistent with the Mössbauer-derived value of 36 %.

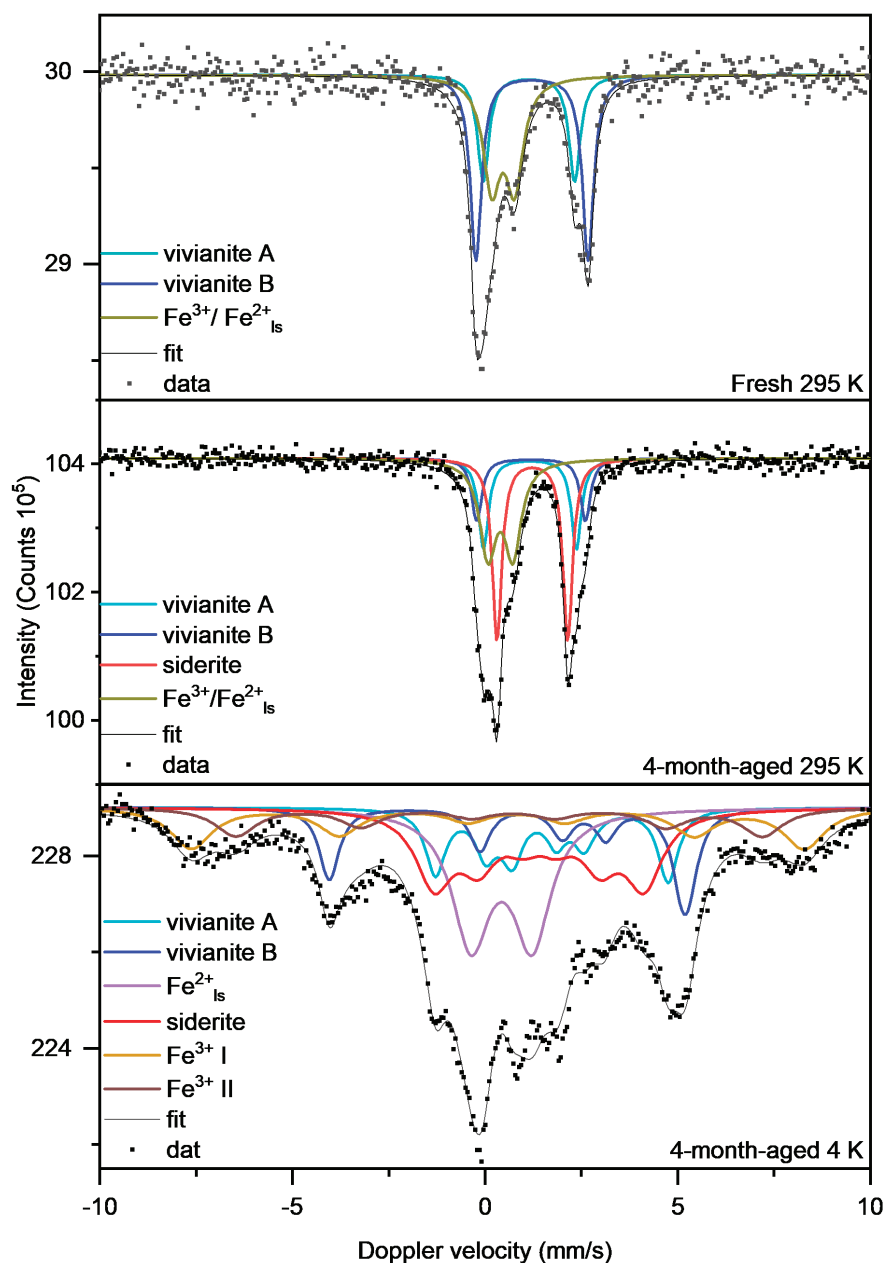


Figure 3-3 Mössbauer spectra at 295 K of fresh manure and at 295 K and 4 K of 4-month-aged (4-m) manure with fitted iron phases.

Vivianite could also be observed in 4-month-aged manure. While the parameters are well aligned with literature [44], the distribution between the two vivianite sites A and B is not according to the stoichiometric ratio. Theoretically, site B should have double the contribution of site A, since two iron atoms are in site B and one is in site A as defined for the

vivianite crystal structure. However, here, the site A contribution is 1.5 times higher than site B. Partial substitution of iron by magnesium could explain this distortion [47], but could not be proven with SEM-EDX (Figure A 3-3). A preferred oxidation at site B could explain the smaller contribution of this site in 4-month-aged manure better. Counting only iron(II) vivianite contributions 49% of the phosphate would be bound as vivianite. To improve iron phase discrimination, low-temperature (4 K) Mössbauer measurements were conducted. However, the complexity of the spectrum increased, likely due to fine particle size and compositional heterogeneity [48]. At 4 K the two fully split sextuplets of vivianite can be identified, indicating that 27% of total iron was in vivianite, translating to ~41% of the phosphate present. In this case, the site ratio A/B was one, still indicating a reduced contribution of site B as observed at 295 K. Oxidation of the vivianite remains a likely explanation for this, with Fe (III) contributions clearly distinguishable in the 4 K spectrum (light and dark brown lines for oxidation in site A and B respectively in Figure 3-3). Adding Fe(II) and Fe(III) components, the total amount of iron would be 22 % in site A and 29 % in site B. Even then, the B/A ratio is only 1.3, so impurities such as magnesium remain an option even though since SEM-EDX might not have been sensitive enough to detect them.

A substantial difference between the fresh and 4-month-aged manure iron speciation is the siderite present in 4-month-aged manure, accounting for approximately 36% of the total iron content, as determined by Mössbauer spectroscopy. The isomer shift and quadrupole splitting closely match the characteristic values reported for siderite (IS=1.22, QS=1.80) [49] confirming its presence. The competitive formation of siderite and vivianite has been documented in both natural and engineered environments. For instance, Chen et al. (2022) observed reduced phosphate precipitation in the presence of equimolar concentrations DIC and phosphate in synthetic kitchen waste, suggesting that DIC can compete with phosphate and thus inhibit vivianite formation [50]. The presence of siderite in the same place as vivianite has also been reported in lake sediments and has been related to pH, with vivianite prevailing at pH 6 and siderite at pH 8 [51]. However, the nature of the composition in iron-dosed manure is very different from lake sediments, with magnitudes higher concentrations of iron, phosphate, and carbonate. In the present study, the pH was 7.0 in fresh manure and 7.2 in 4-month-aged manure at the end of the experiment, which is a minor difference compared to the concentrations of these ions, and therefore unlikely to be the dominant factor influencing the iron phase formation. Instead, the markedly higher DIC concentration in the aged manure—approximately 320 mM (20 g/L HCO_3^-) compared to 110 mM (7 g/L HCO_3^-) in the fresh manure—likely shifted the chemical equilibrium toward siderite precipitation. Similar observations were made for calcium phosphate granulation in cow manure [27]; and struvite formation in dairy manure [52] where a high DIC precipitated the calcium and magnesium cations instead of phosphate. With the experiments here, it is shown that the inhibitory effect of DIC in manure also extends to ferrous phosphate formation.

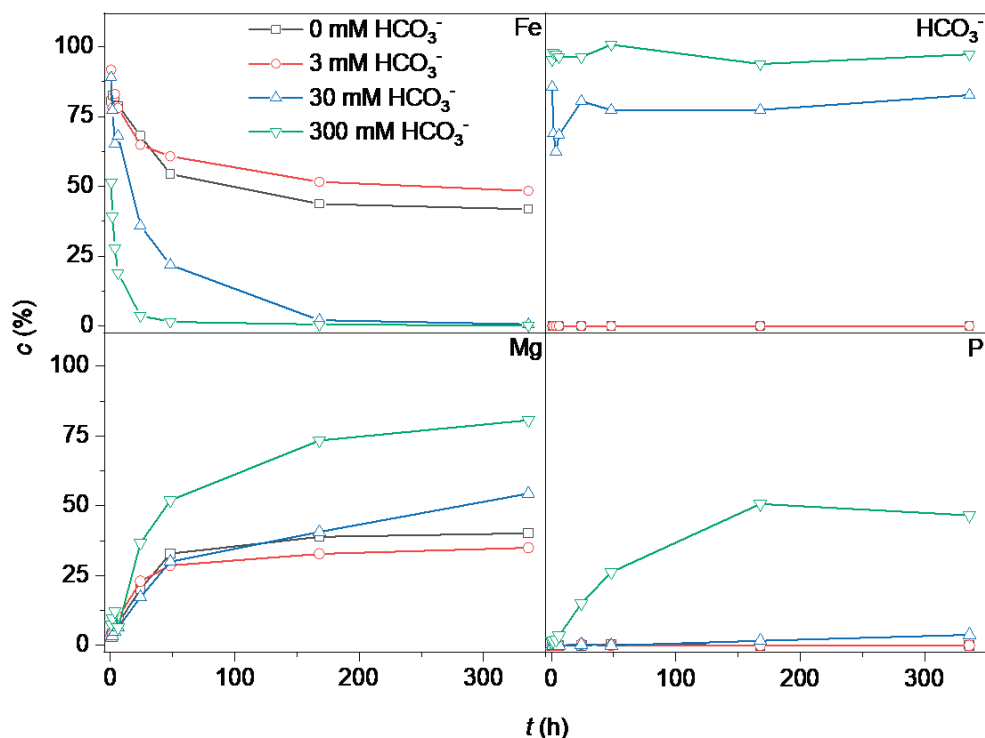


Figure 3-4 Time-dependent concentrations of dissolved species in ultrapure water at varied NaHCO₃ concentrations, with 5 mM struvite, 7.5 mM FeCl₂, and pH 8.

3.3.2 Vivianite vs siderite formation in ultrapure water

To reproduce the influence of DIC on struvite dissolution and vivianite formation, precipitation in ultrapure water with increasing DIC concentrations (3, 30, 300 mM) was evaluated. The temporal evolutions of iron, magnesium, phosphorus, and DIC in the liquid phase are presented in Figure 3-4. The results indicate that increasing DIC concentrations accelerate iron precipitation in the form of siderite. Concurrently, magnesium and phosphorus—initially present as struvite—were released into solution as struvite dissolved. Notably, higher DIC concentrations led to a more pronounced release of both ions. This observation is in contrast with the results from iron dosing in 4-month-aged manure, where elevated DIC did not result in significant phosphorus and magnesium release. The DIC of the 30 mM sample displayed an interesting pattern, with the DIC decreasing at the beginning only to increase again after 24 h. This suggests that first DIC precipitated as siderite and then redissolved. The pH decreased in the 3 and 30 mM experiments from 7.7 to 7.3 and 7.8 to 7.5, respectively, and slightly increased in the 0 and 300 mM samples from 7.5 to 7.6 and 7.9 to 8.1, respectively. A decrease in pH could be due to the addition of FeCl₂, an acidic salt, and due to the deprotonation of bicarbonate during siderite formation. Struvite dissolution, however, increases the pH due to the release of deprotonated phosphate. Vivianite formation should not change the pH much since the depro-

onated phosphate would be incorporated into the vivianite structure. It seems struvite dissolution is the dominant factor influencing the pH in the 0 and 300 mM samples, while siderite precipitation seems to mainly influence the pH in the 3 and 30 mM samples.

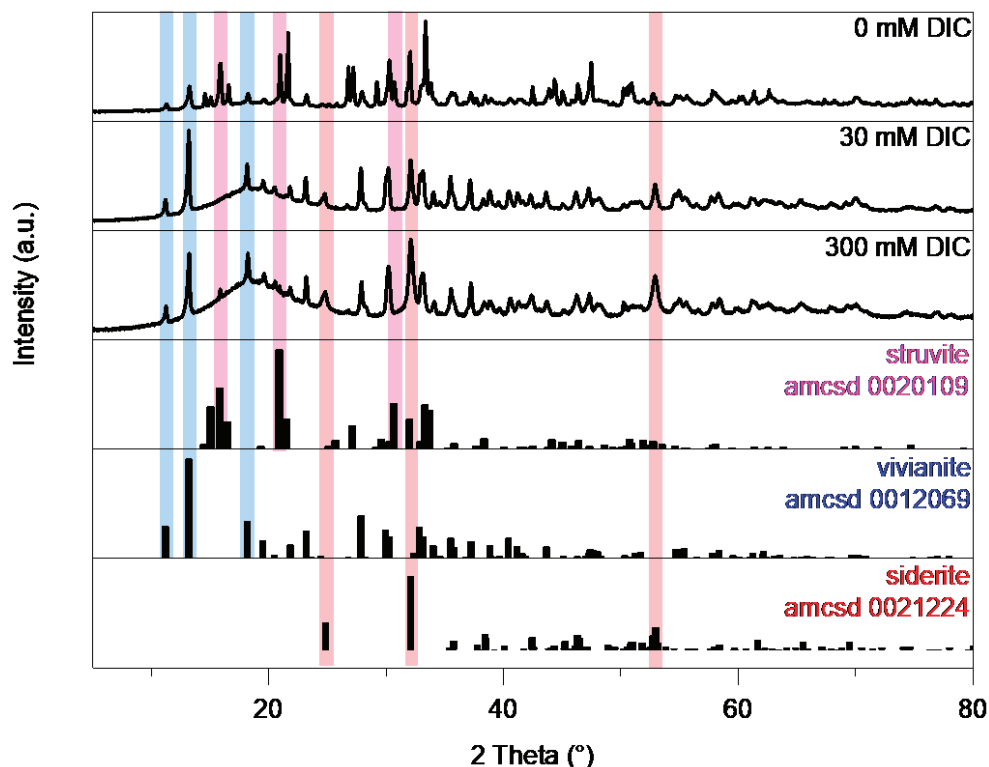


Figure 3-5 Baseline corrected XRD patterns of the precipitates in the vivianite vs siderite formation experiment in ultrapure water with varied NaHCO_3 concentrations, 5 mM struvite, 7.5 mM FeCl_2 , and at pH 8, together with the identified crystal phases [70].

X-ray diffraction analysis (Figure 3-5) supported the trends observed in the liquid phase. Siderite reflections were detected at elevated DIC, confirming that both carbonate and phosphate were competing for iron under these conditions. However, at low DIC concentrations, vivianite reflections were relatively weak, while higher DIC concentrations corresponded with diminished struvite. At the highest DIC levels, a broad hump in the XRD patterns between 15° and 25° 2θ suggested the formation of an amorphous or nanoparticulate phase which could be related to the precipitation of fine iron minerals or the dissolution of struvite to small particles.

Despite the qualitative similarities, notable discrepancies exist between the ultrapure water system and the manure matrix. One key difference was, as mentioned in 3.2, that struvite and iron were less concentrated than in manure. Moreover, the higher ionic

strength in manure will influence the solubility of the ions and crystallisation in the system. Generally, an increased ionic strength decreases the activity coefficient of ions and their likelihood to precipitate. However, if more ions of the same type are present, they are more likely to precipitate [53]. In fresh manure, more vivianite precipitation than in the ultrapure system was observed, which could be due to the higher concentration of iron that was added to the solution. Nevertheless, assessing the effect of ionic strength is more complicated due to the diverse composition of ions in manure.

Another notable difference between the ultrapure system and the manure system is the counter ion of carbonate. Sodium bicarbonate was used in the ultrapure system, whereas DIC is known to balance out ammonium in manure matrices [54]. Given that struvite solubility is sensitive to the concentrations of its constituent ions—magnesium, phosphate, and ammonium—the high ammonium levels in manure (Table 3-1) are likely to suppress struvite dissolution at higher DIC. Modeling the experimental conditions in ultrapure water at pH 8 using MINTEQA2 confirmed that increasing ammonium concentrations theoretically reduce the extent of struvite dissolution, as indicated by dissolved magnesium (Figure A 3-4). In the absence of ammonium, struvite dissolution could be increased in the presence of DIC due to the formation of dissolved magnesium carbonate and bicarbonate complexes. MINTEQA2 predicted all magnesium to be dissolved at 300 mM DIC using sodium as a counter ion, with 36 % present as magnesium bicarbonate and 10 % present as magnesium carbonate. Hence, the choice of the carbonate counter ion plays an important role in reproducing the manure system in ultrapure water. However, in the case of fresh manure, ammonium concentrations are similarly elevated as those in 4-month-aged manure (390 mM and 400 mM, respectively). Therefore, the high DIC seems to play a more significant role in preventing vivianite formation from struvite than high ammonium concentrations in solution.

3.3.3 DIC stripping of digested manure

Since a high DIC seems to be the main reason for the absence of vivianite formation in manure systems, working with fresh manure could be recommended. An alternative could be progressively removing DIC from aged or digested manure, which can even be combined with ammonia stripping of digested manure, reducing both DIC and ammonium in the manure (section 2.2). Figure 3-6 presents Mössbauer spectra of the solids of five iron dosed digested manure samples subjected to ammonia stripping, hence with different DIC levels. Relevant Mössbauer parameters are summarized in Table 3-5. Consistent with previous observations in fresh and 4-month-aged manure, iron speciation in digested manure was dominated by phosphate-, sulfide-, or carbonate-bound forms. In the sample with the highest DIC concentration, siderite and iron(III)/low-spin iron(II) species—which could be attributed to iron sulfides similarly to what was done in section 3.1—were the only identified iron-containing phases. As DIC concentrations decreased, the relative spectral contribution of vivianite increased, accompanied by a decline in

the siderite and iron(III)/low-spin iron(II) phases' abundance. However, the proportion of the iron(III)/low-spin iron(II) sulfide phase in the less stripped digested manure samples appears disproportionately high when compared to the sulfur content in manure, assuming the maximum Fe/S molar ratio of 1 (see section 3.1). This discrepancy suggests that part of this spectral contribution may arise from unidentified iron(III) and/or low-spin iron(II) phases distinct from iron sulfides (see Table 3-5). In fact, the elevated line width of these contributions also supports a small particle size, which could stem from small iron(III) particles such as ferrihydrite. Table 3-6 illustrates that decreasing DIC concentrations correlate with a lower contribution from these unattributed iron phases. Due to the limitation of having Mössbauer spectra only from measurements performed at 295 K, further identification of these phases remains speculative. At this temperature, the phase is consistent with either a low-spin iron(II) or an iron(III) species. However, low-spin iron(II) phases other than iron sulfides are unlikely to form in manure, as such species typically require strong-field ligands like cyanide, carbonyl, or synthetic chelators (e.g., bipyridine) [55], which are not typically found in manure matrices [54]. Consequently, the presence of iron(III) species appears more plausible, suggesting an oxidized siderite phase.

Siderite oxidizes easily [56,57] and it is conceivable that partial oxidation occurred during sample preparation. Rothwell et al. (2025) demonstrated that synthetic siderite oxidizes within hours under ambient conditions, although partial Fe(II) preservation was observed for up to 500 hours in the presence of low-molecular-weight organic acids, compounds also found in manure [58]. These acids could therefore account for the coexistence of the preserved siderite together with the oxidized iron(III) phases, while vivianite oxidized more slowly. Alternatively, kinetic constraints may have influenced phase development. Like in fresh manure, magnesium went into solution upon iron addition to the digested manure samples, indicating the dissolution of struvite. Equilibrium was assumed to be reached after 48 hours based on the stabilization of dissolved magnesium concentrations, indicative of struvite dissolution (see Figures A 3-3, A 3-5, A 3-6). Unlike magnesium, no dissolved phosphate was detected post-treatment, suggesting that phosphate was incorporated into another solid phase, presumably vivianite. Notably, in a separate proof-of-concept experiment, Prot et al. (2021) conducted Mössbauer spectroscopy on samples of manure dosed with 11 g/L iron after one day and five weeks [20]. They observed a significant reduction in the iron(III)/low-spin iron(II) spectral contribution—from 63% to 27%, respectively — concurrent with increased vivianite and siderite signals. This finding suggests that additional vivianite and siderite may have formed in high-DIC samples when the experiments had been conducted over longer timeframes.

While vivianite formation correlates with lowering the DIC, struvite dissolution could also be related to lowering the ammonium concentration, as elaborated in 3.2. In this set of experiments, both DIC and ammonium concentrations were lowered through stripping. In comparison to magnesium dissolution in fresh manure, the magnesium dissolution

happened faster in the stripped digested samples. The magnesium release seemed to stabilize after 24 h in the former, while it was after 4 h in the latter. As was discussed by Schott et al. (2023a, 2023b) [27,28], and in 3.2, DIC is the main barrier in the formation of calcium and iron phosphates, respectively. However, lowered ammonium concentrations influence the kinetics of struvite dissolution, and this could have a further influence on the formation of the iron phosphate phase. To fully elucidate the transformation pathways of iron species in manure, further time-resolved solid-phase characterization in the initial hours following iron addition is necessary.

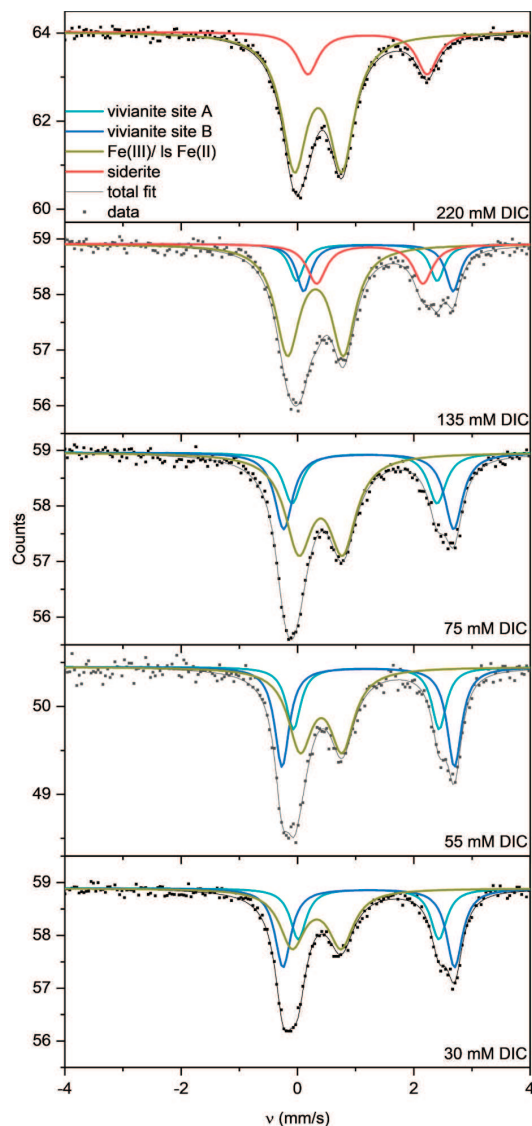


Figure 3-6 Mössbauer spectra at 295 K of stripped digested manure with different DIC content, with fitted iron phases.

Table 3-5 Distribution of Fe species according to Mössbauer analysis at 295 K of stripped digested manure with different DIC content, with isomer shift (IS), quadrupole splitting (QS), line width (LW), and related Fe spectral contribution percentage (% Fe). The last column shows the estimated percentage of P in vivianite based on vivianite quantification from Mössbauer analysis. Error IS, QS, LW ± 0.01 mm/s; % Fe ± 3 %.

	Fe species	IS (mm/s)	QS (mm/s)	LW	% Fe	% P in vivianite
220 mM DIC	siderite	1.2	2.05	0.44	21	
	Fe(III)/ Is Fe (II)	0.35	0.82	0.53	79	
135 mM DIC	vivianite A	1.23	2.36	0.29*	11	
	vivianite B	1.20	2.94	0.29*	15	
	siderite	1.23	1.89	0.42	19	36
	Fe(III)/ Is Fe (II)	0.37	0.84	0.52	57	
75 mM DIC	vivianite A	1.23	2.44	0.34*	17	
	vivianite B	1.24	2.93	0.34*	25	
	siderite	1.28	1.91	0.45	7	53
	Fe(III)/ Is Fe (II)	0.34	0.86	0.55	52	
55 mM DIC	vivianite A	1.18	2.5	0.30*	21	
	vivianite B	1.22	2.96	0.30*	34	65
	Fe(III)/ Is Fe (II)	0.41	0.72	0.5	44	
30 mM DIC	vivianite A	1.22	2.41	0.33*	23	
	vivianite B	1.23	2.96	0.33*	36	67
	Fe(III)/ Is Fe (II)	0.33	0.85	0.52	41	

*fixed same line width for vivianite A and B contributions

Table 3-6 Mössbauer spectral contributions of total iron(III)/ low spin iron(II) at different DIC concentrations (from Table 3-5), and their estimated fractionations in maximum FeS phase content (based on total sulfur in the manure sample), and unattributed Fe phases (other than FeS) content.

sample	Iron(III)/low spin iron(II)	Max. FeS (%)	Unattributed Fe (%)
220 mM DIC	79	34	45
135 mM DIC	57	33	24
75 mM DIC	52	37	14
55 mM DIC	44	40	5
30 mM DIC	40	41	-

3.3.4 DIC thresholds for vivianite formation in digested manure, THP digested sludge, and raw manure

As discussed in Section 3.3, a reduction in dissolved inorganic carbon (DIC) in digested manure significantly promotes the formation of vivianite. Mössbauer spectroscopy enabled quantification of iron incorporated into vivianite, allowing for correlation with the DIC concentration of each sample. To facilitate a more accurate comparison, the estimated amount of iron present as iron sulfide—assuming a stoichiometric Fe/S ratio

of 1—was subtracted from the total iron content. This correction yielded the percentage of iron attributed to vivianite, adjusted for sulfur interference, as outlined in Section 3.1. The molar amount of iron in vivianite was calculated using Equation 4:

$$Fe \text{ in vivianite} = (\% Fe \text{ vivianite A} + \% Fe \text{ vivianite B}) \bullet total Fe \quad [\text{Equation 4}]$$

The sulfur-corrected percentage of iron in vivianite was then determined using Equation 5:

$$\% Fe \text{ in vivianite corrected for S} = \frac{Fe \text{ in vivianite}}{total Fe - total S} \bullet 100\% \quad [\text{Equation 5}]$$

With % Fe vivianite A and B as determined by Mössbauer spectroscopy, total Fe and S, the total molar concentration of the element determined at the end of the experiment.

Figure 3-7a illustrates the inverse relationship between DIC concentration and sulfur-corrected % Fe in vivianite. The data exhibits a slightly sigmoidal trend, with vivianite formation approaching a maximum at approximately 55 mM DIC. A more pronounced increase in vivianite content is observed below 30 mM DIC, suggesting a threshold for optimal vivianite formation between 30 and 55 mM DIC. This corresponds to a bicarbonate concentration of approximately 2–3 g/L. This threshold aligns with typical bicarbonate concentrations in digested sludge, which are around 3 g/L [59], supporting the hypothesis that vivianite formation in sludge is generally limited by sulfide availability rather than DIC [35,37,60]. However, minor siderite formation has been reported in Finnish sludge samples, potentially due to elevated iron concentrations [17]. Prot et al. also reported higher DIC concentrations in sludge—up to 6.3 g/L HCO_3^- (approximately 100 mM DIC)—which, based on the present findings, may inhibit vivianite formation. Such elevated DIC levels are particularly relevant in thermal hydrolysis plants (THPs), where ammonium concentrations can reach approximately 120 mM due to enhanced protein degradation [61,62]. This increase in ammonium is typically balanced by a corresponding rise in DIC. Indeed, THP-derived digested sludge samples (Table A 3-2) exhibited both elevated DIC and siderite formation, along with reduced vivianite content was detected with Mössbauer spectroscopy (Figure A 3-7, Table A 3-3). Notably, the vivianite content at these DIC levels aligns with the trend observed in stripped digested manure (blue triangle in Figure 3-7a), suggesting that the findings from digested manure can be extrapolated to wastewater treatment systems with elevated DIC, such as THPs.

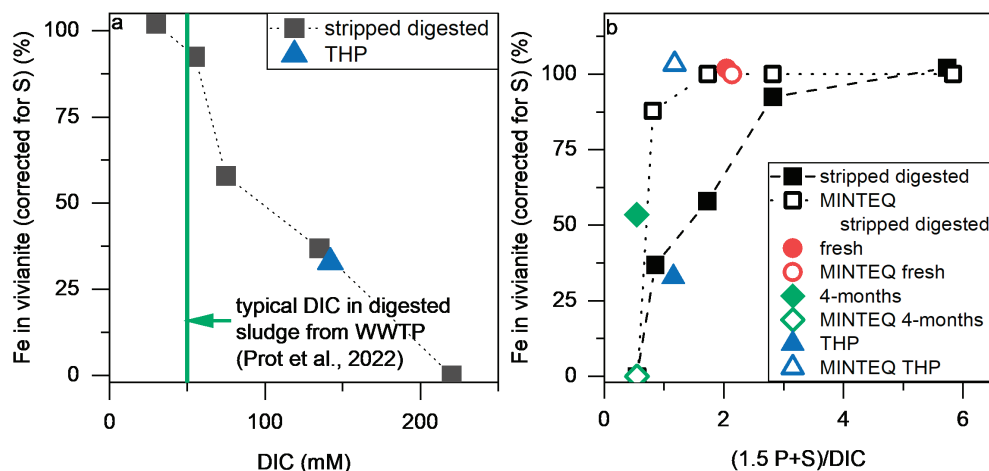


Figure 3-7a Relative amount of iron in vivianite corrected for the sulfur content at different DIC concentrations in stripped digested manure and THP samples. **b** Relative amount of iron in vivianite corrected for the sulfur content (assumed Fe/S molar ratio of 1), against the $(1.5 P + S)/DIC$ molar ratio, in the stripped digested manure, fresh manure, 4-month-aged manure, and THP samples. For all cases, both experimental data (full symbols) and simulated data from MINTEQ (outlined symbols) are represented.

Whether the observed relationship between DIC concentration and iron incorporation into vivianite also applies to fresh and 4-month-aged manure remains to be fully established. Additionally, the extent to which this relationship can be predicted using the MINTEQ software for chemical equilibrium modeling was explored (Table 3-2 and Table A 3-2). Notably, both fresh and 4-month-aged manure exhibited elevated phosphate concentrations, attributed to higher total solids (TS) content (see Table 3-1), which necessitated proportionally higher iron dosing to achieve comparable vivianite formation. To enable consistent comparison across samples with varying DIC and competing anion concentrations, the absolute DIC values from Figure 3-7a were normalized. This was achieved by dividing the combined molar concentrations of phosphate and sulfide by the DIC concentration of each sample. A stoichiometric Fe/S molar ratio of 1 was assumed (as discussed in Section 3.1), while for phosphate, the stoichiometric Fe/P ratio of 1.5—corresponding to vivianite—was applied. This yielded the dimensionless parameter:

$$(1.5 P + S)/DIC,$$

Figure 3-7b presents a comparison of this normalized parameter across stripped digested manure, fresh and 4-month-aged manure, and THP-derived digested sludge (represented by squares, dots, diamonds, and triangles, respectively). Experimental data are contrasted with MINTEQ predictions, with filled symbols representing measured values and outlined symbols representing model outputs. Experimentally, vivianite formation plateaued at a normalized ratio of approximately 2–3 in both fresh and stripped digested manure. In-

terestingly, 4-month-aged manure supported more efficient vivianite formation at lower normalized ratios. However, quantification of vivianite in the 4-month-aged manure sample via Mössbauer spectroscopy proved more challenging, likely due to sample-specific complexities such as mineral inhomogeneity or particle size effects. In contrast, for the other manure samples, the extent of struvite dissolution—assessed via magnesium and ammonium release—correlated well with phosphate incorporation into vivianite as determined by Mössbauer analysis (Figure A 3-6), supporting the reliability of the method in those cases. In the 4-month-aged manure sample, however, the observed struvite dissolution was lower than expected based on Mössbauer-derived vivianite content. This discrepancy suggests a potential overestimation of vivianite by Mössbauer spectroscopy in this specific case, possibly due to the aforementioned factors.

Geochemical modeling using MINTEQA2 was employed to assess the thermodynamic predictability of DIC as a barrier to vivianite formation. The MINTEQA2 simulations predicted a sharp increase in vivianite formation—from 0% to 90%—at normalized DIC ratios below 1. In contrast, experimental data revealed a more gradual increase in vivianite formation, especially in stripped digested manure samples with intermediate DIC concentrations (75–135 mM) and in thermal hydrolysis process (THP) sludge (140 mM DIC). These discrepancies could be attributed to shortcomings of the thermodynamic model and kinetic factors influencing phase transformations in real complex matrices. To improve the thermodynamic predictions, the model could be extended by incorporating more accurate solubility constants for impure mineral phases, for example. Moreover, the limitations of the model are particularly pronounced under high ionic strength conditions, where solubility and equilibrium behavior become increasingly complex. Ionic strength values calculated by MINTEQA2 ranged from 0.3 M (30 mM DIC digested manure) to 0.6 M (4-month-aged manure). As noted by Hafner and Bisogni (2009), modeling solubility and pH-dependent equilibria in matrices rich in ammonia and carbonate presents significant challenges [63]. Although the Specific Ion Interaction Theory (SIT) implemented in MINTEQA2 provides ionic activity corrections, it may still fall short in accurately capturing solubility dynamics in manure systems. Shorter retention times also play a role in real matrices, potentially favoring the precipitation of one phase over another kinetically. This has been observed in calcium phosphate formation in solid waste streams [64]. It is important to recognize the relevance of kinetic limitations in wastewater and manure treatment systems, since they operate on shorter, standardized timescales, unlike geochemical processes in soils. Ultimately, while MINTEQA2 simulations were instrumental in identifying siderite formation as a potential barrier to vivianite precipitation at elevated DIC levels, the model—originally developed for geological systems—lacks the resolution to predict phase speciation near threshold values in complex waste matrices, which could lead to underestimation of the role of siderite around these values. Further research is needed to develop these models and understand kinetic limitations in complex waste matrices and their treatment processes.

Overall, a normalized ratio of approximately 2.5 appears to serve as a practical threshold for maximizing vivianite formation in both raw and digested manure. The required molar iron concentration for vivianite formation can be estimated using Equation 6:

$$Fe = (1.5 \text{ total } P + \text{total } S) \bullet 2.5 \text{ DIC} \quad [\text{Equation 6}]$$

Above this threshold, vivianite formation increases only marginally, indicating a plateau effect. Below this ratio, vivianite yields decline sharply, particularly in digested manure, where competing iron carbonate phases such as siderite may form and sequester iron, thereby reducing the efficiency of vivianite precipitation.

3.3.5 Outlook on vivianite formation in systems high in DIC

In pig farming in the Netherlands, livestock densities are high with limited land to manure production, leading to a surplus of nutrients and removing P and other nutrients in a targeted way would be beneficial for their redistribution [10]. The limitation of dissolved inorganic carbon (DIC) as a limiting factor for vivianite formation in pig manure introduces a new possibility for phosphate recovery through iron dosing strategies. One potential approach involves promoting vivianite crystallization directly within the fresh manure, a process demonstrated to be feasible in this study (97% of the phosphorus bound as vivianite). Nevertheless, this method presents notable challenges. The high solids content in fresh manure complicates magnetic separation, but the implementation of such a phosphate recovery system would require substantial adjustments to current manure management practices to avoid storage, a condition not always operationally feasible.

An alternative strategy involves utilizing digested pig manure, with the known benefits from anaerobic digestion processes that not only stabilize organic matter but also generate biogas [34], thus enhancing overall resource circularity. Integrating vivianite recovery into manure digestion could enable the simultaneous extraction of multiple resources: energy via biogas, ammonia through stripping (potentially coupled with carbon capture), and phosphate. However, based on the characteristics of the digested manure used in this study, approximately 90% of the dissolved DIC would need to be removed to achieve a bicarbonate concentration of 3 g/L—necessary for efficient vivianite formation. Some facilities already couple ammonia stripping of manure or food waste to CO₂ stripping to keep the pH high enough, reducing the addition of base (biosys, 2025). Such processes could be adapted to reach a lower DIC suitable for vivianite formation. However, practical application substituting nitrogen gas with other stripping gases such as air and methane, or vacuum stripping [65] should be tested, since using pure nitrogen gas is too expensive. Moreover, vivianite particles in digested manure were smaller than those found in digested sludge (Figure A 3-8). Their magnetic separation from digested manure has yet to be demonstrated at a larger scale. Hence, further testing is necessary to perform an economic analysis of this process. Ultimately, the viability of this technology will depend

on market demand for refined vivianite-based products and the availability of sustainable electricity for energy-intensive pumping processes [66].

Overall, the limitation of vivianite formation at elevated DIC concentrations provides new insights into the geochemical conditions favoring vivianite precipitation. DIC levels in most lake sediments or wastewater sludges are generally lower, thereby exerting a less significant influence. However, the high DIC in certain wastewater treatment contexts, such as THP digested sludge, poses a barrier to vivianite formation in line with the observations in digested manure in these plants. Interestingly, Wang et al. (2024) observed higher vivianite formation (based on XANES quantification) in hydrothermally digested samples compared to conventionally digested sludge [67]. In contrast, Wang et al. (2021) identified barriers to vivianite formation in hydrothermally treated digested sludge, attributing these to magnesium availability and pH [68], while Cui et al. (2024) pointed to iron-organic complexation as the limiting factor [69]. Notably, none of these studies investigated the potential role of DIC. Therefore, the role of siderite formation in iron dosed sludges high in DIC might have been overlooked so far. One reason could be that siderite is not detected due to oxidation prior to the measurements if the samples were not protected accordingly. Further research using techniques such as Mössbauer spectroscopy could help clarify the influence of DIC in vivianite formation in sludge matrices high in DIC.

3.4 CONCLUSION

This study demonstrated that elevated DIC concentrations are the main barrier to vivianite formation in both raw and digested manure experiments, as well as THP digested sludge. A stoichiometric iron dose of; $Fe = (1.5 P + S) \bullet 2.5 DIC$ was identified as critical for optimal vivianite precipitation. Longer retention times may further enhance yields and merit future investigation. In the absence of ammonium and high ionic strength, vivianite formation from struvite at decreased DIC could not be reproduced in ultrapure water, with thermodynamic modeling indicating ammonium to be a relevant ion in vivianite formation from struvite besides DIC.

While challenging, vivianite recovery from pig manure offers potential for integrated biomethane, nitrogen, and phosphorus recovery as well as carbon capture. A possible approach involves stripping DIC and ammonia from digested manure, followed by iron dosing and magnetic separation of vivianite. However, practical implementation requires further testing with alternative stripping gases and at larger scales to evaluate feasibility.

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SUPPLEMENTARY INFORMATION

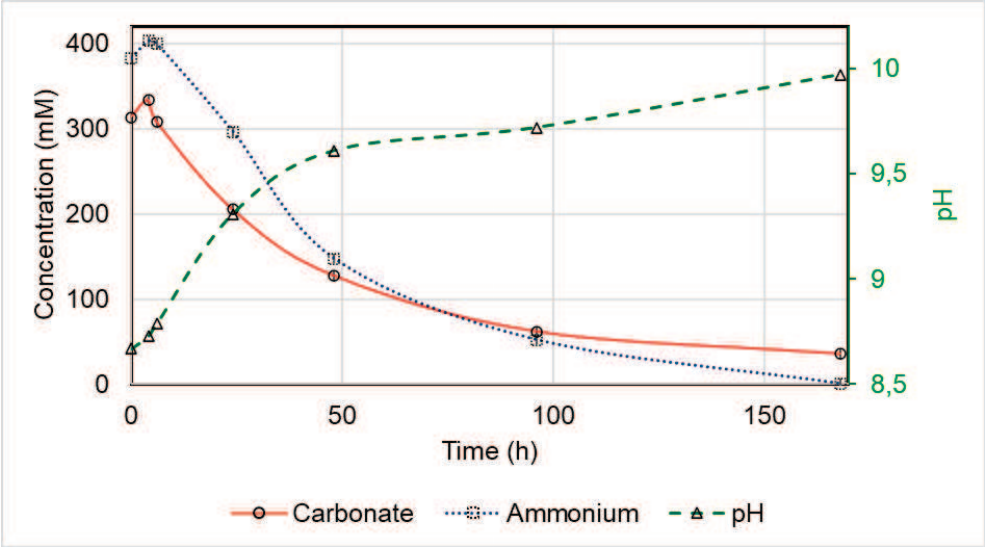


Figure A 3-1 DIC, and ammonium concentrations (left y-axis), and pH value (right y-axis) over the course of 168 h stripping of the digested manure with N₂ gas.

Table A 3-1 Experimental conditions of the struvite-iron-DIC system.

	0 mM DIC	3 mM DIC	30 mM DIC	300 mM DIC
c Struvite (mM)	5.22	5.21	5.20	5.22
c NaHCO ₃ (mM)	0.00	3.31	33.6	334
Initial pH	7.5	7.7	7.8	7.9
Final pH	7.6	7.3	7.5	8.1

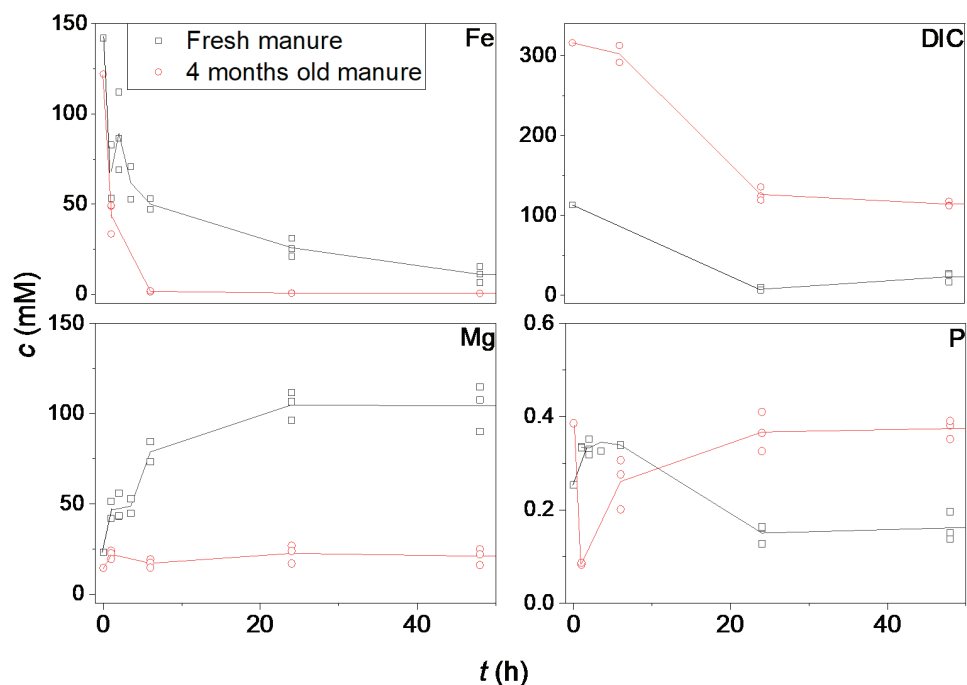


Figure A 3-2 Evolution of the concentration of iron, DIC, magnesium and phosphorus in the soluble fraction of the fresh and 4-month-aged manure over 48 h after iron dosing. Iron precipitated in both manures, but more gradually in the fresh. DIC decreased in both fresh and 4-month-aged manure. Precipitation alone is unlikely since no siderite was found in the fresh manure; hence, CO₂ release during foaming after iron addition is possible. Magnesium release into the solution indicates struvite dissolution, to a greater extent in fresh than 4-month-aged manure. Phosphorus in solution slightly increases in fresh manure and then precipitates, while the opposite is observed in 4-month-aged manure. The peak in iron and phosphorus concentrations at 2 h in fresh manure could be indicative of the vivianite formation process.

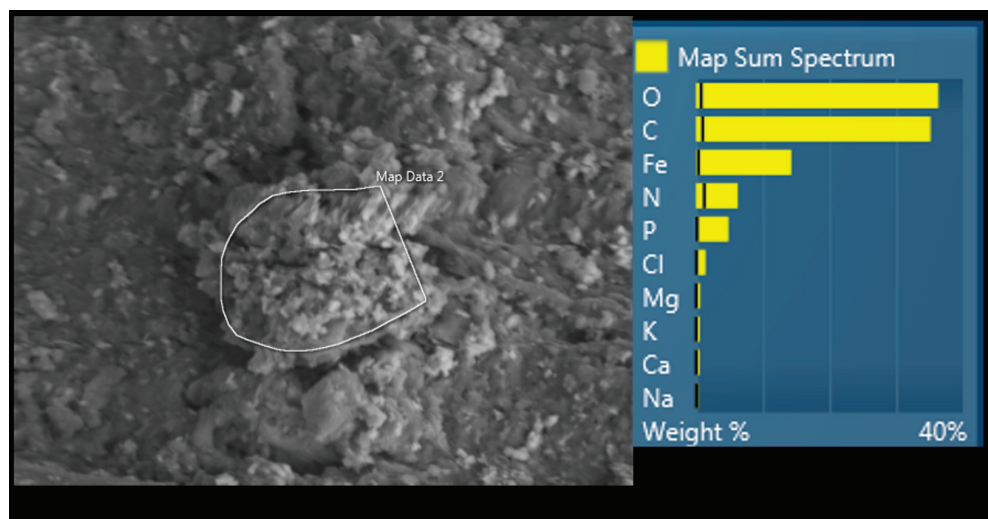


Figure A 3-3 Vivianite precipitate in 4-month-aged manure. Iron and phosphorus are present/overlapping in the circled section; O, C, and N are considered omnipresent in the sample and not considered for this overlap.

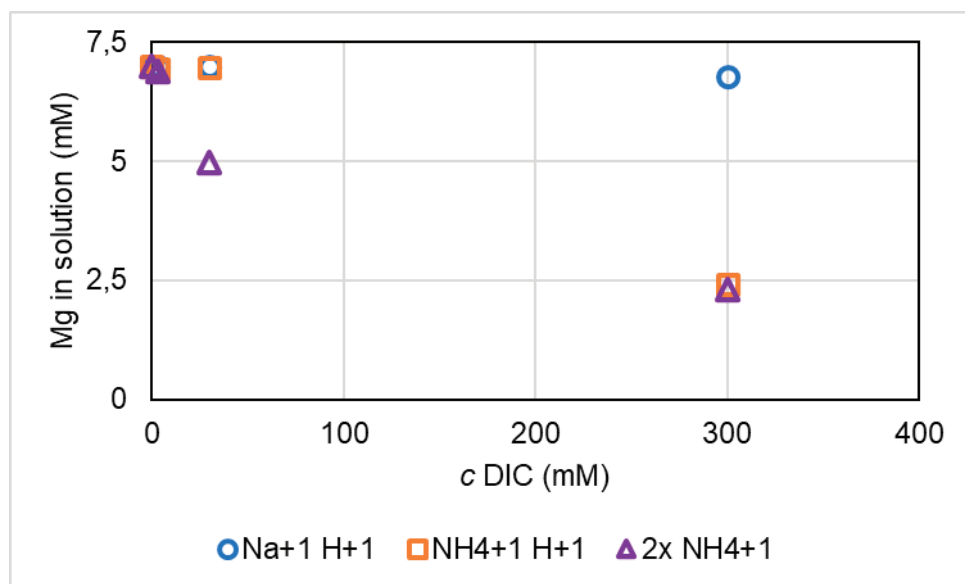


Figure A 3-4 MINTEQ simulation of magnesium release from struvite against DIC concentration depending on whether H+ / Na+, H+ / NH4+ or 2x NH4+ are used as counter ions of CO₃²⁻. Input: 5 mM struvite, 7.5 mM FeCl₂, pH 8. A higher DIC leads to less magnesium release, only if at least one NH₄⁺ is used as counter ion.

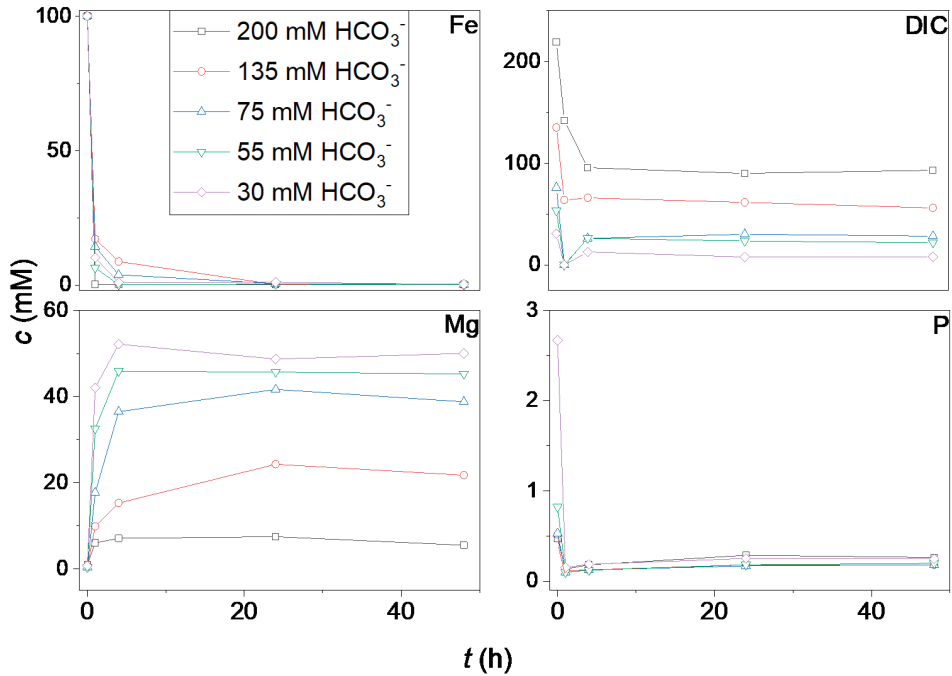


Figure A 3-5 Evolution of the concentration of iron, DIC, magnesium and phosphorus in the soluble fraction of the digested manure over 42 h after iron dosing. Stripped digested manure has an asymptotic magnesium release with a very steep increase at the beginning, indicating fast kinetics.

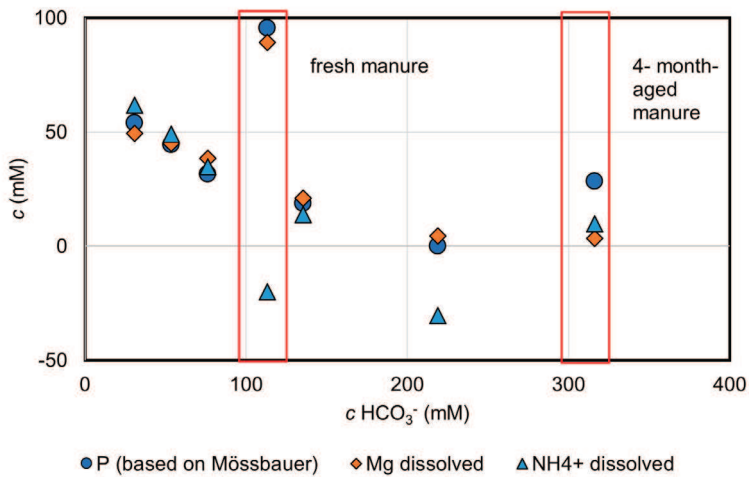


Figure A 3-6 The amount of phosphorus bound in vivianite (as determined from the amount of vivianite measured with Mössbauer spectroscopy), compared with magnesium, and ammonium released in solution against the DIC of the stripped digested, fresh, and 4-month-aged manure samples. Magnesium and ammonium dissolved indicate the amount of struvite dissolved. At lower DIC in the stripped digested manure samples, the amounts of phosphorus in vivianite and dissolved struvite are similar, indicating the phosphorus from struvite was bound in vivianite. At higher DIC in

the digested samples ammonium does not correlate with phosphorus in vivianite and dissolved Mg concentrations. In the case of 4-month-aged manure this is also the case. In the case of 4-month-aged manure dissolved magnesium and ammonium are lower than the amount of P that should be bound in vivianite. Hence, it is more difficult to correlate struvite dissolution and vivianite formation in the 4-month-aged manure.

Table A 3-2 Total elements of microwave-digested and soluble fraction of 0.45 μm filtered THP digested sludge from Hengelo wastewater treatment plant (24-06-2025) and input values for MINTEQ calculations based on the SIT ionic activity model. For MINTEQ, CO32- was the sum of DIC and the equimolar concentration of total calcium, assuming most calcium was bound as calcite, and NH_4^+ was the sum of soluble NH_4^+ and the equimolar concentration of total magnesium, assuming most phosphorus was bound as struvite. List of possible solids: $\text{Ca}_3(\text{PO}_4)_2$ (am2), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (s), Mackinawite, Vivianite, Struvite, Siderite, $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ (s), Calcite, Magnesite, $\text{Fe}(\text{OH})_2$ (am), $\text{Al}(\text{OH})_3$.

measured	c (g/kg dried)	MINTEQ input	c (mM)
total elements (N=3)			
Al	6.5 ± 0.2	Al^{3+}	15
Mg	7.8 ± 0.9	Mg^{2+}	20
P	50 ± 2	PO_4^{3-}	90
Fe	62 ± 2	Fe^{2+}	60
S	16.7 ± 0.6	HS^-	30
Ca	27 ± 1	Ca^{2+}	40
TS	55.5 ± 0.2		
VS	35.7 ± 0.1		
soluble fraction (N=3)			
	c (mg/L)	Acetate ⁻	75
Al	0.57 ± 0.02		
Mg	01.42 ± 0.02		
P	389 ± 3		
Fe	11.57 ± 0.06		
S	62.3 ± 0.7		
Ca	62.0 ± 0.7		
K^+	339 ± 3	K^+	10
Na^+	159 ± 2	Na^+	5
Cl^-	214 ± 1	Cl^-	5
NH_4^+	4170 ± 10	NH_4^+	250
HCO_3^-	8700 ± 20	CO_3^{2-}	180
pH	7.6	pH	7.6

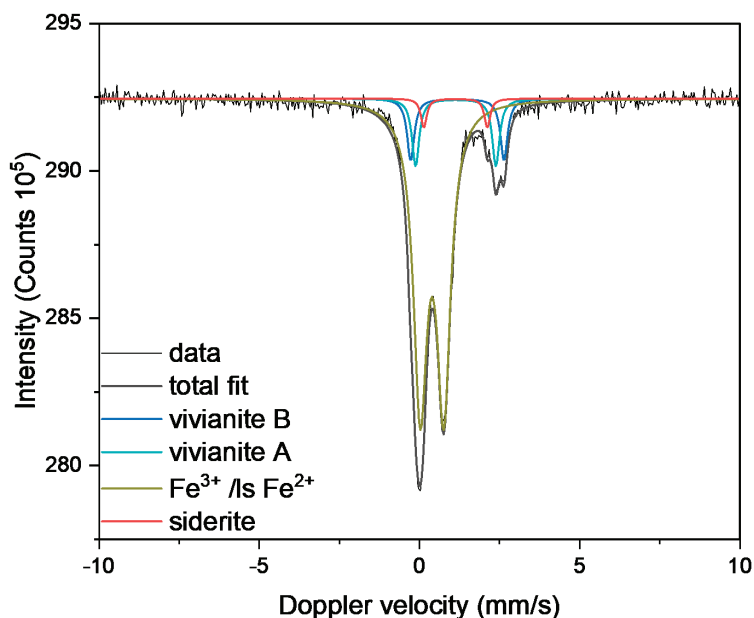


Figure A 3-7 Mössbauer spectrum at 295 K of THP digested sludge, DIC = 140 mM.

Table A 3-3 Distribution of Fe species according to Mössbauer analysis at 295 K of THP digested sludge, with isomer shift (IS), quadrupole splitting (QS), line width (LW), and related Fe spectral contribution percentage (% Fe). The last column shows the estimated percentage of P in vivianite based on vivianite quantification from Mössbauer analysis. Error IS, QS, LW $\pm$ 0.01 mm/s; % Fe $\pm$ 3 %.

	Fe species	IS (mm/s)	QS (mm/s)	LW (mm/s)	% Fe	% P in vivianite
140 mM DIC THP	vivianite A	1.13	2.51	0.27*	9	
	vivianite B	1.23	2.91	0.27*	9	8
	siderite	1.13	1.98	0.21	3	
	Fe ³⁺ /Is Fe ²⁺	0.39	0.73	0.52	79	

*fixed same line width for vivianite A and B contributions, ^fixed parameters

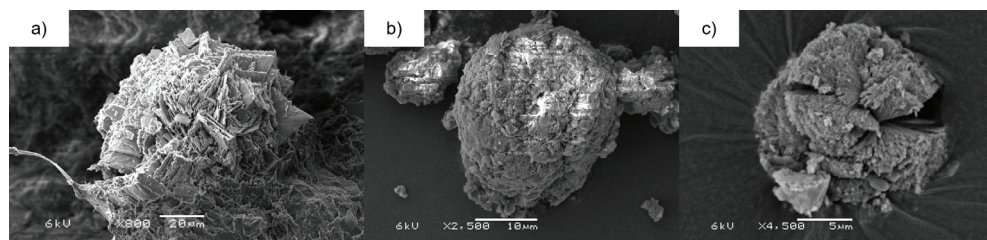


Figure A 3-8 Comparison between vivianite crystals formed in a) anaerobically incubated excess sludge by Prot et al., 2022, b) fresh manure and c) stripped digested manure at 30 mM HCO_3^- (lowest DIC content). The vivianite crystals formed in digested sludge are bigger than the ones formed in the manure matrices (see different picture scales) and dependent on the iron reduction kinetics (48-96 h). The fast kinetics of vivianite formation and magnesium release in solution in fresh manure and digested manure could have played a role in the small crystal size (Figure A 3-4, Figure A 3-5). Moreover, the crystal formed in sludge has more pronounced plated edges while the ones formed in manure seem more round/spherical. High ionic strength and adsorption of other compounds onto the growing vivianite crystal could have induced these morphological.

4

Evaluating phosphate recovery as vivianite from lake sediments

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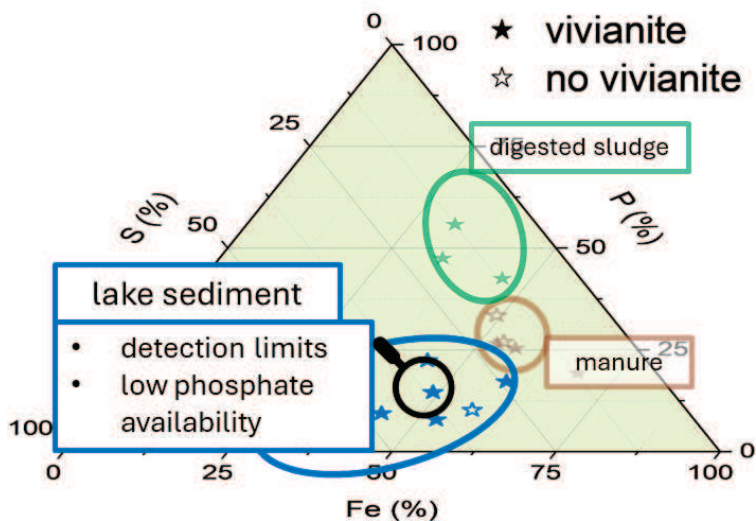
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ABSTRACT

Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) plays a significant role in phosphorus sequestration within anaerobic lake sediments and has recently gained interest as a recoverable phosphate resource from wastewater due to its paramagnetic properties. This study examines vivianite formation and detectability in the context of dredging-based remediation of the eutrophic Lake Ormstrup (Denmark), focusing on whether iron(II) dosing to dredged lake sediment can enhance vivianite production for magnetic recovery. Vivianite was detected only when iron and phosphate were added simultaneously, indicating that phosphate availability, not iron supply, is the key constraint in dredged sediments. Furthermore, low native vivianite concentrations prevented reliable detection using Mössbauer spectroscopy. To improve vivianite quantification, alternative Mössbauer fitting approaches and bipyridine extractions were compared. However, iron-spiked samples showed no measurable increase in Fe(II)-P relative to controls, highlighting persistent analytical challenges. These findings show limited potential for vivianite-based recovery from dredged sediment in Lake Ormstrup. Nevertheless, the results also provide new insights into carbonates and organics likely outcompeting phosphate for iron binding, outline methodological improvements needed to detect vivianite in low-concentration environments, and highlight differences in Fe/P/S ratios in lake sediments compared to those in digested sludge.

Graphical Abstract



4.1 INTRODUCTION

Phosphorus (P) is widely recognized as the key nutrient driving eutrophication in freshwater systems[1]. Agricultural runoff, following the application of manure or synthetic fertilizers, plays a significant role in supplying external phosphorus to lakes [2]. Even after external P loading ceases, lakes that have experienced prolonged eutrophication may continue to release P from internal sediment stores, thereby sustaining eutrophic conditions. To mitigate eutrophication and restore lake ecosystems, various remediation strategies have been implemented. These include chemical approaches (e.g., lanthanum oxides, aluminium (Al) or iron (Fe) dosing to immobilize P), biological interventions such as removal of planktivorous fish, and physical dredging of the upper sediment layers (typically the top 20 cm) [3,4]. Dredged sediments have been proposed for land application [5,6]; however, logistical constraints such as high transportation costs and the need for dewatering pose significant challenges [4,7]. Moreover, knowledge on the agronomic value of dredged sediments is limited by uncertain nutrient ratios, variable P availability, and elevated concentrations of heavy metals [8,9].

One P-bearing mineral already present in some sediments is vivianite, a ferrous phosphate that typically forms in organic-rich environments with low sulphidation rates [10]. A novel and promising method for P recovery from digested sewage sludge involves magnetic separation of vivianite, which also forms under reducing conditions in iron-coagulated sludge [11,12]. This raises the question of whether vivianite could similarly be targeted for magnetic recovery from dredged lake sediments, contributing to nutrient circularity in sustainable lake restoration, as identified by Tammerog et al. (2025). Vivianite has previously been observed in the Danish Lake Ormstrup [13], a system with favourable Fe and P concentrations for vivianite formation that has undergone dredging as part of restoration efforts [5,7]. However, predicting and quantifying vivianite in sediments remains challenging [14,15]. For example, sulphidation rate and kinetic factors are known to inhibit vivianite formation despite a favourable vivianite supersaturation index in the pore water [15]. For effective phosphorus reduction via magnetic separation, most of the mobile sedimentary P must occur as vivianite. In some lakes, iron dosing is commonly employed to suppress internal P release and has been shown to promote vivianite formation in Lake Groß-Glienicke [15]. Laboratory studies have demonstrated the transformation of phosphate adsorbed onto iron(III) oxyhydroxides into vivianite under anaerobic conditions [16,17]. However, in situ vivianite formation from iron(III) oxyhydroxide dosing without additional P supply was unsuccessful in aquatic sediments [17]. Consequently, further investigation is needed to determine whether vivianite formation can be stimulated by iron dosing, with or without supplemental phosphate.

The dredging of Lake Ormstrup provided a unique opportunity to investigate vivianite formation as a novel pathway for phosphorus recovery within lake restoration measures. In this study, iron dosing combined with anaerobic incubation of dredged lake sediment was applied to immobilize sedimentary phosphorus in the vivianite phase, which can subsequently be recovered magnetically. Moving forward, optimizing the conditions that promote phosphorus availability for vivianite formation and developing robust approaches to quantify the vivianite already present in the sediment will constitute key challenges for advancing this method.

4.2 MATERIALS AND METHODS

4.2.1 Lake sediments

A gravity core sampler was used to collect lake sediments from different sampling stations (Figure A 4-1 [13]). To achieve a representative mix of dredged sediment across Lake Ormstrup the upper 20 cm from the stations were mixed, forming LO1 from the sampling of October 2023 and LO2 from the sampling of September 2023. Experiments with LO1 were conducted from October to December 2023, the cores for LO2 were stored in a dark place and used for experiments from June to August 2024. The composition of LO1 and LO2 is shown in Table 4-1.

Table 4-1 Total elements, soluble elements, dry weight (DW), and organic matter (OM) as determined as loss on ignition (450°C) of LO1 and LO2 (N=3).

	LO1		LO2	
	total c µmol/ g DW	soluble c mM	total c µmol/ g DW	soluble c mM
Al	710 ± 10	-	650 ± 40	-
Ca	224 ± 5	0.79 ± 0.08	250 ± 10	0.7±0.4
Fe	420 ± 10	0.04 ± 0.06	400 ± 20	0.01±0.02
Mg	125 ± 1	0.17 ± 0.02	116 ± 8	0.16±0.08
Mn	36 ± 1	0.053 ±0.004	42 ± 3	0.04±0.06
P	90 ± 2	0.04 ± 0.05	104 ± 7	0.02±0.01
S	450 ± 10	0.08 ± 0.01	360 ± 20	1.12±0.07
DM %	5.54 ± 0.04			
OM %	2.40 ± 0.01			

4.2.2 Vivianite formation experiments

To stimulate vivianite formation, iron(II) and phosphate salts were added to LO1 (250 mL) in plastic bottles (VWR® High Performance) in triplicate in different treatments (Table 4-2, Figure 4-1).

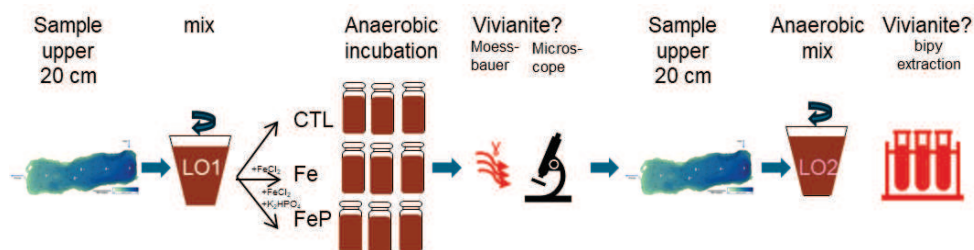


Figure 4-1 Schematic of study process, featuring sampling and mixing of the sediment, anaerobic incubation, and vivianite detection.

- LO1-CTL: An anoxic control treatment with no iron or phosphate addition.
- LO1-CTL 2: A control treatment with no iron or phosphate addition, opened more frequently for monitoring of soluble iron and phosphate.
- LO1-Fe: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (9.8 mM, expected pH 3-4 [18]) was added to study if a deficiency of Fe due to sulphide or organic binding [14,19] could explain the absence of significant vivianite. The concentration of the added iron was chosen to be the double of the total phosphorus already present in the sediment $\text{Fe}_{\text{dose}}/\text{P}_{\text{sediment}}=2$ similar to a previous vivianite formation studies in manure [20].
- LO1-FeP: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (9.8 mM) and K_2HPO_4 (4.7 mM) were added to ensure vivianite formation and study, if matrix effects further limit vivianite formation. Next to the iron dose mentioned above, phosphorus equal to the amount already in the sediment was dosed $\text{Fe}_{\text{dose}}/\text{P}_{\text{dose}}/\text{P}_{\text{sediment}}=2/1/1$

Bottle lids were sealed with parafilm, and the bottles were incubated at room temperature on a rotary platform shaker (HS 501 digital, IKA Labortechnik) at 150 rpm for seven (LO1-CTL), five (LO1-CTL 2) and four weeks (LO1-FeP). Longer incubation times were set for LO1-CTL to ensure phosphate adsorption on iron(III)(hydr)oxides and their reduction, as was demonstrated in Heinrich et al. (2021). In contrast, shorter incubation times in the LO1-Fe and LO1-FeP treatments could be justified by the dosing of iron(II) and thus additional time for iron reduction was necessary. Samples (10 mL) were collected at 0 and 1176 h for LO1-CTL treatment, at 0, 24, 168, 336, and 840 h for LO1-CTL 2 and LO1-Fe treatments, and at 0, 1.5, 168, and 672 h for LO1-FeP treatment to monitor soluble components.

Table 4-2 Molar Fe, P, and S contents (N=3), added Fe, added P, molar S/Fe, and Fe/P ratios of control (LO1-CTL, LO1-CTL 2), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1.

μmol/g DW	addition	Fe μmol/g DW	S μmol/g DW	P μmol/g DW	Fe/S	Fe/P
LO1-CTL, LO1-CTL 2	none	420 ± 10	450 ± 10	90 ± 2	0.9	4.7
LO1-Fe	Fe(II)	420 ± 10 + 185 added	450 ± 10	90 ± 2	1.3	6.7
LO1-FeP	Fe(II) & P	420 ± 10 + 185 added	450 ± 10	90 ± 2 + 90 added	1.3	3.4

4.2.3 Sediment characterization

Soluble components

For soluble phase analysis, samples were centrifuged at 4750 rpm for 10 minutes (Sigma 4-5 L, Sigma Laborzentrifugen), and the porewater supernatant was filtered through 0.45 μm syringe filters (Q-Max RR syringe filters). To minimize Fe oxidation, samples were filtered into a beaker, with the headspace continuously purging with N₂. Fe and P were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Optima 2100 DV, Perkin Elmer).

Iron and phosphorus extractions

Sequential P extractions were based on the protocol by Reitzel (2005) [21] and Wang et al. (2021)[22] as presented by Haasler et al. (2025)[8] (Table 4-3). For each sequence, 1 g of wet sediment was extracted with 25 mL of extractant. After every addition, the sample was shaken, then centrifuged, and the supernatant was removed. The pellet was washed with ultrapure water before the next extractant was added. The collected fractions of each extractant, including the washing step, were then analyzed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES; Thermo Scientific iCAP Pro, with yttrium standard). LO1 was extracted using ultrapure water, bicarbonate-dithionite (BD), and NaOH extraction steps. LO2 was extracted using the same sequence as LO1, with an additional bipyridine extraction step between ultrapure water and BD.

Table 4-3 Extractants and details of the extraction steps with assigned P fractions for the P sequential extraction used on LO1 and LO2. The bipyridine step was only used in an additional extraction on LO2.

Extractant solution	Extraction conditions	Washing step	Assigned P fraction
N ₂ -purged ultrapure water	1 h, RT	1 x ultrapure water	porewater/exchangeable
0.2%-2,2'-bipyridine +0.1 M KCl	24 h, 50°C	1x0.2% Bipy in 0.1 M KCl, 2x0.1 M KCl, 1x ultrapure water	Fe(II)-bound / vivianite

Table 4-3 Extractants and details of the extraction steps with assigned P fractions for the P sequential extraction used on LO1 and LO2. The bipyridine step was only used in an additional extraction on LO2. (*continued*)

Extractant solution	Extraction conditions	Washing step	Assigned P fraction
0.11 M bicarbonate-dithionite (BD)	1 h, RT	2×0.11 M BD, 1× ultrapure water	Redox-sensitive Fe/Mn bound
0.1 M NaOH	16 h, RT	1×0.1 M NaOH, 1× ultrapure water	Metal Fe/Al bound

The Fe extraction was based on the HCl-extraction step described by Muench et al. (2024) [23], adapted from Claff et al. (2010)[24], to distinguish between HCl-soluble iron (II) and iron (III) phases. 1 mL wet sediment from LO1-CTL, LO1-Fe, and LO1-FeP was extracted with N₂-purged HCl (1 M) (9 mL), shaken at 60 rpm for 4 h, filtered through 0.45 µm syringe filters in a N₂ stream, and analyzed for Fe²⁺ and Fe³⁺ using the ferrozine method [25].

Total elemental composition and solid phase characterization

- Elemental composition: 2 mL of wet samples were microwave digested in 8mL 69% HNO₃ using a sludge and solids protocol (Milestone Ethos Easy), followed by ICP-OES analysis (Thermo Scientific iCAP Pro). It is worth noting that this establishes an upper limit for reactive iron, as iron silicates are not solubilized using this technique [19,26].
- Crystal imaging: Vivianite could be identified by its characteristic blue color using a stereoscope (Leica). Scanning Electron Microscopy (SEM; JEOL JSM-6480LV) coupled with Energy Dispersive X-ray Spectroscopy (EDX; Oxford Instruments x-act SDD Energy Dispersive X-ray spectrometer), was used to further investigate the morphology and elemental composition of the minerals identified under the stereoscope. Samples were first gold-coated (10 nm) under vacuum (15 Pa, 25 mA), and measurements were taken at 12 kV with a 10 mm working distance. Data acquisition and analysis were performed using JEOL and Aztec software.
- Crystal phase determination: X-Ray Diffraction (XRD; Rigaku mini flex 600 X-Ray diffractometer), was performed by mounting ground sediments on Si510 wafers, scanned with Cu Kα radiation (5°–90° 2θ, 0.02° step size, 1 s/step).
- Iron mineral phase quantification: Mössbauer Spectroscopy was performed at 295 K, with a conventional constant acceleration or sinusoidal velocity spectrometer, using a ⁵⁷Co(Rh) radioactive source with α-Fe as calibration reference. Samples (50 mL) were dried in the air, ground, and sent for measurements. Spectra were analyzed using MossWinn 4.0 [27]. Two fitting procedures are presented: the original assigned fit according to distinguishable peaks and an alternative fit, using vivianite hyperfine parameters obtained from the LO1-FeP spiked sample for specific vivianite identification in LO1-CTL and LO1-Fe (Text A 4-1, Table A 4-3).

Vivianite quantification approach

Due to the complexity of vivianite quantification and the difficulty in assessing treatment differences, the original sediment from Lake Ormstrup was analyzed in greater detail. For this purpose, a new composite sample, designated LO2, was prepared by mixing material from multiple stations within the lake. The sediment was stored under anaerobic conditions for several weeks prior to analysis, making it broadly comparable to LO1-CTL. To understand the amount of vivianite in amended and unamended sediment, the bipyridine-extracted LO2 quantification was compared with the original and alternative Mössbauer fits of LO1.

4.2.4 Supersaturation Index calculations

Visual MINTEQ was used to calculate vivianite supersaturation indices (Table A 4-1), using soluble iron, phosphorus, and sulphur concentrations measured with ICP-OES (Thermo Scientific iCAP Pro, with yttrium standard) and dissolved inorganic carbon concentrations determined via total organic carbon analysis (TOC-L CPH, Shimadzu).

4.3 RESULTS

4.3.1 Iron and phosphate precipitation with and without spiking

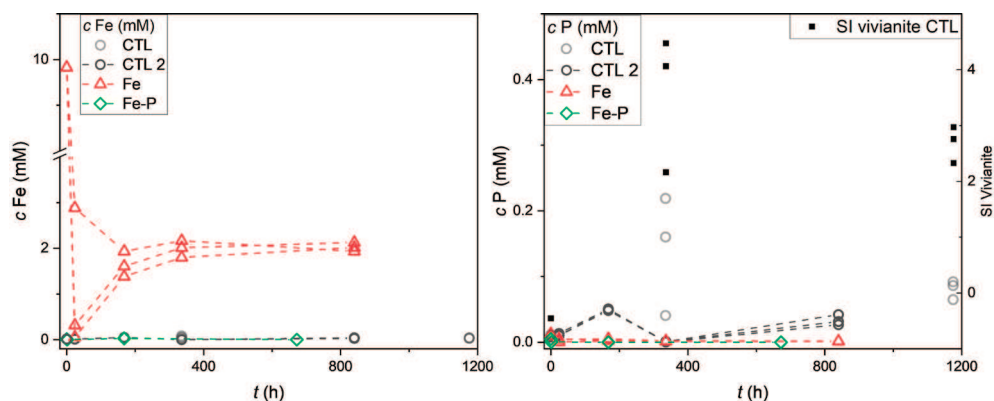


Figure 4-2 Time-dependent porewater concentrations of iron and phosphorus in control (LO1-CTL, LO1-CTL 2), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1. Supersaturation index (SI) for vivianite in pore water in LO1-CTL on the right axis of the soluble phosphorus graph.

Table 4-4 Difference in soluble calcium, magnesium, manganese, sulphur and pH at 168 h in control (LO1-CTL 2), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1. Colour highlights differences to the start, the darker the colour, the bigger the difference.

mM	Ca	Mg	Mn	S	pH end
start	0.79 ± 0.08	0.17 ± 0.02	0.053 ± 0.004	0.08 ± 0.01	
LO1-CTLO2 168 h	1.22 ± 0.07	0.24 ± 0.01	0.104 ± 0.06	0.3 ± 0.2	6.6 ± 0.1
LO1-Fe 168 h	6 ± 1	1.0 ± 0.2	0.8 ± 0.2	1 ± 1	6.0 ± 0.1
LO1-FeP 168 h	3.5 ± 0.1	0.32 ± 0.02	0.25 ± 0.01	3 ± 2	6.0 ± 0.1

In anaerobically incubated samples (Figure 4-2), rapid Fe precipitation occurred following dosing in both LO1-Fe and LO1-FeP treatments; however, approximately 2 mM Fe remained in solution in the LO1-Fe treatment. Phosphate precipitated rapidly in the LO1-FeP treatment, as seen by the low P concentrations at the beginning, and remained consistently low in the LO1-Fe treatment. In contrast, phosphate concentrations fluctuated in the LO1-CTL and LO1-CTL-2 samples, with minor variations also observed in Fe concentrations. These fluctuations influenced the calculated supersaturation index (SI) for vivianite in LO1-CTL treatment, which increased to approximately 4 during incubation and then declined. Spot checks at 168 h revealed temporal variations in soluble calcium, magnesium, manganese, and sulphur concentrations (Table 4-4). Iron dosing was associated with cation release, and LO1-Fe and LO1-FeP treatments exhibited elevated dissolved sulphur concentrations, although measurement uncertainty for sulphur was considerable. When enabling iron sulphide precipitation in Visual MINTEQ with the measured Fe, P and S concentrations, vivianite SI from 4 to 0 (Table A 4-1), indicating inhibition of vivianite formation. Additionally, Fe addition reduced pH, with values declining from 6.6 to 6.0 by the end of the experimental period in the LO1-Fe and LO1-FeP treatments compared to LO1-CTL.

Further characterization of precipitated Fe was achieved through HCl extractions of LO1-CTL, LO1-Fe, and LO1-FeP treatments (Figure 4-3). The majority of HCl-extractable Fe was present as Fe(II). Relative to LO1-CTL, LO1-Fe and LO1-FeP treatments exhibited additional Fe(II) recoveries of 135 $\mu\text{mol g}^{-1}$ DW and 170 $\mu\text{mol g}^{-1}$ DW, respectively. Considering the theoretical Fe(II) spike of 185 $\mu\text{mol g}^{-1}$ DW, these results suggest that most of the added iron remained extractable and in a reduced state.

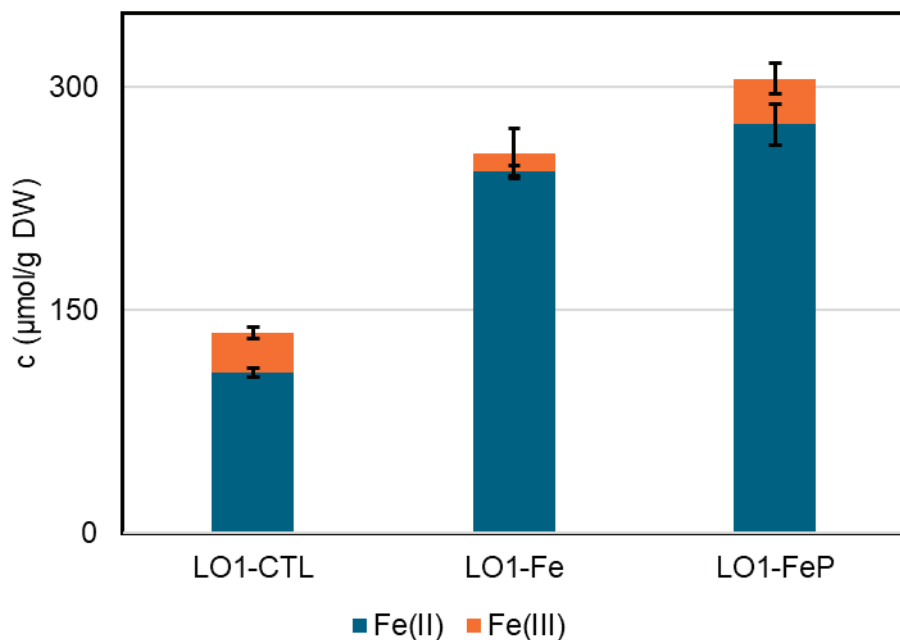


Figure 4-3 HCl extracted Fe from control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup LO1. ($Fe_{\text{sediment}} 420 \pm 10 \mu\text{mol/g DW}$, $Fe_{\text{dose}} 185 \mu\text{mol/g DW}$).

4.3.2 Vivianite detection and quantification approaches

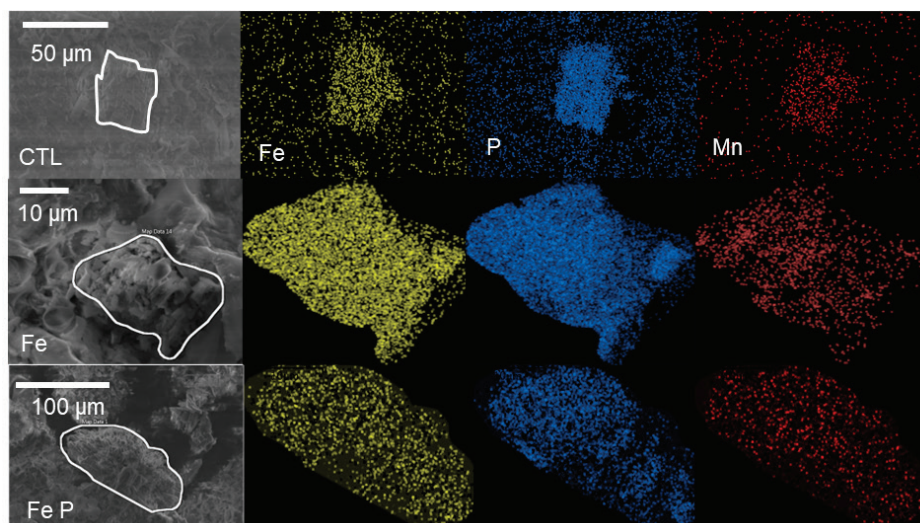


Figure 4-4 Electron microscopy images of control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1. The EDX maps of Fe, P, and Mn show Mn-substituted vivianite in all samples.

Vivianite was identified in all three samples using light microscopy (Figure A 4-2) and SEM-EDX analysis. Manganese (Mn) incorporation into vivianite was evident, with Mn contents corresponding to 22%, 14%, and 26% of Fe for representative phases in LO1-CTL, LO1-Fe, and LO1-FeP, respectively (Figure 4-4, Table A 4-2). Although these values do not represent the entire sample, they confirm that Mn substitutes for Fe within vivianite across treatments. Despite clear microscopic evidence, only weak signals corresponding to vivianite were observed in the initial control sediment using XRD at 14° 2 Theta, while LO1-FeP exhibited pronounced reflections after 1.5 h, which diminished by 168 h (Figure 4-5). A similar trend was noted between LO1-Fe treatment at 168 h and 336 h, with a reflex visible in the former but absent in the latter.

Further information on the iron mineral phases was gathered with Mössbauer spectroscopy. Vivianite typically exhibits two distinct high-spin (hs) Fe(II) doublets (A and B) with isomer shifts (IS) of 1.16 and 1.20 mm s^{-1} and quadrupole shifts (QS) of 2.45 and 2.91 mm s^{-1} , respectively [28]. Spectra for LO1-CTL and LO1-Fe (Figure 4-6; Table 4-5) were fitted with a high-spin Fe(II) doublet and an additional low-spin Fe(II)/Fe(III) component, originating from iron sulphides and iron (III) minerals [12]. The hs doublet in LO1-CTL exhibited IS and QS values of 1.11 mm s^{-1} and 2.57 mm s^{-1} , while LO1-Fe showed a slightly higher IS (1.19 mm s^{-1}) with similar QS. If these deviations reflected an overlapping vivianite signal, the mixed QS would typically be around 2.75 mm s^{-1} . Since the QS observed in this study is lower, it is more likely that a third unattributed phase with low IS is present next to the vivianite, such as Fe(II) silicates (IS $\approx$ 1.15 mm s^{-1} , QS $\approx$ 2.57 mm s^{-1} ; [29]) or Fe(II)-organic complexes, which exhibit comparable Mössbauer characteristics [30].

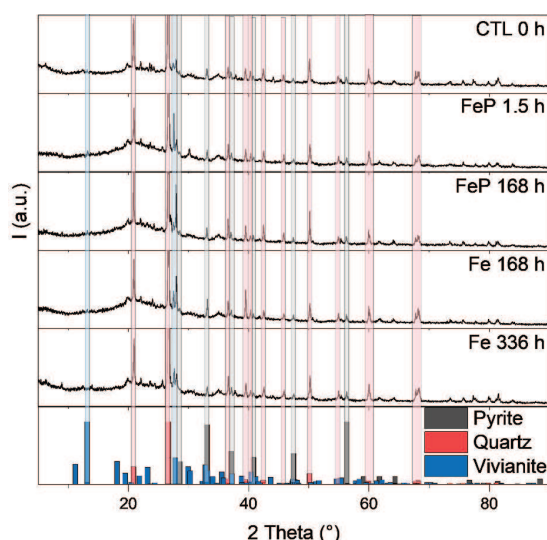


Figure 4-5 XRD patterns of initial, iron-spiked (Fe), and iron and phosphate-spiked (FeP) lake sediment mixes from Lake Ormstrup mix LO1 at different times with the identified crystal phases pyrite (R050070), quartz (amcsd 0006212), and vivianite (amcsd 0012069) [55].

In contrast, LO1-FeP amended with Fe(II) and phosphate displayed distinct hs Fe(II) signals consistent with vivianite ($IS = 1.21$ and 1.19 mm s^{-1} ; $QS = 2.44$ and 2.96 mm s^{-1}). However, the A/B intensity ratio was 0.67, exceeding the expected crystallographic ratio of 0.5 [31] indicating substitution of iron with impurities [32] or higher oxidation at site B than A. Moreover, the fit for LO1-FeP did not account for the Fe phase identified in LO1-CTL, which likely persisted post-amendment. When overlaying the spectral data for all three amendments, a clear increase in the hs Fe(II) region is observed for the LO1-FeP treatment, indicative of the newly formed vivianite. Based on this difference and assuming structural similarity between vivianite in LO1-FeP and LO1-CTL, an alternative vivianite fit to estimate the vivianite present in the LO1-Fe and LO1-CTL treatment is presented in the Supplementary (Text A 4-1, Table A 4-3, Table A 4-4, Figure A 4-3).

Table 4-5 Original fit distribution of Fe species according to Mössbauer analysis at 295 K measurements control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1, with isomer shift (IS), quadrupole splitting (QS), magnetic field (B), line width (LW), and related Fe spectral contribution percentage (% Fe). Errors: IS, QS, LW $\pm 0.01 \text{ mm/s}$; % Fe $\pm 3 \%$.

sample	type	T K	IS	QS	Lw	%
LO1-CTL	Fe(II)	295	1.11	2.55	0.73	20
	Fe(III)/Is Fe(II)	295	0.33	0.64	0.48	80
LO1-Fe	Fe(II)	295	1.14	2.57	0.63	18
	Fe(III)/Is Fe(II)	295	0.34	0.66	0.5	82
LO1-FeP	Fe(II) Vivianite B	295	1.19 [^]	2.96	0.54*	12
	Fe(II) Vivianite A	295	1.21 [^]	2.44	0.54*	18
	Fe(III) ^a	295	0.46 [^]	0.59 [^]	0.48 [^]	9
	Fe(III)/Is Fe(II)	295	0.3	0.68	0.53	61

*fixed same line width for vivianite A and B contributions, [^]fixed parameters, ^ahypothesized based on Fe(III) in pure oxidized vivianite

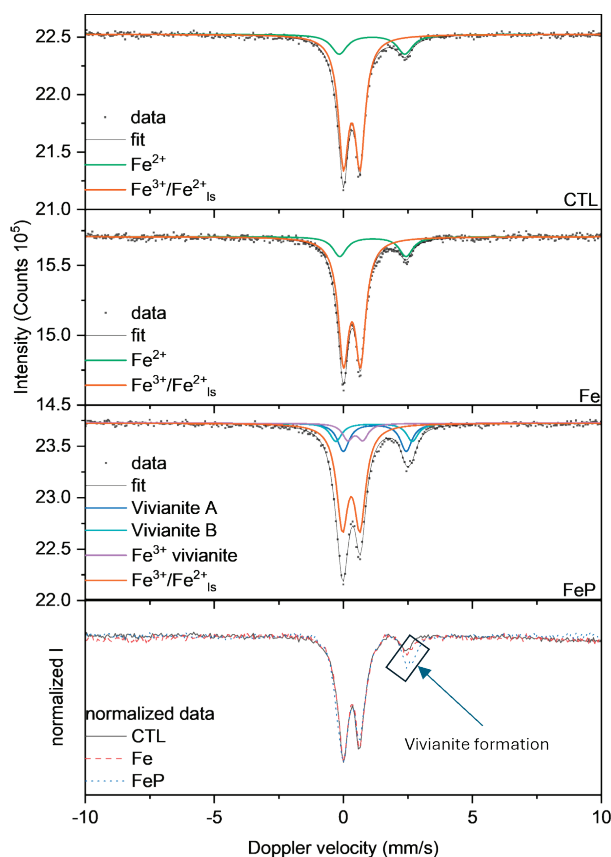


Figure 4-6 Mössbauer spectra at 295 K control (LO1-CTL), iron-spiked (Fe), and iron and phosphate-spiked (FeP) lake sediment mixes from Lake Ormstrup mix LO1, with original fitted iron phases. Bottom: Overlap of baseline-subtracted, normalized Mössbauer spectral data at 295 K of LO1-CTL, Fe, and FeP without fitted phases with spectral area of newly formed vivianite highlighted.

4.3.3 Extending quantification of vivianite in unamended sediment with bipyridine extraction

To characterize P speciation, sequential phosphorus extractions were performed on the unamended sediment (Figure 4-7). Due to the limitations in quantifying the vivianite native to the sediment with Mössbauer spectroscopy in the LO1-CTL treatment, a bipyridine step specific for Fe(II)- bound P was included to characterize a second, unamended Lake Ormstrup sedimentary mix (LO2) (Figure 4-7). In the standard extraction sequence (excluding bipyridine), approximately 90% of total P was recovered during the BD (reductive) and NaOH (alkaline) steps for both samples. Phosphorus distribution was relatively uniform in LO1, whereas LO2 exhibited a slightly higher proportion in the BD fraction. The BD step also extracted the largest share of iron ($\approx 30\%$) in both samples. However, NaOH-extracted iron differed markedly between sediments: 10% in LO1 versus only 2% in LO2, suggesting minor variations in metal-bound P phases. Incorporation of the bipyri-

dine step in LO2 substantially altered the extraction profile. Most Fe and P were recovered during this step, with an Fe/P molar ratio of approximately 2. This resulted in a 65% reduction in BD-extracted Fe and P and a 60% reduction in NaOH-extracted phosphorus. The bipyridine fraction also contained manganese equivalent to 10% of extracted iron and magnesium equivalent to 23%, along with a significant calcium release ($\approx 91\%$ of extracted iron). In the absence of bipyridine, manganese, magnesium, and calcium were primarily recovered in the BD fraction. These findings indicate that the bipyridine step targeted vivianite, which incorporates manganese, magnesium, and calcium as minor constituents.

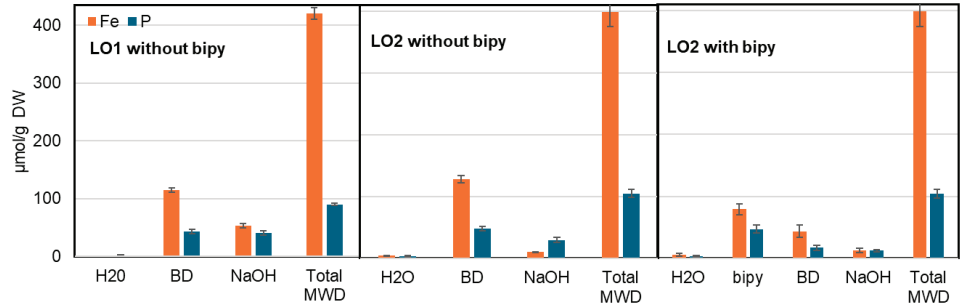


Figure 4-7 Iron and phosphorus extracted from LO1 and LO2 by different extractants with the total iron and phosphorus content as determined by digestion in nitric acid.

4.3.4 Estimating vivianite in sediment

Table 4-6 Overview of the amount of Fe(II) quantified by Mössbauer spectroscopy (Mb) of control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1 with original and alternative fit, versus bipyridine extraction from Lake Ormstrup mix LO2.

		Fe _{total} (μmol/g DW)	% Fe(II)	P _{total} (μmol/g DW)	%P
LO2	bipyridine	400	11 ^a	104	45
LO1-CTL	original Mb	400	20	90	89 ^a
	alternative Mb	400	9	90	40 ^a
LO1-Fe	original Mb	585	18	90	117 ^a
	alternative Mb	585	13	90	85 ^a
LO1-FeP	original Mb	585	30	180	98 ^a
	alternative Mb	585	20	180	65 ^a

^acalculated stoichiometrically with Fe(II)/P=1

Based on the Mössbauer spectroscopy analyses of the LO1 samples and the bipyridine extraction of the LO2 samples, the vivianite content in the sediment mixes was assessed (Table 4-6). The first section of Table 4-6 is dedicated to the extraction of bipyridine in

LO2, where the Fe in vivianite was calculated with a Fe/P ratio of 1, as determined by the SEM-EDX characterizations (Table A 4-2). The following rows contain the quantifications based on the original Mössbauer fit assuming all hs Fe(II) were vivianite (Table 4-5, Figure 4-6), and the alternative Mössbauer fit (Table A 4-3, Figure A 4-3). The respective phosphorus in vivianite was calculated with a Fe/P of 1 as well. Yet the question is: which of these quantifications is most likely to accurately assess the amount of vivianite?

4.4. DISCUSSION

4.4.1 Vivianite identification and quantification

By incubating dredged lake sediment anaerobically without amendment (LO1-CTL), with Fe dosing (LO1-Fe), and with Fe and P dosing (LO1-FeP), vivianite formation was studied in the three treatments. Only in the LO1-FeP treatment, vivianite could be reliably detected with Mössbauer spectroscopy, but bipyridine extractions were needed in addition to estimate the vivianite already present in the unamended sediment. Furthermore, SEM-EDX, bipyridine extraction, and the shifted A/B ratio in the LO1-FeP Mössbauer spectrum of vivianite indicate that vivianite is present in the sediment and contains impurities, which is relevant for the vivianite quantification. Especially Mn and Mg are known to be incorporated into the vivianite structure [32]. Elevated manganese concentrations in the sediment, likely resulting from high amounts of manganese in the grain used for duck hunting [33], support this interpretation. Based on the SEM-EDX measurements, the Fe/P ratios were below 1.5 in the treated LO1 samples, specifically 0.8, 1.1, and 1.2 in LO1-CTL, LO1-Fe, and LO1-FeP, respectively, which can be partly explained by manganese substitution (Table A 4-2). Magnesium substitution could further explain the remaining discrepancies since magnesium release was observed within the bipyridine extraction indicating its incorporation into the vivianite structure [34]. However, the bipyridine extracted Fe/P ratio was 2, and the inclusion of the other cations in this ratio further shifts the (Fe+Mg+Mn)/P ratio way above what was expected for the stoichiometric Fe/P ratio of 1.5. Fe/P ratios above 1.5 in bipyridine extractions are not uncommon and can be explained by the additional extraction of oxide, carbonate, and organic phases, containing iron [8]. The best assumption for vivianite present should therefore be based on the P content of the bipyridine extraction and not the Fe extracted [8].

Both the bipyridine extraction of LO2 and the amount of phosphate in vivianite, based on the alternative Mössbauer quantification of LO1-CTL, indicate a similar amount of vivianite (Table 4-6), at 40-45% of the total P, which could validate the alternative Mössbauer fit. The key to this comparison is the assumption that LO1-CTL and LO2 are indeed similar enough, based on similar conditions (anaerobic storage, no extra salts added), and comparable P extractions in Figure 4-7. However, the alternative Mössbauer fit on LO1-Fe estimated that 85% of the total P is bound as vivianite, which is too high considering the

lack of additional evidence. Moreover, the assumption of all hs Fe(II) to be present as vivianite in the original Mössbauer fit would overestimate the amount of P bound in vivianite unrealistically (117%). First, the reliability of the Mössbauer fit for LO1-Fe is questionable due to the relatively small amount of Fe(II) in vivianite compared to the total Fe in the sample, the inherent quantification error of $\pm 3\%$, and the elevated χ^2 (Table A 4-4). Second, a vivianite reflex at $14^\circ 2\theta$ was only distinguishable in the LO1-Fe 168 h sample, but not in the later one (Figure 4-5), further reducing the likelihood of increased vivianite presence in the end sample. In contrast to LO1-Fe, LO1-FeP exhibits clear indications of vivianite formation within the Mössbauer spectrum, as well as in XRD and microscopy, at an estimated 65% of P present in vivianite based on the alternative Mössbauer quantification of LO1-FeP, making the LO1-Fe alternative Mössbauer quantification even less likely.

In summary, bipyridine extraction of LO2 indicates that 45% of the P is bound in vivianite, in good agreement with the alternative Mössbauer fitting of LO1-CTL. However, the alternative fit failed to quantify vivianite, and Fe dosing alone did not significantly increase vivianite in the sediment, in contrast to the clear increase observed in the LO1-FeP sample. This means that iron dosing induced vivianite formation for recovery from dredged sediments is not promising within the approach tested in this study. Reasons for the limitations of this approach will be discussed in the following section.

4.4.2 Barriers in vivianite detection and formation in lake sediments

Magnetic recovery of vivianite has gained attraction in P recovery from digested sludge, with successful pilot implementations and growing technological interest [11,35]. Extending this approach to other matrices, such as pig manure and dredged sediments, is promising, as removing surplus P would make both matrices more suitable for further use. In Figure 4-8, the Fe/P/S ratios for selected studies on vivianite in digested sludge, manure and lake sediments are compared. In these studies, vivianite was analyzed using Mössbauer spectroscopy, XRD, or microscopy, and the presence of vivianite is indicated by filled shapes. Vivianite reliably forms in digested sludge, located at higher P levels within the Fe/P/S scheme, while some exceptions can be seen for manure, with a relatively lower P content. Especially in lake sediments, at the lower end of the P within the Fe/P/S ratio, vivianite absence is observed more often, making it less promising for vivianite-mediated phosphorus recovery. In the following subsections, the different reasons for less promising vivianite formation in lake sediments will be explored and contrasted with those in other matrices.

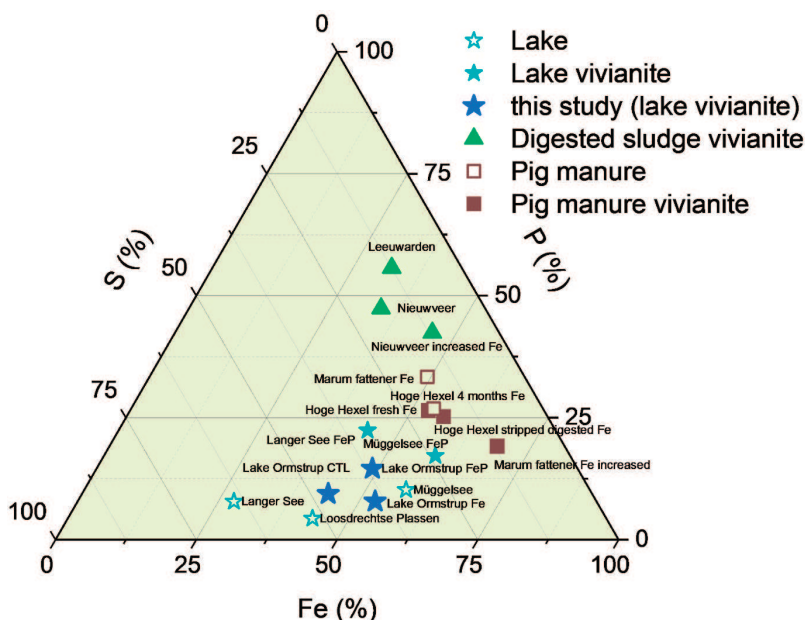


Figure 4-8 Vivianite formation studies in different matrices and according to their Fe/S/P ratio. The presence of vivianite was confirmed in the filled-in shapes within these studies using Mössbauer spectroscopy, XRD or microscopy. Clustering shows clear differences in P abundance in lake sediment vs manure and sludge.

Muggelsee, Langer See [16]; Lake Ormstrup (this study); Loosdrechtse Plassen [23]; Leeuwarden [12]; Nieuwveer [36]; Marum fattener [37]; Hoge Hexel [20].

Difficulties in vivianite detection

Common methods for detecting vivianite in sediments include equilibrium modeling, sequential P extraction, and characteristic X-ray analysis [15], often complemented by electron microscopy or microprobe techniques [38]. However, equilibrium modeling and sequential extraction alone cannot provide definitive evidence of vivianite, as they lack mineralogical confirmation. Characteristic X-ray-based approaches are highly effective for identifying vivianite but typically require preselection of candidate particles through sieving [38] or visual inspection under a light microscope, as applied in this study. Quantification using these methods remains challenging. Solid-state analytical techniques offer more robust characterization of vivianite phases, including X-ray diffraction (XRD) [16,39], X-ray absorption spectroscopy (XAS) [8], and Mössbauer spectroscopy [34]. Nevertheless, XRD often fails to detect vivianite reflections due to low abundance [16,34,38], small particle size [34,40], poor crystallinity [34], Mn substitution [41], or interference from clay minerals [38]—all factors likely relevant for LO1 sediment. Mössbauer spectroscopy is highly reliable for detecting vivianite in digested sludge [12,36] and manure [20], but is more challenging to interpret in heterogeneous sediment matrices [30,42]. Measuring above and below the magnetic ordering temperature of vivianite (12 K [43]) could help detect the vivianite phase, but a high degree of impurities could hinder magnetic order-

ing [12]. Further, Haasler et al. (2025) [8] attributed the reduced vivianite detection by XAFS to the high iron and organic content, which may also have complicated the Mössbauer interpretation for LO1. The inclusion of a bipyridine step in sequential phosphorus extraction has improved identification of Fe(II)-associated phosphate [8,22,44]. However, this method is sensitive to particle size and purity, which limits its reliability [34]. Ultimately, a combined approach—bipyridine-modified extraction coupled with solid-state analysis—remains essential for obtaining robust estimates of vivianite in sediments, as demonstrated by Haasler et al. (2025)[8].

Phosphate competition with sulphide, carbonate and organics

The lower relative P content in lake sediments compared to manure and digested sludge may lead to less vivianite formation when iron precipitates with other components in the matrix. Of course, iron sulphides are already more thermodynamically favoured over vivianite formation [45]; however, carbonate and organics could also play a larger role in inhibiting vivianite formation in lake sediments.

Despite the S/reactive Fe ratio below the empirical threshold of 1.1 in both LO1-Fe and LO1-FeP, vivianite formation could only be confirmed in the latter. In section 4.3.1, it was shown that the fluctuating sulphur concentrations in the sediment would favour iron sulphide precipitation over iron phosphate. If sulphate reduction proceeds faster than P is made available, the probability of vivianite formation decreases. Iron sulphide formation would also explain the smaller high-spin Fe(II) region in LO1-Fe compared to LO1-FeP, as iron sulphide phases are typically measured as low-spin Fe(II), contributing to the low-spin Fe(II)/Fe(III) section of the spectrum. Combined with the high amount of HCl extractable iron(II) (Figure 4-3), this would support a good portion of the dosed Fe in LO1-Fe being present as low-spin Fe(II), namely iron sulphide. Elevated sulphide concentrations are common in eutrophic lakes, particularly in hypolimnetic waters during summer stratification [46] and in porewaters of shallow systems [47]. In conclusion, the high sulphide availability compared to phosphate is a key challenge in stimulating and predicting vivianite formation in eutrophic lake dredged sediments such as the one from Lake Ormstrup.

While iron sulphide can be clearly distinguished from vivianite in Mössbauer spectroscopy thanks to its low-spin iron(II) disposition, there were other high-spin iron(II) species that interfered both with vivianite formation and detection in Lake Ormstrup. Iron(II) silicates could contribute to the difficulty in detection; however, due to their slow formation [48], they are unlikely to play a significant role in the Fe dosing experiments. Another group of high-spin iron(II) compounds that may have formed are iron(II)-organic complexes, exhibiting Mössbauer shifts similar to the ones of the silicates [30]. As mentioned in 4.1, iron(II)-organic binding could explain the elevated Fe concentrations extracted with the bipyridine extraction step. Indeed, Muench et al. (2024) [23] hypothesized the existence

of iron(II)/iron(III) containing phases, stabilized by organic matter when both Fe-sulphide and Fe-phosphate binding could be excluded in the researched sediment (Loosdrechtse Plassen Figure 4-8). This stabilization may have prevented the formation of the more redox-stable vivianite, leading to an easier release of internal phosphate [23]. The interaction between iron and organic matter has been previously documented [49,50], and its role in suppressing vivianite formation has been noted [14,51]. Nevertheless, Rothe et al. (2016) [10] reported that vivianite preferentially forms in Fe- and organic-rich environments, indicating that the presence and degradation of organic matter create reducing conditions and supply inorganic P, which is necessary for vivianite formation. Hence, organic matter plays a dual role in vivianite formation, ensuring suitable conditions while potentially complexing iron.

Recently, Notini (2023) [52] et al. and Kubeneck et al. (2024, 2025) [17,42] showed the relevance of green rust as a product of iron transformations in soils and sediments ($IS=1.24-1.28$ mm/s and $QS=2.70-2.90$ mm/s). Green rust is a mixed-valence Fe(II)–Fe(III) double-layer hydroxide with intercalated anions $[(Fe(II)_{1-x}Fe(III)_x(OH)_2]^{x+} \cdot [(x/n)A^{n-} \cdot (m/n)H_2O]^{x-}$, where $A^{n-} = CO_3^{2-}, SO_4^{2-}, Cl^-, OH^-$ [30]. When investigating the reductive dissolution of ferrihydrite in saltwater sediment, the metastable mineral green rust was identified using ^{57}Fe -labelled samples in Mössbauer spectroscopy and Fe-EXAFS, rather than vivianite, which could have formed according to thermodynamic predictions [17]. Green rust was likely stabilized by components present in the porewater, such as phosphate, silicate, and organic ligands [17]. This makes a combination of these parameters with organically complexed iron likely. Dissolved carbonate is present in the lake sediment at 1.5–4 mM based on exploratory measurements in the mixed sediments of Lake Ormstrup (results not shown). At the dissolved Fe and phosphate concentrations of LO1-CTL, this concentration does not influence vivianite SI. However, once the iron in solution is increased to 9.8 mM of the Fe dose, Visual MINTEQ predicts the precipitation of the ferrous carbonate siderite ($FeCO_3$) at a near-stoichiometric carbonate concentration. Siderite is a more pure and reduced form of iron carbonate, compared to green rust, and this further indicates the formation of ferrous carbonates over ferrous phosphates. Interestingly, ferrous carbonate (siderite) formation also plays a role in inhibiting vivianite formation in aged manure (Figure 4-8), despite otherwise favourable Fe/S/P ratios, due to higher carbonate availability compared to phosphate. Hence, at an elevated iron dose, iron carbonate minerals are likely to play a role in suppressing vivianite formation in Lake Ormstrup.

4.4.3 Implications for phosphate recovery from dredged sediments

The use of Fe(II) salt has been shown to be an effective way to form vivianite both in manure [20] and anaerobically incubated sludge [53]. In this study, iron(II) chloride tetrahydrate was selected to ensure sufficient iron(II) is available for vivianite formation in the sediment, thereby ensuring independence from the iron reduction process. However, based on the observation using XRD (Figure 4-5), vivianite that may have formed upon

iron(II) addition was disappearing over time. Moreover, this acidic iron salt induced a measurable pH decline from 6.6 to 6.0, with the initial drop likely more pronounced due to concentration effects. This can further alter sediment speciation, potentially mobilizing heavy metals or releasing hydrogen sulphide ($pK_a(\text{HS}^-) \approx 7.0$ [54]), both of which pose environmental and health risks. The low efficiency and high acidity of the Fe(II) salt added make it inadequate to stimulate vivianite formation in sediments. An alternative approach could involve the use of more alkaline iron(III) salts, such as iron(III) (hydr)oxides. These compounds would mitigate pH decline and form iron sulphides less readily. Interestingly, vivianite was only found in the presence of phosphate adsorbed to iron(III)oxyhydroxides and not in the iron(III)oxyhydroxides samples alone [16,42]. The proximity of iron and phosphate likely creates a microenvironment with a higher SI for vivianite formation upon reductive dissolution [17]. This could occur in parallel with vivianite formation in digested sludge, where vivianite is also hypothesized to form after phosphorus associates with iron(III) prior to digestion [12]. Therefore, facilitating phosphate adsorption to iron(III) could be a relevant way to increase vivianite formation in sediments. However, this approach remains unexplored, and overall, vivianite yields from dredged sediments would be too small to be of interest for its magnetic recovery compared to the recovery from digested sludge or perhaps manure.

4.5 CONCLUSION

The feasibility of vivianite-mediated phosphate recovery from dredged sediment was explored in Lake Ormstrup. Reliable quantification of native vivianite required a bipyridine extraction step, as Mössbauer spectroscopy fitting could not be reliably refined to account for the vivianite. Moreover, the addition of iron(II) salt failed to enhance vivianite formation in the sediment. Consequently, the magnetic extraction of vivianite from dredged sediments is less promising than from digested sludge or manure. Nevertheless, the roles of phosphate availability for iron binding and the adsorption on iron(III) oxides as precursors to vivianite formation should be further explored to improve the mechanistic understanding of phosphorus sequestration and potential recovery strategies in sediments.

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SUPPLEMENTARY INFORMATION

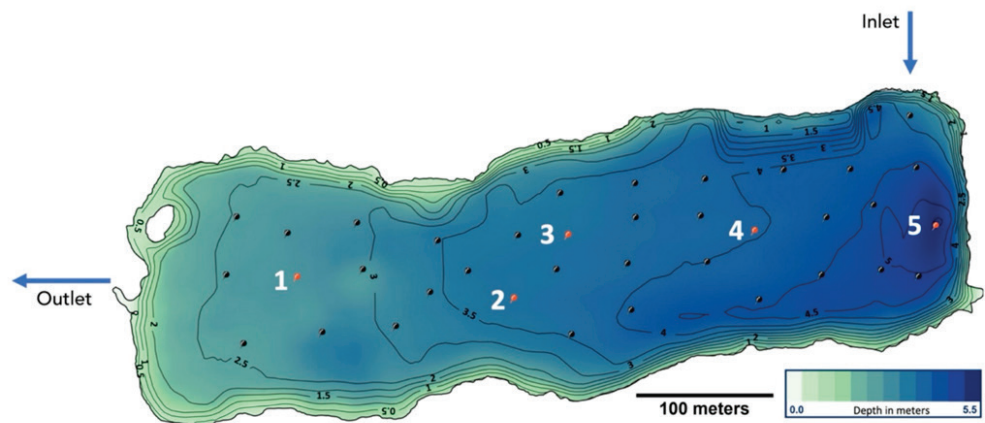


Figure A 4-1 Lake Ormstrup (56°19'38"N 9°38'45"E) bathymetric map showing water depth at 0.5 m intervals, with markings of the inlet and outlet (arrows) (Polauke, 2025). The five permanent stations, 1–5, were used to form the Lake Ormstrup mixes LO1 and LO2.

Table A 4-1 MINTEQ simulation using the soluble iron, phosphorus, and sulphur in LO1-CTL to LO2 at 168 h as measured with ICP, excluding and including FeS(ppt) precipitation.

SI without FeS (ppt) precipitation			SI with FeS precipitation		
LO1-CTL 2(1)	LO1-CTL 2(2)	LO1-CTL 2(3)	LO1-CTL 2(1)	LO1-CTL 2(2)	LO1-CTL 2(3)
3.694	3.964	4.035	-0.11	-1	1.56

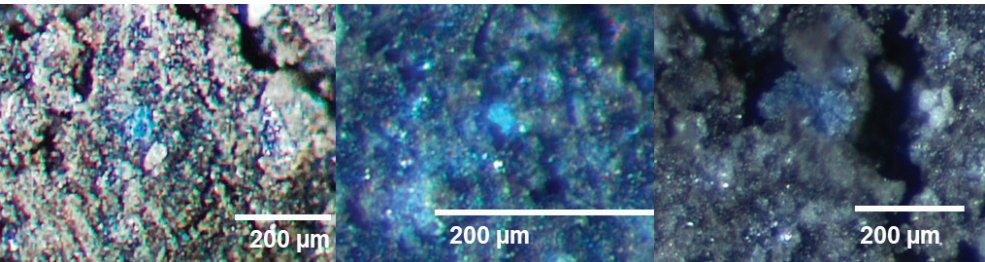


Figure A 4-2 Blue vivianite crystal under the stereoscope in control (LO1-CTL), iron-spiked (Fe), and iron and phosphate-spiked (FeP) lake sediment mixes from Lake Ormstrup mix LO1

Table A 4-2 Elemental distribution for singled out vivianite crystals (Figure 4-4) with Fe/P and (Fe+Mn)/P in control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1.

Atomic %				
Element	LO1-CTL	LO1-Fe	LO1-FeP	
C		35.3	28.1	56.2
O		54.3	60.2	38.2

Table A 4-2 Elemental distribution for singled out vivianite crystals (Figure 4-4) with Fe/P and (Fe+Mn)/P in control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1. (*continued*)

Atomic %			
Al	0.3	0.3	0.7
Si	1.1	1.3	3.3
P	3.4	4.3	0.5
S	0.1	0.2	0.3
Ca	0.2	0.1	0.2
Mn	1.1	0.7	0.1
Fe	4.2	4.8	0.5
Fe/P	1.2	1.1	0.9
(Fe+Mn)/P	1.6	1.3	1.1

Text A 4-1 Alternative fitting procedure for the Mössbauer spectra

1. The parameters of the high spin Fe(II) contribution from the LO1-CTL treatment were fixed and applied on the LO1-FeP treatment.
2. The leftover high spin Fe(II) contribution in the LO1-FeP treatment was fitted for the two vivianite doublets (LO1-FeP Figure A 4-3, Table A 4-4).
3. The characteristic parameters for vivianite grown from Fe(II) and P spiked into the sediment were saved from this fit ($IS=1.23, 1.22$; $QS=2.49, 3.00$). Interestingly, the best fit arose from an amplitude distribution of $A/B=0.67$ instead of the stoichiometric 0.5, hence the amplitude ratio $A/B=0.67$ was used for further fitting.
4. The characteristic IS and QS of both vivianite doublets identified in LO1-FeP, as well as the A/B amplitude ratio of 0.67 were copied into the LO1-CTL and LO1-Fe treatments. The χ^2 improved when adapting the QS of vivianite B to 2.91, so this QS was used for further fitting. Moreover, the line width was adjusted to 0.4 mm/s to account for the more continuous nature of the iron phases in these samples.
5. The samples were fit using only these vivianite parameters, and then the resulting areal fit was fixed, leaving space to add the unattributed Fe(II) contribution of LO1-CTL with fixed parameters ($IS=1.11$; $QS=2.55$).
6. The unattributed Fe(II) high spin contribution was added with fixed IS , and QS , with the mathematically most fitting LW at 0.5 mm/s. The spectra were fit again (LO1-CTL and LO1-Fe Figure A 4-4, Table A 4-3).

Parameters for this alternative fit are presented in Figure A 4-3, Table A 4-3 and Table A 4-4. It is important to note that this approach quantified only the additional vivianite formed in LO1-FeP. Thus, the vivianite contribution identified for LO1-CTL needs to be added to the spiked vivianite detected in LO1-FeP to account for spiked and native vivianite in LO1-FeP.

Table A 4-3 Alternative fit Fe spectral contribution percentage (% Fe) at 295 K of control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1, with respective χ^2 . Errors: % Fe $\pm$ 3 %.

	Vivianite A (%)	Vivianite B (%)	unattributed Fe(II) (%)	Fe(III)/Is Fe(II) (%)	χ^2
LO1-CTL	4	5	10	82	1.36
LO1-Fe	5	8	5	83	2.05
LO1-FeP	5	6	18	70	1.33

Table A 4-4 Alternative fitting parameters of Fe species according to Mössbauer analysis at 295 K measurements of control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1, with isomer shift (IS), quadrupole splitting (QS), line width (LW), and restrictions for the amplitude.

sample/fit	type	IS (mm/s)	QS (mm/s)	LW (mm/s)	Amplitude
	Fe(II) unattributed	1.11	2.55	0.73	manually changed
LO1-CTL, LO1-Fe	Vivianite A	1.23	2.49	0.40	A/B=0.67
	Vivianite B	1.22	2.91	0.40	
	Vivianite A	1.23	2.49	0.27	free
LO1-FeP	Vivianite B	1.22	3.00	0.27	free

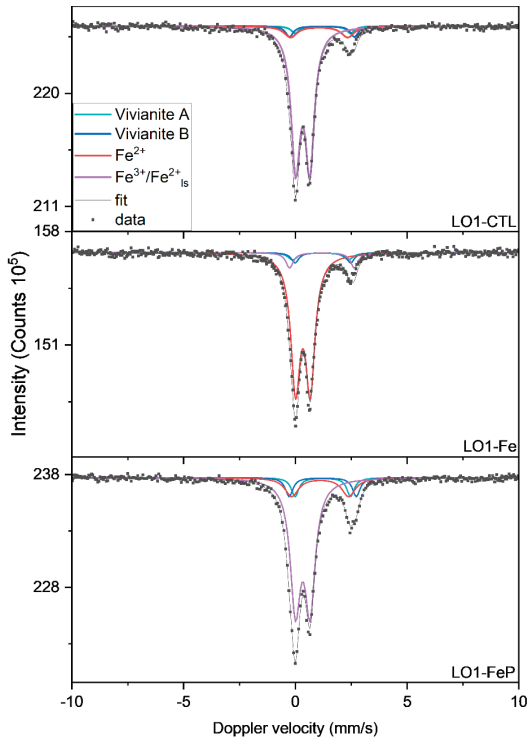


Figure A 4-3 Mössbauer spectra at 295 K control (LO1-CTL), iron-spiked (LO1-Fe), and iron and phosphate-spiked (LO1-FeP) lake sediment mixes from Lake Ormstrup mix LO1, with alternative fitted iron phases according to Text A 4-1.

Bibliography A

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5

Leveraging iron sulphide destruction via ORP-controlled microaeration to improve phosphate recovery

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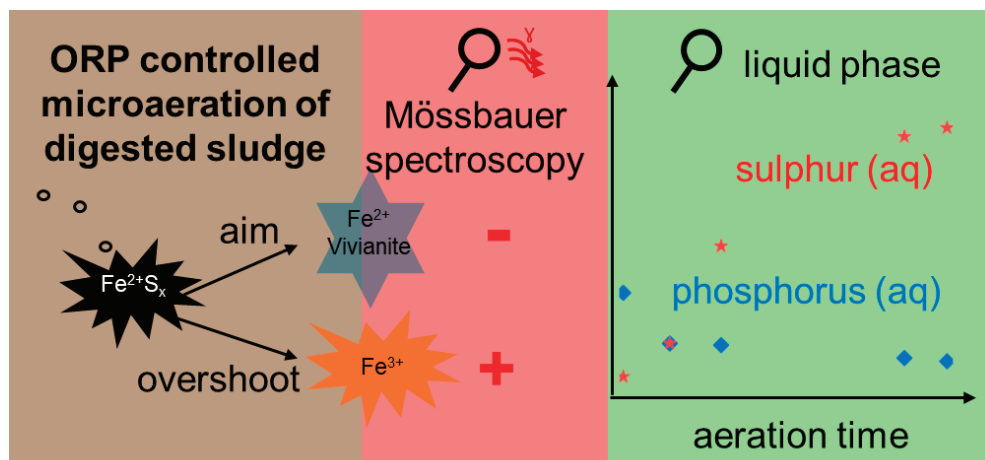
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ABSTRACT

Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is an attractive product for phosphorus recovery and can form in digested sludge, sediments, and manure when sufficient Fe(II) is available. In wastewater treatment, however, iron sulphides typically outcompete vivianite under anaerobic conditions. To reduce the iron dosage required for vivianite formation, this study investigated whether controlled microaeration at oxidation–reduction potential (ORP) levels ranging from -220 to 0 mV can oxidize iron sulphides, release Fe(II), and thereby promote vivianite formation. Microaeration produced two contrasting effects. Mössbauer spectroscopy indicated a loss of ~20% of the Fe(II) vivianite fraction across all ORP conditions, while a pyrite-like iron sulphide phase remained largely unchanged. In contrast, in the soluble phase, sulphur species increased (~40% of total sulphur), and phosphorus decreased (~70% of soluble phosphorus), suggesting iron–phosphate binding or adsorption under microaerobic conditions. These observations support a time-dependent reaction sequence. During early aeration, more labile FeS_x phases are likely to have oxidized to elemental sulphur, providing free iron sites for phosphorus binding/adsorption. After prolonged aeration (24 h), both sulphur and iron species shifted toward oxidized products, including sulphate and Fe(III) minerals. Targeting only the initial microaeration phase may offer a pathway to selectively convert iron sulphides into more desirable recovery products—elemental sulphur and vivianite. Additionally, phosphorus removal, at ORP as low as -220 mV highlights microaeration as a potential low-chemical alternative to peroxide-based treatments.

Graphical Abstract



5.1 INTRODUCTION

Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$) has gained attention as a promising mineral for phosphate recovery from digested sludge due to its paramagnetic properties, which enable magnetic separation—a technique successfully demonstrated at pilot scale [1,2]. This ferrous phosphate mineral typically forms under anaerobic conditions, as in the sludge digesters of wastewater treatment plants (WWTPs). Its low solubility and stability within a pH range of 6–8 favour its formation over other phosphate minerals, including calcium phosphates and magnesium phosphates such as struvite [3,4]. The formation of vivianite is contingent upon the presence of iron, typically introduced via iron-based coagulants used in WWTPs for the removal of phosphate, sulphide, and other contaminants [5]. However, prior to phosphate precipitation, iron preferentially binds with sulphide due to the higher thermodynamic stability of iron sulphide species [6]. This competitive interaction is well-documented in lake sediments, where vivianite formation is inhibited unless the molar ratio of reactive iron to sulphur remains above 0.9 [7]. Prot et al. (2020) [8] further demonstrated that vivianite can form in digested sludge when the Fe/S ratio is above 1. While lake sediments exhibit a range of FeS species—from amorphous phases to mackinawite (Fe_{1+x}S), greigite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{S}_4$) and pyrite (FeS_2) [9]—crystalline forms such as pyrite are rarely observed in sludge environments [8,10,11]. Since the iron sulphide composition is not well defined and difficult to analyze due to small particle size and low crystallinity, they are denominated FeS_x [11–13].

The preferential formation of iron sulphides necessitates additional iron dosing to enable subsequent vivianite precipitation, thereby increasing operational costs. For instance, assuming a sulphur content of 10 g S /kg dry weight (DW) [11] and an Fe/S ratio of 1, an additional 17 g/kg DW of iron must be dosed to satisfy sulphide binding before promoting vivianite precipitation. If iron sulphide formation could be suppressed, this additional iron could instead contribute directly to vivianite formation, potentially satisfying up to 19% of the required iron for phosphate precipitation in RZWI Nieuwveer, based on 38 g P/kg DW [11] and the stoichiometric vivianite Fe/P ratio of 1.5. One potential strategy involves the controlled oxidation of iron sulphides to liberate iron for vivianite formation. Ma et al. (2023) [14] demonstrated that vivianite can form from FeS via a dissolution–precipitation mechanism under conditions of continuous sulphide removal. An approach to remove sulphide involves oxidizing it to species such as elemental sulphur or sulphate, preventing the formation of the toxic H_2S gas. Pyrite oxidation is assumed to progress via an initial dissolution of the mineral producing iron(II) [15,16], indicating a potential window for selective FeS destruction and vivianite formation. Although vivianite formation under such conditions has not yet been empirically demonstrated, the oxidation of iron sulphides in sludge has been investigated. Yin et al. (2021) [17] evaluated various oxidants and found that hydrogen peroxide (500 mg/L) was effective in controlling H_2S release, improving sludge dewaterability, and precipitating phosphate. However, the use

of peroxides involves the use of chemicals and promotes Fenton-like reactions, increasing Fe(III) concentrations [18]. This can lead to the formation of ironhydroxyphosphates or oxidized iron (III) minerals such as ferrihydrite ($\text{Fe}^{3+}_2\text{O}_3 \cdot 0.5 \text{H}_2\text{O}$) that are known to adsorb phosphate to a certain extent [19]. Yet, the formation of vivianite would be more interesting, enabling both a more favorable Fe/P binding of 1.5 in comparison to the Fe(III) precipitates [20] as well as the magnetic recovery of iron and phosphate. Aeration presents a more promising alternative for iron sulphides oxidation, as it avoids the formation of radicals and is less environmentally aggressive compared to peroxides. Yin et al. (2021) [17] also explored aeration for sulphide removal but dismissed its application due to elevated H_2S production at pH ~ 6 , which enhances H_2S volatility and increases pumping costs. Microaeration, in contrast, has attracted attention as a method for H_2S scavenging in anaerobic digestion systems [21]. Microaerobic conditions are typically defined by oxidation-reduction potentials (ORP) between -230 and -180 mV [21,22]. The primary objective of this research was to investigate an ORP-based controlled aeration in order to oxidize iron sulphides to Fe^{2+} and S^0 , and the subsequent use of the iron for the formation of the Fe(II)-phosphate vivianite in digested sludge for more efficient phosphate recovery.

5.2 MATERIAL & METHODS

5.2.1 Digested sludge

Digested sludge was collected in April 2025 from RWZI Nieuwveer, and experiments were conducted from May to July of the same year. The composition of the digested sludge analyzed according to the procedure described in 2.3 is summarized in Table 5-1.

Table 5-1 Total elemental composition of microwave-digested sludge measured with ICP-OES and composition IC of the soluble fraction after $0.45 \mu\text{m}$ filtration, measured with ICP-OES and IC, including total solids (TS), volatile solids (VS), pH, and oxidation-reduction potential (ORP). Replicates are represented with N.

Elements/ Parameter	Total elements wet sludge (N=3) c (g/kg)	Compounds	Composition soluble fraction(N=2) c (mg/L)
Mg	210 ± 7	Mg	1.43 ± 0.05
P	1990 ± 40	P	116 ± 1
Fe	1580 ± 20	Fe	1.5 ± 0.4
S	630 ± 20	S	10 ± 1
Ca	1580 ± 10	Ca	56 ± 1
Al	330 ± 10	SO_4^{2-}	7 ± 3
TS	45.8 ± 0.2	K^+	250 ± 20
VS	29.4 ± 0.2	Na^+	110 ± 7
ORP (mV) (N=1)	-350	Cl^-	143 ± 1

Table 5-1 Total elemental composition of microwave-digested sludge measured with ICP-OES and composition IC of the soluble fraction after 0.45 μm filtration, measured with ICP-OES and IC, including total solids (TS), volatile solids (VS), pH, and oxidation-reduction potential (ORP). Replicates are represented with N. (*continued*)

Elements/ Parameter	Total elements wet sludge (N=3) c (g/kg)	Compounds	Composition soluble fraction(N=2) c (mg/L)
pH (N=1)	8.7	NH_4^+ (N=1)	3160
		HCO_3^- (N=1)	5990

5.2.2 Aeration experiments

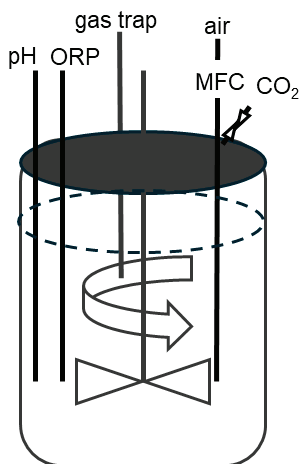


Figure 5-1 Schematic of the reactor system used in aeration experiments, MFC=Mass flow control.

A total of 1.5 L of digested sludge was aerated under continuous stirring in the reactor system schematically depicted in Figure 5-1. Both pH and oxidation–reduction potential (ORP) were regulated using limit switches, and all measurements were recorded via a data logger. A gas trap containing 0.01 M NaOH was installed to capture any H_2S potentially released during the experiments. Samples (15 mL) were withdrawn through an outlet at predefined intervals over 168 h (0, 3, 24, 48, 144, and 168 h). At the final sampling point, an additional 50 mL was collected for solids characterization.

To investigate the oxidative dissolution of iron sulphide, aeration was applied to maintain ORP setpoints of -220 mV, -150 mV, and 0 mV. These ORP targets were selected based on preliminary modelling using Visual MINTEQ, which used equimolar concentrations of iron, sulphur, and phosphorus at pH 7.8 as inputs. Mackinawite (Fe_{1+x}S) was selected as the representative iron sulphide phase, as it is hypothesized to be structurally similar to the initially forming FeS_x species [23,24] Ferrihydrite was used to represent iron(III) oxyhydroxides, and vivianite was included as the relevant iron-phosphate mineral (Figure 5-2).

The thermodynamic predictions indicated that vivianite should dominate the iron mineralogy within an ORP window of approximately -250 mV to 0 mV.

During aeration, the pH increased to approximately 8.4, exceeding the typical optimum range for vivianite formation (pH 6–8) [25,26]. Therefore, pH was controlled at 7.8 using CO_2 dosing. Hydrochloric acid was deliberately avoided based on prior laboratory observations that local acidic microenvironments created by HCl dosing may promote undesired vivianite dissolution. The temporal evolution of pH and ORP for all experimental conditions is presented in Figures A 5-1–3.

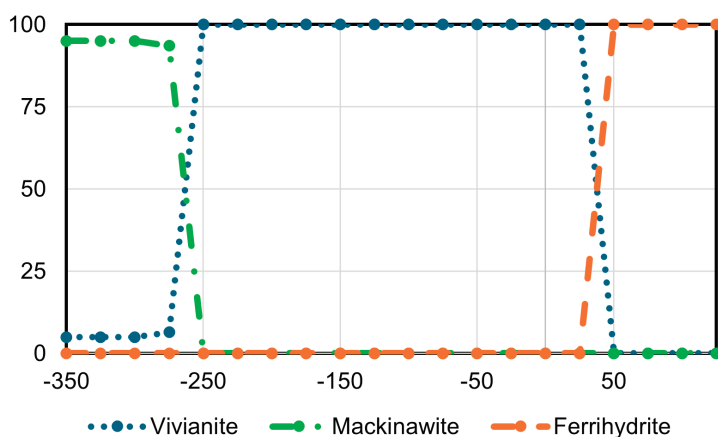


Figure 5-2 Visual MINTEQ predictions for vivianite, mackinawite, and ferrihydrite distribution among different oxidation reduction potentials with Fe^{2+} , HS^- , PO_4^{3-} at equimolar concentrations of 10 mM, and pH fixed at 7.8.

5.2.3 Characterization

Soluble components

For the analysis of the soluble fraction, samples were centrifuged at 4750 rpm for 10 min (Beckman Coulter Avanti J-15R). The supernatant was subsequently filtered through $0.45\ \mu\text{m}$ syringe filters (Millipore). To minimize oxidation during filtration, the beaker headspace was continuously flushed with N_2 . Elemental concentrations were quantified using inductively coupled plasma optical emission spectroscopy (ICP-OES; Thermo Scientific iCAP Pro). Ionic species were measured via ion chromatography (IC; Metrohm Compact IC Flex 88), and dissolved inorganic carbon (DIC) was determined using a total organic carbon analyzer (Shimadzu TOC-L CPH).

Evaporative losses resulted in sludge volume variations of up to 25% during the experiments. To correct for this, concentrations of soluble constituents were normalized using a correction factor (cf) derived from measured Na^+ and K^+ concentrations, which were

assumed to remain constant throughout the experiment. The correction factor was calculated as:

$$cf = \left(\frac{c(Na^+)_t}{c(Na^+)_{0h}} + \frac{c(K^+)_t}{c(K^+)_{0h}} \right) / 2$$

where $c(Na^+)_{0h}$ and $c(K^+)_{0h}$ denote the initial sodium and potassium concentrations, and $c(Na^+)_t$ and $c(K^+)_t$ represent their concentration at time t .

Solid phase

The total elemental composition of the initial sludge was determined by microwave digestion of 2 mL wet sludge in 8 mL of 69% HNO₃, using a sludge-specific digestion protocol (180 °C, 15 min) on a Milestone Ethos Easy system, followed by ICP-OES analysis. In addition, both the initial sludge and the samples treated at −220, −150, and 0 mV were dried for one week under N₂ atmosphere in a glovebox (≤0.1% O₂). Subsequently, 50 mg of each dried sample were digested in 10 mL of 69% HNO₃ using the same microwave method. Solid-phase characterization comprised the following analyses:

- **Iron speciation:** Iron extractions were conducted by mixing 1 mL of sludge with 9 mL of 1 M HCl. Samples were shaken at 65 rpm for 4 h, filtered through 0.45 μm syringe filters under a continuous N₂ stream, and analyzed for Fe(II) and Fe(III) using a colorimetric assay (LCK 320, Hach Lange) (based on [27]).
- **Crystal phase determination:** X-ray diffraction (XRD) analysis (Bruker D8 Advance diffractometer) was used to identify crystalline phases. Powdered samples were mounted on Si510 wafers and scanned using Cu Kα radiation over 5°–80° 2θ with a step size of 0.008° and a dwell time of 2 s per step. Diffractograms were evaluated using Bruker DiffracSuite EVA software.
- **Iron mineral phase quantification:** Mössbauer spectroscopy was employed to quantify and speciate iron phases. Samples were dried, ground, and sealed under N₂ (≤0.1% O₂) in the glovebox prior to analysis. Measurements were performed using a conventional constant-acceleration or sinusoidal-velocity spectrometer equipped with a ⁵⁷Co(Rh) source and calibrated against α-Fe. Spectra were fitted using MossWinn 4.0 [28]. Interpretation of Mössbauer spectra required differentiation among iron(III), low-spin (ls) Fe(II), and high-spin (hs) Fe(II) species. At room temperature, many iron-bearing compounds appear as paramagnetic (pm) doublets due to superparamagnetic behaviour or their electronic configuration. Some phases become magnetically ordered below their Curie or Néel temperatures and are thus observed as sextets or octets—for example, vivianite forms antiferromagnetic (afm) octets below its Néel temperature [29].
 - o **4 K measurements:** Spectra acquired at 4 K provide the most accurate quantification [30]. However, at this temperature, more phases become magnetically ordered, increasing spectral complexity.

- o **20 K measurements and vivianite fitting:** To maintain vivianite in its paramagnetic state, measurements were also conducted at 20 K, above its Néel temperature of 12 K [29], while minimizing temperature-related noise. Paramagnetic vivianite is characterized by two *hs*-Fe(II) doublets with isomer shifts (IS) of approximately 1.3 mm s^{-1} and quadrupole splittings (QS) of $\sim 2.6 \text{ mm s}^{-1}$ and $\sim 3.2 \text{ mm s}^{-1}$ (at 77 K; Dyar et al., 2014), corresponding to the A and B crystallographic sites. The expected A/B intensity ratio of ~ 0.5 reflects the structural occupancy of vivianite [31]. Deviations from this ratio may indicate Fe(II) oxidation, substitution by other cations such as Mg^{2+} [32], or overlapping spectral contributions.
- o **Distinguishing low-spin Fe(II) from Fe(III):** Low-spin Fe(II) in iron sulphides, common in digested sludge [11], typically overlaps with *pm*-Fe(III) doublets. Most iron sulphides observed in sludge, including thermodynamically stable pyrite [33], remain paramagnetic at 4 K, facilitating their distinction from magnetically ordered Fe(III).
- o **Fe(III) in vivianite versus other Fe(III) phases:** Fe(III) within oxidized vivianite is expected to become magnetically ordered at the same Néel temperature as Fe(II) in vivianite. Thus, Fe(III) appearing as a paramagnetic doublet at 20 K but as an *afm* sextet at 4 K may be indicative of oxidized vivianite.
- o **Green rust identification:** Green rust, a mixed-valence Fe(II)–Fe(III) double-layer hydroxide with intercalated anions ($[\text{Fe(II)}_{1-x}\text{Fe(III)}_x(\text{OH})_2]^{x+} \cdot [(x/n)\text{A}^{n-} \cdot (m/n)\text{H}_2\text{O}]^{x-}$, where $\text{A}^{n-} = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{Cl}^-, \text{OH}^-$) [33], has recently been reported to form in aquatic sediments as an alternative to vivianite [34]. Evidence of green rust presence was also observed in the present samples (Text A 5-1, Figure A 5-4).

5.3 RESULTS & DISCUSSION

5.3.1 Increasing sulphur and decreasing phosphorus concentrations in solution are ORP-independent

Across all aeration experiments, sulphur species were released into the liquid phase, as quantified by ICP-OES, with release rates slowing after approximately 72 h (Figure 5-3). The 0 mV treatment exhibited the highest overall sulphur release. Interestingly, the -220 mV experiment showed a higher release than the -150 mV experiment, which may be attributable to overshooting of the ORP setpoint during operation (Figure A 5-1). Throughout the experiments, measured sulphur and sulphate concentrations were closely aligned, indicating that sulphate was the predominant dissolved sulphur species. During the first 24 h, however, sulphate concentrations were notably lower—particularly under more reducing conditions—suggesting the transient presence of other sulphur species. Thiosulphate concentrations were below the detection limit and therefore cannot account for this discrepancy. A plausible explanation is the formation of elemental sulphur particles smaller than $45 \mu\text{m}$. In wastewater systems, biological oxidation of

sulphides to elemental sulphur has been reported to proceed more rapidly than chemical oxidation to sulphate or thiosulphate [35]. Thus, the initial formation of fine elemental sulphur particles could explain the temporarily lower sulphate concentrations observed in the first 24 h. An increase in soluble Fe (Figure A 5-4) during the first 48 h—most notably at -220 mV—supports the interpretation of early FeS_x dissolution. This transient Fe release coincides with both sulphur mobilization and the rapid initial decrease in dissolved phosphorus.

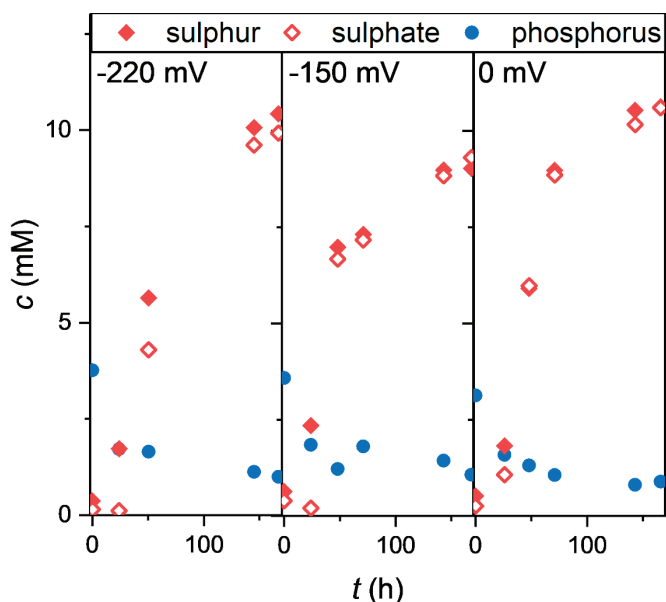


Figure 5-3 Evolution of soluble sulphur, sulphate, and phosphorus concentrations during aeration.

In addition to sulphide oxidation and dissolution, a net decrease of approximately 70% in soluble phosphorus was observed, indicating substantial phosphorus precipitation. Phosphorus concentrations declined sharply at the start of the experiments and stabilized after roughly 72 h. To relate the extent of sulphur release to phosphorus removal, the $\Delta\text{S}/\Delta\text{P}$ molar ratio was calculated for each experimental condition (Table 5-2). Ratios were 3.6 and 3.3 for -220 mV and -150 mV, respectively, and 4.5 for 0 mV. The elevated value of -220 mV relative to -150 mV may again reflect the aforementioned ORP overshoot.

Assuming the released sulphur originates from iron-bound sulphides with a Fe/S molar ratio of 1 [8], the corresponding amount of iron would become available to bind phosphate. Precipitation of phosphate with Fe(II) would likely result in vivianite formation, which exhibits a Fe/P molar ratio of 1.5. In contrast, Fe(III) and phosphate commonly form iron hydroxyphosphates with Fe/P ratios ranging from 1.7 to 2 under neutral pH conditions [20]. The observed $\Delta\text{S}/\Delta\text{P}$ ratios (>2) therefore align more closely with the stoichi-

ometry associated with iron hydroxyphosphate formation. However, this interpretation is based exclusively on liquid-phase measurements, whereas solid-phase mineralogy also plays a crucial role in determining phosphorus binding stoichiometry. The amount of iron liberated to bind phosphate depends on the specific sulphide and iron species present initially. Furthermore, phosphate previously incorporated in struvite (as confirmed by XRD; Figure A 5-7) may have undergone cation exchange or re-precipitation, supported by the slight release of magnesium into solution (Figure A 5-6).

Table 5-2 Total amount of sulphur species in solution (ΔS) and phosphorus precipitated (ΔP) with the $\Delta S/\Delta P$ ratio for each experiment.

	c (mM)		
	-220 mV	-150 mV	0 mV
ΔS (increased in solution)	10.1	8.3	10.0
ΔP (decreased in solution)	2.8	2.5	2.2
$\Delta S/\Delta P$	3.6	3.3	4.5

5.3.2 Iron sulphide stability and vivianite lability to microaeration

As described in Text A 5-1, changes in vivianite content were assessed by tracking the spectral area of the vivianite B site at 20 K. Aeration resulted in a reduction of the B-site contribution by 22% (from 29% initially to 17% in the -220 mV and 0 mV treatments), indicating that microaeration led to partial oxidation or degradation of vivianite. To evaluate whether this loss originated from vivianite oxidation, the increase in antiferromagnetically ordered (afm) Fe(III) between 20 K and 4 K was examined. Magnetic ordering below 20 K is expected for Fe(III) within vivianite or green rust (Section 2.3, Text A 5-1). Only an increase of 10–12% afm Fe(III) was detected in the -220 mV and 0 mV samples. Even if this entire increase were attributed to oxidized vivianite rather than Fe(III) present in green rust, it would correspond to only a small fraction of the total reduction in vivianite B-site signal. Thus, another portion (10–12%) of originally crystalline Fe(II)-vivianite was converted into non-magnetically ordered iron (III) phases, demonstrating that microaeration induces both oxidation and structural breakdown of vivianite.

The fraction of Fe(II)-vivianite not transformed into afm Fe(III) was likely detected as paramagnetic (pm) low-spin (ls) Fe(II)/Fe(III). This pm contribution (orange doublet at 4 K) increased considerably in both microaerated samples. This increase is attributable not only to vivianite alteration but also to oxidation of a pm high-spin (hs) Fe(II) phase (yellow doublet at 4 K). Notably, this pm hs Fe(II) partially overlaps with the pm signal of vivianite site A, complicating precise deconvolution of vivianite and green rust-like phases (Text A 5-1, Figure A 5-5). The presence of paramagnetic phases at 4 K may be due to very small particle sizes (<30 nm) or lattice disorder—both conditions known to suppress magnetic ordering [33]. Such disorder may arise from impurities within vivianite

crystals [11]. Alternatively, these pm signatures could originate from green rust, which may remain incompletely magnetically ordered even at 4 K [36].

In summary, microaeration converted both (i) part of the afm Fe(II)-vivianite and (ii) the pm hs Fe(II) phases—originating either from nanocrystalline/impure vivianite or from green rust—into pm Fe(III). This demonstrates that microaeration promotes broad oxidation processes affecting multiple Fe-bearing mineral phases.

The presence of paramagnetic (pm) Fe(III) at 4 K considerably complicated the quantification of iron sulphides, as the pm Fe(III) signal continued to overlap with the low-spin (ls) Fe(II) contribution (orange component). XRD analysis did not resolve the iron sulphide phases either, indicating that these phases lacked sufficient crystallinity for detection (Figure A 5-7). To assess whether microaeration led to the destruction of iron sulphides, changes in other Mössbauer-assigned iron fractions, particularly antiferromagnetic (afm) vivianite and pm high-spin (hs) Fe(II), were therefore interpreted. Figure 5-5 (top) summarizes the evolution of five key spectral contributions between the initial and microaerated samples: afm vivianite (blue), pm hs Fe(II) (yellow), afm Fe(III) (purple), ls Fe(II)/Fe(III) (orange), and a species with a magnetically distributed fit (gold-green), only in the initial sample. Because the initial sample had a very low oxidation state (Figure 5-5, bottom) and pm Fe(III) formed predominantly during microaeration, the ls Fe(II)/Fe(III) fraction in the orange component of the initial sample was assumed to represent ls Fe(II) primarily. Based on this assumption, the iron sulphide content in the microaerated samples was estimated using:

$$ls\ Fe(II) = \Delta_{orange} - \Delta_{gold-green} - \Delta_{yellow} - (\Delta_{blue} - \Delta_{purple})$$

The resulting estimates $9 \pm 9\%$ for the $-220\ mV$ sample and $10 \pm 9\%$ for the $0\ mV$ sample carry substantial uncertainty due to the cumulative 3% fitting uncertainty for each spectral component. Despite the large error margins, these values are similar to the 9% ls Fe(II) measured in the initial sample, suggesting that the iron sulphide fraction likely remained largely intact during microaeration. Thus, the influence of aeration on iron sulphide oxidation appears limited. Nevertheless, a portion of the initial ls Fe(II) signal may have originated from more labile FeS_x phases. At 20 K, the emergence of a magnetically ordered Fe(II)/Fe(III) component was observed, but fitting was challenging and a magnetically distributed fit was applied (Table A 5-1, gold-green contribution Figure 5-5, Figure A 5-6). Previous studies have shown that FeS_x minerals can exhibit irregular magnetic ordering and poorly defined Mössbauer signatures [12,33], complicating spectral deconvolution. Although the QS parameter obtained here ($IS = 0.40\ mm/s$, $QS = 0.51\ mm/s$, $B=21\ T$ at 21 K, Table A 5-1) does not fully align with literature values ($IS = 0.40\ mm/s$, $QS = 0.13\ mm/s$, $B=17-20\ T$ at 77 K) [32], the observed irregularity could indicate the presence of a FeS_x species.

Complementary HCl-extractable iron measurements (Figure 5-5, bottom) revealed a decreasing Fe(II) fraction with increasing ORP. Moreover, total extractable iron decreased by approximately 20% in the -150 mV and 0 mV samples compared with the initial and -220 mV samples, suggesting the formation of more crystalline or otherwise less acid-soluble Fe(III) phases under more oxidizing conditions. This trend contrasts with the Mössbauer results, which showed strong similarities between the -220 mV and 0 mV samples. One possible explanation is partial oxidation during the prolonged drying period, despite the low oxygen levels in the glovebox ($<0.1\%$).

Despite these limitations, the combined analyses clearly demonstrate that microaeration leads to substantial oxidation and structural alteration of vivianite and other mixed Fe(II)/Fe(III) phases such as green rust. In contrast, the ls Fe(II) iron sulphide fraction appears resistant to oxidation under the conditions tested. This raises important questions regarding the nature of the iron and sulphur phases in the initial sludge and the mechanisms by which sulphur was mobilized, and phosphorus was removed from solution.

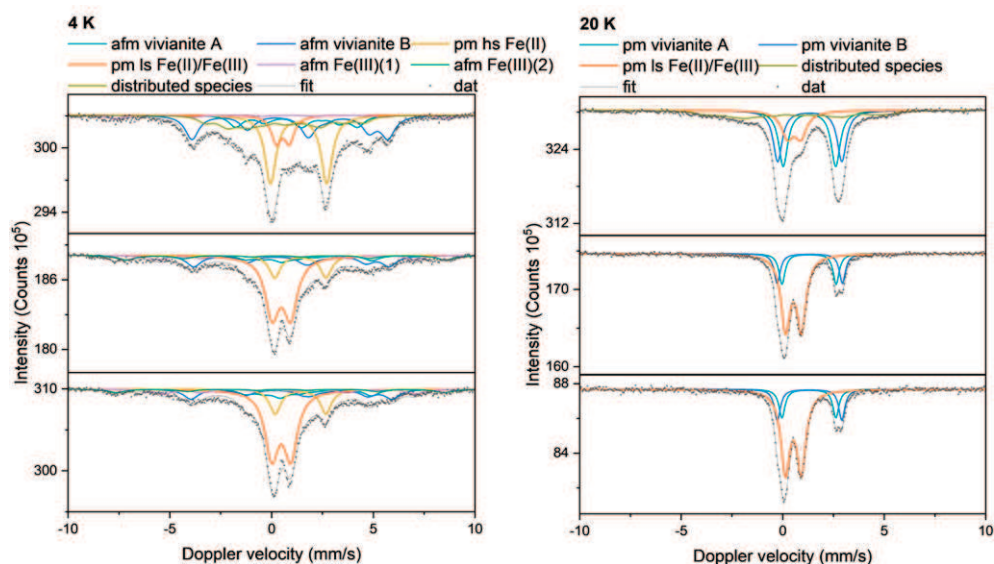


Figure 5-4 Mössbauer spectra at 20 K and 4 K of initial, -220 mV, and 0 mV sludge samples with fitted iron phases.

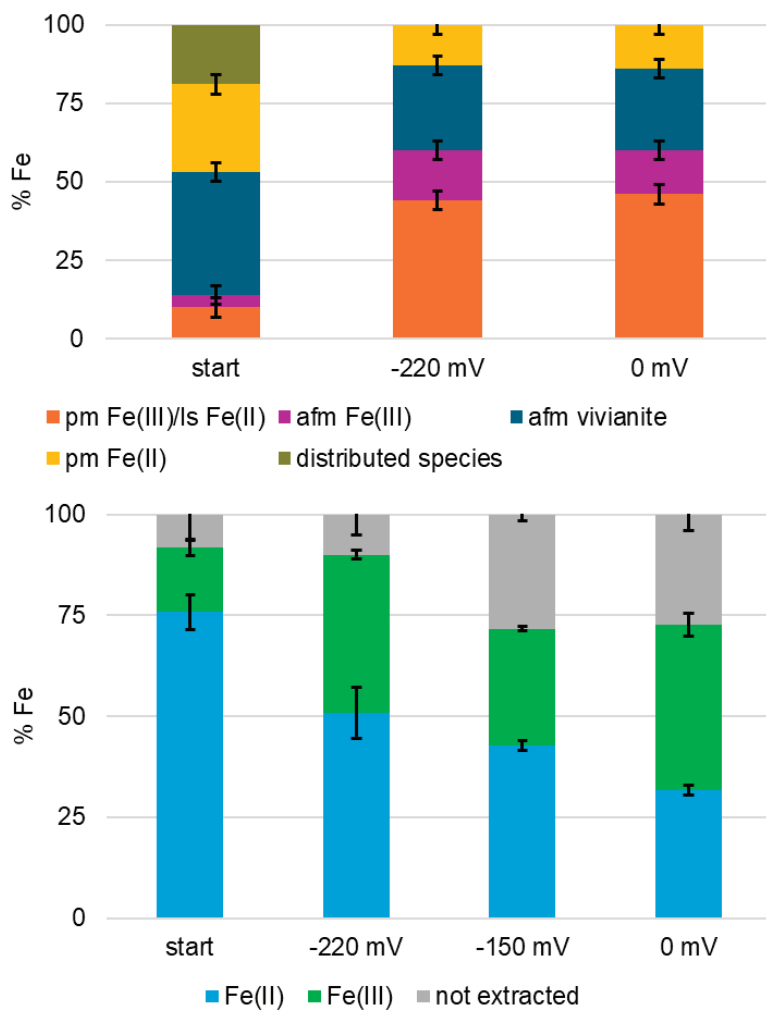
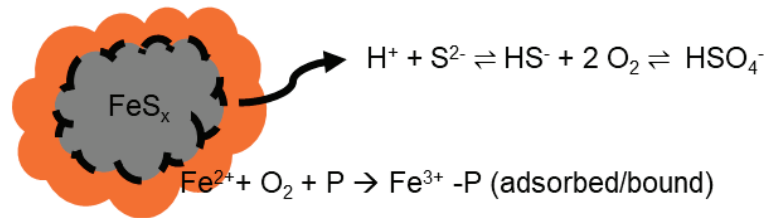


Figure 5-5 % Fe in different iron phases as per 4 K Mössbauer spectroscopy (top) and HCl extraction (bottom).

5.3.3 Mechanistic scenarios for Fe–S–P transformations during microaeration

Scenario A: Surface oxidation combined with iron sulphide dissolution



Scenario B: Elemental sulphur oxidation and iron(II) compound oxidation

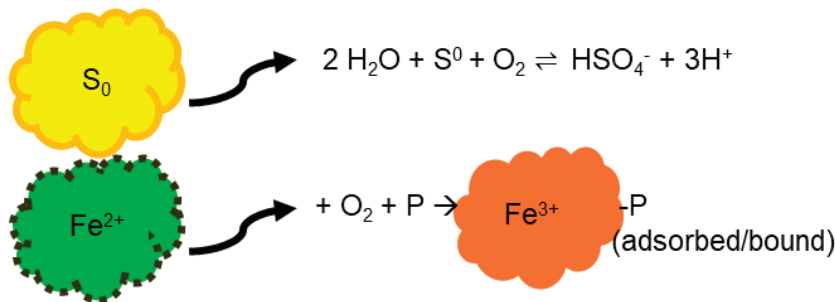


Figure 5-6 Scenarios for iron and sulphur species that could react upon oxidation and provoke phosphorus decrease in the solution.

Table 5-3 Comparison of Scenario A (Surface oxidation combined with iron sulphide dissolution) and Scenario B (Elemental sulphur oxidation and iron(II) compound oxidation) on their potential to match the observations.

Observation	Scenario A	Scenario B
	Sulphide oxidation	Elemental sulphur oxidation
Sulphur release	x	x
Delayed sulphate release	x	
	Surface oxidation of iron(II) sulphide to iron(III)oxyhydroxydes	Destruction of other iron(II)/ (III) binding
Phosphate adsorption/binding	x	x
Magnetically distributed species	x	

To interpret the aeration response of the initial sludge sample, two mechanistic scenarios were developed based on the combined observations (Table 5-3; Figure 5-6). These observations include: (i) the release of sulphur to solution with delayed sulphate formation under low ORP conditions (–220 and –150 mV; section 5.3.1), (ii) a pronounced decrease

in dissolved phosphorus due to adsorption or precipitation (section 5.3.1), and (iii) the presence of a magnetically split Fe(II)/Fe(III) Mössbauer component at 20 K exclusively in the initial sample.

Scenario A – Coupled Fe–S Oxidation: In this scenario, iron and sulphur oxidation processes proceed together. Surface oxidation of FeS_x leads to sulphide dissolution, explaining the increase in dissolved sulphur and the initially delayed formation of sulphate. The lag in sulphate formation can be attributed to transient elemental sulphur, which is commonly produced during early-stage oxidation of sulphides (section 5.3.1). The transient rise in soluble Fe during the first 48 h (Figure A 5-4) is consistent with FeS_x dissolution expected under early microaeration. In consequence, the decrease in dissolved phosphorus is consistent with Fe losing sulphide as its primary ligand and binding phosphorus, and after prolonged aeration, the formation of Fe(III) hydroxyphosphates or ferric oxyhydroxides that adsorb phosphate. The 20 K Fe(II)/Fe(III) Mössbauer component may correspond to a weakly ordered FeS_x phase, although the fit uncertainty makes precise comparison to literature challenging. Meanwhile, the persistent pm ls Fe(II) signal at 4 K likely represents a more stable FeS_x species, such as pyrite. Previous work has shown that iron sulphide oxidation at near-neutral pH can yield lepidocrocite, elemental sulphur, and sulphate [37]. Moreover, the formation of passivating surface layers may shield remaining FeS_x from complete oxidation [38]. Overall, Scenario A suggests that labile FeS_x phases undergo surface oxidation to form Fe(III) oxyhydroxides capable of binding phosphorus, while sulphide is released and ultimately oxidized to sulphate.

Scenario B – Decoupled Fe and S Oxidation: In the alternative scenario, iron and sulphur oxidation proceed independently. If part of the sulphur pool existed as solid elemental sulphur, its oxidation during aeration would explain the observed sulphur release; however, it would not account for the initially low sulphate concentrations. Phosphorus removal would then be less directly linked to sulphide dissolution. Instead, aeration may shift carbonate equilibria through CO_2 stripping, destabilizing ferrous carbonate or green rust phases and thereby promoting phosphate precipitation or adsorption onto newly formed Fe(III) oxyhydroxides—similar to the outcome of Scenario A, but driven by different mechanisms. The indications of green rust in the Mössbauer spectra (section 5.3.2, Text A 5-1) are also consistent with this scenario, and phosphate adsorption on green rust has been demonstrated [12,34]. A mass-balance consideration further supports the presence of multiple sulphur pools: the $\approx 10\%$ persistent pm ls Fe(II)/Fe(III) signal at 4 K corresponds to roughly $60 \text{ mmol Fe g}^{-1} \text{ DW}$. If this were entirely pyrite ($\text{Fe/S} = 0.5$), it would imply $\sim 130 \text{ mmol S g}^{-1} \text{ DW}$ —representing only about one-third of the total sulphur. If the magnetically distributed species observed by Mössbauer spectroscopy in the initial sample is indeed FeS_x , this would account for another 40% of the sulphur, at a $\text{Fe/S} = 1$. The remaining 30% sulphur could therefore be present as organic sulphur or elemental sulphur. In literature, only $\sim 40\%$ of sulphur was found as FeS_x -bound, with $\sim 30\%$ present

as reduced organic sulphur and ~20% as elemental sulphur [39]. Moreover, elevated Fe/S ratios, such as in the digested sludge used in this sample, are also known to favour polysulphide and elemental sulphur formation [40]. Yet, elemental sulphur was not detected with SEM-EDX analysis of anaerobically dried samples, but this may reflect small particle size—typically 1–20 µm in biological desulphurization [41,42], or even nanoparticulate forms in natural waters [43]—or sample-preparation artifacts that could lead to iron sulphide oxidation (Wilfert et al., 2018; section 3.2). In summary, Scenario B suggests that elemental sulphur was solubilized and oxidized during microaeration, while iron phases such as green rust exchanged ligands or were oxidized, enhancing their ability to bind phosphate.

The magnetically distributed species detected with Mössbauer spectroscopy in the initial sample and the absence of sulphate during the early aeration stage are most consistently explained by FeS_x dissolution (Scenario A). The absence of sulphate in the solution also coincides with the major decline in dissolved phosphorus. Over longer aeration periods, oxidation may shift towards non-Fe-bound sulphur pools such as elemental sulphur (Scenario B). Prolonged aeration also likely disrupted vivianite and mixed Fe(II)/Fe(III) phases (e.g., green rust), supporting elements of Scenario B. Overall, the aeration behaviour aligns predominantly with Scenario A, indicating that time-controlled microaeration may simultaneously promote phosphate precipitation and elemental sulphur formation.

5.3.4 Opportunities and limitations of microaeration for phosphorus recovery in digested sludge

Table 5-4 Comparison of phosphorus precipitation and presumed iron sulphide destruction by oxidizing agents, in literature and in this study.

matrix	oxidizing agent	dose	soluble P start (mM)	P precipitated (mM)	FeS _x start (mM)	FeS _x (mM) destroyed	S product	study
sludge W sedimentation tank	H ₂ O ₂	500 mg/L	3.1	1.8	2.0	0.3-1.7	SO ₄ ²⁻ /SO ₃ ²⁻ /S ⁰	Yin 2021
sludge sedimentation tank	ClO ₂	400 mg/L	3.1	2.9	2.0	0-0.5	SO ₄ ²⁻ /SO ₃ ²⁻	Yin 2021
spiked wastewater	H ₂ O ₂	300 mg/L	16.1	5.2	5.1	5.1	S ⁰	Ismail 2022
digested sludge to -220 mV	air	1 L/min +CO ₂	3.7	2.8	9	5.2	SO ₄ ²⁻ /?	this study

Although microaeration did not enhance vivianite formation, it did promote substantial phosphate precipitation, which is relevant for wastewater treatment applications. Lower

dissolved phosphate concentrations reduce the demand for iron coagulants typically required for further phosphate removal. However, aeration is not the only oxidative strategy capable of generating this effect. Previous studies by Ismail et al. (2022) and Yin et al. (2021) evaluated the ability of several oxidants—including hydrogen peroxide (H_2O_2) and chlorine dioxide (ClO_2)—to oxidize iron sulphides and thereby induce phosphate precipitation [17,18]. Their findings are compared with those of the present study in Table 5-4. Among the tested oxidants, H_2O_2 was the most effective: Yin et al. (2021) reported that $500 \text{ mg L}^{-1} \text{H}_2\text{O}_2$ removed up to 90% of phosphate [17], and Ismail et al. (2022) observed maximum FeS_x oxidation at $300 \text{ mg L}^{-1} \text{H}_2\text{O}_2$ with a corresponding $\Delta\text{S}/\Delta\text{P}$ ratio of 1 [18]. In the aeration experiments of the present study, phosphate removal was slightly lower but exceeded that observed with ClO_2 . This comparison is of practical interest because ClO_2 appears to be a milder oxidant toward iron, potentially preserving Fe(II) and thereby favouring vivianite formation.

Quantifying iron sulphide oxidation in sludge solids remains challenging. Yin et al. (2021) and Ismail et al. (2022) used Fe(II) oxidation as an indirect proxy for FeS_x destruction [17,18]; however, oxidized iron in their systems may not have originated exclusively from FeS_x . In our study, solid-phase sulphur loss between the initial and -220 mV samples was used as an indicator (Text A 5-2, Table A 5-2), though it remains uncertain whether this sulphur originated from FeS_x or other sulphur pools. Compared with aeration, H_2O_2 induced more extensive iron sulphide oxidation and produced elemental sulphur, a valuable product for sulphur recovery [44]. Nevertheless, aeration presents a chemical-free alternative for sulphur oxidation and phosphate removal, though its performance requires further optimization.

Future optimization should focus on enhancing phosphate precipitation. Promoting elemental sulphur and vivianite formation also remains attractive because vivianite binds more phosphorus per mole of iron ($\text{Fe/P} = 1.5$), and the products are interesting for recovery. One possible strategy is to refine aeration duration: after 24–48 h, phosphorus removal plateaued, likely due to excessive Fe(III) formation. Transitioning to anaerobic incubation after this point could promote vivianite formation if vivianite nucleates more rapidly than FeS_x [45]. A systematic investigation of ORP, pH, and the interplay between aeration and anaerobic conditions is needed. Finally, experiments combining ultrapure water and digested sludge supernatant could provide valuable insight into the mineral transformation pathways. Comprehensive solid-phase characterization using Mössbauer spectroscopy, sulphur extractions, and X-ray absorption spectroscopy (XAS) [39] may further elucidate the coupled evolution of iron, phosphorus, and sulphur.

5.4 CONCLUSION

This study investigated the potential micro-aeration for conversion iron sulphide into elemental sulphur and Fe(II), with subsequent precipitation of vivianite. The potential to use an ORP based control for microaeration was tested to oxidize iron sulphides and its impact on iron phosphate formation, with the goal of promoting vivianite formation for targeted phosphorus recovery. Despite the observed increase of sulphur and decrease of phosphorus in solution, the vivianite present at the start was oxidized and destroyed rather than observing new vivianite forming throughout ORPs from -220 mV to 0 mV.

Optimizing ORP, pH, and shorter aeration periods followed by anaerobic incubation could increase the amount of phosphorus leaving the solution, potentially enabling the formation of vivianite and elemental sulphur species, instead of overshooting the oxidation. This could open a new technological route for combined sulphur and phosphorus recovery from digested sludges or simply help reduce coagulant consumption for phosphorus removal. Furthermore, a more thorough characterization of the mineral species, supplementing Mössbauer spectroscopy with XAS and sulphur extractions, is necessary to better understand iron sulphide and iron phosphate binding and transformations in digested sludge.

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SUPPLEMENTARY INFORMATION

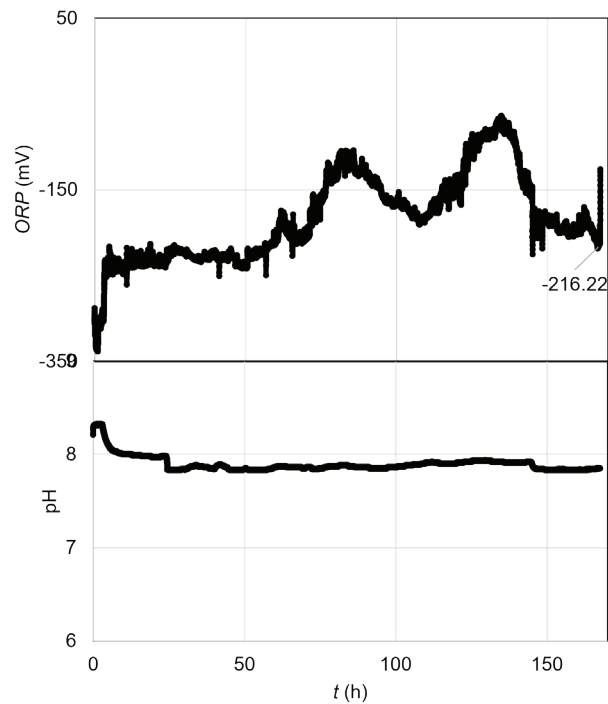


Figure A 5-1 ORP and pH over the course of the -220 mV experiment.

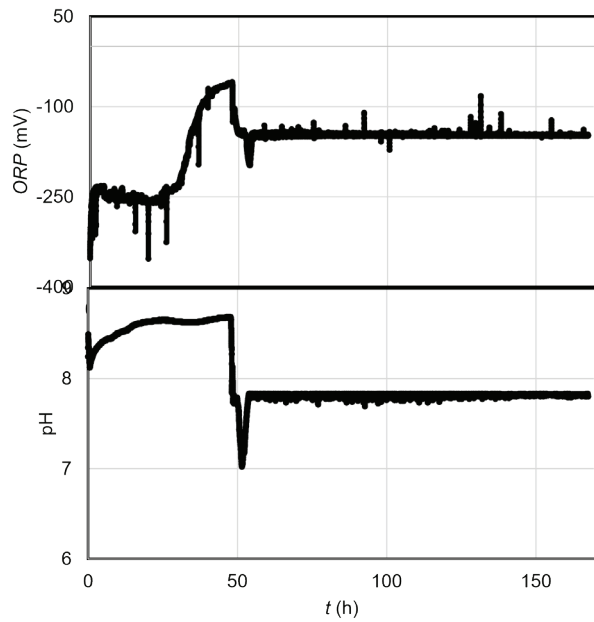


Figure A 5-2 ORP and pH over the course of the -150 mV experiment.

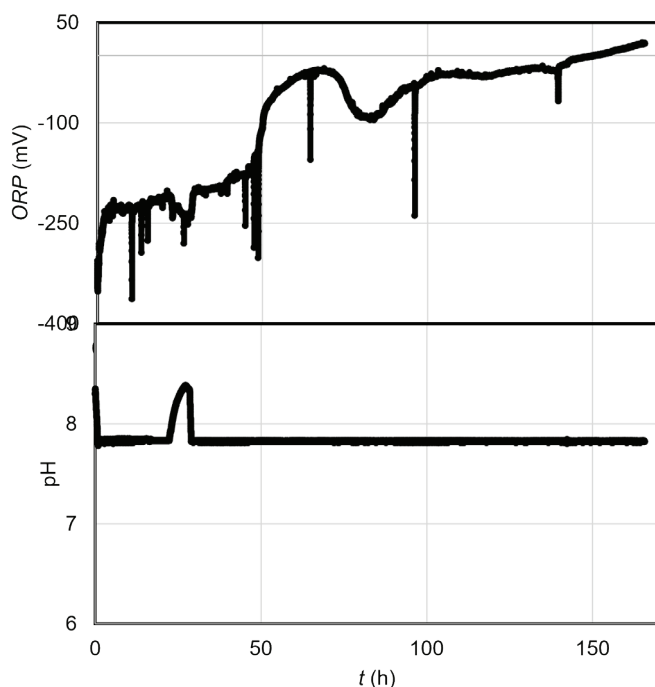


Figure A 5-3 ORP and pH over the course of the 0 mV experiment.

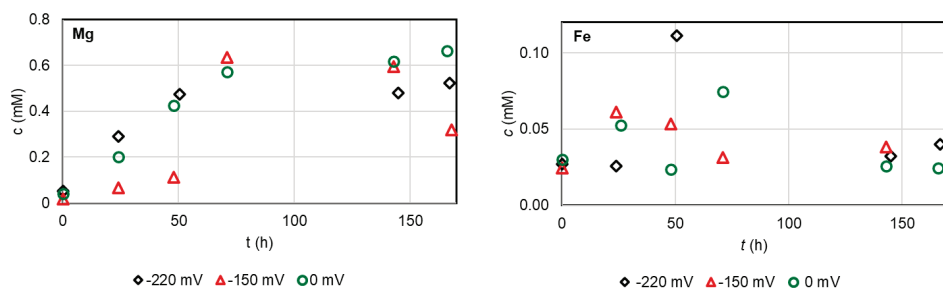


Figure A 5-4 Evolution of soluble magnesium and iron concentrations during aeration.

Text A 5-1 Impure/fine vivianite versus green rust in the Mössbauer spectrum

At 4 K, a paramagnetic high-spin (pm hs) Fe(II) contribution (yellow) was observed in all samples, with hyperfine parameters of $IS = 1.21 \text{ mm s}^{-1}$ and $QS = 2.74 \text{ mm s}^{-1}$ in the initial sludge. These values fall within the reported ranges for pm Fe(II) in green rust ($IS = 1.24\text{--}1.28 \text{ mm s}^{-1}$; $QS = 2.70\text{--}2.90 \text{ mm s}^{-1}$ at 77 K; [34]) and also overlap with those of vivianite site A ($IS \approx 1.3 \text{ mm s}^{-1}$; $QS \approx 2.6 \text{ mm s}^{-1}$; [46]). To distinguish between these possibilities, Néel temperatures, A/B doublet ratios, and the characteristics of co-occurring Fe(III) species were compared.

Both green rust (Néel temperature ~ 5.2 K; [47]) and vivianite (Néel temperature ~ 12 K; [29]) are expected to be magnetically ordered at 4 K. However, incomplete magnetic ordering at 4 K has been reported for green rust [36], and also vivianite can remain paramagnetic when present as fine particles or containing structural impurities. Pure vivianite exhibits a characteristic A/B intensity ratio of 0.5 [31]. In contrast, our samples displayed A/B ratios of 0.4–0.6 for antiferromagnetic vivianite at 4 K and ~ 1.0 for paramagnetic vivianite at 20 K. These deviations indicate the presence of impurities, partial oxidation, or overlapping contributions. The strongly elevated A/B ratio at 20 K, in particular, suggests the coexistence of a second Fe(II) phase—potentially green rust—which overlaps with the vivianite A site. Additional insight comes from the Fe(III) species resolved at 4 K (green-gold component). Oxidized vivianite typically exhibits $IS = 0.35$ mm s $^{-1}$, $QS = 0.45$ mm s $^{-1}$ and $B = 44$ T [11], whereas green rust shows $IS = 0.49$ – 0.58 mm s $^{-1}$, $QS = -0.35$ to -0.06 mm s $^{-1}$, and $B = 49$ – 51 T [33]. The negative QS of the Fe(III) sextets measured in initial and 0 mV samples, therefore, supports the presence of a green-rust-like or Fe(III) oxyhydroxide phase, and the QS and lower magnetic fields of the 0 mV and -220 mV sextets could stem from oxidized vivianite (Table A 5-1). Furthermore, Fe(III) originating from green rust or iron oxyhydroxides may contribute to the low-spin Fe(II)/Fe(III) doublet (orange) observed at 4 K, particularly in aerated samples. Taken together, these observations suggest that green rust may have formed at the expense of vivianite. Such vivianite-to-green-rust transformations have been reported in soils [12], and carbonate-rich green rust is known to coexist with siderite [34], inhibiting vivianite formation under elevated carbonate concentrations [48]. The relatively high carbonate levels in our sludge (~ 6 g L $^{-1}$; Table 5-1), therefore, provide favourable conditions for green rust formation.

In conclusion, the Fe(III) hyperfine parameters and the elevated A/B ratios strongly indicate the presence of a green-rust-like phase, although contributions from impure or partially oxidized vivianite cannot be fully excluded. For assessing vivianite evolution within an experimental series, the 20 K B-site doublet remains the most distinct indicator. Nonetheless, complete quantification requires assumptions about the A/B ratio, and 4 K measurements remain essential to resolve the full spectrum of paramagnetic and antiferromagnetic Fe(II) phases.

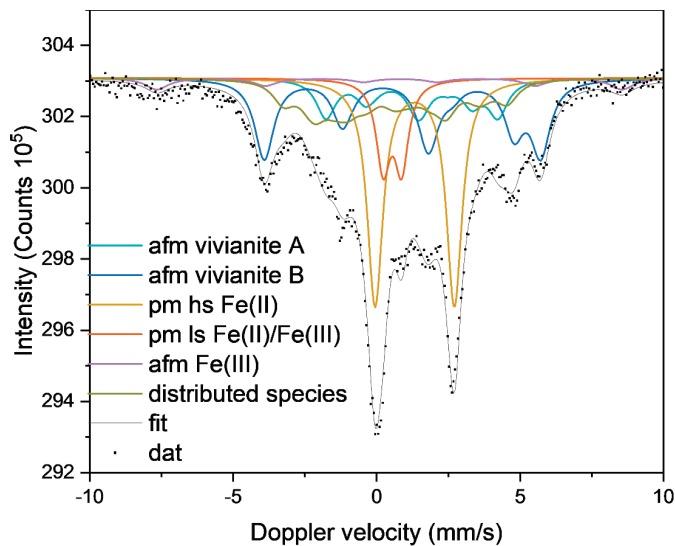


Figure A 5-5 Mössbauer spectrum at 4 K of the initial sludge sample with fitted iron phases.

Table A 5-1 Distribution of Fe species according to Mössbauer analysis at 20 and 4 K of the initial, -220, and 0 mV sludge samples, with isomer shift (IS), quadrupole splitting (QS), line width (LW), magnetic field (B), and related Fe spectral contribution percentages (% Fe). Error: IS, QS, LW $\pm$ 0.01 mm/s; % Fe $\pm$ 3 %.

20 K		IS (mm/s)	QS (mm/s)	B (T)	LW	%	A/B
initial (-350 mV)	pm Viv A	1.33	2.58		0.54*	30	1.0
	pm Viv B	1.31	3.16		0.54*	29	
	pm ls Fe(II)/Fe(III)	0.56	0.66		0.70	19	
	magnetically distributed species	0.40	0.51	21	0.85^	20	
-220 mV	pm Viv A	1.29	2.67		0.36*	18	1.1
	pm Viv B	1.33	3.21		0.36*	17	
	pm ls Fe(II)/Fe(III)	0.62	0.83		0.53	38	
0 mV	pm Viv A	1.28	2.65		0.36*	16	0.9
	pm Viv B	1.32	3.17		0.36*	17	
	pm ls Fe(II)/Fe(III)	0.53	0.79		0.51	67	
4 K		IS (mm/s)	QS (mm/s)	B (T)	LW	%	A/B
initial (-350 mV)	afm Viv A	1.35^	2.45^	15^	0.81*	13	0.5
	afm Viv B	1.35^	3.35	26	0.81*	26	
	pm hs Fe(II)	1.32	2.76		0.66	28	
	pm ls Fe(II)/Fe(III)	0.55^	0.64^		0.58^	10	
	afm Fe(III)	0.64^	-0.37	50	0.97^	4	
	magnetically distributed species	0.40^	0.51	18	0.85^	19	

Table A 5-1 Distribution of Fe species according to Mössbauer analysis at 20 and 4 K of the initial, -220, and 0 mV sludge samples, with isomer shift (IS), quadrupole splitting (QS), line width (LW), magnetic field (B), and related Fe spectral contribution percentages (% Fe). Error: IS, QS, LW $\pm$ 0.01 mm/s; % Fe $\pm$ 3 %. (*continued*)

20 K		IS (mm/s)	QS (mm/s)	B (T)	LW	%	A/B
-220 mV	afm Viv A	1.35 [^]	2.52 [^]	15 [^]	0.87*	8	0.4
	afm Viv B	1.35 [^]	3.21 [^]	26 [^]	0.87*	19	
	pm hs Fe(II)	1.41	2.52		0.65 [^]	13	
	pm Is Fe(II)/Fe(III)	0.48	0.9		0.82	44	0.6
	afm Fe(III)	0.48*	0.53	39	0.97*	8	
	afm Fe(III)	0.48*	0.46	49	0.97*	8	
	afm Viv A	1.35 [^]	2.45 [^]	15 [^]	0.87*	10	
0 mV	afm Viv B	1.35 [^]	3.10 [^]	27 [^]	0.87*	16	
	pm hs Fe(II)	1.42	2.49		0.65 [^]	14	
	pm Is Fe(II)/Fe(III)	0.48	0.93		0.81	46	
	afm Fe(III)	0.48 [^]	0.76	38	0.97 [^]	8	
	afm Fe(III)	0.48 [^]	-0.09	50	0.97 [^]	6	

*equal between vivianite A and B contributions, [^]fixed parameters

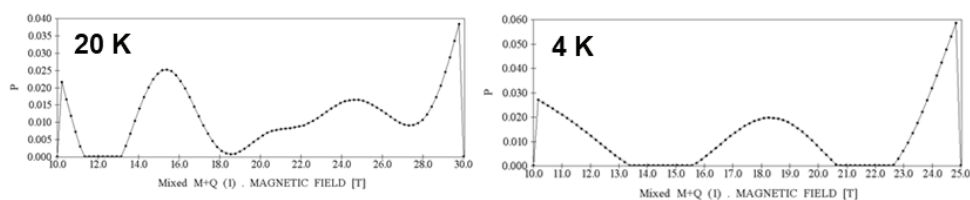


Figure A 5-6 Magnetic field distribution for magnetically distributed fit for Mössbauer spectra at 20 and 4 K.

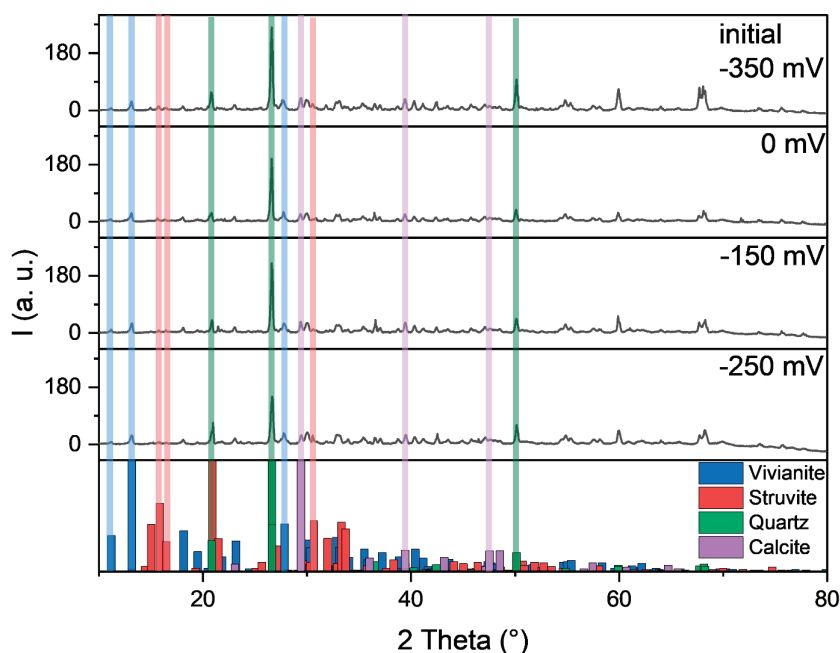


Figure A 5-7 Normalized and baseline corrected X-Ray diffractograms of the initial, 0 mV, -150 mV, and -250 mV samples; vivianite (amcsd 0012069), struvite (amcsd 0020109), quartz (amcsd 0006212), and calcite (amcsd 0000098)[49].

Text A 5-2

Removal of sulphur from the solid phase was also evident in the digested, dried solids obtained after decanting the supernatant (Table A 5-2). All elemental concentrations decreased from the initial to the aerated samples, which may reflect a reduction in the total inorganic fraction due to particle sedimentation during the experiment, or differences in microwave digestion efficiency. To minimize these matrix-related effects, Fe/S Smolar ratios were used for comparison rather than absolute concentrations. The Fe/S ratio increased from 1.8 in the initial sample to 2.6 in the 0 mV treatment. In the -220 mV sample, the increase from 1.8 to 2.5 corresponds to the loss of approximately 115 mmol S kg⁻¹ DW (5.2 mM). If this sulphur had been present entirely as iron sulphide with a Fe/S ratio of 1, the released sulphur would represent ~20% of the iron being affected. This proportion closely matches the ~20% magnetically split Fe(II)/Fe(III) contribution observed in the initial sample at 20 K (sections 3.2 and 3.3). These calculations therefore support the interpretation that the sulphur released during microaeration may originate from a more labile FeS_x phase. Such a phase would be consistent with the unattributed Fe(II)/Fe(III) signal detected in the initial sample's 20 K Mössbauer spectra.

Table A 5-2 Total elements of microwave-digested dried solids after centrifugation and removal of supernatant and Fe ratios.

c (mmol/kg DW)	Fe	P	S	Mg	Ca	Fe/S	Fe/P	Fe/Mg	Fe/Ca
start	700	1015	388	178	815	1.8	0.7	3.9	0.9
-220 mV	681	1030	270	156	784	2.5	0.7	4.4	0.9
-150	621	934	264	146	708	2.4	0.7	4.3	0.9
0	615	954	233	141	742	2.6	0.6	4.4	0.8

6

Conclusion & Outlook

Vivianite is increasingly explored as a route for phosphate recovery from manure, lake sediments, and digested sludge. In this chapter, the feasibility of vivianite formation and recovery in pig manure, dredged sediments, and from iron sulphides in digested sludge is discussed. Knowledge gaps on iron mineral phase chemistry, modelling, and characterization are identified. Finally, the evaluation of vivianite-based phosphorus recovery is extended to a broader perspective across the three matrices.

6.1 VIVIANITE FORMATION ACROSS MANURE, LAKE SEDIMENTS, AND DIGESTED SLUDGE

The competition for ferrous iron—between phosphate and ligands such as organic matter, carbonates, and sulphides—controls vivianite formation in pig manure, (dredged) lake sediment, and digested sludge, yet different chemical limitations were explored in the three matrices.

In manure, vivianite formed only when iron was dosed at levels three times higher than those required in digested sludge, suggesting a strong competition for iron. Although iron–organic binding was initially suspected, organics did not inhibit vivianite formation (Chapter 2). Instead, elevated dissolved inorganic carbon in aged and digested manure promoted siderite (FeCO_3) formation at the expense of vivianite (Chapter 3). Working with fresh manure or reducing carbonate concentrations below a threshold could overcome this barrier.

In dredged lake sediments (Chapter 4), iron dosing alone did not enhance vivianite formation. Only when phosphate salts were added did vivianite precipitate, indicating that low phosphorus availability limits its formation. As a result, dredged lake sediments appear to have limited potential for vivianite-based phosphate recovery.

Finally, the influence of sulphide competition was assessed using ORP-controlled microaeration in digested sludge (Chapter 5). Microaeration dissolved sulphur-containing compounds and reduced dissolved phosphorus, which may be useful for phosphorus removal. However, it also oxidized and degraded vivianite, reducing its suitability for recovery, warranting optimization if this technology should become of interest.

Feasibility of vivianite recovery from manure

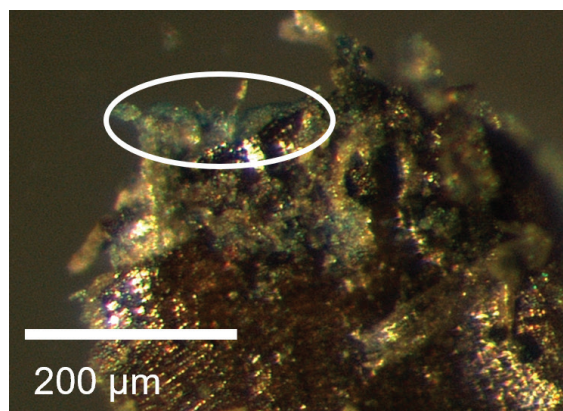


Figure 6-1 Stereoscope image of blue vivianite particles (white circle) on top of organic matter, magnetically recovered at lab-scale with a μ -Jones separator from stripped digested manure.

Vivianite formation in manure is strongly constrained by alkalinity. Low alkalinity is essential, as high dissolved inorganic carbon (DIC) favours siderite formation, with carbonate outcompeting phosphate for ferrous iron. The use of fresh manure and stripping carbonate from digested manure proved feasible to reduce DIC under controlled laboratory conditions. Yet, the magnetic recovery of vivianite formed in fresh and stripped manure has not been systematically explored and the physical characteristics of the vivianite could present practical challenges. The mineral typically precipitated as very small particles (~ 10 – $20\ \mu\text{m}$ Supplementary, Chapter 3), which could limit the effectiveness of magnetic separation if particles fall below the $10\ \mu\text{m}$ threshold [1]. Figure 6-1 further illustrates that the magnetically recovered particles may come attached to organic matter due to electrostatic interactions. Moreover, the high dry matter content (12–13 %, Chapter 3) and small particle size in fresh manure could make the magnetic recovery route challenging compared to digested sludge, where dry matter content is lower (4 %) and particle sizes bigger [2].

Future work should explore if laboratory-scale approaches to reduce carbonate—such as working with fresh manure or applying carbonate stripping—are feasible under farm conditions. In the Netherlands, manure is typically stored in pits, solid liquid separated, or deep litter bedded [3], with storage times ranging from 6 months to a year [4]. Treating fresh manure directly would necessitate a change in farm procedure which could be complicated by routine work. Furthermore, the feasibility of stripping the carbonate with air rather than N_2 needs to be explored, as N_2 is too expensive for farm-scale use. Using air holds the risk of making turning the conditions in the digested manure more aerobic. If iron is dosed into more aerobic conditions, iron(II) might be oxidized instead of forming vivianite. Therefore, the return to anaerobic conditions within the system needs to be

monitored, alongside with the influence of oxidation on other components present in manure, as for example sulphides. Addressing the particle size and purity of the recovered product would also be essential. The use of iron(III) in place of iron(II) salts could facilitate the slower release of ferrous iron, which in turn would for ferrous phosphate precipitates more gradually, thereby aiding crystal growth.

Taken together, the findings show that manure-based vivianite formation is scientifically achievable. Optimization of the stripping procedure and magnetic recovery techniques, along with an economic assessment, would be necessary to demonstrate it at a farm scale.

Vivianite formation in dredged lake sediments

Vivianite has been reported in various lake sediments [5,6], and therefore, vivianite-mediated phosphate recovery could be an interesting approach for lake remediation. However, in this thesis, even iron(II) supplementation did not increase the vivianite phase already present in the dredged sediment. Iron(II) was more likely to precipitate carbonate, organic matter, and sulphides than phosphate. In previous research, only phosphate adsorbed on iron(III) oxyhydroxide phases could form vivianite [7,8], but not iron(III) oxyhydroxides alone. This indicates that the geochemical conditions in lake sediments—particularly phosphate availability and competition between iron phases—do not readily support significant transformation into vivianite. Moreover, vivianite already present in the sediment was difficult to detect with Mössbauer spectroscopy, a reliable tool in manure and digested sludge. The limited formation, the difficulty of detection, and the low phosphate availability collectively make lake sediments an unpromising source for generating recoverable quantities of vivianite.

Looking forward in research, to form vivianite in lake sediments, several fundamental geochemical questions should first be addressed:

- **Phosphate availability:** Iron-phosphate binding could be increased by concentrating the phosphate closer to the iron oxides. For example, indications of increased phosphorus immobilization within the matrix were observed when phosphate adsorbed onto iron oxyhydroxide phases was spiked into the matrix, suggesting that the pre-adsorbed phosphate may act as a catalyst for more phosphate adsorption [8].
- **Phase transitions:** The transition from iron oxyhydroxides or green rust phases to vivianite and back remains poorly understood. The specific minerals, their incubation in anaerobic media, and in the presence of different compounds (organics, carbonates, sulphides, phosphates) should be studied in more detail.
- **Improving characterization:** Combining extraction schemes, microscopy, and solid-phase characterization methods will be essential, as the iron phases and transitions are poorly defined and less crystalline, making their detection challenging.

Advancing mechanistic understanding and detection sensitivity could inspire new approaches for enhancing long-term phosphorus immobilization in sediments. From an applied perspective, vivianite formation is not a suitable pathway for phosphate recovery from dredged lake sediments, given the extremely low phosphorus concentrations and limited phosphate availability. However, vivianite may still hold relevance in the broader context of lake restoration, where the primary aim is to reduce internal phosphorus loading rather than to recover a concentrated product [9]. Here, promoting stable iron–phosphate phases *in situ* could contribute to long-term sediment phosphorus retention, complementing other in-lake remediation measures.

Thus, vivianite will not play a role in recoverable phosphorus pools in dredged sediments, yet its stabilization could help reduce internal loading in lake sediments during restoration efforts. Progress in detection and mechanistic insights will determine whether this potential can be meaningfully integrated into broader restoration approaches.

Vivianite formation from iron-sulphides in digested sludge

The transformation of iron sulphide phases in digested sludge to vivianite was unsuccessful, as microaeration oxidized and destroyed the vivianite already present in the sludge, independently of ORP setpoint. Despite this effect, sulphur was mobilized into solution, mainly as sulphate, and the concentration of dissolved phosphate decreased, indicating that iron–phosphate interactions were enhanced. This effect could be relevant for phosphorus removal, but from a recovery perspective, vivianite and elemental sulphur would be more interesting products of targeted iron sulphide oxidation. Finally, Mössbauer analysis revealed unexpected speciation complexity, indicating that a significant portion of the sulphur was not iron-bound but may instead accumulate as an elemental sulphur phase. At the same time, part of the iron appeared to be associated with mixed-valence, green-rust-like phases instead of vivianite, highlighting uncertainties in iron speciation under anaerobic digestion conditions.

Future research on vivianite formation from iron sulphides in digested sludge should focus on resolving the remaining uncertainties in iron–sulphur speciation. As in lake sediments, clarifying mineral transition pathways will be essential for understanding whether iron-binding dynamics can be steered to favour vivianite formation. Another key direction lies in optimizing microaeration parameters. Exploring modified microaeration regimes, including alternating microaerobic and anaerobic phases, may help avoid over-oxidation while enhancing phosphate binding to reduced iron phases. Such strategies should also address the potential for elemental sulphur formation, as well as the operational and economic feasibility of integrating redox-controlled treatments into existing sludge lines.

Ultimately, the speciation of iron sulphide and its transformation to vivianite remain unanswered questions. Nevertheless, microaeration-induced phosphate removal could be an interesting add-on for further sludge processing pending its viability.

6.2 IRON CHEMISTRY AND MINERAL TRANSFORMATIONS ACROSS MATRICES

Iron chemistry

Across manure, lake sediments, and digested sludge, iron interactions with the different matrix components are defining for vivianite formation. Four interactions dominated the outcomes: iron-organic, iron-carbonate, iron-sulphide, and iron-phosphate.

Organics are frequently invoked as the “black box” explanation for poor vivianite yields since iron-organic binding in complex matrices is difficult to characterize due to the heterogeneity of organic matter itself [10–13]. The evidence in this thesis indicates a more nuanced role. Pig manure dissolved organic matter did not inhibit vivianite formation; instead, it influenced crystal morphology and particle size, likely modifying crystal growth via surface adsorption. In contrast to iron-organic interactions, iron-carbonate interactions were likely underestimated. Carbonate consistently and strongly competed for Fe(II). Siderite can scavenge Fe(II), while less defined green-rust phases containing both iron and carbonate ($[\text{Fe}^{2+}_{1-x}\text{Fe}^{3+}_x(\text{OH})_2]^{x+} \cdot [(x/n)\text{A}^{n-} \cdot (m/n)\text{H}_2\text{O}]^{x-}$ with $\text{A}^{n-} = \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{Cl}^-, \text{OH}^-$) further complicate detection and mass balances. These Fe(II)–carbonate and mixed-valence phases reduce the window in which Fe(II) remains available for phosphate, thereby suppressing vivianite formation. The iron sulphide speciation initially forming in the different matrices remains difficult to resolve. In sludge, less sulphur than assumed was observed to be bound to iron, putting the assumed binding ratio of Fe/S=1 into question. In eutrophic sediments, ongoing sulphate reduction rates could hamper iron(II) phosphate binding because of the constant supply of HS^- . However, kinetic factors within the initial phase of formation could benefit vivianite over iron sulphide formation [14], but have not yet been explored to benefit vivianite formation over iron sulphide formation. Iron–phosphate interactions are governed by availability and mineral transitions. Even with available Fe(II), phosphate availability limited the formation of vivianite in sediments. Across matrices, the role of iron hydroxyphosphate and phosphate adsorbed on iron oxyhydroxides or green rust phases should be explored in more detail. These phases likely exhibit a dual role, a precursor for vivianite thanks to facilitating an initial iron-phosphate binding/proximity, and at the same time they could stabilize, acting as a competitor to vivianite instead.

Building on the cross-matrix evaluation of vivianite formation, several mechanistic research questions emerge that are central to understanding and, ultimately, controlling iron–phosphate mineralization in complex environmental systems. A first direction is to clarify how organic matter and other co-occurring inorganic compounds influence the nucleation, morphology, and aggregation of vivianite. The surface potential of freshly formed phases likely plays a decisive role in determining crystal size as well as particle interactions and agglomeration [15,16]. Understanding these effects may open the possibility of deliberately tuning crystal properties—either to promote compounds that enhance crystallization or to eliminate compounds that suppress crystal growth. This is particularly relevant for magnetic separation, where particle size and surface charge directly affect recoverability. A second important research direction is the systematic investigation of transformation pathways between key iron phases under controlled conditions. Experiments in synthetic solutions should examine the conversion of green rust/iron oxyhydroxides and iron sulphides of different crystallinity toward and away from vivianite. Gradually increasing system complexity—by introducing soluble components from real matrices in a stepwise manner and finally the soluble phase of real matrices as an aqueous phase—can help bridge the gap between simplified experiments and environmental conditions. Coupling these studies with magnetic susceptibility measurements would additionally reveal how these transformations translate to the practical performance of magnetically mediated phosphate recovery.

While the competition of phosphate with other ligands (carbonate, sulphide, organics) is strongly matrix-specific, the underlying chemistry is shared. Further experiments on mineral transitions and vivianite crystallization in a synthetic environment could significantly advance understanding of vivianite formation while enabling further optimization of the process. Further progress is needed to characterize transient iron phases and to improve thermodynamic and kinetic predictions in real matrices.

Predicting iron binding using thermodynamic modelling

Thermodynamic software (e.g., Visual MINTEQ) proved useful as an indicator of iron binding and mineral formation across matrices, particularly for predicting supersaturation and precipitation tendencies. In this thesis, modelling was applied to predict vivianite vs. siderite formation, assess supersaturation in iron-dosed and control lake sediments, and explore ORP-dependent competition among vivianite, iron sulphides, and iron(III) oxyhydroxides. These simulations supported the measurements by providing mechanistic explanations for decreased iron–phosphate binding, indications of which phases might form experimentally, and scenario testing across concentration/pH/ORP ranges.

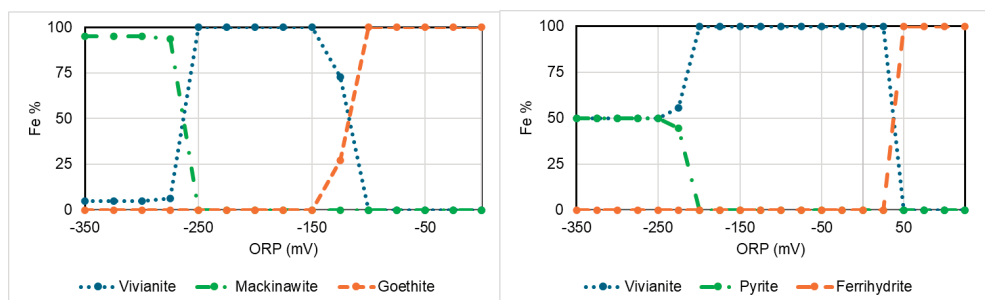


Figure 6-2 Repartition of iron minerals at 10 mM Fe²⁺, PO₄³⁻, HS⁻, each, pH 7.8, across different ORPs.

However, thermodynamic predictions also showed important limitations in complex matrices. A central challenge is selecting the relevant input components; often the system is oversimplified, but more data input does not necessarily increase model accuracy [17] and can lead to a costly, time-consuming matrix analysis. Even when the input dissolved composition is reasonably known, endpoint mineral phase selection in the model introduces uncertainty. In Chapter 5, modelling the ORP-dependent occurrence of iron sulphide, vivianite, and iron(III) oxyhydroxides required choosing proxy minerals: mackinawite (FeS) versus pyrite (FeS₂) for sulphides, and goethite (α -FeOOH) versus ferrihydrite ((Fe³⁺)₂O₃·0.5 H₂O) for Fe(III) phases (Figure 6-2). These choices have consequences: on the one hand, pyrite stoichiometry (Fe/S=0.5) favoured vivianite formation, leaving half of the Fe potentially available. On the other hand, pyrite was more stable, up to $\sim$ -200 mV, whereas mackinawite stability reached only $\sim$ -250 mV, thus iron sulphide speciation as mackinawite creates a bigger margin for vivianite formation. For Fe(III) phases in this simulation, it was also difficult to know which iron(III) phase formed, for example, the more crystalline goethite, or the more amorphous ferrihydrite, a precursor of the former [18]. In the model, goethite appeared already between $\sim$ -150 and -100 mV, while ferrihydrite formed only above $\sim$ 0 mV. In the laboratory experiments, no favourable ORP zone for vivianite formation was observed; limited sulphide destruction occurred, while substantial Fe(III) formed already at $\sim$ -250 mV—a discrepancy pointing to kinetic effects not captured by equilibrium models. More broadly, thermodynamic frameworks describe geochemical endpoints, whereas engineered recovery processes do not necessarily operate at equilibrium due to shorter timescales than those of natural systems, making direct translation difficult [19]. In natural matrices (e.g., lake sediments), lower phosphate concentrations may further slow reaction rates, complicating process-oriented predictions of vivianite formation.

To enhance predictive reliability in secondary phosphate streams, three lines of development are most promising: First, a sensitivity analysis should be conducted to identify key parameters (e.g., Fe, PO₄³⁻, CO₃²⁻, S²⁻/S⁰, Mg²⁺, Ca²⁺, NH₄⁺) that most strongly govern outcomes. The results should be cross-checked between the model and practical

laboratory experiments. Second, closer alignment between mineral phase models and observations could be achieved by better characterizing the mineral phases of interest, including the impact of impurities on solubility. Third, full kinetic modelling may be out of scope for routine design but allowing kinetically favoured phases to precipitate over the thermodynamically favoured ones could improve modelling in engineered systems. This underscores the need for kinetic studies to identify which phases dominate at given timescales. Such timescale details could be added to thermodynamic databases to show at which point different minerals are technically possible.

Overall, thermodynamic modelling was indispensable for formulating hypotheses, identifying controlling factors, and revealing knowledge gaps between theory and practice, thereby opening the path to future research. Yet its predictive power can be improved by more sensitive input selection, better understanding of the solubility of the minerals forming in secondary phosphate streams, including precursor, metastable or poorly defined phases, and a better understanding of the kinetics governing the processes.

6.3 CHARACTERIZATION OF VIVIANITE AND COMPETING MINERAL PHASES

Microscopy

Microscopy offers a practical complement to advanced spectroscopic techniques for identifying mineral phases in complex environmental matrices. Larger particles with characteristic colour or morphology can already be detected using stereoscopic microscopy, as is the case of the blue aggregates indicative of vivianite in lake sediments. Electron microscopy provides higher resolution and reveals finer morphological details: the plate-like, radial, or stacked structures typical of vivianite [20], the smooth cuboid morphology of struvite [21], and the framboidal textures characteristic of pyrite [22]. Coupling SEM with EDX further enables semi-quantitative determination of elemental composition and stoichiometry, allowing, for example, the confirmation of Fe–P-rich structures as vivianite and Fe–S clusters as iron sulphides. Figure 6-3 shows an example of the identification of vivianite in iron- and phosphorus-spiked lake sediments under a stereoscope, with electron microscopy and with EDX mapping.

However, light microscopy and SEM-EDX also face clear limitations. First, careful sample preparation in an anaerobic environment followed by a rapid insertion into the machine is necessary to minimize oxidation. Second, FeS_x encountered in this thesis were often $<10\text{ }\mu\text{m}$ and highly dispersed, making their identification and quantification challenging. Similarly, very diffuse or small iron–phosphate phases can be difficult to resolve, and the readily occurring binding of iron to organic matter, carbonates, or oxides cannot be reliably identified because carbon and oxygen are omnipresent in the sample and their

quantification in EDX is inherently unreliable [23]. Finally, electron microscopy remains only semi-quantitative; localized observations cannot be easily translated into absolute abundances for the entire sample.

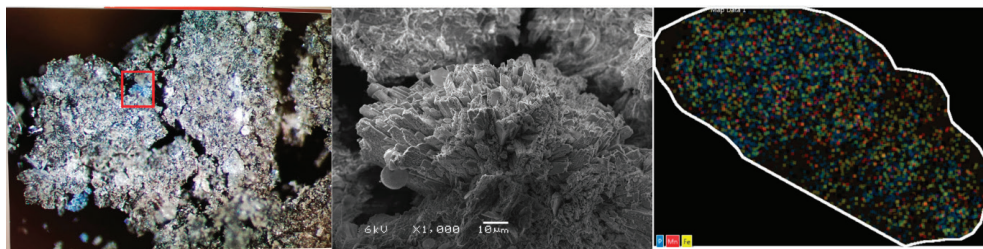


Figure 6-3 Microscopy images in iron and phosphate spiked lake sediment samples (Chapter 4), blue crystals under the stereoscope (left), aggregated vivianite crystals fanning out from a central point under the electron microscope (middle), and the elemental distribution of phosphorus, iron, and manganese detected with EDX (right).

Moving forward, one promising direction is the development of statistically rigorous image-processing workflows to quantify recognizable mineral structures across large numbers of frames. Such approaches could help estimate the abundance of vivianite, struvite, pyrite, or FeS_x phases at the scale of entire samples rather than in isolated micrographs. Improved automated particle recognition, shape-based classification, and machine-learning-assisted mapping may allow microscopy to evolve into a quantitative method suitable for monitoring mineral transformations during process optimization. Furthermore, microscopy will play a role in monitoring particle morphology to understand how operational conditions influence crystal growth, particle size, and aggregation, key factors for magnetically mediated vivianite recovery.

Microscopy, particularly SEM-EDX, provides valuable structural and compositional insights that complement Mössbauer spectroscopy and help contextualize mineral morphology. Optimizing image processing could be a promising route to quantifying mineral phases. So far, advanced spectroscopic methods are necessary for a decent quantification of iron phases.

Mössbauer spectroscopy

Mössbauer spectroscopy proved essential for identifying and quantifying iron phases in complex matrices, as demonstrated previously for vivianite in digested sludge [24,25] and further expanded in this thesis. The technique provides diagnostic information on the electronic environment around ^{57}Fe nuclei and on temperature-dependent magnetic ordering through hyperfine parameters: isomer shift (IS), quadrupole splitting (QS), and magnetic hyperfine field, allowing iron species to be distinguished. Yet, some limitations arose, where the vivianite content was low (especially in lake sediments), vivianite was

impure, or phase transformations between vivianite and other phases were difficult to resolve.

At room temperature, vivianite can be recognized by its characteristic A and B doublets ($IS=1.16$ and 1.20 mm/s, $QS=2.45$ and 2.91 mm/s [26]) with an ideal A/B ratio of 0.5, as governed by the crystal structure [27]. Deviations in A/B ratios above the approximate special contribution error of $\pm 3\%$ indicate the presence of impurities [28], or partial oxidation [24]. Further complications arise when green rust and other iron(II) species overlap with vivianite site A, as observed in Chapters 4 and 5 in this work and in the literature [8]. This potential overlap makes the vivianite quantification of site A doublet less reliable. Another problem at room temperature is the greater recoil effect and thermal motion of fine particles [29,30], which could lead to underestimating vivianite in a sample compared to iron sulphides such as pyrite.

Within Chapter 5 of this thesis, vivianite and other relevant iron minerals were analyzed at 20 and 4 K, as illustrated in Figure 6-4. The lower the measurement temperature, the more quantification of iron mineral phases becomes accurate, as thermal and recoil effects decrease, and eventually become minimized at 4 K. Yet, the presence of multiple peaks due to magnetically split components makes spectral fitting more difficult at 4 K. For vivianite, the magnetic ordering temperature (Néel temperature) is 12 K [31]. In Chapter 5 of this thesis, at 4 K, a site A-like doublet was still visible, suggesting the presence of a less pure or ultrafine (super)paramagnetic vivianite phase, or the coexistence of vivianite with an overlapping phase, such as green rust (Kubeneck, 2025). So far, no clear distinction guideline between impure/fine vivianite and green rust has been found. Therefore, the best solution is to quantify vivianite based on the spectral area of site B at 20 K, just above the Néel temperature of vivianite. This approach combines a more accurate quantification with the simpler fit of the vivianite site B doublet.

The characterization of coexisting iron sulphides and iron(III) species is further complicated. At room temperature, these phases appear as overlapped low-spin iron(II)/iron(III) doublets, which are challenging to separate. At 4 K, iron(III) phases are usually magnetically ordered, while low-spin Fe(II) phases, such as pyrite, remain paramagnetic, which enables their distinction. Yet difficulties persist when ultrafine or impure iron(III) species do not order magnetically at 4 K, as observed in Chapter 5. Anyway, iron sulphide characterization will remain challenging since the magnetic ordering behaviour of less-defined FeS_x compounds varies widely. For now, a magnetically distributed fit as carried out by Kubeneck et al. (2024) [32] was adopted, with the magnetically distributed species distinguishable at 20 K (Figure 6-4).

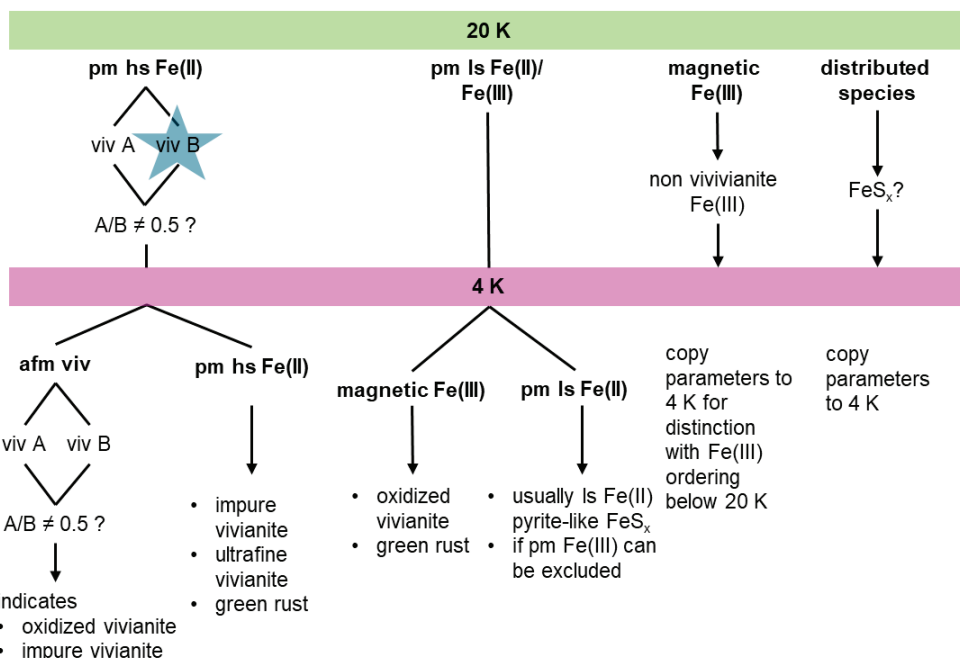


Figure 6-4 Flow scheme for identifying vivianite (viv) and other iron minerals relevant in organic-rich matrices, using Mössbauer measurements at 4 and 20 K, above and below vivianite Néel temperature (12 K, Meijers, 1967), with vivianite site B (viv B) at 20 K marked as the most characteristic peak to identify vivianite.

Future Mössbauer characterization could be improved by measuring synthesized reference iron phases likely to occur in secondary phosphate streams and using these parameters to ‘fingerprint’ the fit. Nevertheless, Mössbauer spectroscopy must always be complemented by a multi-method characterization, especially given the complexity of real matrices. In particular, Fe, S, and P K-edge XAS can provide detailed insights into local coordination environments [6,32,33]. At the same time, both XAS and Mössbauer techniques remain costly and technically demanding [10,34], underscoring the need to identify practical, more accessible analytical methods for routine phosphorus recovery applications.

Taken together, these results show that vivianite is most reliably quantified using the B-site signal at 20 K, and that 4 K spectra are valuable for separating magnetically ordered phases from paramagnetic phases. However, low concentrations, fine particles or a high impurity content hampers this distinction, warranting combined measurements.

Extraction protocols

Sequential extraction protocols combined with solid-state characterization can offer a useful means of characterizing iron, phosphorus, and sulphur species in secondary phosphate streams [6]. The classical extraction schemes developed in soil and sediment sciences distinguish five operationally defined fractions—water-soluble, exchangeable/acid-soluble, reducible, oxidizable, and residual—commonly used for metals such as iron [35]. In this thesis, phosphorus extractions were used to approximate iron-phosphate binding in sediments. More specifically, adding a bipyridine extraction step to classical sequential phosphorus extraction protocols can more effectively target Fe(II)-bound phosphate phases, such as vivianite [36,37]. Iron extractions were used to complement Mössbauer spectroscopy in sediments and digested sludge. Extraction in hydrochloric acid, followed by characterization of the resulting iron(II)/(III) species, provides indications of the oxidation state of HCl-labile phases and, in comparison to the total iron, the presence of more stable, often more crystalline phases that do not dissolve in HCl.

The chemical extraction of sulphur species would be of particular interest, as their detection by microscopy or XRD is hampered by their small particle size, low crystallinity, and lability to oxidation [38,39]. Yet, sulphur extraction schemes remain less developed than those for iron and phosphate [40]. Approaches such as acid-volatile sulphur (AVS) analysis provide only a broad classification of S phases and do not directly correspond to specific FeS minerals [41]. Elemental sulphur extraction frequently relies on Soxhlet methods, making routine multi-sample analysis laborious [42,43]. Additional downsides of chemical extractions in general include incomplete selectivity, potential reprecipitation, and changes in speciation during extraction steps, sensitivity to particle size, impurities and substrate-solvent ratios, which limit their accuracy and complicate the reliable assignment of mineral phases [35,44,45].

To advance iron speciation in a more practical setting, extraction protocols should be prioritized and specifically validated for complex waste matrices. This includes optimizing parameters such as extraction selectivity, solvent ratios, and stabilization procedures to minimize artifacts and improve reproducibility. For sulphur speciation, there is a clear need to develop simpler methods to detect elemental sulphur, replacing labour-intensive approaches. Nevertheless, integrating AVS extraction with solid-state methods such as Mössbauer spectroscopy could already enhance the quantification of FeS_x phases. Yet, the development of chemical extraction methods should not be the primary concern. Compared with spectroscopic techniques, extractions will continue to provide less information on the actual chemical binding and will remain high in chemical use, which is not sustainable. In the meantime, online and in-line use of techniques, such as IR spectroscopy, is becoming more accessible and reliable for identifying specific compounds in complex matrices [46,47]. While this has not been developed for vivianite, vivianite

has characteristic IR and Raman bands [48] that could be leveraged in combination with advanced data analysis.

Overall, sequential extractions remain a necessary complement to solid-state analyses until on- or in-line technologies become reliable for quantifying vivianite in secondary phosphate streams. For now, it is important to validate the extraction procedures for new matrices to ensure appropriate use.

6.4 BROADER PERSPECTIVES ON VIVIANITE-BASED PHOSPHATE RECOVERY TECHNOLOGIES IN DIFFERENT MATRICES

Within this section, non-chemical barriers to vivianite-based recovery from pig manure, (dredged) lake sediment, and digested sludge are discussed. Apart from technological readiness, the political and economical landscape, as well as stakeholder synergies are vital in bringing new phosphate recovery technologies forward.

Pig manure

At decreased carbonate in the manure, vivianite formation and its magnetic recovery is feasible, but remains to be proven at farm-scale. The broader agricultural context strongly influences the viability of manure-based vivianite recovery. Current subsidy structures in the EU predominantly support animal production, with 82% reportedly directed toward animal-based foods [49]. This incentivizes manure accumulation while providing limited financial or political support for manure treatment technologies, making large-scale implementation of vivianite recovery, including the use of iron salt and magnetic equipment, unlikely in the short term. Additionally, the fertilizing quality of the recovered phosphorus is a critical factor for local reuse. Vivianite has lower plant availability compared with struvite or calcium phosphate products [50], reducing its competitiveness as a recycled fertilizer. Given these structural and economic constraints, cooperative or regionally coordinated approaches appear more promising than individual farm-level solutions. Initiatives such as the ReFarM project—a cross-border effort between northwest Germany and the Netherlands exploring regional phosphorus recycling alongside calcium phosphate granulation technologies [51–54]—demonstrate how shared infrastructure can support nutrient recovery. Similarly, the RePhoKUs project in Northern Ireland has shown that stakeholder engagement, farmer training, and the introduction of Nutrient Management Plans can effectively mitigate phosphorus losses and improve nutrient handling [55]. These examples highlight that successful phosphorus management often depends on collaborative networks that integrate farmers, analytical institutes, environmental agencies, and regional authorities. A comparable networked model would likely be necessary for any future vivianite-based manure treatment system, enabling shared

investment in technologies such as magnetic separation and facilitating local reuse of recovered phosphorus. However, establishing such coordinated systems remains challenging under the current agricultural and policy landscape, where economic incentives for manure treatment remain limited.

In the end, the practicality of future vivianite-based recovery from manure depends on regional collaboration and supportive policy frameworks rather than on farm-level applications alone.

(Dredged) lake sediments

Beyond phosphate recovery, restoration is the primary concern in phosphate management in aquatic sediments, with eutrophication a major water quality issue in most freshwater and marine ecosystems [56]. Lake restoration typically integrates in-lake techniques—such as dredging, phosphorus immobilization, and the biological control of cyanobacteria—with nature-based shoreline solutions, including buffer zones, physical barriers, and pre-treatment of inflowing water [57]. The choice of techniques also depends on the specific conditions of the lake [58]. Yet, restoration efforts lack tangible long-term effects due to insufficient data or continued eutrophication caused by internal phosphate loading into the sediment [59–61]. For the latter, vivianite stabilization in the sediment is one element of effective phosphorus management, yet its immobilization potential is hampered by elevated sulphide concentrations [62]. The liability of vivianite in sediment to sulphide concentrations would require vivianite recovery before it can be destroyed by sulphide interesting again. For this, the circumstances would need to differ from those of dredged sediment. There are indications that certain depths in the sediment favour vivianite formation [63] which in turn could be used for a different magnetic recovery strategy. Developing robots equipped with magnets to extract sediment from the lake at a specific depth (e.g., 10 cm), as envisioned by L. Korving, could be an innovative approach. Yet this vision would need adequate design, detection, and recovery yields.

As with sustainable manure management, these efforts rely on coordinated stakeholder management to establish long-term, locally anchored restoration strategies [57]. Moreover, long-term action. Understanding and promoting phosphorus immobilization in vivianite could be part of these strategies, provided destruction by sulphide is limited or it can be removed magnetically.

Digested sludge

Independent of iron-sulphide utilization for vivianite formation, vivianite-based recovery from digested sludge has attracted the most attention and remains the most promising matrix for implementation [1,64–66]. One reason for this is the typical use of iron coagulants in wastewater treatment [67], driving vivianite formation. The potential of vivianite recovery is further highlighted by stakeholders developing the technology, with the LIFE Phos4EU project aiming to advance it until 2027, including the construction of a demonstrator at the Nieuwveer wastewater treatment plant [68]. These efforts will help test the technology at scale and evaluate its marketability, as no clear application routes have emerged so far. Vivianite could be used as a fertilizer for iron chlorosis in the Mediterranean [69], with possible infrastructural applications for recovery and reuse in Spain [70]. Furthermore, splitting vivianite into phosphate for fertilizer production and iron for recirculation in wastewater treatment has been explored [71]. Finally, emerging applications, such as the production of iron phosphate battery materials, could create new opportunities for vivianite.

Overall, progress in technology development and stakeholder efforts to implement it further are promising indicators for the future of vivianite in wastewater treatment. Advances in scaling up the process and materials science could mature magnetic vivianite recovery into a robust phosphate recycling technology.

6.5 CHALLENGES IN TRANSDISCIPLINARY PHOSPHATE MANAGEMENT

This thesis set out to bridge knowledge on phosphorus from the agricultural, environmental, and sanitation sectors, each of which has developed its own technical vocabulary, priorities, and measurement practices. These sectoral differences complicate comparison and cooperation. For example, the terminology and analytical focus in agricultural research emphasise soil carbon interactions and plant-available phosphorus, reflected in the use of Olsen-P or Mehlich-P extractions [72,73]. Phosphorus is often expressed as P_2O_5 [74], although more recent work increasingly uses elemental P per unit of wet manure [75]. In environmental science, the dominant concerns—eutrophication, management, and lake water quality—lead to pore-water measurements in ppm or ppb to assess trophic status [76], as well as depth-resolved sediment analyses for iron–phosphate burial [12,63] and sequential extraction schemes to evaluate P mobility [6]. In sanitation, the primary objectives relate to removal efficiency, effluent compliance, and operational costs, requiring measurement of soluble phosphorus concentrations and quantification of phosphorus in sludge on a wet- or dry-mass basis [77,78].

These divergent methods, units, and objectives underscore the challenge of developing a trans-sectoral perspective. However, they also point to the path forward. A shared analytical foundation—such as consistently reporting phosphorus in elemental P and adopting comparable extraction and quantification approaches across matrices—would substantially improve communication and interoperability between sectors. Such harmonization would not replace sector-specific methods but would strengthen cross-sector assessments of phosphorus pools, transformations, and recovery potential. Establishing this common analytical basis, together with a clearly articulated collective goal for phosphorus management, provides a practical foundation for advancing coherent and effective strategies across agriculture, environmental science, and sanitation.

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USE OF AI TOOLS

Microsoft Copilot (Chapters 1, 3, 4, 5, 6) and ChatGPT (Chapter 2) were used during preparation to assist with tasks such as text editing, correcting grammar, improving readability, restructuring paragraphs, providing phrasing suggestions, and translating the summary into Dutch. These tools did not generate original research content, arguments, or conceptual contributions. All substantive academic work—including data analysis, theoretical reasoning, and final interpretations—was performed by the author. All AI-assisted text was reviewed, verified, and edited by the author to ensure accuracy and compliance with academic integrity guidelines.

CV

After completing a volunteer year with an environmental NGO in Argentina, Sophie began her academic career in the Franco-German Chemistry bachelor's program *Regio Chimica*. In 2016/17, she studied at the Université de Haute Alsace in Mulhouse (France), and from 2017 to 2019 at the Albert-Ludwigs-Universität Freiburg (Germany), where she completed a bachelor's thesis on the fluorometric detection of phosphates in water. Following a short internship through the German Academic Exchange Service (DAAD) RISE program at the Pontificia Universidad Católica de Chile in Santiago, working on metal–organic frameworks, she began her master's degree at the Dresden University of Technology (Germany). There, she worked as a student assistant on battery materials at the Fraunhofer Institute for Material and Beam Technology and completed a master's thesis in water chemistry on the anaerobic biodegradation and enzymatic activity of benzophenone-type UV filters. During both her bachelor's and master's studies, Sophie was a recipient of the Cusanuswerk scholarship for gifted students. In late 2021, Sophie started her PhD within the EU Horizon 2020 Marie Skłodowska-Curie Innovative Training Network *RecaP*, which focused on interdisciplinary phosphorus management. Based at Wetsus and supervised by Delft University of Technology, she investigated vivianite formation in organic-rich matrices. During her PhD, she also conducted research visits to the Ecology laboratory at the University of Southern Denmark in Odense and to the R&D department of Kemira in Espoo (Finland).



CV

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