Geoderma 193–194 (2013) 189–199

Contents lists available at SciVerse ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Does vivianite control phosphate solubility in anoxic meadow soils?

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ARTICLE INFO

Article history:
Received 4 August 2011
Received in revised form 20 June 2012
Accepted 1 October 2012
Available online 17 November 2012

Keywords:
Wetland
Gyttja
Vivianite
Sorption
Iron(II)
Phosphate

ABSTRACT

Vivianite ($Fe_3(PO_4)_2.8H_2O$) may precipitate in anoxic wetland soils where it may control orthophosphate (P_i) equilibrium solution concentrations at micromolar levels, and thus be of key importance in reducing excessive P from agricultural sources and eutrophication. However, vivianite equilibria and kinetics under *in situ* conditions are not fully understood and the occurrence of vivianite in wetland soils is rarely documented. In the present investigation we have monitored the temporal (November to June) variation in the pore water chemistry of a wet meadow soil (Sapric Medihemist) including a vivianite-containing gyttja layer. Pore water concentrations of Ca, Fe^{II}, HCO_3, and NH_4 in the gyttja layer were higher than in adjacent horizons. In contrast, dissolved P_i concentrations were the lowest observed in the profile and showed only minor fluctuations (between 0.1 and 6 μM). Pore water composition in the gyttja layer was close to equilibrium with vivianite (saturation index, SI_{viv}, 2.01 ± 0.53) at constant pH (~ 6.8). Dissolution and precipitation experiments in the laboratory with soil suspensions from the gyttja layer demonstrated that vivianite solubility equilibria were only slowly restored. Even after 120 days following perturbation the supersaturation was still high (SI_{viv}~6). It seems that vivianite does contribute to P_i immobilization in anoxic soil horizons, but due to slow precipitation kinetics such soils cannot maintain P_i concentrations at levels below critical thresholds for eutrophication (~1 μM), except if pore water geochemistry is kept stable.

1. Introduction

The geochemistry of orthophosphate (P_i) in anoxic soils and sediments has been intensively investigated for many years without a clear picture emerging (e.g. Brand-Klibanski et al., 2007; Gächter and Müller, 2003; Hoffmann et al., 2009; Reddy et al., 1999; Roden and Edmonds, 1997; Zhang et al., 2003).

It is well documented that anoxic conditions lead to reductive dissolution of iron(III) oxides, followed by release of sorbed phosphate to solution (House et al., 1998; Kjaergaard et al., 2012; Patrick and Khalid, 1974; Ponnamperuma, 1972; Scalenghe et al., 2002; Szilas et al., 1998). This is an integral part of the internal phosphorous cycling in eutrophic lakes having seasonally anoxic bottom waters (Boström et al., 1988; Roden and Edmonds, 1997) and in wetland soils (de Mello et al., 1998; Heiberg et al., 2010; Zak and Gelbrecht, 2007). Knowledge gaps exist relating to the fate of P_i released during reductive dissolution, as in most cases the amount of P_i released to solution is much less than expected based on the amount of iron(III) oxide reduced (Jensen et al., 1998; Kirk, 2004; Willett, 1989). Possible explanations for this include resorption to redox-stable sorbents (e.g. aluminum oxides, phyllosilicate clays and calcite), assimilation by microorganisms and plants, or precipitation as calcium, magnesium or mixed metal phosphates, or as iron(II) phosphates, e.g. vivianite ($Fe_3(PO_4)_2 . 8H_2O$), (Kirk et al., 1990). Furthermore, iron(III) oxides with a high P_i saturation are less readily reduced than oxides without P (Borch and Fendorf, 2008).

As iron(II) concentrations are often rather high in the anoxic soils and sediments, precipitation of iron(II) phosphates is likely to take place. Equilibrium modelling indicates that occurrence of vivianite and vivianite-type compounds in wetland soils, lake and river sediments is not uncommon, but direct evidence is rarely presented (e.g. in Hearn et al., 1983; Manning et al., 1991; Nanzyo et al., 2010; Nriagu and Dell, 1974; Postma, 1981; Taylor and Boult, 2007).

The solubility of vivianite is given by:

$$Fe_3(PO_4)_2 \cdot 8H_2O \rightleftharpoons 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$$

and has an equilibrium constant of $pK_{sp} = 35.767 \pm 0.076$ at 25 °C (Al-Borno and Tomson, 1994). The pH of anoxic soils and sediments is often relatively high (~pH 7) due to the acid consuming process of iron(III) oxide reduction. At the concurrent high release of Fe^{2+} the concentration of phosphate in equilibrium with vivianite and in

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http://dx.doi.org/10.1016/j.geoderma.2012.10.003

absence of strong metal complexing ligands is rather low (Willet, 1985), e.g. decreasing from 2.5 to 0.05 µM for Fe^{2+} concentrations between 50 and 2000 µM. Fig. 1 shows calculated "sorption isotherms" where P_i is added to an Fe^{2+}-rich model pore water. In the low total Fe^{2+} (200 µM)/low alkalinity case (Fig. 1a), P_i concentrations in equilibrium with vivianite remain below 3.5 µM at initial solution P_i concentrations from 1 to 100 µM and reach a "sorption" maximum thereafter. At a ten times higher Fe^{2+} concentration and alkalinity (Fig. 1b) the zero equilibrium P_i concentration (EPC_0, at which sorption equals desorption, Froelich, 1988), decreases to 0.12 µM, and the buffer capacity of the solid phase increases, keeping soluble P_i below 0.6 µM over a wider range of initial P_i concentrations (up to 500 µM). For comparison, the effect of the presence of siderite ($FeCO_3$) and vivianite on soluble P_i is shown in Fig. 1c. Siderite is a common mineral in waterlogged soils where sufficient Fe^{2+} and alkalinity is generated (Zachara et al., 2002). If siderite equilibrates with the pore water (Fig. 1c) and controls the Fe^{2+} activity, vivianite will not precipitate until P_i solution concentrations exceed 44 µM. Hence, if the solution phase is in equilibrium with vivianite and siderite is not present, anoxic soils and sediments should be able to control soluble P_i concentrations at low levels and in particular at levels below critical threshold concentrations for algal growth in surface waters (~1 µM P_i, Kristensen et al., 1991).

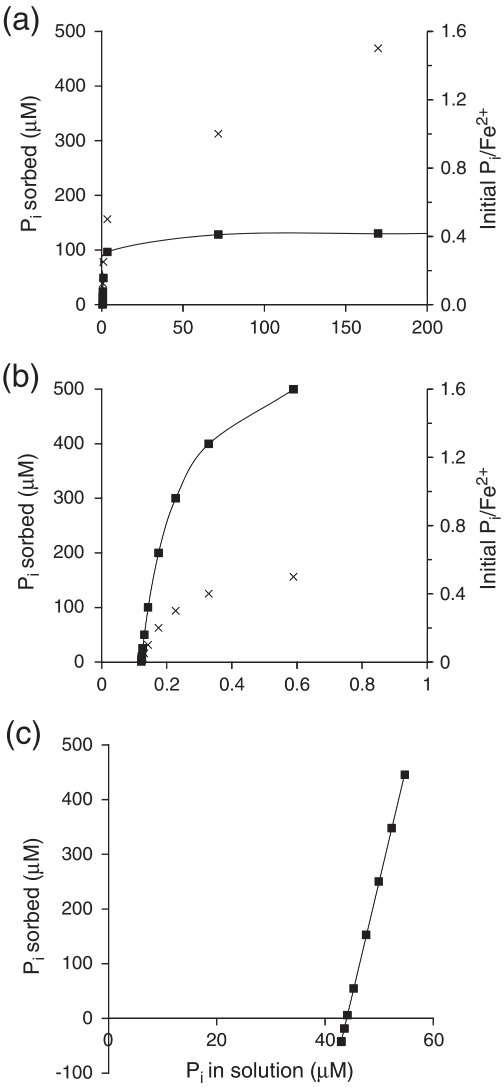

Fig 1. Modelled solution concentrations of P_i (solid symbols) at pH 7 for initial P_i concentrations of 1 to 500 µM in equilibrium with vivianite (a, b) and vivianite and siderite (c). Calculations were done using VisualMINTEQ for total concentrations of 500 µM Ca^{2+}, 520 µM CO_3^{2-}, 200 µM Fe^{2+}, 100 µM Mg^{2+}, 1000 µM Cl^- (a), and 1200 µM Ca^{2+}, 5200 µM CO_3^{2-}, 1000 µM Fe^{2+}, 100 µM Mg^{2+}, 500 µM Cl^-, 250 µM Na^+ (b, c). Concentration levels are comparable to *in situ* conditions in winter as found in the gyttja layer. The intersection of the trend lines with the x-axis is the point of zero net sorption (EPC_0). Crosses indicate the initial P_i/Fe^{2+} ratio (same for b and c) and vivianite precipitates when this ratio is ≤ 0.67.

The possible precipitation of vivianite and vivianite-type phases has important practical implications. Vivianite precipitation is regarded as an important buffer mechanism under steady state conditions in anoxic lake sediments regulating interstitial concentrations and phosphorus release to the overlying water (Nriagu and Dell, 1974). A disturbance, e.g. restoration of thermally stratified lakes with anoxic bottom water by hypolimnetic oxygenation, may increase P_i solubility rather than reduce it (Gächter and Müller, 2003). This may also have implications for the fate of vivianite contained in waste water sludge and anoxic river sediments, which have received treated sewage (Frossard et al., 1997; Hearn et al., 1983; Taylor and Boult, 2007). Wetlands may function as phosphorus traps (Axt and Walbridge, 1999; Darke and Walbridge, 2000; Nowak and Watts, 2006; Nowak et al., 2004; Richardson, 1999) and currently new wetland areas are being established in order to retain phosphate leaching from agricultural land and to remove phosphorus from river water occasionally flooding the wetland (e.g. Biebighauser, 2007). However, complex interactions of the hydrological regime and local biogeochemical properties complicate prediction of the phosphorus assimilation capacity (Hoffmann et al., 2009), and in particular investigations of P_i cycling in the anoxic soils often lack evidence for the occurrence of vivianite.

The present study for the first time combines solid phase characterization with a detailed *in situ* time course monitoring of the pore water chemistry in a vivianite-containing soil for a ~ 7 months hydrological period including the period of fully waterlogged conditions in winter and water table decrease during spring. Our aims were: 1) to characterize the vivianite, 2) to investigate the *in situ* geochemical equilibrium conditions and biogeochemical processes contributing to it, 3) to study dissolution and precipitation kinetics in laboratory experiments using soil material from the gyttja layer to elucidate if and how fast a vivianite-controlled equilibrium establishes, and 4) to evaluate the ability of vivianite to control pore water phosphate concentration at low levels.

2. Materials and methods

2.1. Study site and profile description

A field site near Vejrumbro (56° 26 09 56 N, 9° 33 13 20 E) in the Nørreå river valley in the central part of Jutland, northern Denmark, was investigated. The study area is a former groundwater-fed fen wetland with deep (>5 m) peat and gyttja layers receiving nutrients from surrounding watershed through drainage and surface runoff. Within the past 50 years, intensive agriculture and the establishment of a system of subsurface drains and open ditches has caused both degradation and subsidence of the soil. Presently the water table fluctuates moderately between a minimum of ~50 cm below the surface in summer and fully waterlogged conditions during the winter season. The area is used as permanent grassland for grazing and hay harvesting.

A profile of a wet meadow soil (Sapric Medihemist, Soil Survey Staff, 1992, Fig. 2a) was described and sampled on 3 November 2009. The uppermost horizons of the soil profile comprise an A (0 –15 cm) and an oxic B ($B_{ox,}$ 15–35 cm) horizon consisting of hemic material which is intensively penetrated by roots and biopores (predominantly from earthworms). The B_{ox} horizon is mottled by reddish brown Fe oxide precipitates (2.5 YR 3/6, Munsell soil colour code) in a brown reddish matrix (>70%, 5 YR 3/2). The underlying reduced horizons of black/dark brown to grey colour consist of a sapric B horizon (B_{red}, 35–60 cm) with many old lignified roots, and reddish brown Fe oxide