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Mineralogical associations with soil carbon in managed wetland soils

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Abstract

Carbon (C) rich wetland soils are often drained for agriculture due to their capacity to support high net primary productivity. Increased drainage is expected this century to meet the agricultural demands of a growing population. Wetland drainage can result in large soil C losses and the concentration of residual soil minerals such as iron (Fe) and aluminum (Al). In upland soils, reactive Fe and Al minerals can contribute to soil C accumulation through sorption to poorly crystalline minerals and precipitation of organo-metal complexes, as well as C loss via anaerobic respiration by Fe-reducing bacteria. The role of these minerals in soil C dynamics is often overlooked in managed wetland soils and may be particularly important in both drained and reflooded systems with elevated mineral concentrations. Reflooding drained soils has been proposed as a means to sequester C for climate change mitigation, yet little is known about how reactive Fe and Al minerals affect C cycling in restored wetlands. We explored the interactions among soil C and reactive Fe and Al minerals in drained and reflooded wetland soils. In reflooded soils, soil C was negatively associated with reactive Fe and reduced Fe(II), a proxy for

anaerobic conditions (reactive Fe: R^2=0.54-0.79; Fe(II): R^2=0.59-0.89). In drained soils, organo-Al complexes were positively associated with soil C and Fe(II) (Al R^2 =0.91; Fe(II): R^2=0.54-0.60). Soil moisture, organo-Al, and reactive Fe explained most of the variation observed in soil C concentrations across all sites ($P<0.01$). Reactive Fe was negatively correlated to soil C concentrations across sites, suggesting these Fe pools may drive additional C losses in drained soils and limit C sequestration with reflooding. In contrast, reactive organo-Al in drained soils facilitates C storage via aggregation and/or formation of anaerobic (micro)sites that protect residual soil C from oxidation and may at least partially offset C losses.

1. Introduction:

Wetlands represent only 3% of the world's soils, but account for approximately 21% of the global soil organic carbon (C) stock (Scharlemann et al., 2014; Yu et al., 2010). Under natural, waterlogged conditions, slow decomposition favors the accumulation of soil organic matter, leading to a net C sink (Dise, 2009; Wilson et al., 2016). However, >10% of wetlands worldwide have been drained for agriculture (Kramer & Shabman, 1993; Leifeld, 2013; Stephens et al., 1984), and future increases in drainage are expected this century to meet growing demands for food production (Verhoeven & Setter, 2010). These land use-related disturbances to soil and hydrologic conditions often result in large soil C losses and currently contribute to substantial greenhouse gas emissions globally (1.91 Gt CO_{2eq} yr^{-1}, Hemes et al., 2019; Leifeld & Menichetti, 2018; Wilson et al., 2016). Following drainage, rapid oxidation enhances soil organic matter decomposition, leading to significant land surface subsidence and carbon dioxide (CO_2) emissions (Deverel et al., 2016; IPCC, 2013; Teh et al., 2011). Reflooding has been proposed as a restoration approach on drained soils to reintroduce anaerobic conditions, reverse land

50 subsidence, and enhance soil C sequestration. Eddy-covariance studies suggest that reflooded
51 soils have the potential to become net C sinks (on the order of 4.1 Mg ha^{-1} yr^{-1}, Hemes et al.,
52 2019), but C emissions following flooding can hinder or delay net C storage (Hatala et al., 2012;
53 Hemes et al., 2018; Knox et al., 2015; Miller et al., 2008). Given their large soil C stocks, high
54 soil C sequestration potential, and the potential for large greenhouse gas emissions, better
55 understanding of the mechanisms controlling soil C dynamics in both drained and restored
56 reflooded wetlands is needed (Spivak et al., 2019).
57 When wetland soils are drained for agriculture, extensive losses of organic matter can lead to
58 the concentration of minerals in soils. The role of soil minerals in soil C sequestration and loss
59 has been studied extensively in upland soils (Hall & Silver, 2015; Markus Kleber et al., 2015;
60 Kögel-Knabner et al., 2008, Chen et al. 2020), but the relationships between soil minerals and C
61 storage in organic-rich soils has not been explored. Reactive iron (Fe) and aluminum (Al)
62 minerals are thought to contribute to soil C accumulation in soils through direct sorption to
63 poorly crystalline minerals and/or precipitation of organo-metal complexes, particularly under
64 aerobic conditions (Chen et al., 2020; W. Huang et al., 2020; Markus Kleber et al., 2015). In
65 contrast, Fe minerals can also contribute significantly to C loss via anaerobic respiration of Fe-
66 reducing bacteria (Baldock & Skjemstad, 2000; Kaiser & Guggenberger, 2000; Peretyazhko &
67 Sposito, 2005; Wagai & Mayer, 2007). In upland tropical forest soils, microbial Fe reduction
68 accounted for up to 44% of organic C oxidation from soils on an annual basis (Dubinsky et al.,
69 2010).
70 Most research exploring the role of reactive Fe and Al minerals in soil C dynamics has been
71 conducted either in relatively low C soils or natural wetlands (X. Huang et al., 2018; Kaiser et
72 al., 2002; LaCroix et al., 2018; Takahashi & Dahlgren, 2016; Wagai et al., 2013). Wetland soils

recently drained for agriculture tend to be C-rich and often experience extremes in water table height (Holden et al., 2004), with farmers maintaining an artificially low water table interspersed with periodic flood irrigation. Drainage and periodic flooding events lead to fluctuating oxidation-reduction (redox) conditions (Niedermeier & Robinson, 2007). Some research has highlighted the effects of fluctuating redox conditions on Fe redox cycling in wetlands (Chamberlain et al., 2018; Niedermeier & Robinson, 2007; Todorova et al., 2005), but the importance of Fe and Al biogeochemistry as controls on soil C accumulation or loss in drained or reflooded soils is not well understood.

Redox-active Fe minerals can be readily reduced or oxidized through a number of biogeochemical pathways (Coby et al., 2011; Mejia et al., 2016; Melton et al., 2014; Weber et al., 2006) and the oxidation states of Fe form a dominant redox couple in many soils (Conrad, 1996; Lovley, 1991). In fact, the concentrations of reactive Fe often exceed concentrations of most other electron acceptors in soils. Fluctuating redox conditions with abundant reactive Fe and high C concentrations essentially create a biogeochemical engine for anaerobic microbial metabolism (Barcellos et al., 2018; Bhattacharyya et al., 2018; Hall & Silver, 2015; Weber et al., 2006). The combination of high concentrations of reactive Fe, abundant C availability, and fluctuating redox could thus drive considerable soil C losses (Dubinsky et al. 2010). However, reactive Fe minerals can also protect soil C from microbial oxidation via sorption or complexation mechanisms (M. Kleber et al., 2005; Wagai & Mayer, 2007). While oxidized Fe is generally thought to be important for soil C storage, anoxic conditions can mobilize mineral-bound C that can subsequently be oxidized under fluctuating redox conditions (Chen et al. 2020, Huang et al. 2020).

Aluminum also plays a key role in soil C storage and loss. The decomposition of Al-associated soil C can be inhibited via the direct recalcitrance of ligand exchange (M. Kleber et al., 2005). Reactive Al species have also been shown to lower soil C lability to microbes, and can be positively correlated with soil C concentrations (M. Kleber et al., 2005; Takahashi & Dahlgren, 2016; Torn et al., 1997). Aluminum is not redox-active, but can limit the decomposition of Al-associated organic matter under anaerobic conditions (Hall & Silver, 2015). Given the low metal to C ratios (M/C) observed in other studies (Bazilevskaya et al., 2018; Hall & Silver, 2015; Jansen et al., 2004) the direct recalcitrance of soil C associated with reactive Al species is improbable in C-rich wetland soils. This suggests other mechanisms, such as a bulk soil conditions or soil aggregation may limit the decomposition of Al-associated soil C.

Here, we hypothesized that the concentration of reactive Fe and Al minerals limit soil C losses in drained wetland soils due to the formation of mineral-C associations. We also hypothesized that reactive Fe and Al mineral concentrations would not be related to patterns in C storage in reflooded systems where persistent anaerobic conditions limited decomposition rates. We sampled nine mineral-rich sites encompassing a range of drained and restored conditions in a regional complex of active agricultural land, recently reflooded farmland, and older restored wetlands. Previous research has focused on utilizing wetland restoration to combat climate change by increasing soil C sequestration and regulating further soil C loss by limiting aerobic respiration (Hatala et al., 2012; Hemes et al., 2019; Knox et al., 2015). Understanding the interactions between reactive Fe and Al minerals and soil C in both drained and reflooded soils could highlight potential mechanisms controlling the rates of C accumulation and loss across a range of soil conditions. A better understanding of these pathways can facilitate wetland

117 restoration efforts that maximize long-term soil C sequestration and minimize future CO_2
118 emissions.
119
120 **2. Methods**
121 *2.1. Site descriptions*
122 The study was conducted in the Sacramento-San Joaquin Delta region of California
123 (hereafter referred to as the Delta). The Delta experiences a Mediterranean climate with hot dry
124 summers and cool wet winters. The region's historical mean annual temperature is 15.1° C and
125 has a yearly average rainfall of 326 mm (Hatala et al., 2012). Much of the Delta was drained for
126 agriculture in the mid-19th century, which has led to high rates of peat oxidation and substantial
127 soil subsidence (Drexler et al., 2009). Given the differences in management practices and time
128 since drainage across the Delta, the region now consists of Fe-rich soils encompassing a large
129 range of soil organic matter contents. In addition to drained sites, wetland restoration projects
130 have been conducted across the Delta in an effort to reverse soil subsidence and promote soil C
131 sequestration. The combination of historical and current water management practices sampled
132 across a small geographical area (~60 km^2) provided a unique template to explore the importance
133 of mineralogical controls on soil C storage across a range of substrate and redox conditions.
134
135 *2.1.1. Drained and degraded agricultural sites*
136 The drained and degraded agricultural sites were located on Bouldin, Sherman, and
137 Twitchell Islands. Land uses included a continuous corn site (38.11 N, -121.5 W, Ameriflux ID:
138 US-Bi2), two continuously grazed pasture sites (38.04 N, -121.74 W; US-SND and 38.04 N, -
139 121.7 W; US-Snf), and three perennial alfalfa sites (38.10 N, -121.5 W, US-Bi1; 38.12 N, -121.6

W, US-TW3; and 38.11 N, -121.5 W). The continuous corn site was a highly organic Histosol, with a partially oxidized peat layer approximately 2 m deep; the other agricultural sites were predominantly mineral alluvium Mollisols (Eichelmann et al., 2018; Hemes et al., 2019). Although all agricultural sites were drained, they still experienced spud ditch or flood irrigation during the growing season, and possible short-term winter floods associated with storms or water management activities. As these sites were dominantly unflooded, we refer to them as "drained".

2.1.2. Reflooded restored wetland sites

The wetland sites were perennially flooded and are referred to hereafter as "reflooded". Sites were located on Twitchell and Sherman Islands. West Pond wetland (38.11 N, -121.6 W; US-TW1) was reflooded in 1997 and the accreted layer since restoration was largely undecomposed, saturated plant detritus with a Histosol beneath. Before restoration this site was used for agriculture through the 19th century and was primarily a corn field prior to restoration (Miller et al. 2008, Fleck et al. 2004). Mayberry wetland (38.05 N, -121.8 W; US-MYB), previously a pasture, was reflooded in 2010 and was predominantly a Histosol. East End wetland (38.10 N, -121.6 W, US-TW4) was previously a continuous corn field and was reflooded in 2014 on an iron-rich alluvium Mollisol (Chamberlain et al. 2018, Eichelmann et al. 2018).

2.2 Soil sampling and analyses:

Samples were collected along three 20 m transects per site; soil cores were taken at five locations at 5 m intervals along each transect. Recognizable surface litter was removed prior to sampling. Each soil core was collected to a depth of 30 cm at all sites as separate 0-15 cm and

15-30 cm samples. Additionally, visible differences across depths in reflooded soils were used to operationally define these soils as "accreted" and "residual" soil in an parallel study (Chamberlain et al., 2018). With the exception of air-dried analyses, soils and in-field extractions were transported in an insulated cooler to maintain soil temperatures within the seasonal range. Samples were processed less than 24 hours after sampling and all laboratory analyses were conducted at U.C. Berkeley.

For total soil C and N analyses, subsamples were air-dried, sieved to < 2 mm, and had visible roots removed before being ground to a fine powder. In reflooded soils, large undecomposed organic material and roots were removed before sieving. Samples were then analyzed in duplicate for total C and N on a CE Elantech elemental analyzer (Lakewood, New Jersey). Soil pH was determined by creating a 1:1 soil to water solution, vortexing for 1 minute, then measuring the solution pH after 10 minutes (McLean, 1982). Soil moisture was determined gravimetrically by weighing fresh soil, oven drying for 24 hours at 105 °C, reweighing the dried soil, and calculating the difference as percent soil moisture.

Table 1. Description and the interpretations of measured reactive Fe and Al pools

Variable	Description	Interpretation	Extraction condition
$Fe(III)_{HCl}$	0.5 M HCl extractable Fe(III)	Poorly crystalline, weak acid soluble short-range order and organo-Fe(III) complexes; proxy for a reactive fraction of Fe(III)	Field
$Fe(II)_{HCl}$	0.5 M HCl extractable Fe(II)	Weak acid soluble Fe(II), proxy for anaerobic conditions	Field
Fe_{CA}	Citrate-ascorbate extractable Fe	Poorly crystalline, redox-active short-range order (oxy)hydroxides and organo-Fe complexes; proxy for microbially reducible Fe	Field
Al_{CA}	Citrate-ascorbate extractable Al	Al-substituted in short-range order (oxy)hydroxides and organo-Al complexes; proxy for substitutable Al	Field

Fe_{AO}	Ammonium-oxalate extractable Fe	Organo-Fe complexes, short-range order (oxy)hydroxides; proxy for chelatable Fe	Ground, air-dried
Al_{AO}	Ammonium-oxalate extractable Al	Organo-Al complexes, short-range order (oxy)hydroxides; proxy for chelatable Al	Ground, air-dried

Interpretations from: Hall & Silver (2015), Loeppert & Inskeep (1996) and Wagai & Mayer (2007); Hyacinthe et al. (2006)

2.2.1 Reactive Fe and Al pools

We utilized separate soil extractions to characterize three operationally defined indices of reactive Fe and Al. These indices have been mechanistically linked to microbial and geochemical interactions between Fe or Al and organic C storage and loss (Table 1, see also Hall & Silver, 2015; Wagai & Mayer, 2007). First, a 0.5 M hydrochloric acid (HCl) extraction was used to measure both weak-acid soluble, reactive short-range order Fe(III) ($Fe(III)_{HCl}$) and soluble Fe(II) ($Fe(II)_{HCl}$) complexes (Fredrickson et al., 1998). $Fe(II)_{HCl}$ concentrations were also used as an index of reducing conditions, while $Fe(III)_{HCl}$ was used as a proxy for a reactive fraction of Fe(III) (Fredrickson et al., 1998; W. Huang & Hall, 2017). Approximately 3 g soil (oven dry equivalent (ODE)) was added to a 30 ml 0.5 M HCl solution in the field within 1 min of sampling to minimize soil oxidation. The low pH of this extraction also inhibits the oxidation of Fe(II) in solution (Hall & Silver, 2015). Determination of expected ODE masses was determined using residual soil parameters known prior to sampling. An estimated soil-to-volume ratio was determined, then a known volume of soil was added to a preweighed, prefilled Falcon tube. Upon return to the lab, the Falcon tube was reweighed to determine the soil mass added, shaken for 1 h, and centrifuged at 4700 relative centrifugal force (rcf) for 15 min. Samples were subsequently measured colorimetrically within 24 h of sampling using a ferrozine assay buffered with 50 mM HEMES (Viollier et al., 2000). Soil extracts with high colored dissolved organic C

(CDOC) concentrations can lead to $Fe(II)_{HCl}$ overestimations up to 10% during ferrozine assays through either autoreduction or direct absorbance (W. Huang & Hall, 2017; Verschoor & Molot, 2013). Additional samples blanks were run using deionized water (H_2O) instead of ferrozine to determine the interference of CDOC. Interferences from CDOC were generally negligible overall, with maximum interferences of 2.5%. To examine the possible overestimation of $Fe(II)_{HCl}$ via autoreduction in the 0.5 M HCl assay (Verschoor and Molot, 2013), we added an Fe(III) spike as FeCl to 5 mL subsamples of extract from sites with > 10% C (n = 10, 5 from each depth), corresponding to an increase of 0.2 mM Fe(III)/L (Supplemental Material). Samples were rerun with the ferrozine analysis. The recovery rate of the Fe(III) spike was always > 95%, within the error of the method. While this test does not confirm that autoreduction did not occur in our samples, it does highlight that autoreduction was not a significant source of $Fe(II)_{HCl}$ measured. To further test the potential effects of autoreduction, we determined the impacts of decreasing $Fe(II)_{HCl}$ concentrations by 10% in all drained soil samples, as well as simply removing samples with soil C > 10% from the dataset and redoing the trend analyses. These changes did not significantly alter the patterns observed (Supplemental Figure 3a and 3b). We acknowledge the potential for overestimation, particularly via autoreduction, in $Fe(II)_{HCl}$ data, although it does not appear to have affected the results reported here.

A second, separate field extraction was performed utilizing a 0.2 M sodium citrate and 0.05 M ascorbic acid (citrate-ascorbate) with a pH of 6 to provide a separate estimate of reducible (redox-active) short-range order Fe oxides (Fe_{CA}) and substituted Al oxides (Al_{CA}), (Torrent, 1997). These assays are an index of microbially reducible Fe and substitutable Al. Approximately 1.5 g soil (ODE) was added to 45 ml of solution within 1 minute of sampling utilizing the same in-field methods described in the HCl extractions above. Extracts were shaken

for 16 h, centrifuged at 1000 rcf for 20 min, and then decanted and refrigerated until analysis. A third, separate index of chelatable Fe (Fe_{AO}) and Al (Al_{AO}) oxides and organo-metal complexes (organo-Fe and organo-Al complexes) used an ammonium-oxalate extraction consisting of 0.17 M ammonium oxalate and 0.1 M oxalic acid performed in the dark at pH 3 (Loeppert & Inskeep, 1996). Subsamples were air-dried and ground to directly compare with previously published ammonium oxalate extractions (Hall & Silver, 2015; Loeppert & Inskeep, 1996), and because oxalate can extract crystalline Fe in the presence of Fe(II) (Phillips et al., 1993), which was elevated in some soils. Approximately 0.5 g was added to 30 ml of solution, shaken for 2 h, centrifuged at 1000 rcf for 20 min, and decanted and refrigerated until analysis. The ammonium-oxalate extraction represents chelatable Fe and Al species, previously defined as organo-Fe or organo-Al complexes and may also represent some redox-active Fe species. The citrate-ascorbate extraction readily solubilizes Fe via reductive dissolution and can be considered both redox-active Fe species and poorly crystalline Fe and Al species. Both citrate-ascorbate and ammonium-oxalate extractions were analyzed for Fe and Al in triplicate via inductively coupled plasma optical emission spectroscopy (ICP-OES; Perkin Elmer Optima 5300 DV). These three separate, non-sequential soil extractions are commonly used to quantify operationally-defined reactive Fe and Al phases (Table 1; Coward et al., 2018; Hall & Silver, 2015; Thompson et al., 2011; Wagai et al., 2013) that interact in different ways with soil C.

2.3 Statistical analyses

Statistical analyses were performed using JMP Pro 13 (SAS Institute Inc., Cary, NC). To determine differences across site, land use type (restored or drained), and soil depths, we performed one-way ANOVAs followed by post-hoc Tukey tests using soil C, soil N, pH, soil moisture, Fe_{AO}, Al_{AO}, $\ln(Fe_{CA})$, $\ln(Al_{CA})$, $\ln (Fe(II)_{HCl})$, and $\ln(Fe(III)_{HCl})$ concentrations, nested

within depth values and soil conditions. Data were log-transformed when necessary to create a log-normal distribution to meet ANOVA assumptions.

A multiple regression model was used to further test the relationships between soil C concentrations and the other biogeochemical variables measured and the interactions among them. Three sets of separate sample groups were used with one group containing all sites, and the second and third groups were split into drained or reflooded soils. Depth was again included as a blocking factor to account for sampling design and unexplained depth-related variations in soil C concentrations. Generalized pairwise regression analyses were used to explore the relationships between measured biogeochemical variables and soil C concentrations at the scale of individual samples within and across soil type and conditions. Relevant fits for pairwise regression analyses are included in Supplemental Table 1.

2.4 Upscaling

To determine the potential impacts of redox-active Fe species on C stocks over time, we used data from a nearby drained Delta wetland site reported in Yang and Liptzin (2015). They measured Fe reduction rates of 1.18 mg Fe g $soil^{-1}$ d^{-1}. Assuming 0.025 mol C oxidized per mol of Fe(III) reduced and a bulk density of 0.25 g cm^{-3} (Deverel et al., 2016), we estimated a microbial respiration rate from Fe reduction of 0.47 g C m^{-2} d^{-1}. We then assumed 5.5-d of Fe(III) reduction (Yang & Liptzin, 2015) during 7-d or 14-d redox cycles throughout the year. Note that 5.5-d reduction periods would yield only 65% of the reduced Fe concentrations measured in flooded soils in this study, and thus is likely a conservative estimate. Further explanation, including sample calculations, are located in the Supplemental Material.

3. Results

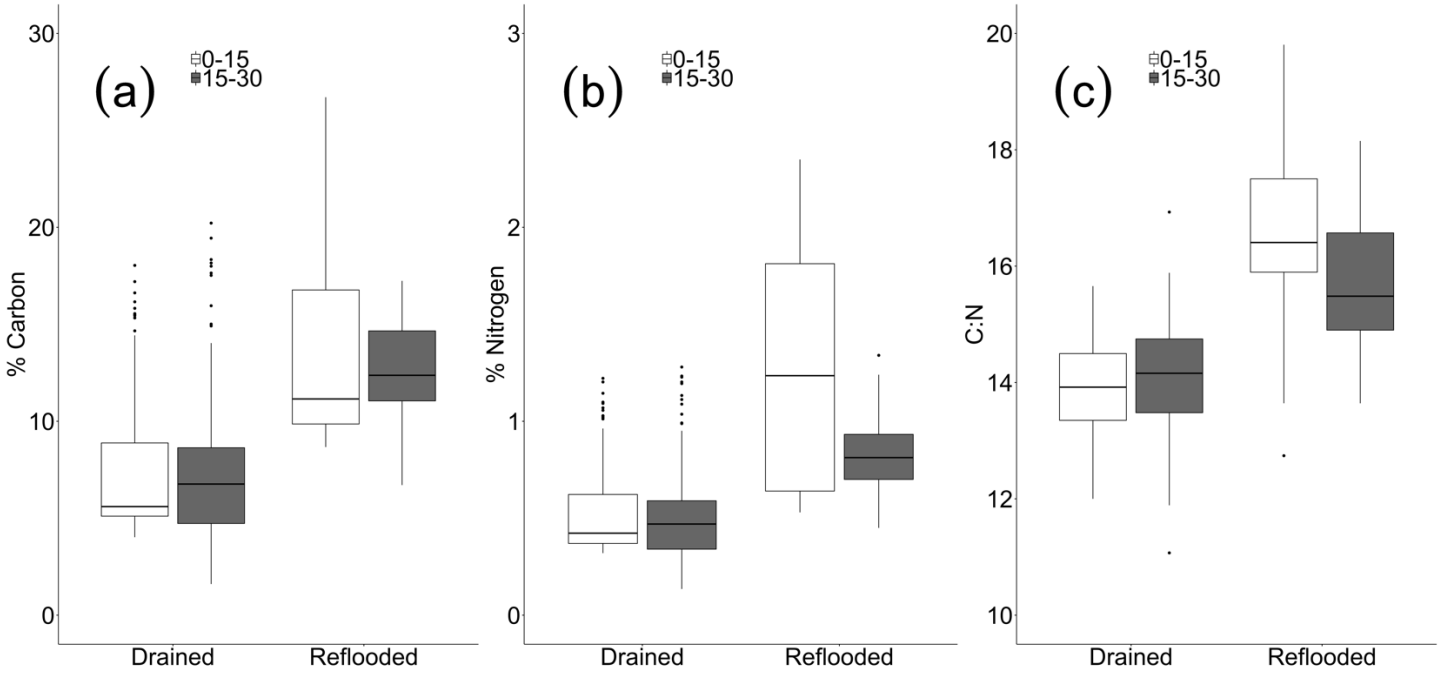

Fig. 1 Boxplots of (a) % Carbon, (b) % Nitrogen, and (c) C:N ratios in 0-15 cm and 15-30 cm depths across drained and reflooded soils. Note the difference across y-axes.

3.1 Carbon and nitrogen in drained and restored wetland soils

There was a strong gradient in soil C concentrations across sites and depths with values ranging from 3.6 to 44.6% C. Reflooded sites had higher total C and N concentrations than drained soils at both 0-15 cm and 15-30 cm depths ($P < 0.0001$; Fig. 1a, Table 1). Soil C concentrations were greatest in the reflooded surface soils (0-15 cm) but varied considerably with a range of 8.7-44.6% C, compared to drained surface soils with a range of 3.6-16.0% C. Reflooded surface soils had significantly higher soil C concentrations than reflooded soils at 15-30 cm depths ($P < 0.0001$), but soil C concentrations in drained surface soils did not differ significantly from drained 15-30 cm depths. Soil N concentrations showed trends similar to C across depths and drainage status. Reflooded soils had significantly higher C:N ratios than

drained soils in both 0-15 cm and 15-30 cm depths ($P < 0.0001$). The C:N ratio was significantly higher in the reflooded surface soils than those from the lower depth (P = 0.01).

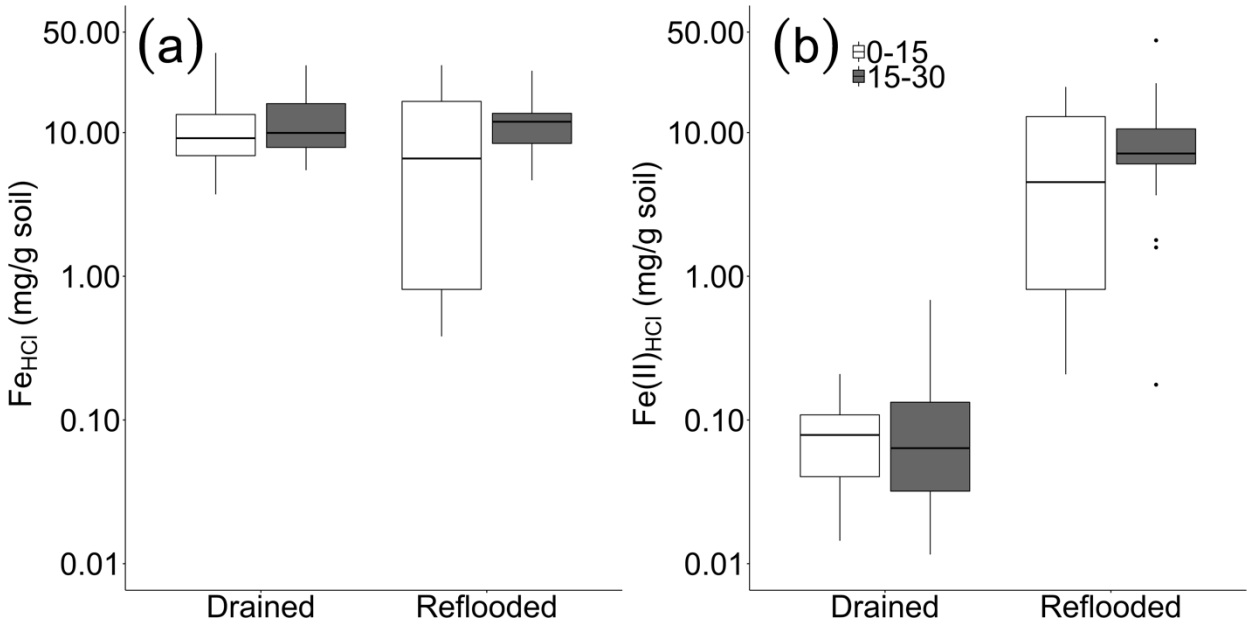

Fig. 2 Log-scale boxplots of concentrations of total HCl-extractable Fe (a) and Fe(II) (b) in 0-15 cm and 15-30 cm depths across drained and reflooded soils.

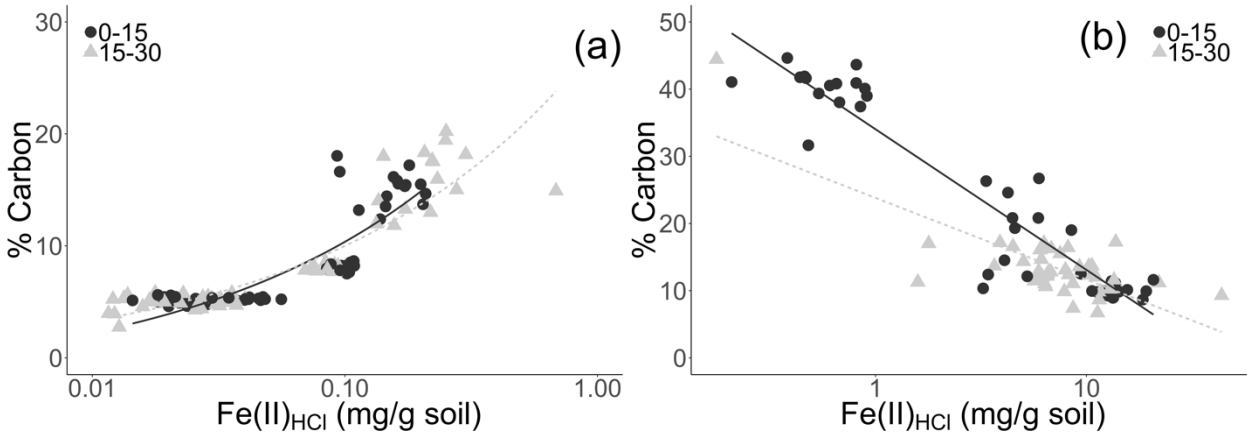

Fig. 3 Log-linear relationships between soil carbon and HCl-extractable Fe (II) concentrations at 0-15 cm (black circles) and 15-30 cm (grey triangles) depths across (a) drained soils (0-15 cm R^2

292 = 0.49, $P < 0.0001$; 15-30 cm $R^2 = 0.58$, $P < 0.0001$) and (b) reflooded soils (0-15 cm $R^2 = 0.89$,
293 $P < 0.0001$; 15-30 cm $R^2 = 0.59$, $P < 0.0001$). Note the log scale on the x-axis and the different
294 scales on both axes.
295
296 *3.2 HCl-extractable Fe(II) and Fe(III)*
297
298 HCl-extractable soil Fe pools tended to accumulate in drained soils. Total concentrations of
299 Fe_{HCl} were elevated at all sites and were significantly greater in drained surface soils ($P <$
300 0.0001). Concentrations in reflooded surface soils ranged across two orders of magnitude.
301 Expectedly, reduced Fe concentrations ($Fe(II)_{HCl}$), a proxy for the extent of anaerobic conditions,
302 were significantly greater in reflooded soils in comparison to drained soils across both depths (P
303 < 0.0001). $Fe(II)_{HCl}$ concentrations were positively correlated with C concentrations in drained
304 soils at both 0-15 and 15-30 cm depths ($R^2 = 0.49$ to 0.58, $P < 0.0001$; Fig. 3a). $Fe(II)_{HCl}$
305 concentrations were roughly an order of magnitude higher in reflooded soils and were negatively
306 correlated with soil C at both 0-15 and 15-30 cm depths ($R^2 = 0.59$ to 0.89, $P < 0.0001$; Fig 3b).
307

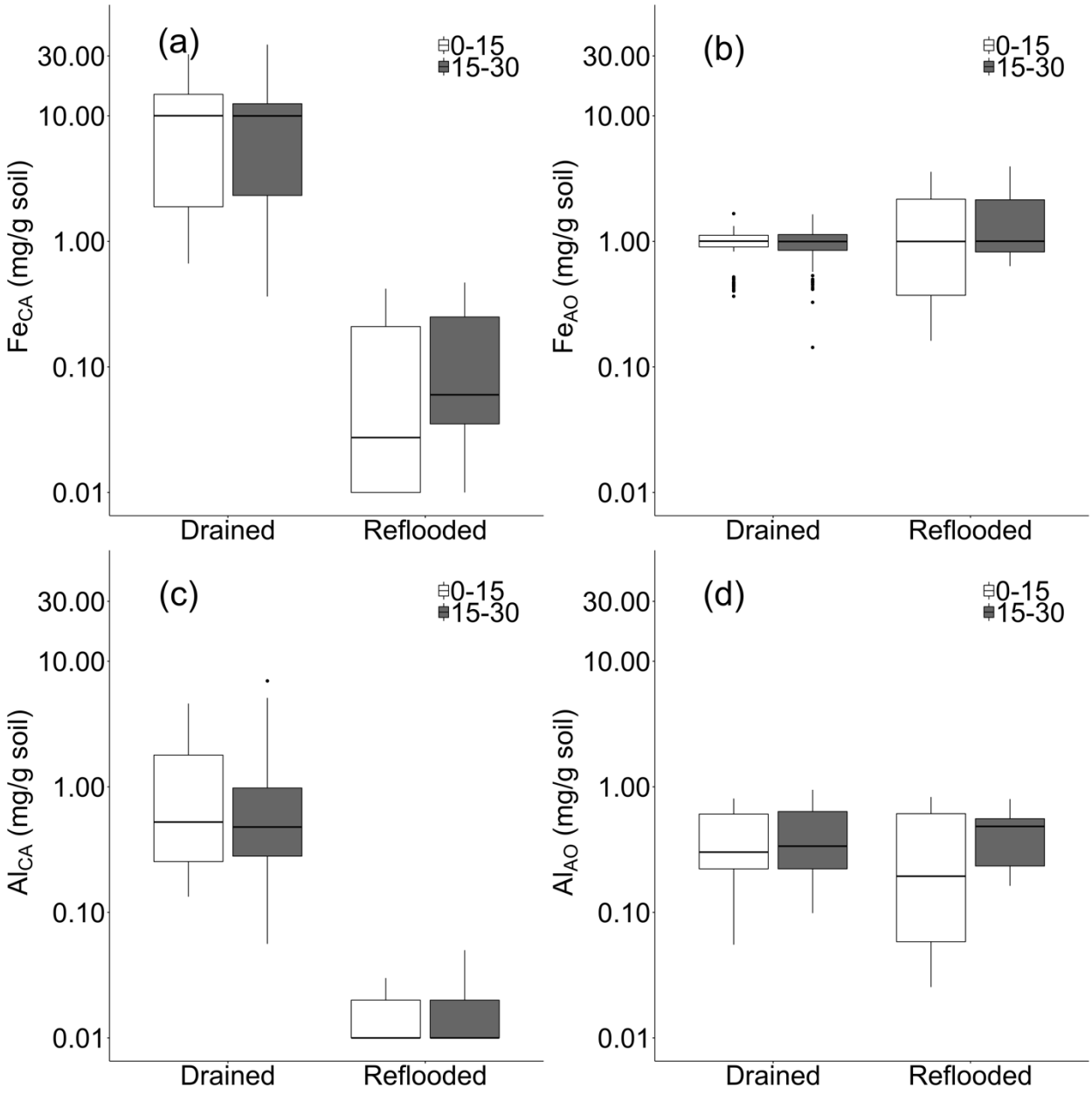

Fig 4. Log-scale boxplots of reactive Fe and Al concentrations in 0-15 cm and 15-30 cm depths separated into drained and reflooded soils: a) citrate-ascorbate extractable Fe; c) citrate-ascorbate extractable Al, b) ammonium-oxalate extractable Fe; d) ammonium-oxalate extractable Al.

3.3 Reactive, poorly crystalline and organo-metal complexes of iron and aluminum

Concentrations of both Fe_{CA} and Al_{CA}, representing reactive, poorly crystalline Fe and Al species, were significantly higher in drained soils than reflooded soils at both 0-15 and 15-30 cm depths ($P < 0.0001$). Extractable Al_{CA} concentrations did not differ across depths in either drained or reflooded soils. Many values were close to the detection limit in reflooded soils (Fig. 4c). Extractable Fe_{CA} increased with depth in reflooded systems ($P < 0.05$). Ammonium-oxalate extractable Fe (Fe_{AO}) and Al (Al_{AO}), representative of reactive organo-mineral complexes, were similar in magnitude across drained and reflooded systems, but lower than Fe_{CA} and Al_{CA} in drained systems and greater than Fe_{CA} and Al_{CA} in reflooded systems. Fe_{AO} concentrations were significantly higher in reflooded soils than drained soils at both depths ($P < 0.01$), but Al_{AO} concentrations did not differ across drainage classes.

Concentrations of Fe_{CA} were negatively correlated with C concentrations across soils, regardless of drainage status. There was a strong negative log-linear correlation between mean soil C concentrations and mean Fe_{CA} values in soils at both 0-15 cm ($R^2 = 0.81$, $P < 0.0001$) and 15-30 cm depths ($R^2 = 0.69$, $P < 0.0001$; Fig. 5). In reflooded soils, there was a strong negative log-linear correlation between soil C and Fe_{AO} ($R^2 = 0.59$, $P < 0.001$) and Fe_{CA} ($R^2 = 0.54$, $P < 0.001$) in the 0-15 cm depths (Fig. 6). This correlation was much weaker at 15-30 cm for both Fe_{AO} ($R^2 = 0.22$, $P < 0.001$) and Fe_{CA} ($R^2 = 0.31$, $P < 0.001$).

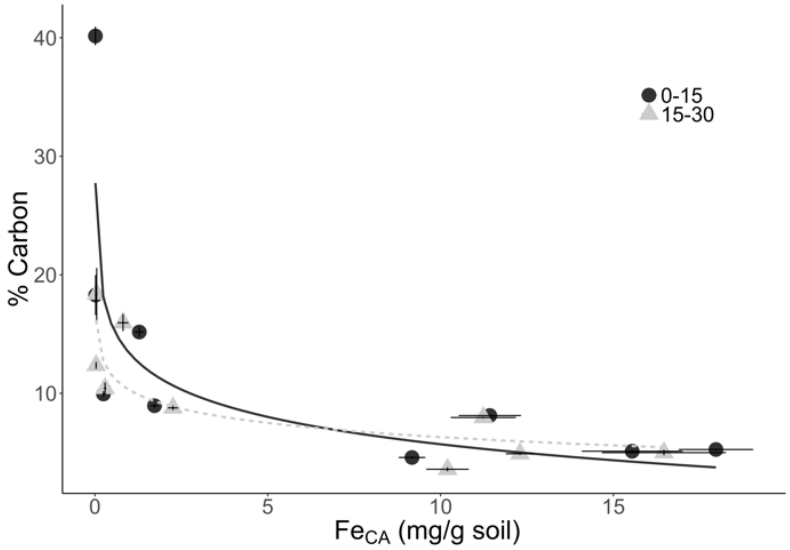

Fig. 5 Log-linear relationships between site mean concentrations of soil carbon and reactive poorly crystalline Fe_{CA} (reactive poorly crystalline Fe from the citrate-ascorbate extract) in 0-15 cm (black circles; $R^2 = 0.81$, $P < 0.0001$) and 15-30 cm (grey triangles; $R^2 = 0.69$, $P < 0.0001$) depths across all sites.

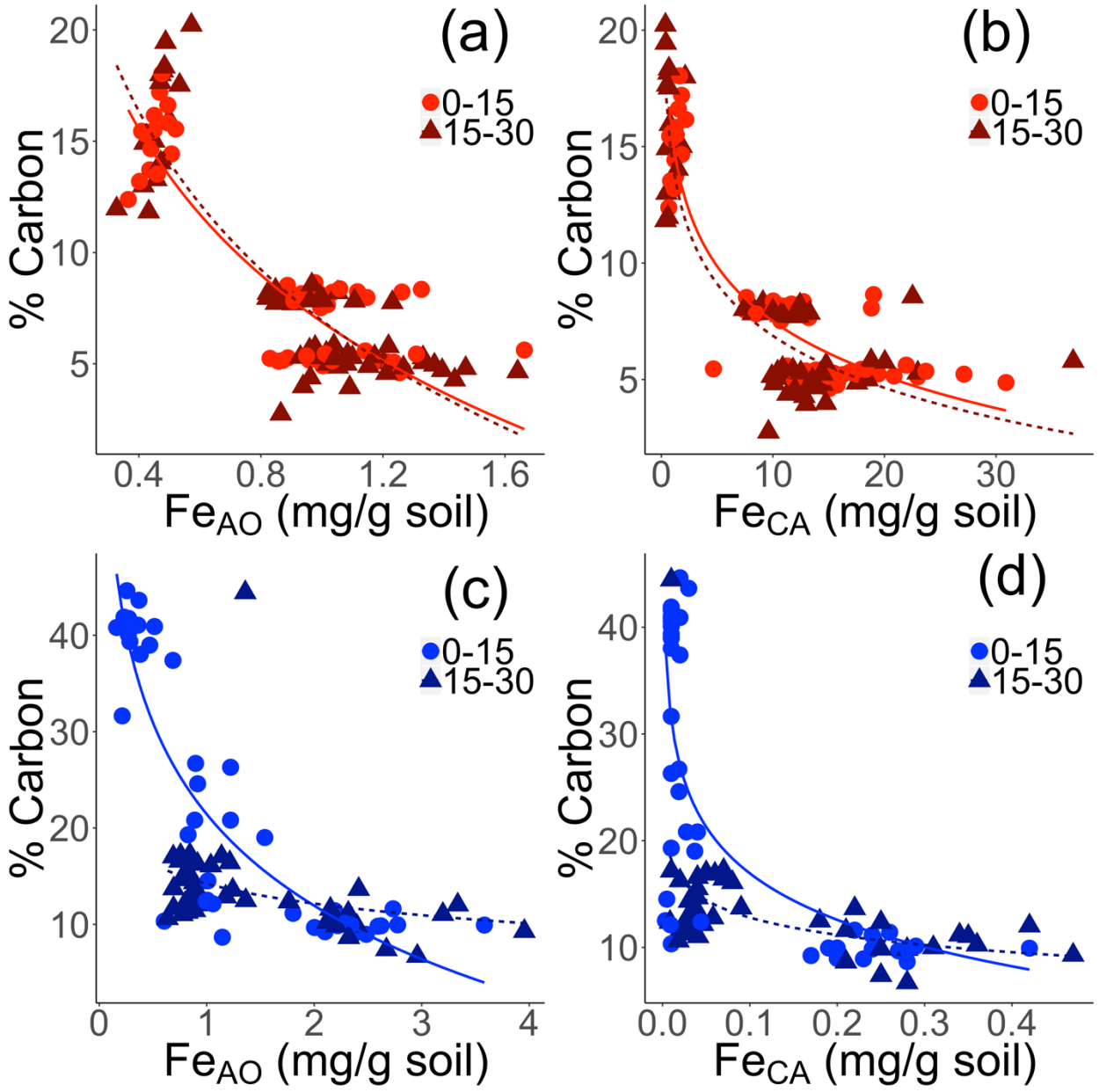

Fig. 6 a and c: Log-linear relationships between % soil carbon and Fe_{AO} (reactive organo-Fe complexes from the ammonium-oxalate extract); a) drained 0-15 cm depth: $R^2 = 0.59$, $P < 0.001$, 15-30 cm depth: $R^2 = 0.45$, $P < 0.001$; c) reflooded 0-15 cm depth: $R^2 = 0.59$, $P < 0.001$, 15-30 cm: $R^2 = 0.22$, $P < 0.001$); and Fe_{CA} (reactive poorly crystalline Fe from the citrate-ascorbate extract); b) drained 0-15 cm depth: $R^2 = 0.46$, $P < 0.001$,15-30 cm depth: $R^2 = 0.41$, P

344 < 0.001; d) reflooded 0-15 cm: R^2 =0.54, $P < 0.001$, 15-30 cm: $R^2 = 0.31$, $P < 0.001$. Drained
345 soils are in red and reflooded soils are in blue. Note differences in scales across axes.
346
347 Concentrations of Al_{AO} were strongly correlated with soil C concentrations in drained
348 soils when pasture sites were removed from the dataset (0-15 cm: $R^2 = 0.91$, $P < 0.0001$; 15-30
349 cm: $R^2 = 0.91$, $P < 0.0001$) (Fig. 7, Supplemental Figure 2). Pasture sites were characterized by
350 much higher soil bulk density values in surface soils compared to other drained sites, as
351 continuous grazing practices may have increased surface soil compaction and altered the
352 mechanism for C-Al interactions (see discussion below; Supplemental Table 3). In reflooded
353 sites, there was a negative log-linear relationship between Al_{AO} and soil C concentrations in
354 surface soils ($R^2 = 0.64$, $P < 0.0001$) but no trend at depth (Supplemental Figure 2b). There was
355 also a strong log-linear correlation between Al_{AO} and increasing $Fe(II)_{HCl}$ concentrations in
356 drained systems across depths (0-15 cm: $R^2 = 0.71$, $P < 0.0001$; 15-30 cm: $R^2 = 0.50$, $P <$
357 0.0001; Fig. 8). On a molar basis, mean total soil C values exceeded mean Al_{AO} values by more
358 than 720 times (M/C ratio < 0.006; C:Al molar ratio 179 ± 9) in all samples.
359

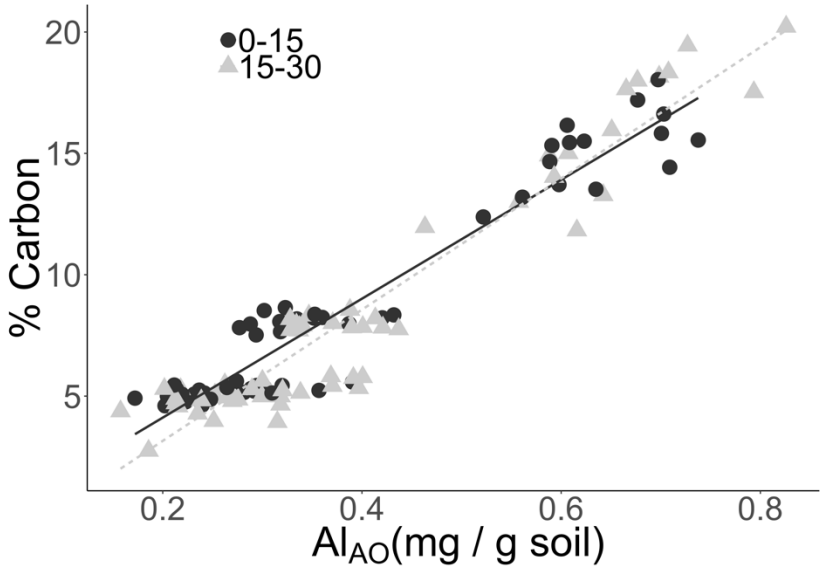

Fig. 7 Linear relationships between concentrations of soil carbon and Al_{AO} (reactive organo-Al complexes from the ammonium-oxalate extract) across 0-15 cm (black circles; $R^2 = 0.91$, $P < 0.0001$) and 15-30 cm (grey triangles; $R^2 = 0.91$, $P < 0.0001$) depths in drained soils. Pasture soils were removed from this analysis (see text; Supplemental Figure 2).

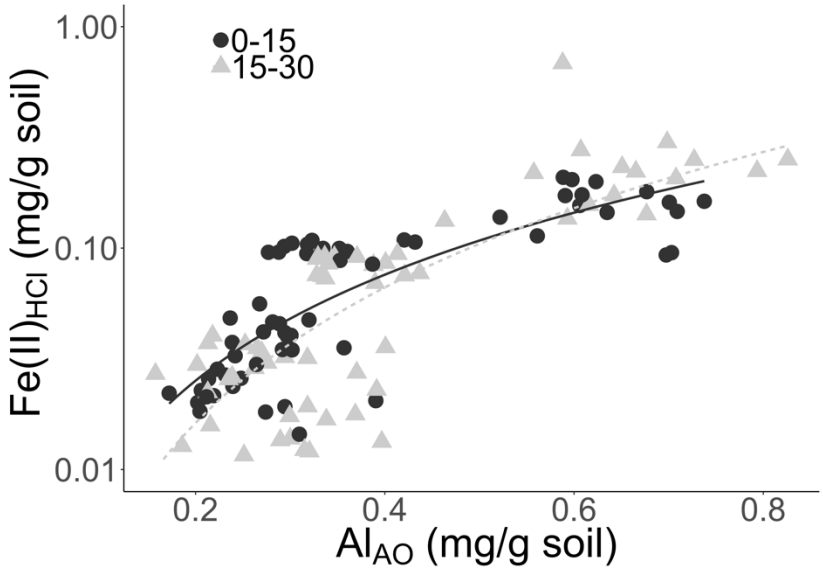

Fig. 8 Log-linear relationships between $Fe(II)_{HCl}$ and Al_{AO} (reactive organo-Al complexes from the ammonium-oxalate extract) concentrations across 0-15 cm (black circles; $R^2 = 0.71$, $P <$

0.0001) and 15-30 cm (grey triangles; $R^2 = 0.50$, $P < 0.0001$) depths in drained soils. Pasture soils were removed from this analysis (see text).

3.4 *Multiple regressions model for predicting soil C concentrations*

In the combined dataset, indices of reactive Fe pools were negatively associated with soil C values, while organo-Al complexes were positively associated with soil C values. Across all sites, soil C concentrations declined as the concentrations of reduced and reactive Fe [$\ln(Fe(II)_{HCl})$, $\ln(Fe_{HCl})$, $\ln(Fe_{CA})$, and Fe_{AO}] increased in the 0-15 cm depth ($P \leq 0.02$). A similar negative relationship was also observed for soil C, $\ln(Fe_{HCl})$, and $\ln(Fe_{CA})$ at 15-30 cm depths ($P \leq 0.01$, Supplemental Table 4). In contrast, soil C concentrations were significantly positively correlated with Al_{AO} in the 0-15 cm depth, and with Al_{AO}, soil moisture, pH in the 15-30 cm depth ($P \leq 0.02$, Supplemental Table 4).

Similar trends between soil C and active Fe and Al pools were observed when datasets were divided into reflooded and drained soils. In reflooded sites, surface soil C concentrations were positively correlated with soil moisture and negatively associated with $\ln(Fe(II)_{HCl})$ ($P < 0.10$; Supplemental Table 5). At 15-30 cm in reflooded soils, soil C concentrations were positively correlated with soil moisture, pH, and Al_{AO}, and negatively correlated with $\ln(Fe_{HCl})$ ($P \leq 0.05$, Supplemental Table 5).

In drained sites at 0-15 cm, soil C was positively correlated with pH, $\ln(Al_{CA})$, and Al_{AO}, and negatively associated with Fe_{AO} concentrations ($P \leq 0.03$, Supplemental Table 6). Soil C concentrations from 15-30 cm depths at drained sites increased with soil moisture, pH, $\ln(Al_{CA})$, Al_{AO}, and $\ln(Fe(II)_{HCl})$, and decreased with $\ln(Fe_{HCl})$ and $\ln(Fe_{CA})$ ($p \leq 0.03$, Supplemental Table

391 6). Generally, soil C concentrations were negatively correlated with Fe species and positively
392 correlated with organo-Al complexes across both depths and drainage status.
393 *3.5 Upscaling*
394 Using Fe reduction rates from a nearby drained Delta site (Yang and Liptzin 2015), we
395 estimated that 6.5 mg Fe(II) were produced per g soil during a 14-d oxidation-reduction cycle. If
396 we assume that these 14-d cycles occur throughout the year, Fe reduction would yield
397 approximately 678 kg C ha^{-1} y^{-1}. Using a weekly oxidation-reduction cycle yielded a C flux of
398 1.4 Mg C ha^{-1} y^{-1} from Fe reduction.
399
400 **4. Discussion**
401 *4.1 Relationships between reactive Fe pools and soil C in drained and restored wetlands*
402 Reactive Fe species are typically thought to increase C concentrations in soils and sediments,
403 as they can preferentially facilitate soil C accumulation via direct Fe-C associations (Coward et
404 al., 2017; Lalonde et al., 2012; Wagai et al., 2013). However, we observed the opposite trend in
405 both drained and reflooded wetlands. The negative correlation between Fe_{AO} and soil C
406 concentrations in drained soils was surprising, as Fe_{AO} is thought to represent organo-mineral
407 complexes that protect soil C from microbial decomposition (Hall & Silver, 2015; Loeppert &
408 Inskeep, 1996). This soil C protection mechanism has been observed in both dominantly aerobic
409 and anaerobic systems, including sediments, C-rich paddy soils, and upland soils (Kögel-
410 Knabner et al., 2010; Lalonde et al., 2012; Wagai & Mayer, 2007). The negative relationship
411 observed here suggests that reactive organo-Fe complexes are not the predominant mechanism of
412 soil C protection in drained soils (Wang et al., 2019). Alternatively, organo-Fe complexes may
413 also be utilized by microbial Fe reducers in these soils following depletion of other reactive Fe

414 pools (i.e. Fe_{CA}) when soils experience reducing conditions associated with rainfall or irrigation
415 events.

416 Reactive Fe species (Fe_{CA}, Fe_{AO}) and reduced Fe ($Fe(II)_{HCl}$) concentrations were also
417 associated with lower soil C concentrations in reflooded sites. The negative correlation between
418 $Fe(II)_{HCl}$ and soil C concentrations across reflooded soils suggests an important role for
419 microbial Fe reduction in C oxidation and loss and a limitation on soil C sequestration potential
420 in mineral-rich soils following wetland restoration. The production of Fe(II) via anaerobic
421 microbial respiration coupled to Fe-reduction is known to be a pathway of soil C loss in upland
422 soils and fens (Bhattacharyya et al., 2018; Emsens et al., 2016; Hall & Silver, 2013). Strong
423 negative relationships between soil C and Fe_{CA} and Fe_{AO} values suggest that a residual or
424 recycled redox-active Fe pool is limiting the rate of soil C accumulation in the restored wetlands.
425 Although reduced Fe concentrations were much lower than the soil C concentrations measured in
426 the reflooded systems (up to 30 moles C per mole $Fe(II)_{HCl}$), fluctuating redox conditions as
427 well as dissolved sources of O_2 (Mejia et al., 2016; Weber et al., 2006), can rapidly and
428 repeatedly replenish the reducible Fe so it can be used again and again for anaerobic microbial
429 respiration. Thus, redox fluctuations can facilitate significant soil C oxidation associated with Fe
430 redox cycling. Replenishment of the reducible Fe pool can occur following redox fluctuations
431 driven by a range of processes such as root and rhizome oxygenation of wetland plant
432 rhizospheres (Kaplan et al., 2016; Nikolausz et al., 2008), changes in the water table height
433 (Catallo, 1999), or anaerobic Fe oxidation (Mejia et al., 2016; Weber et al., 2006). Our results
434 suggest that high concentrations of reactive, reducible Fe species limit soil C accumulation in
435 reflooded soils and increase C loss in drained soils.

As a preliminary upscaling exercise, we used measured Fe reduction rates from a nearby site (Yang & Liptzin, 2015) and bi-monthly and weekly redox cycling to determine the potential impacts on soil C fluxes. These upscaled C fluxes ranged from 0.7 to 1.4 Mg C ha^{-1} y^{-1}. For comparison, Knox et al (2015) estimated net ecosystem greenhouse gas losses from the drained corn and pasture sites of 5.7 and 3.9 Mg C_{eq} ha^{-1} y^{-1}. Heterotrophic respiration associated with Fe reduction thus accounted for 12 and 17% of these C_{eq} losses, respectively, assuming a 14-d redox cycle. For the reflooded wetlands, a 14-d Fe-redox cycle would oxidize 128% of the C emitted from methane fluxes (0.53 Mg C ha^{-1} y^{-1}) annually (Knox et al., 2015). Previous studies have shown daily redox fluctuations in wetland soils during the growing season (Nikolausz et al., 2008; Vorenhout et al., 2004). These restored wetlands have long growing seasons of roughly 150 days (Knox et al., 2015), suggesting an important role for reactive Fe in C losses.

While reactive Fe pools were negatively related to soil C concentrations, we observed a positive correlation between Fe(II) concentrations and soil C concentrations in drained soils. In upland soils, $Fe(II)_{HCl}$ may represent a proxy for the extent of soil anaerobic conditions (Hall & Silver, 2015). We posit that the positive relationship between soil C and Fe(II) concentrations in drained soils could be indicative of an increasing number of anaerobic (micro)sites characterized by slower decomposition rates than well-aerated soils. Reduced Fe concentrations in drained soils were roughly an order of magnitude lower than in flooded soils, likely resulting from a generally more oxidized soil volume. The opposite pattern between Fe(II) and soil C concentrations was observed in restored wetlands, with Fe(II) concentrations increasing as soil C concentrations decreased. The much higher concentrations of Fe(II) in the reflooded soils would have resulted in significant C losses from these ecosystems as highlighted above.

459 *4.2 Relationships between reactive Al pools and soil C in drained and restored wetlands*

460 As with Fe, Al can react with soil organic matter and facilitate C preservation (Porras et al.,
461 2017; Scheel et al., 2007). However, unlike Fe, Al is not redox active and thus does not directly
462 drive microbial metabolism. We found that organo-Al complexes were strongly positively
463 correlated with soil C in drained soils, but given the high C:Al molar ratio (179 ± 9), this is
464 probably not an important direct mechanism of C protection in these sites. Rather, we
465 hypothesize that the relationship between soil Al_{AO} and soil C concentrations may be a result of
466 increased aggregation via associations between reactive Al species and larger organic molecules
467 (Oades & Waters, 1991; Totsche et al., 2017; Wiseman & Püttmann, 2006). This soil
468 aggregation mechanism would also explain the strong positive correlation between $Fe(II)_{HCl}$
469 concentrations, a proxy for anaerobic conditions, and organo-Al complexes in drained soils. Soil
470 aggregation facilitates the development of anaerobic microsites, a mechanism for potential soil C
471 accumulation even in well drained soils (Keiluweit et al., 2016; Six & Paustian, 2014). There
472 was no observed trend between $Fe(II)_{HCl}$ and organo-Al complexes in flooded soils
473 (Supplemental Figure 1a). This is also expected as bulk soil anaerobic conditions and decreased
474 soil aggregation limit the importance of anaerobic microsites within aggregates (De-Campos et
475 al., 2009).

476 The relationship between soil C and organo-Al complexes was not observed in the drained
477 pasture sites we sampled. The continuous grazing at these sites likely led to surface soil
478 compaction (Silver et al., 2010), observed through higher soil bulk density in pasture soils
479 (Supplemental Table 3). Soil compaction would result in a direct loss of aggregation in surface
480 soils (Warren et al., 1986), and directly inhibit O_2 diffusion through reduced soil pore space

(Stepniewski et al., 1994). Soil C concentrations in the pasture sites are thus more likely to be influenced by an increase in anaerobic bulk soil conditions associated with compaction.

4.3 Interacting controls on soil C accumulation and loss in drained and restored wetlands

Multiple regression analyses suggested an important role for Fe and Al in patterns in soil C storage with wetland drainage and reestablishment. Soil C was negatively associated with concentrations of reactive and reduced Fe pools under both drained and reflooded conditions, suggesting that Fe reduction coupled to C oxidation may be more important than Fe-C bonding as a driver of C cycling in these soils. Soil C was also positively correlated with soil moisture and organo-Al complexes, particularly in drained soils, again emphasizing the likely importance of anaerobic microsites, facilitated by soil aggregation, for soil C accumulation in these systems. The contrasting trends observed between Al and Fe species and soil C also suggest these relationships are driven by both direct and indirect effects of the concentration of residual soil minerals following wetland drainage.

5. Conclusion

Our results suggest that the concentration of mineral material in residual soils following the drainage of wetlands can impact C cycling on drained soils as well as patterns in C concentrations following wetland restoration. In reflooded soils, high concentrations of both reactive Fe and reduced Fe(II) were negatively correlated with soil C concentrations, suggesting that Fe reduction and subsequent organic matter oxidation may at least partially limit soil C sequestration in these ecosystems. Reactive Fe minerals, likely the most abundant alternative electron acceptors under anaerobic conditions across sites, were also associated with decreasing

soil C concentrations in drained sites. This suggests that periodic redox fluctuations and reactive, reducible Fe pools may also further increase C emissions from drained wetland soils. However, both soil moisture and a proxy for anaerobic conditions, $Fe(II)_{HCl}$, were positively correlated with soil C concentrations in drained soils, suggesting that reducing conditions may counteract at least some of these C losses. Additionally, we found that reactive organo-Al species were positively correlated with soil C concentrations across drained soils. We hypothesize that these organo-Al species may facilitate soil aggregation or anaerobic (micro)sites that protect residual soil C from oxidation. Our results highlight the potential role of mineral in C cycling, storage and loss with ecosystem management in wetlands. Understanding the underlying mineral composition of soils can help determine if, and how quickly wetland restoration can result in a net C sink for climate change mitigation. Our results also show that the presence of reactive Fe minerals in soils does not necessarily infer increased C sequestration, as redox dynamics can drive microbial C oxidation at potentially high rates in both drained and reflooded ecosystems. Increased understanding of the relationships between Fe and Al biogeochemistry and soil C is necessary to prioritize wetland restoration projects that balance maximizing soil C sequestration and limiting future soil C losses.

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