Decomposition of carbon adsorbed on iron (III)-treated clays and their effect on the stability of soil organic carbon and external carbon inputs

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Abstract The interaction of organic carbon (OC) with clay and metals stabilizes soil carbon (C), but the influence of specific clay-metal-OC assemblages (flocs) needs further evaluation. This study aimed to investigate the stability of flocs in soil as affected by external C inputs. Flocs representing OC-mineral soil fractions were synthesized using dissolved organic C (DOC) combined with kaolinite (1:1 layer structure) or montmorillonite (2:1 layer structure) clays in the absence or presence of two levels of Fe (III) (named low or high Fe). Flocs were mixed with soil (classified as Luvisol) and incubated with or without ^{13}C labelled plant residue (i.e., ryegrass) for 30 days. The CO_2 emissions and DOC concentrations as well as their ^{13}C

signatures from all treatments were examined. Total C mineralization from flocs was approximately 70% lower than non-flocced DOC. The flocs made with montmorillonite had 16–43% lower C mineralization rate than those made with kaolinite with no Fe or low Fe. However, when flocs were made with high Fe, clay mineralogy did not significantly affect total C mineralization. A positive priming effect (PE) of flocs on native soil OC was observed in all treatments, with a stronger PE found in lower Fe treatments. The high-Fe clay flocs inhibited ryegrass decomposition, while the flocs made without clay had no impact on it. Interestingly, flocs significantly decreased the PE of ryegrass on native soil OC decomposition. These results indicate that the adsorption of DOC onto clay minerals in the presence of Fe (III) stabilizes it against decomposition processes and its stability increases as Fe in flocs increases. Flocs also protect soil OC from the PE of external degradable plant C input. This study showed that Fe level and clay mineralogy play an important role in controlling soil C stability.

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Introduction

The adsorption of organic carbon (OC) onto mineral surfaces is an important mechanism of stabilizing soil organic carbon (SOC) (Kahle et al. 2002; Mikutta et al. 2007; von Luetzow et al. 2006; Han et al. 2016; Rasumssen et al. 2018). Phyllosilicate clays and iron minerals have long been recognized as reactive surfaces that adsorb OC (Balcke et al. 2002; Mikutta et al. 2006; Kaiser and Guggenberger 2007). The OC stabilization effect in the absence of metals depends on particle size and surface charge (Eusterhues et al. 2005; Feng et al. 2005; Zhang et al. 2012). For example, kaolinitic clays with a 1:1 layer structure occur as larger particles but carry less charge compared to 2:1 clays (Greenland 1971), though the mineral size of kaolinites in soils varies (Singh and Gilkes 1992; West et al. 2004; Prandel et al. 2017). Six et al. (2002) found that soil dominated by 1:1 clays exhibited a lower C sequestration potential compared to soil dominated by 2:1 clay minerals. The stability of OC on clay often occurs with hydrous Fe oxides, a common bridging metal (Saidy et al. 2012). The stability of organo-mineral associations (referred to as flocs) differs with clay type, and undoubtedly affects the priming effect (PE) outcomes in the presence of degradable C inputs.

Many studies have investigated the role of phyllosilicate clay minerals in stabilizing dissolved organic carbon (DOC) through adsorption interactions (Kahle et al. 2004; Saidy et al. 2012, 2013; Sodano et al. 2016). DOC is a mobile and reactive OC pool in soil that can adsorb and desorb from metal-clay assemblages (Wang et al. 2003). By measuring C mineralization following adsorption, these studies found that different clay minerals imparted various degrees of stability to OC. Moreover, Saidy et al. (2015) showed that plant C adsorbed to pure phyllosilicate clays had a significant lower C mineralization rate compared to the absence of clay. Characteristics of clay minerals such as specific surface area (SSA) and cation exchange capacity (CEC) determine the degree to which DOC is adsorbed (Kahle et al. 2004). For example, coating of kaolinite with hydrous Fe oxide enhanced DOC sorption, but this phenomenon was not observed with montmorillonite due to its relatively limited available surface after coating of Fe (Saidy et al. 2012).

Co-precipitation of DOC and Fe commonly occurs in soils, sediments, and surface and ground water. It is believed that these floc formations are stable and have limited mobility following formation (Larsen 2009). The stability of flocs is in part promoted by the adsorbed OC's ability to protect Fe oxides from reduction to Fe (II) (Henneberry et al. 2012). Eusterhues et al. (2008) mentioned the important role of floc in immobilizing DOC and protecting it from microbial degradation. Studies in paddy soil and aquatic environments (Sodano et al. 2016) have shown that the rate of floc C decomposition was faster in wet than in dry seasons. The stability of OC in hydromorphic soils, such as rice paddies and wetlands, can be strongly controlled by its adsorption onto Fe (hydr)oxide (Henneberry et al. 2012; Sodano et al. 2016). These studies shed light on C associated with clays and Fe but do not provide insight into the PE that they potentially exert on other soil C pools, such as litter or other labile sources of C.

The objectives of this study were to understand the decomposition of flocced OC formed through the interaction between DOC and clay sized minerals (i.e., phytosilicates with and without the presence of Fe species), and the effect of these minerals on the stability of other SOC pools as well as the decomposition of degradable C in plant residues. We hypothesized that (1) the decomposition rate of C in clay-Fe-OC flocs would decrease as Fe content in the flocs increased, (2) OC in kaolinite flocs would decompose faster than in montmorillonite flocs, and (3) the flocs made with low Fe and kaolinite would stimulate SOC and plant residue decomposition. To test these hypotheses, we conducted a laboratory incubation experiment using flocs made with kaolinite or montmorillonite clays precipitated with DOC in the absence or presence of different levels of Fe. Our results provide information on the role that Fe plays in stabilizing OC on clay surfaces as a function of clay mineralogy and how SOC and the degradable plant C substrate can be affected by flocs containing different Fe contents.

Materials and methods

Sample preparation

Extraction of dissolved organic carbon

The DOC used to prepare floc products was extracted from mature corn residue (leaves and stems) (*Zea mays* L.). Before extraction, the corn residue (approximately 2 cm pieces) was inoculated with 2% soil solution (soil: water = 1:50) and pre-incubated at 40 °C for 30 days. The soil used for extracting soil solution was a silty clay loam (classified as Luvisol according to World Reference Base for Soil Resources) and collected from the Russell Ranch Sustainable Agricultural Facility, University of California-Davis, California. The purpose of this pre-incubation was to allow soil microorganisms to consume labile C in the residue to better reflect characteristics of soil DOC (Bertrand et al. 2006). After the pre-incubation, the residue (2 kg dry mass equivalent) was suspended in deionized water (8 L). The suspension was shaken at 170 r min⁻¹ for 48 h, left to settle for 48 h, and filtered through a 0.45 µm glass fiber filter. The DOC concentration in the filtrate was 1.6 g C L⁻¹, determined by UV-persulfate digestion (Teledyne-Tekmar Phoenix 8000). The $\delta^{13}\text{C}$ value of the DOC solution was -15.8‰, determined by using a TOC analyzer (1010 OI Analytical, College Station, TX, USA) coupled to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) at the Stable Isotope Facility, the University of California-Davis. Working DOC standards prepared with glucose of known mass and ^{13}C enrichment were used for quality control. Four analytical replicates of DOC solution were made and the standard deviation of the replicated ^{13}C analyses in this coupling system was 0.13‰.

Preparation of iron–OC floc

A flocculant solution (1.75 M) was prepared consisting of $\text{Fe}_2(\text{SO}_4)_3$ powder in reagent grade 9 M H_2SO_4 . The optimal dose of $\text{Fe}_2(\text{SO}_4)_3$ required to remove maximum DOC from the corn residue filtrate was determined in a parallel experiment by adding different amounts of $\text{Fe}_2(\text{SO}_4)_3$ into the filtrate solution until the concentration of the remaining DOC in the solution did not change anymore (Henneberry et al.

2012). Flocs were subsequently prepared using the optimal dose of coagulant and recovered by filtering the suspension through a 0.45 µm glass fiber filter. The floc retained on the filter was oven-dried at 50 °C.

Preparation of clay–OC flocs

Two clays were obtained from the Clay Minerals Society: kaolinite (low-defect kaolin, Warren Count, Georgia, USA; SSA: 10.0 m² g⁻¹) and Ca-rich montmorillonite (Gonzales County, Texas, USA; SSA: 83.8 m² g⁻¹). Clays adsorbed DOC from the filtrate solution (described above) by shaking 20 ml DOC solution with 1 g clay for 12 h at 22 °C. The pH of the mixtures was adjusted to 6.0 with NaOH before shaking (Saidy et al. 2013). The suspensions were then centrifuged and the pellets were washed with deionized water and centrifuged again; this step was repeated until no DOC was detected in the supernatant. The precipitates were oven-dried at 50 °C and then ground to pass 200 µm. The C concentration and $\delta^{13}\text{C}$ value analyses of all the floc products were determined by using a VarioEL CHN combustion analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to an isotope ratio mass spectrometer (PDZ Europa 20–20 IRMS, Sercon Ltd., Cheshire, U.K.). All the floc products had a similar $\delta^{13}\text{C}$ value of -15.8‰.

Preparation of clay-iron–OC flocs

The Fe (hydr)oxide-coated clays were prepared by suspending clay (1 g) in coagulant solution (pH = 2.5, NaOH adjusted) with different concentrations of Fe as $\text{Fe}_2(\text{SO}_4)_3$: 20, 40, 80, 120, 160, 200, 240, 280, 320, and 360 mg Fe L⁻¹. The minimum and maximum amounts of Fe coated with clays were chosen and named as “low Fe” and “high Fe”. The clay-Fe mixtures were shaken for 48 h at 22 °C, and then centrifuged. This process was repeated numerous times until no Fe was detected in the supernatant using phenanthroline indicator (Saidy et al. 2012). The Fe-coated clays were then oven-dried at 50 °C and gently ground by mortar to pass a 200 µm sieve. The Fe content of the Fe-coated clays was determined by suspending a known amount of the product in 1 M HCl, shaking for several hours to dissolve the iron species, and determination of dissolved iron. The “low Fe” products (Fe_{low}) contain 5.4 mg Fe g⁻¹ clay and

11.4 mg Fe g⁻¹ clay for kaolinite and montmorillonite, respectively. The “high Fe” products (Fe_{high}) contain 199.0 mg Fe g⁻¹ clay and 219.0 mg Fe g⁻¹ for kaolinite and montmorillonite, respectively. Clays with Fe coating were then used to adsorb DOC from the filtrate solution (described above) to form clay-iron-OC flocs using the same procedure as described in “[Preparation of clay-OC flocs](#)”.

Incubation experiment

Soil incubation preparation

The soil used for preparing the incubation medium was the same as that mentioned above for preparing the soil inoculum. The soil contained 19.39 g kg⁻¹ OC, 2.58 g kg⁻¹ total N, and a $\delta^{13}\text{C}$ value of -26.7‰ . The sand was washed with hydrochloric acid numerous times to remove nutrients and other ions. No C or N was detected in the washed sand. The washed sand was then mixed with soil at a ratio of 19: 1 (by mass) and air dried. Aliquots of the dried sand/soil (10 g dry mass) mix (hereafter referred to as soil medium) were placed into 60 ml glass serum vials, wetted to 40% water holding capacity with deionized water, and pre-incubated at 22 °C in dark for 7 days.

Experimental design

After the pre-incubation, floc material or unflocced DOC was added to the soil medium at a rate of 0.2 mg C g⁻¹ and mixed thoroughly with a glass rod. The soil medium alone (no floc or DOC additions) was treated as control. A separate set of treatments received enriched ¹³C-labeled mature ryegrass residue (*Lolium perenne* L.) at a rate of 1 mg C per treatment (equals to 0.4 mg C g⁻¹) at the same time as floc addition. The ryegrass, with a $\delta^{13}\text{C}$ value of 538.0‰, was labeled by frequent ¹³CO₂ pulse labeling events according to Bird et al. (2003). The use of ¹³C-enriched ryegrass residue allowed us to sufficiently differentiate C mineralization from ryegrass vs. soil/floc mixtures to estimate the PE of ryegrass on soil/floc C and the effect of floc on ryegrass decomposition during incubation. For each treatment, a nutrient solution containing (NH₄)₂SO₄ and K₂HPO₄ was added to reach a final C: N and C: P of the soil/floc mixture of 10: 1 and 25: 1, respectively, to ensure no nutrient limitation. The moisture content of all the treatments was adjusted to 60% of water

holding capacity with deionized water. Sample vials were closed with butyl rubber septa and crimp-sealed following the addition of nutrient solution and moisture adjustment. The headspace of sample vials was then immediately flushed with CO₂-free air to ensure no background CO₂ remained in the headspace. All the vials were incubated at 22 °C in the dark for 30 days. The experiment was set up as a completely randomized design with 18 treatments (summarized in Table 1), each with 4 replicates.

Gas sampling and analysis

Aliquots of 20 ml gas samples were removed from the headspace of the vials on days 1, 3, 5, 7, 9, 11, 14, 17, 20, 23, 26, and 30 and transferred to evacuated exetainers (Labco, Ceredigion, United Kingdom). At each sampling event, all vials were flushed immediately after gas sampling with CO₂-free air to ensure no CO₂ remained in the headspace. The CO₂ concentration in the gas samples was analyzed on a gas chromatograph with a thermal conductivity detector (Model 2014, Shimadzu Scientific Instruments). Stable C isotope analysis of CO₂ in gas samples were analyzed on days 1, 5, 17, and 30 on a Thermo GC combustion isotope ratio mass spectrometer (GC/C-IRMS) consisting of a Trace GC Ultra gas chromatograph (Thermo Electron Corp., Milan, Italy) coupled to a Delta V Advantage IRAM through a GC/C-III interface (Thermo Electron Corp., Bremen, Germany).

Soil analysis

At the end of the incubation, all treatments were extracted with 0.5 M K₂SO₄ (2:1 extractant volume-to-soil mass ratio). The extracts were filtered, and the supernatant analyzed for DOC concentration using UV-persulfate oxidation (Phoenix 8000, Teledyne-Tekmar) and ¹³C-DOC content using a TOC analyzer (1010 OI Analytical, College Station, TX, USA) coupled to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) at the UC Davis Stable Isotope Facility. Working DOC standards prepared with glucose of known mass and ¹³C enrichment were used for quality control.

Table 1 Summary of the treatments

Treatment	Description
Control	No floc or DOC solution was added into soil medium
DOC	Only DOC solution was added into soil medium
Fe–OC	The floc made with Fe and DOC was added into soil medium
M–OC	The floc made with montmorillonite and DOC was added into soil medium
Felow–M–OC	The floc made with low Fe-coated montmorillonite and DOC was added into soil medium
Fehigh–M–OC	The floc made with high Fe-treated montmorillonite and DOC was added into soil medium
K–OC	The floc made with kaolinite with adsorbed C was added into soil medium
Felow–K–OC	The floc made with low Fe-coated kaolinite and DOC was added into soil medium
Fehigh–K–OC	The floc made with high Fe-treated kaolinite and DOC was added into soil medium

Calculation

Treatments without ryegrass addition

The difference in $\delta^{13}\text{C}$ natural abundance of soil medium (-26.7‰) and flocs (-15.8‰) was used to calculate the contribution of these C pools to CO_2 production. The fraction of CO_2 (f_{floc}) and CO_2 production ($\text{CO}_{2, \text{floc}}$) derived from flocs was calculated as follows:

$$f_{\text{floc}} = (\delta^{13}\text{C} - \text{CO}_{2, \text{treatment}} - \delta^{13}\text{C} - \text{CO}_{2, \text{control}}) / (\delta^{13}\text{C}_{\text{floc}} - \delta^{13}\text{C}_{\text{control}}) \quad (1)$$

$$\text{CO}_{2, \text{floc}} = \text{CO}_{2, \text{total}} \times f_{\text{floc}} \quad (2)$$

where $\delta^{13}\text{C}-\text{CO}_{2, \text{treatment}}$ and $\delta^{13}\text{C}-\text{CO}_{2, \text{control}}$ are the $\delta^{13}\text{C}$ value of mixed CO_2 produced from the treatments of soil medium amended with flocs and control (soil without floc), respectively. $\Delta^{13}\text{C}_{\text{floc}}$ and $\delta^{13}\text{C}_{\text{control}}$ refer to the $\delta^{13}\text{C}$ signature of the flocs and soil medium in the control, respectively. $\text{CO}_{2, \text{total}}$ represents the total CO_2 production in the floc treatments.

The CO_2 production ($\mu\text{g g}^{-1}$) derived from soil medium only was derived from native SOC ($\text{CO}_{2, \text{SOC}}$) and was determined as follows:

$$\text{CO}_{2, \text{SOC}} = \text{CO}_{2, \text{total}} \times (1 - f_{\text{floc}}) \quad (3)$$

The PE ($\mu\text{g g}^{-1}$) of flocs on native SOC mineralization was defined as follows:

$$\text{PE} = \text{CO}_{2, \text{SOC}} - \text{CO}_{2, \text{control}} \quad (4)$$

where $\text{CO}_{2, \text{control}}$ was the CO_2 production from the treatment of soil medium alone (control, no floc and DOC addition).

In the DOC-only treatment, the fraction of CO_2 (f_{DOC}) and CO_2 production ($\text{CO}_{2, \text{DOC}}$) derived from DOC was calculated using the same approach as described above by replacing floc pool with DOC pool in the calculation.

Treatments with and without ryegrass straw addition

The fraction of CO_2 derived from ryegrass straw was calculated as follows:

$$f_{\text{straw}} = (\delta^{13}\text{C} - \text{CO}_{2, \text{with straw}} - \delta^{13}\text{C} - \text{CO}_{2, \text{without straw}}) / (\delta^{13}\text{C}_{\text{straw}} - \delta^{13}\text{C}_{\text{without straw}}) \quad (5)$$

where $\delta^{13}\text{C}-\text{O}_2, \text{with straw}$ and $\delta^{13}\text{C}-\text{CO}_2, \text{without straw}$ are the $\delta^{13}\text{C}$ value of mixed CO_2 produced from the treatments with and without straw for each floc, respectively. $\delta^{13}\text{C}_{\text{straw}}$ and $\delta^{13}\text{C}_{\text{without straw}}$ refer to the ^{13}C signature of the ryegrass straw and the soil/floc mixture, respectively. The soil and flocs ^{13}C (-26.7 to -15.8‰) were considered as background in the presence of highly enriched ryegrass straw (538‰). We carried out the calculation (Eq. 5) using the ^{13}C signature of soil or flocs and the results did not vary ($\text{CV} < 1\%$). Thus, we treated the soil and floc mixture as one C pool, named “soil-floc” pool (with the measured $\delta^{13}\text{C}$ value of -16.1‰). By using this approach, we also acknowledge that CO_2 derived from the soil or the flocs in the ryegrass straw addition

treatments could not be differentiated. The PE of the ryegrass addition on C mineralization of soil-floc pool was estimated to be the difference between the C–CO₂ derived from soil-floc pool in the ryegrass treatments and the total C–CO₂ production in the treatments without ryegrass. The large difference in the ¹³C enrichment between the soil-floc and ryegrass was sufficient to reliably estimate the change in the contribution of ryegrass to total CO₂ production.

The fraction of extracted DOC derived from flocs or soil/floc mixture in the treatments without ryegrass or with ryegrass was calculated using the same approach for CO₂ fraction calculation (see above).

Statistical analyses

A two-way Analysis of variance (ANOVA) was performed using PROC Mixed procedures in SAS (SAS 9.3, SAS Institute Inc., Cary, N.C., USA). Differences were considered significant at $P < 0.05$, with a separation of mean values by a least significant difference (LSD) test. In the treatments without or with ryegrass residue, clay type and Fe level were treated as fixed factors, and replicate as a random factor, to test their effect on cumulative CO₂ production, PE, and DOC content at the end of the incubation.

Results

Properties of flocs

Regardless of Fe levels (none, low, or high), the maximum DOC sorption capacity of montmorillonite flocs was larger than that of kaolinite flocs (Table 2).

Coating clays with Fe enhanced DOC sorption capacity of both montmorillonite and kaolinite clays, with the high Fe-treated clays adsorbing more DOC than the low Fe-treated clays. The CEC decreased in the flocs containing higher Fe content. The floc made without clay adsorbed higher DOC compared to the flocs made with clays (Table 2).

Cumulative CO₂ production and source partitioning

In all treatments, cumulative CO₂ production increased gradually throughout the entire incubation (Fig. 1). In treatments without ryegrass, total CO₂ production in DOC treatments were significantly higher than other floc treatments (Table 3). More CO₂ was produced in treatments containing flocs made with kaolinite alone or combined with low level of Fe than comparable treatments with montmorillonite. In treatments with ryegrass, the total CO₂ production in the DOC-only treatment was similar to the treatments of K–OC and Fe_{low}–K–OC significantly higher than other floc treatments. In floc treatments with no or low Fe, higher CO₂ production was found in kaolinite flocs than montmorillonite flocs (Table 3).

The fractional contributions of floc and native SOC to total CO₂ production were determined for all the treatments without ryegrass (Fig. 2A). In all the treatments of flocs made without Fe, floc was the dominant source of CO₂ produced while native SOC contributed significantly to the total CO₂ production in floc treatments made with Fe regardless of its level. The total CO₂ production derived from floc in all treatments was significantly lower than the CO₂ produced from DOC decomposition in the DOC-only

Table 2 Characteristics of flocs

Treatments	Fe-OC ^a	Montmorillonite kaolinite					
		M–OC	Fe _{low} –M–OC	Fe _{high} –M–OC	K–OC	Fe _{low} –K–OC	Fe _{high} –K–OC
CEC ^b (cmol kg ^{−1})	–	84.4	49.0	1.9	2.0	1.3	–
Fe ^c (mg g ^{−1})	9.0	–	11.4	219.0	–	5.4	199.0
Sorbed C (mg C g ^{−1})	340.0	4.0	9.1	26.0	2.4	6.3	22.0

^aFe coagulated with dissolved organic carbon

^bCation exchange capacity

^cCarbon content of flocs

Fig. 1 Cumulative CO₂ production from different floc treatments incubated without (A and C) and with ryegrass (B and D). Error bars represent standard error of the means (n = 4)

Table 3 Cumulative CO₂ production (CO₂-C μg g⁻¹) during incubation period and extracted DOC (μg g⁻¹) at the end of incubation from different treatments without and with ryegrass (n = 4)

Treatments	Added floc mg C g ⁻¹	Without ryegrass		With ryegrass	
		CO ₂ production	DOC content	CO ₂ production	DOC content
Control	0	19.6 (1.2) f	7.35 (0.5) c	302.7 (10.0) e	15.03 (0.6) f
DOC	0.2	148.2 (0.6) a	96.71 (12.0) a	463.2 (13.5) a	111.61 (2.5) a
Fe-OC	0.2	50.7 (2.4) e	46.13 (0.9) b	344.7 (14.4) d	57.13 (2.7) b
M-OC	0.2	87.9 (1.4) d	17.41 (0.7) c	407.2 (11.3) c	31.37 (0.5) c
Fe _{low} -M-OC	0.2	82.6 (1.5) d	27.10 (0.9) c	350.9 (7.0) d	39.94 (1.0) c
Fe _{high} -M-OC	0.2	25.2 (2.5) f	13.92 (0.7) c	256.1 (17.1) f	17.07 (0.7) f
K-OC	0.2	129.7 (1.8) b	15.38 (1.6) c	457.3 (7.9) ab	14.97 (1.2) f
Fe _{low} -K-OC	0.2	106.6 (3.8) c	24.38 (0.7) c	433.2 (8.2) bc	25.92 (1.2) e
Fe _{high} -K-OC	0.2	28.5 (2.6) f	17.32 (1.0) c	268.9 (10.7) f	23.31 (1.2) e

The letters represent the differences in CO₂ production or DOC among different floc treatments without or with ryegrass addition

treatment. At the end of the incubation, 45.4% of DOC was mineralized in the DOC-only treatment while 4.0–30.4% of floc-C was mineralized in floc treatments. The floc-derived CO₂ production was 1.2–2.3 times higher in the treatments of flocs made with kaolinite than that in the treatments with montmorillonite (Fig. 3A). Within the same clay treatment, CO₂

produced from floc decomposition decreased as the Fe level increased. Compared with the control (soil only), the addition of flocs or DOC significantly promoted CO₂ produced from native SOC, with higher SOC-derived CO₂ production found in the flocs made with lower level of Fe. The type of clay minerals in the flocs made with Fe did not significantly impact the CO₂

Fig. 2 Fraction of the CO₂ production from floc and native soil C pools in the treatments without ryegrass (A) and fraction of the CO₂ productions from ryegrass and floc-soil pools in the

treatments with ryegrass (B). Error bars represent standard error of the means (n = 4)

Fig. 3 Quantification of the cumulative CO₂ production from floc and native soil C pools in the treatments without ryegrass (A) and from ryegrass and soil/floc C pools in the treatments with ryegrass (B). The uppercase letters show significant differences in CO₂ derived from soil or ryegrass at $P < 0.05$

produced from native SOC. In the treatments of flocs made without Fe, higher SOC-derived CO₂ production was found in kaolinite compared to montmorillonite treatments (Fig. 3A).

The fractional contributions of soil-floc mixture and ryegrass to total CO₂ production were determined for all the treatments with ryegrass (Fig. 2B). As

among different floc treatments without or with ryegrass. The lowercase letters show significant differences in CO₂ derived from floc or soil/floc mixture at $P < 0.05$ among different floc treatments without or with ryegrass. Error bars represent standard error of the means (n = 4)

expected, ryegrass-derived CO₂ production dominated total CO₂ production in all treatments, ranging from 59 to 76% (Fig. 3B). In all treatments, 45–78% of ryegrass was mineralized by the end of the incubation, with the highest rate found in the DOC-only treatment. The total CO₂ produced from ryegrass treatments was significantly increased by flocs made without Fe.

However, regardless of clay mineralogy, the flocs made with high Fe significantly inhibited ryegrass C decomposition by 14–19% while no impact of Fe–OC floc on ryegrass decomposition was found. The total CO₂ produced from the soil-floc mixture C pool varied significantly among floc treatments, with higher soil-floc mixture-derived CO₂ production found in kaolinite compared to montmorillonite floc treatments.

Dissolved organic carbon and source partitioning

At the end of the incubation, the fractional contributions of the extracted DOC sources were determined for all treatments (Fig. 4). In the treatments without ryegrass, the floc-derived DOC changed significantly among treatments. For example, the floc-derived DOC was 85–420% higher in the Fe-OC floc treatment compared to other treatments. No significant difference in soil-derived DOC was found among all treatments except DOC-only treatment, which had higher soil-derived DOC than control and other floc treatments. Unexpectedly, the addition of ryegrass increased the total extracted DOC was only found in treatments of flocs made with montmorillonite or floc made without clay (Table 3). In ryegrass treatments, 44–95% of the extracted DOC was derived from soil-floc mixture instead of ryegrass (Fig. 4). However, the

addition of ryegrass promoted DOC released from soil-floc mixture compared with non-ryegrass treatments.

Priming effect

The clay mineralogy and Fe level in flocs had a significant impact on the PE of flocs on native SOC in treatments without ryegrass (Table 4). Regardless of Fe level, the flocs made with kaolinite primed 2.9–31.1 $\mu\text{g C g}^{-1}$ more CO₂ from SOC than the montmorillonite flocs (Table 5). Regardless of clay mineralogy, the flocs made with low Fe significantly primed 46.8–49.2 $\mu\text{g C g}^{-1}$ more CO₂ from SOC than the high Fe flocs. The primed SOC-derived CO₂ production in floc treatments made with Fe only or clay only were 11.3–19.7 $\mu\text{g C g}^{-1}$ less than in the DOC-only treatment. At the end of the incubation, a negative PE on SOC-derived DOC was found in all floc treatments while the DOC only significantly primed DOC released from SOC (Table 5).

The addition of ryegrass stimulated 3–34% more CO₂ production from soil-floc mixtures compared to treatments without ryegrass, while in the DOC-only treatment, less soil-floc-derived CO₂ production was observed in ryegrass treatments compared with non-ryegrass treatments (Fig. 3A, B; Table 5). In treatment

Fig. 4 Extracted DOC at the end of the incubation without (A) or with ryegrass (B). Floc material or unflocced DOC was added to the soil medium at a rate of 0.2 mg C g⁻¹. The uppercase letters show significant difference in DOC derived from soil or ryegrass at $P < 0.05$ among different floc

treatments without or with ryegrass. The lowercase letters show significant difference in DOC derived from floc or soil/floc mixture at $P < 0.05$ among different floc treatments without or with ryegrass. Means ($n = 4$) and standard errors are shown

Table 4 Results of analysis of variance on the effect of clay mineralogy and Fe level on cumulative CO₂ production, extracted DOC and priming effect in the treatments without and with ryegrass over 30 days incubation

			Variances	df	Mean square	<i>F</i>	<i>P</i>
Without ryegrass	CO ₂ production	Clay		2	1640.1	88.9	< 0.001
		Fe		2	18,226.2	987.7	< 0.001
		Clay × Fe		3	7912.8	428.8	< 0.001
	PE	Clay		2	5290.5	153.8	< 0.001
		Fe		2	10,202.3	296.6	< 0.001
		Clay × Fe		3	1484.1	43.1	< 0.001
	CO ₂ production	Clay		2	1904.2	7.0	0.003
		Fe		2	15,327.1	56.6	< 0.001
		Clay × Fe		3	7893.2	29.2	< 0.001
With ryegrass	PE	Clay		2	2631.2	22.4	< 0.001
		Fe		2	1005.2	8.6	< 0.001
		Clay × Fe		3	2159.6	18.4	< 0.001

Table 5 Priming effect (PE) of flocs and ryegrass residue on the C mineralization (or extracted DOC) of native soil or soil/floc mixture

Treatment	Without ryegrass PE of SOC		With ryegrass PE of soil/floc mixture	
	CO ₂ -C μg g ⁻¹	DOC μg g ⁻¹	CO ₂ -C μg g ⁻¹	DOC μg g ⁻¹
Control	–	–	48.1(7.5) ab	3.6 (0.6) a
DOC	37.67 (1.5) b	33.4 (11.0) a	– 11.5 (3.5) e	– 106.2 (21.3) b
Fe-OC	23.0 (2.5) c	– 0.4 (0.8) b	46.1 (1.8) ab	7.0 (2.8) a
M-OC	17.9 (1.6) d	– 1.6 (0.9) b	9.4 (5.5) d	– 3.7 (2.3) a
Fe _{low} -M-OC	46.2 (0.9) a	– 3.4 (1.6) b	34.1 (4.3) bc	5.9 (2.5) a
Fe _{high} -M-OC	– 2.8 (0.8) f	– 4.7 (1.1) b	28.1 (3.8) c	0.5 (1.0) a
K-OC	49.0 (2.3) a	– 1.0 (0.8) b	56.2 (2.1) a	– 3.1 (1.6) a
Fe _{low} -K-OC	49.1 (1.8) a	– 2.5 (0.8) b	48.7 (8.5) ab	– 1.5 (1.2) a
Fe _{high} -K-OC	2.3 (2.1) f	– 4.7 (0.6) b	48.6 (7.3) ab	4.1 (0.6) a

PE was calculated as the difference in CO₂ production derived from soil or soil-floc C pool between the treatments and control. Different letters show significant differences ($P < 0.05$) among different floc treatments without or with ryegrass addition

without flocs (control: soil only), the addition of ryegrass residue primed SOC-derived CO₂ production by 48 μg C g⁻¹. Interestingly, the ryegrass primed soil-floc-derived CO₂ in floc treatments was significantly lower than or not different from the ryegrass primed SOC-derived CO₂ (Table 5).

Discussion

The interaction of clay and DOC plays a key role in the stabilization of SOC, which influences its potential for C sequestration (Mikutta and Mikutta 2006; Saidy et al. 2015). The properties of clays significantly affect

the amount of DOC that can be adsorbed. Pedogenic Fe oxides actively interact with DOC and play a pivotal role in the capacity of soil to adsorb DOC (Kahle et al. 2004). In this study, flocs made by adsorbing DOC to montmorillonite contained relatively more C than those with kaolinite (Table 2). Previous studies attribute the higher CEC and SSA of montmorillonite as factors affecting DOC adsorption (Saidy et al. 2013). The role of cation bridging, where Fe is bound to both clay and DOC was summarized by Stevenson (1994). In our treatments, high Fe-treated clays were found to adsorb more DOC than low Fe-treated clays. A positive correlation was found between Fe content and the amount of C in clay-Fe-

OC flocs (Table 2). The floc made with Fe and DOC without clay contained the highest amount of C among all the floc treatments (Table 2). The high capacity of DOC to sorb to actively forming Fe (III) precipitated (co-precipitation) has been shown to remove DOC from wetlands and water streams in situ (Ye et al. 2015; Zou et al. 2018).

Adsorbing DOC to clay and/or Fe decreased its mineralization rate by up to 85% compared to the DOC alone (Table 3); the extent to which mineralization rate was reduced depends on clay mineralogy and Fe levels (Saidy et al. 2012). These results are in line with previous studies, which showed that mineralization of OC adsorbed to clay minerals was reduced by 27–43% compared with free OC (Chenu and Plante 2006; Saidy et al. 2015). Generally, simple compounds such as glucose and citrate can be easily mineralized even after they adsorb to clay minerals (Jones and Edwards 1998). The reduction in mineralization rate of adsorbed C over extended periods is most likely due to the reduced mineralization rate of complex compounds (e.g., lignin and polyphenols) that have been adsorbed. In this study, significantly more C was mineralized from flocs made with kaolinite than montmorillonite when no Fe or low Fe was included in the flocs; however, in flocs made with high Fe, the difference in C mineralization rate between the two types of clay mineralogy disappeared (Fig. 3). These results indicate that the surface of clay mineralogy and Fe levels play a positive interactive role in controlling C stability of flocs. A similar result was also reported by Saidy et al. (2015), who found that microbial degradation differences between OC adsorbed to kaolinite and smectite depended on the presence of Fe in flocs. The mineralization rate of the adsorbed OC decreased as the Fe content in flocs increased (Fig. 3).

In flocs made with clays, Fe (III) adheres to the clay surface or incorporates into the clay lattice without influencing floc adsorptive properties (Carroll 1958; Bhattacharyya and Sen Gupta 2008). In instances where Fe is present as a (hydr)oxide coating, the surface (and adsorption) properties of the floc change. In this study, when the highest amount of Fe was present in flocs, no significant difference in C mineralization was observed between kaolinite and montmorillonite flocs, indicating that mineralization of C in these flocs was controlled predominantly by Fe rather than clay mineralogy. Therefore, while clay

mineralogy and Fe both affect C mineralization, the relative amount of each must be considered in defining C stabilization potential.

In general, compared with 1:1 clays (i.e. kaolinite), 2:1 clays (i.e. montmorillonite) have larger CEC, which facilitates greater adsorption of positively charged metals such as ferric ions (Greenland 1971). The net charge on the montmorillonite surface remains negative if a limited amount of Fe is adsorbed. The sorption of DOC to Fe-treated montmorillonite is expected to occur via non-coulombic mechanisms or cation bridging. For kaolinite, a net positive charge occurs when Fe-adsorbs to the surface and allows for absorbing negatively-charged DOC via coulombic mechanisms such as ligand exchange (Zhuang and Yu 2002; Saidy et al. 2013). Consequently, the stability of C adsorbed onto these two types of clays likely differs. This is reflected in our results showing that the PE of flocs made with the two different clays on SOC decomposition varied (Table 5). In this study, the floc made with kaolinite promoted SOC decomposition compared to montmorillonite. However, when Fe was present in flocs, the floc-primed SOC decomposition was decreased as the Fe content increased in flocs, regardless of clay mineralogy (Table 5). These results indicate that the interaction between Fe and clay can enhance the resistance of OC in flocs and in SOC to microbial decomposition.

As expected, the addition of ryegrass increased total CO₂ production from all treatments, with higher CO₂ production found in kaolinite treatments than montmorillonite treatments (Table 3). Interestingly, the decomposition of ryegrass residue was inhibited by flocs made with high Fe combined with clay. This is probably due to the inhibitory effect of large amounts of Fe on microbial activity (Jones and Edwards 1998). However, no impact of Fe–OC floc on the ryegrass was found while significant higher ryegrass decomposition rate occurred in the DOC-only treatment (Fig. 3B). These results indicate that the presence of Fe in flocs can protect OC from decomposition and can therefore slow down the microbial C turnover process.

Over the course of the incubation with ryegrass residue, the majority of total CO₂ was derived from ryegrass but the DOC extracted at the end of the incubation was mainly derived from the soil-floc mixture (Fig. 4). This result was in line with Hagedorn et al. (2004), who reported that an external C input was preferentially respired as CO₂ but the majority of DOC

originated from native SOC. Toosi et al. (2012) also reported that only 8–14.5% of the total extractable DOC was derived from added ryegrass residue. In their study, the addition of ryegrass residue promoted two times more CO₂ derived from SOC compared with the control (soil only), an example of positive PE. In our study, a similar positive PE was also observed for all floc treatments except for the DOC-only treatment (Table 5), where a negative PE was found. Unexpectedly, the PE of ryegrass on soil-floc-derived CO₂ or DOC in floc treatments was significantly lower than or not different from the ryegrass primed SOC-derived CO₂ or DOC (Table 5), indicating that flocs can decrease the PE of ryegrass on native SOC decomposition and therefore increase the potential of soil C sequestration.

Conclusion

In this study, flocs made with montmorillonite absorbed and stabilized more DOC than kaolinite regardless of Fe content in the flocs. The stability of the adsorbed DOC in flocs was also controlled by the nature of the interaction between clay mineralogy and Fe. For flocs made with high Fe content, the stability of adsorbed DOC was not affected by clay mineralogy, showing that higher amounts of Fe overcome the mineralogical characteristics of clay type in adsorbing DOC. The inclusion of synthetic flocs promoted SOC decomposition with kaolinite derived flocs having a higher PE than montmorillonite flocs. Higher primed SOC-derived CO₂ was also found in the floc treatments with low or no Fe compared to those with high Fe content. The addition of ryegrass residue accelerated C mineralization from the soil-floc mixture. On the other hand, flocs significantly decreased the PE of ryegrass on SOC decomposition. The application of high-Fe clay flocs also inhibited the decomposition of ryegrass residue. Considering cumulative C mineralization and extractable DOC remaining in the soil mixture, the flocs made with montmorillonite and/or high Fe content offered better protection of adsorbed C, SOC and recent plant C inputs against microbial decomposition compared to flocs made with kaolinite and/or low Fe. Overall, clay mineralogy and Fe levels in flocs had a significant effect on C mineralization of clay-Fe-C products and soil C stability and provides insights into the role of Fe in affecting PE.

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Data availability The datasets are available from the corresponding author on reasonable request.

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