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Linking dissolved organic carbon cycling to organic carbon fluxes in rice paddies under different water management practices

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Abstract

Aims: Although paddy soils are generally characterized by relatively high dissolved organic carbon (DOC) concentrations and fluxes, little is yet known on how water management influences the cycling of this important organic C pool. This work aims at providing insights into the link between DOC cycling during rice cropping and organic C input to the subsoils and export with surface waters, as well as methane (CH_4) emissions in a temperate paddy soil as a function of different water management practices.

Methods: DOC quantity, quality and fluxes, as well as CH_4 emissions were evaluated at field-scale over two cropping seasons for three water management systems including continuous flooding, dry seeding with delayed flooding, and intermittent irrigation.

Results: DOC cycling in the different water management systems were strongly linked to the reducing soil conditions resulting from field flooding. In contrast to dry seeding or intermittent irrigation, adoption of continuous flooding not only favoured the accumulation of DOC in the topsoil (>10-20 mg C l^{-1}), but also enhanced C inputs to the subsoil (33-51 g C m^{-2}), and exports with surface waters (18-44 g C m^{-2}). Moreover, changes in DOC quality in paddy soils were linked to a positive feedback on the abiotic release of soil-derived DOC, and substrate availability for CH_4 production.

Conclusions: Water management practices in rice paddies strongly affect the temporal trends in DOC quantity and quality over the cropping season, with important implications on organic C fluxes.

Keywords: organic carbon fluxes, soil redox conditions, reductive dissolution, surface waters, subsoil, methane emissions.

Introduction

Rice paddy soils are generally characterized by large concentrations and fluxes of dissolved organic carbon (DOC) in comparison to other ecosystems (Kögel-Knabner et al. 2010; Krupa et al. 2012). Being a relatively mobile and the most bioavailable fraction of soil organic carbon (SOC; Marschner and Kalbitz, 2003), DOC plays a role in many chemical and biological processes, and therefore the most dynamic in terms of ecosystem functionality. In particular, soil processes involving this organic C pool may strongly control the C source/sink functions of paddy soil agro-ecosystems.

Indeed, paddy rice cultivation represents the major source (11%) of global methane (CH_4) emissions, one of the principal greenhouse gases, with annual emissions estimated to range between 493 and 723 Mt CO_2-eq yr^{-1} in 2010 (Kimura et al. 2004; Smith et al. 2014). Seasonal patterns of CH_4 emissions from these soils generally follow the pattern of DOC in the root zone (Lu et al. 2000), suggesting that this labile C pool may serve as a major C source for methanogenic microorganisms. Moreover, DOC may also be responsible for significant C exports to adjacent water bodies with important implications concerning fluvial water quality and agricultural catchment C budgets (Abe et al. 2011; Krupa et al. 2012). Paddy soils are also often associated with a large accumulation of SOC compared to other arable ecosystems (Kögel-Knabner et al.

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2010). Recently, Hanke et al. (2013) challenged the general assumption that increasing SOC contents with paddy soil development is due to a smaller C mineralization under anoxic conditions. They provided evidence showing how successive cycles of DOC desorption and partial mineralization under anoxic conditions, followed by re-adsorption and selective preservation under oxic conditions, may drive the long-term accumulation of more stable organic C and contribute to increasing topsoil C stocks in well-established paddy soils. Moreover, recent studies have shown that, whereas topsoil organic C stocks and concentrations increase with years of paddy management, accumulation of organic C in the subsoils is slower (Kalbitz et al. 2013). This has been attributed to the low-permeability of the plough pan, particularly in finely textured soils, that could limit DOC input into the subsoil (Wissing et al. 2011).

Various studies have shown that the degradation of incorporated crop residues may contribute significantly to DOC (Katoh et al. 2005; Ruark et al. 2010), and also influence its heterogeneity in terms of chemical composition and molecular structures due to the diverse biodegradability as a function of soil redox conditions (Chen et al. 2010). Rice growth is also an important factor affecting DOC in paddy soils through the release of soluble root exudates and rhizodeposits (Ge et al. 2012), although root-derived DOC has been shown to be rapidly mineralized contributing only marginally to DOC fluxes (He et al. 2015). Moreover, the increase in soil pH and the dissolution of Fe and Mn oxyhydroxides when acidic soils are subjected to anoxic conditions may result in the release of significant amounts of DOC previously stabilized on the mineral matrix (Grybos et al. 2009). These mechanisms, are all considered to affect DOC concentrations and fluxes in rice paddies. However, little is yet known on the numerous biotic and abiotic factors that control the temporal and spatial variations in DOC quantity and quality in soils subjected to alternating redox conditions (Kalbitz et al. 2000), particularly for rice paddies (Hanke et al. 2013).

Agricultural practices in rice cropping systems are expected to influence DOC cycling and related ecosystem functions. In the last decades, various studies have shown that management options involving the adoption of water systems alternative to continuous flooding have a high potential to mitigate CH_4 emissions (Corton et al. 2000; Wassmann et al. 2004; Liu et al. 2014) and impact the timing and magnitude of DOC exports from soils to rivers (Abe et al. 2011; Krupa et al. 2012; Oh et al. 2013; Xu et al. 2013). In fact, water management practices play an important but still not well understood role in the production, mineralization and leaching of DOC in paddy soils, although they are crucial processes affecting the ecosystem C balance (Kindler et al. 2011). On the basis of a two-year field experiment carried out in a temperate paddy field (NW Italy), the objectives of this study were to: (i) evaluate the trends in DOC concentrations, composition and fluxes in paddy soil solution, water supply and drainage canals during rice cropping, and (ii) identify the main mechanisms and drivers that link soil solution DOC cycling to the input of organic C to subsoils, export to surface waters, and CH_4 emissions, as a function of different water management practices.

Materials and Methods

Experimental site description

The field experiment was carried out over two rice cropping seasons (2012 and 2013) at the Rice Research Center of Ente Nazionale Risi, Castello d'Agogna, Pavia (45°14'48"N, 8°41'52"E), located in the plains of the river Po (NW Italy). The study area has a temperate climate with a mean annual temperature of 12.4°C and annual precipitation of 684 mm over the experimental period. Mean daily air temperatures and cumulative precipitation over the experimental period are shown in Fig. 1 (data from Meteorological Station 125, ARPA Lombardia). The soil of the experimental field was classified as a Fluvaquentic Epiaquept coarse silty mixed mesic (Soil Survey Staff, 2010), while general soil properties are reported in Table 1.

Experimental design and irrigation management

Field treatments involved the comparison of three water management systems including water seeding with continuous flooding (WFL), dry seeding with flooding at tillering stage (DFL), and dry seeding with intermittent irrigation (DIR), with two replicate plots for each treatment. Each plot was hydrologically-isolated, had an area of 1600 m^2 (20 × 80 m), and was seeded with rice (*Oryza sativa* L. cv. Gladio; 160 kg ha^{-1}). In all plots, crop residues were incorporated with tillage in spring (2 April 2012 and 9 May 2013).

In the WFL treatment, water seeding was carried out on May 28 and June 7, for the 2012 and 2013 cropping seasons, respectively. A 6–18 cm standing water depth was constantly maintained during the cropping season, except for two 5-day mid-season drainage periods about 18-23 and 45-50 days after seeding (DAS). In the DFL treatment, dry seeding was carried out on May 15 and May 28, and the field kept without standing water for 35 and 24 DAS, for the 2012 and 2013 seasons, respectively. Subsequently, water management followed the same regime as for WFL. In the DIR treatment, dry seeding was carried out on May 15 and May 28 for the two cropping seasons. Ponding water was not maintained throughout the cropping season, and irrigation was applied when the soil moisture tension at a depth of 10 cm approached – 30 kPa (9 events in 2012, and 12 events in 2013). In all treatments, drainage was allowed at the ripening stage, 20–30 days before harvest that was carried out between the end of September and the first 15 days of October. Throughout the cropping seasons, soil pH and Eh were measured potentiometrically in each plot at a soil depth of 10 cm.

For each field treatment 160 kg N ha^{-1} of urea were applied and split between basal, tillering, panicle differentiation and booting stages as follows: 60-60-40-0 kg N ha^{-1}, 40-70-50-0 kg N ha^{-1} and 50-40-40-30 kg N ha^{-1} for WFL, DFL and DIR, respectively. All fertilizer applications were top-dressed except for the basal fertilization that was incorporated. A different fertilizer N split rate was adopted to optimize crop growth and yield performance, as well as limit N losses for each water management. All plots also received 18 kg P ha^{-1} and 70 kg K ha^{-1} as basal fertilization.

Water sampling and analyses

Ceramic suction cups were installed vertically at 25, 50 and 75 cm depths to collect soil solutions, with two replicates per plot. Surface water samples were collected from supply canals and flumes channelling outflow waters from each plot to drainage canals. All water samples were collected on a weekly basis, filtered through a 0.45 µm nylon membrane filter, and subsequently analyzed for DOC, specific ultraviolet absorbance at 254 nm (SUVA), and Fe(II). Dissolved organic carbon was determined using Pt-catalyzed, high-temperature combustion (850°C) followed by infrared detection of CO_2 (VarioTOC, Elementar, Hanau, Germany), after removing inorganic C by acidifying to pH 2 and purging with CO_2-free synthetic air. UV absorption at 254 nm was measured (Helios Gamma Spectrophotometer, Thermo Electron, Waltham, MA) after appropriate dilution to DOC <50 mg l^{-1}. The SUVA values calculated by normalizing measured absorbance values to the concentration of DOC, were used as an estimate for the aromatic content of water samples (Weishaar et al. 2003). Dissolved Fe(II) concentrations were measured colorimetrically immediately after sampling, using the 1,10-phenanthroline method (Loeppert and Inskeep 1996).

Calculation of DOC fluxes

Daily DOC concentrations in surface (inflow and outflow) and subsurface (25 cm) waters were extrapolated for the entire cropping season by assuming a linear change in concentration between two successive measured data points. Water fluxes for each irrigation management were determined for both cropping seasons as described by Chiaradia et al. (2013; 2015). Briefly, irrigation inflow (I) and outflow discharges (D) for each plot were measured by long-throated flumes equipped with a level gauge, while net percolation (P) was obtained as the residual term of the water balance according to the equation:

$$I + R = \Delta S + ET + P + D$$

where R is the precipitation, ET is the crop evapotranspiration estimated by the application of Penman-Monteith type models previously calibrated using a discontinuous data series obtained through eddy-covariance measurements as described by Facchi et al. (2013) and Gharsallah et al. (2013), and ΔS is the change in the field soil water storage (including the soil water content of the root zone up to 40 cm depth, and ponded water depth during flooding). The experimental fields were also instrumented with piezometers in order to monitor the groundwater depth and with tensiometers at different depths in order to assess the soil pressure profile. Net percolation was used to compute the percolation fluxes of DOC at 25 cm. Concentrations at 25 cm instead of those at 50 cm have been chosen in light of the following considerations: (i) fluxes in the topsoil were mainly downward, as evidenced by data obtained from piezometers and tensiometers (data not shown), while horizontal water movements may not be excluded at depths > 40 cm, and (ii) the root water uptake between 25 and 40 cm are in any case negligible compared to the magnitude of percolation fluxes, so no significant differences in percolation fluxes between these two depths were expected. Daily inflow, outflow and percolation fluxes of DOC (g m^{-2} d^{-1}) were then calculated by multiplying the concentration of DOC (mg C l^{-1}) by the water flux (l m^{-2} d^{-1}), while cumulative fluxes over the cropping season were calculated as the sum of all daily fluxes. Flow-weighted DOC concentrations for each irrigation management were calculated by dividing the total DOC flux by the total water flux in the same time period.

Gas sampling and methane flux measurements

Methane emissions were measured over the whole rice cropping season by the non-steady-state closed chamber technique. Stainless steel flux anchors were permanently installed into the soil (40 cm deep) prior to seeding, to ensure reproducible placement of gas collecting chambers during successive emission measurements. The top edge of the anchor had a groove for filling with water to seal the rim of the chamber. The chamber was equipped with a circulating fan to ensure complete gas mixing and was wrapped with a layer of polystyrene and aluminium foil to minimize air temperature changes inside the chamber during the gas sampling period. The cross-sectional area of the chamber was 0.27 m^2 (0.75 × 0.36 m). During gas sampling, the chamber was placed over the vegetation with the rim of the chamber fitted into the groove of the anchor. Extension collars were added to increase chamber height in order to accommodate the growing rice plants. During this study, CH_4 efflux was usually measured once a week, except during drainage periods, when a higher sampling frequency was adopted. Gas samples (30 ml) were drawn with airtight syringes at 0, 15 and 30 min after chamber closure, and transferred into 12 ml pre-evacuated vials (Exetainer®, Labco Limited, UK). Gas samples were analysed by gas chromatography with flame ionization detection (Agilent 7890A, Santa Clara CA, USA). Methane emission flux (F, expressed in g C m^{-2} d^{-1}) was calculated from the linear resolution of the rate of increase in gas concentration in the chamber (dC/dt in ppm h^{-1}), according to the following equation (Yang et al., 2012):

$$F = \frac{dC}{dt} \cdot H \cdot \frac{\mu \bar{P} \cdot 24 \cdot 10^{-6}}{R(\bar{T} + 273.2)}$$

where H is the effective height of the static chamber (m), $\bar{P}$ is the mean air pressure in the chamber (Pa), $\bar{T}$ is the mean air temperature in the chamber (°C), R is the universal gas constant (R = 8.31441 J mol^{-1} K^{-1}) and μ is the molecular weight of C. When the rate of increase in gas concentration decreased over the sampling period suggesting a deviation from non-steady state conditions, fluxes were calculated by applying the nonlinear Hutchinson and Mosier (1981) model.

Results

Soil redox conditions and pH

Field flooding in both WFL and DFL treatments led to the establishment of anoxic conditions evidenced by a decrease in soil Eh and a corresponding increase in pH values (Fig. 2). Eh values below –300 mV were observed for WFL over most of the cropping season, except for a couple of more positive peaks in correspondence with mid-season field drainage, while pH values tended to increase from around 5.0 before flooding to a maximum of 6.3-6.9 before final field drainage (Fig. 2a). In DFL, the drop in Eh values and increase in pH occurred later on in the cropping season with respect to WFL, in correspondence with field flooding at tillering stage (Fig. 2b). However, once the fields were flooded, Eh values below –250 mV were recorded, while pH values tended to increase reaching maximum values of 6.3-6.4. In both WFL and DFL treatments, Eh values gradually returned to positive values after final field drainage towards mid-September (only observed in 2012 due to missing data in 2013). In contrast, redox potentials in DIR were generally positive throughout the cropping season with only a number of temporary drops in Eh in correspondence with some irrigation events, particularly in the 2013 season (Fig. 2c). pH values for this treatment were relatively constant with an average value of 5.3.

Soil solution dissolved organic carbon

DOC concentrations generally tended to increase with the onset of anoxic soil conditions during field flooding, although different trends in time and with soil depth were observed among the three management practices (Fig. 3). In WFL, higher topsoil DOC concentrations (25 cm) were observed during flooded (16-48 mg C l^{-1}) compared to drained periods (6-27 mg C l^{-1}; $p < 0.001$; Fig. 3a). Moreover, temporal variations in DOC at this depth followed a bimodal trend, more evident in 2013, with maxima at the beginning (mid-June) and towards the later stages (beginning September) of the cropping season (Fig. 3a). In both years, increasing DOC concentrations during flooding were also observed at 50 cm (11-29 mg C l^{-1}; mean 18.4 ± 7.2 mg C l^{-1}), and to a lesser extent, at 75 cm (8-23 mg C l^{-1}; mean 13.0 ± 4.3 mg C l^{-1}).

In DFL, topsoil DOC concentrations also increased with the onset of flooding though later on in the cropping season with respect to WFL (Fig. 3b). Under flooded conditions DOC concentrations at 25 cm ranged between 9.8 to 33.9 mg C l^{-1} with maximum values occurring towards the end of August just before final field drainage (Fig. 3b). DOC concentrations at greater depths also tended to increase during flooding, although this increase was more evident in 2012 than 2013.

In DIR, maintenance of oxic conditions through intermittent irrigation resulted in relatively lower DOC concentrations throughout the cropping season and at all soil depths with respect to the other treatments ($p < 0.001$; Fig. 3c). Over both cropping seasons, mean DOC concentrations were 9.7 ± 3.1 mg C l^{-1} at 25 cm, 7.4 ± 2.3 mg C l^{-1} at 50 cm, and 6.5 ± 2.1 mg C l^{-1} at 75 cm with little variation in time.

The increase in DOC during field flooding was generally accompanied by an increase in its aromatic character evidenced by increasing SUVA values at all soil depths (Fig. 4). In WFL, mean SUVA values at 25 cm increased from 1.51 l mg^{-1} m^{-1} before flooding to 2.51 l mg^{-1} m^{-1} during flooding and down to 1.91 l mg^{-1} m^{-1} after final field drainage (Fig. 4a). Maximum values of 3.59 and 4.26 l mg^{-1} m^{-1} were observed towards the later stages of the cropping season in 2012 (mid-September) and 2013 (beginning August), respectively. This increase in SUVA values with flooding was not limited to the topsoil since similar trends and maximum values were also observed at 50 cm and, to a lesser extent, at 75 cm.

In DFL, relatively low SUVA values were obtained at all depths at the beginning of the cropping season when the fields were still drained (mean 1.31 ± 0.27 l mg^{-1} m^{-1}), and again after final field drainage before harvest (mean 1.94 ± 0.38 l mg^{-1} m^{-1}; Fig. 4b). With the onset of flooding SUVA values at 25 cm tended to increase steadily reaching maximum values of 3.39 and 3.82 l mg^{-1} m^{-1} in 2012 (mid-September) and 2013 (beginning August), respectively. A similar trend was also observed at the greater soil depths although this was more evident in 2012 when maximum values at 50 and 75 cm corresponded to peak values observed at 25 cm.

In contrast to the other two management systems, significantly lower SUVA values were observed in DIR ($p < 0.001$), although changes over the rice cropping season showed similar trends (Fig. 4c). In 2012, SUVA values at all depths ranged between 1.07-2.25 l mg^{-1} m^{-1} with mean values of 1.70 ± 0.21, 1.53 ± 0.30 and 1.41 ± 0.33 l mg^{-1} m^{-1} at 25, 50 and 75 cm, respectively. In 2013, average values were slightly higher than 2012 mainly due to a small increase in absorbance values towards the middle of the cropping season (beginning August) at all depths. Maximum values during this period reached 2.89, 2.93 and 2.79 l mg^{-1} m^{-1} at 25, 50 and 75 cm, respectively.

Surface water dissolved organic carbon

Inflow and outflow DOC concentrations over the cropping seasons did not show any particular trend over time, and therefore collected data were grouped together (Table 2). Inflow DOC concentrations were significantly lower than those measured in outflow waters from each of the water management treatments. Over the two cropping seasons DOC concentrations in the supply canals ranged from 2.7-7.9 mg C l^{-1} with an average value of 5.1 mg C l^{-1} (Table 2). Outflow waters showed higher mean DOC concentrations ranging from 6.3 to 7.0 mg C l^{-1} with no significant differences between treatments (Table 2), even though slightly higher maximum DOC concentrations were observed for WFL with respect to DFL and DIR (14.1, 8.9 and 10.9 mg C l^{-1}, respectively). Only for WFL, maximum DOC concentrations in the outflow waters corresponded to the peak values in topsoil DOC observed in the first phase of the cropping period (end June; data not shown). No significant differences were observed in SUVA values between inflow and outflow waters from the three water management practices (Table 2). Compared to soil solutions, mean SUVA values in surface waters were relatively low and ranged between 1.87 and 2.20 l mg^{-1} m^{-1}.

Dissolved iron(II) concentrations

Soil solution Fe^{2+} concentrations generally depended on soil redox conditions therefore resulting in different trends in time and with soil depth among water management practices (Fig. 5). In WFL, Fe^{2+} concentrations in the topsoil (25 cm) increased rapidly with field flooding reaching maximum values of around 24-27 mg Fe l^{-1} in less than 20 days (Fig. 5a). These concentrations were sustained for most of the cropping season except for short periods in correspondence with mid-season drainage and after final drainage before harvest, when Fe^{2+} concentrations dropped rapidly. Mean topsoil Fe^{2+} concentrations over the flooded period were 17.5 ± 8.2 and 22.2 ± 6.0 mg Fe l^{-1} for 2012 and 2013, respectively. Also subsoil Fe^{2+} concentrations tended to increase during flooding reaching maximum values of 23-25 and 9-28 mg Fe l^{-1} at 50 and 75 cm respectively.

Flooding also resulted in an increase in soil solution Fe^{2+} concentrations in DFL, though this was more contained and clearly slower with respect to WFL (Fig. 5b). In fact, maximum Fe^{2+} concentrations of 28.3 and 20.7 mg Fe l^{-1} at 25 cm, were only observed after 35 (end July) and 68 (end August) days from initial field flooding in 2012 and 2013, respectively. Similarly, at 50 and 75 cm soil solution Fe^{2+} concentrations tended to increase only slowly, reaching peak values later on during the cropping season (end August). In this treatment, mean Fe^{2+} concentrations during field flooding tended to decrease with soil depth.

Maintenance of oxic soil conditions for most of the cropping season in the DIR treatment resulted in significantly lower soil solution Fe^{2+} concentrations compared to WFL and DFL ($p < 0.001$; Fig. 5c). Over the two years Fe^{2+} concentrations at 25 cm did not exceed 1.0 mg Fe l^{-1}, while at deeper soil depths (50 and 75 cm) concentrations were generally below or close to detection limits (0.2 mg Fe l^{-1}).

Over both cropping seasons and for all water management practices, mean Fe^{2+} concentrations in surface waters (inflow and outflow) were negligible and never exceeded 0.5 mg Fe l^{-1} (data not shown).

Dissolved organic carbon fluxes

The combined effect of water management practices on DOC concentrations and components of the water balance resulted in a strong influence on DOC fluxes in terms of both the total amounts as well as temporal variations. Over both cropping seasons, mean daily inflow of DOC with the water supply for the three treatments ranged between 0.04 and 0.26 g C m^{-2} d^{-1}, with maximum fluxes of 1.32 g C m^{-2} d^{-1} for WFL and DFL, and 0.84 g C m^{-2} d^{-1} for DIR (Fig. 6). As expected, these peak fluxes were mainly recorded in correspondence with the beginning of field flooding in WFL and DFL, or irrigation events in DIR. Cumulative input fluxes calculated over the entire cropping seasons evidenced a greater input of DOC (17.5-46.3 g C m^{-2}) in the WFL and DFL treatments with respect to the DIR treatment (4.8-6.9 g C m^{-2}; Table 3). However, similar flow-weighted DOC concentrations across treatments (4.6-5.1 mg C l^{-1}) suggests that these differences were mainly linked to the different water flow rates in each treatment.

Mean daily DOC fluxes of 0.24, 0.18 and 0.02 mg C m^{-2} d^{-1} with outflow waters were measured over both cropping seasons for WFL, DFL and DIR, respectively, with maximum fluxes reaching values of 1.56, 1.48 and 0.56 g C m^{-2} d^{-1} for the three treatments respectively (Fig. 7). Highest DOC outflow was generally observed during field drainage (WFL and DFL) or irrigation events (DIR). In both years, cumulative DOC outflow over the cropping season were generally greater in WFL and DFL (between 4-18 times) with respect to DIR, although greater cumulative fluxes were measured in 2012 with respect to 2013 (Table 3). For all treatments, flow-weighted DOC concentrations in outflow waters (5.6-6.5 mg C l^{-1}) were slightly greater that the respective concentrations in inflow waters (4.6-5.1 mg C l^{-1}).

In general, higher DOC percolation fluxes were obtained during flooded with respect to drained periods of the cropping season (Fig. 8). In fact, over both cropping seasons, higher mean daily percolation DOC fluxes were obtained for WFL and DFL (0.32 and 0.23 g C m^{-2} d^{-1}, respectively) with respect to DIR (0.03 g C m^{-2} d^{-1}), as were maximum percolation fluxes (1.68, 2.07 and 0.73 g C m^{-2} d^{-1} for WFL, DFL and DIR respectively; Fig. 8). Cumulative percolation DOC fluxes over the entire cropping season ranged from 3.7 to 51.1 g C m^{-2} and tended to decrease in the order WFL>DFL>>DIR, although greater cumulative fluxes were measured in 2012 with respect to 2013 (Table 3). In the WFL treatment, the greatest amount of DOC percolation occurred during the first 30 DAS, accounting for 39-45% of the total cumulative flux (Table 3). In contrast to WFL, percolation of DOC at the beginning of the cropping season (0-30 DAS) in the DFL treatment was relatively limited, accounting for only 1-2% of the total flux, but increased rapidly with the onset of flooding at tillering stage. Much lower amounts of DOC were percolated in DIR and most of this was concentrated between 31-60 DAS (44-51% of the total DOC percolation flux). Flow-weighted DOC concentrations in percolation waters were markedly higher than those obtained in inflow and outflow waters for all treatments under study (Table 3). Moreover, significantly higher values were obtained for WFL and DFL (18.5-27.0 mg C l^{-1}) with respect to DIR (9.7-12.1 mg C l^{-1}; Table 3). The high flow-weighted DOC concentrations obtained for WFL were generally maintained throughout the cropping season. In contrast, DFL showed relatively lower concentrations in the first 30 DAS with respect to the rest of the season, in both years studied. Flow-weighted DOC concentrations in DIR were generally similar throughout the cropping season, except for the beginning of the 2013 cropping season where lower than average concentrations were observed in the first 30 DAS and higher concentrations in the 31-60 DAS period.

Net methane emissions

Water management practices strongly influenced both the extent and temporal variations in net CH_4 fluxes from the soil during the rice cropping season (Fig. 9), that were generally related to the establishment of anoxic soil conditions and therefore linked to the duration of field flooding. In WFL, CH_4 emissions were recorded a few days after initial field flooding, and rapidly increased to reach maximum fluxes of 0.59 and 0.69 g C m^{-2} d^{-1} within 15-20 days in 2012 and 2013, respectively (Fig. 9a). Emission rates fell drastically in correspondence with mid-season drainage events, only to increase again with subsequent flooding. However, during the cropping season, emission fluxes generally tended to decrease with time and returned to background levels (< 0.01 g C m^{-2} d^{-1}) when fields were drained prior to harvest (end September). Mean CH_4 fluxes over the flooded period were 0.19 ± 0.03 and 0.30 ± 0.03 g C m^{-2} d^{-2} in 2012 and 2013, respectively.

Similarly, in DFL, CH_4 emissions increased in correspondence with field flooding, and, after reaching maximum fluxes towards mid-July, tended to decrease with time (Fig. 9b). However, mean CH_4 fluxes during field flooding (0.14 ± 0.02 and 0.10 ± 0.01 g C m^{-2} d^{-2} in 2012 and 2013, respectively) were smaller, and lower maximum emissions were measured (0.30 and 0.20 g C m^{-2} d^{-1} in 2012 and 2013, respectively), with respect to WFL (p < 0.001). In both years we observed singular high emission peaks just after final drainage in September, probably due to the release of methane trapped in the soil or dissolved in soil solution during drainage.

The maintenance of oxic soil conditions in DIR resulted in measured fluxes that were generally below detection limits, except for some sporadic emissions in 2013 that however, did not exceed 0.08 mg C m^{-2} d^{-1} (Fig. 9c).

Discussion

Quantity and quality of DOC in paddy soils

Water management strongly affected trends in pore-water DOC concentrations with time and depth, clearly showing a dependence on soil water status, and consequently redox conditions. Cropping systems managed under continuous flooding led to the accumulation of important amounts of DOC, with mean topsoil concentrations of 19.4 mg C l^{-1} and maximum values up to 48 mg C l^{-1}. High DOC concentrations in flooded rice paddies have frequently been reported with values often in excess of 10-20 mg C l^{-1} (Katoh et al. 2004; Maie et al. 2004; Xu et al. 2013; He et al. 2015). This has generally been attributed to the limited or incomplete decomposition of organic matter and accumulation of water soluble intermediate metabolites under anoxic conditions (Sahrawat 2004). Moreover, although similar C mineralization rates have been reported under both anoxic and oxic conditions (Hanke et al. 2013), the higher substrate use efficiency by the microbial biomass under anaerobic conditions may lead to a reduced mineralization of straw-derived C with an enhanced preference for the most labile C pools (Devêvre and Horwáth 2000). The relatively high DOC concentrations and low SUVA values observed at the beginning of the cropping season under continuous flooding seem to suggest that most of the accumulated soluble organic C derived from decomposing crop residues. Post-harvest incorporation of crop residues represents the main input of organic C into paddy soils (Kimura et al. 2004), which in our experimental platform, accounted for a organic C input of 270-385 g C m^{-2} y^{-1} in the form of rice straw alone (i.e. excluding below-ground biomass C; *unpublished*). The decomposition of these residues may supply important amounts of DOC, predominantly during the first stages of the cropping season (Katoh et al. 2005). However, the extent of this contribution also depends on the timing of crop residue management practices. In fact, we attributed the generally higher DOC concentrations observed in 2013 (Fig. 3a) to the shorter time span between crop residue incorporation and field flooding with respect to 2012 (27 and 53 days, respectively). As a consequence of the particularly abundant precipitation in the spring of 2013, soil tillage had to be delayed, probably influencing the amount of labile straw-derived C present in the soil during the cropping season.

The increasing trend in SUVA with time under flooded conditions (up to values of 3.6-4.3 l mg^{-1} m^{-1}) points to an increasing contribution of more aromatic, soil-derived organic C, although the selective preservation of aromatic, residue-derived constituents under anoxic conditions could have also partly contributed to this increase. The important release of Fe^{2+} due to the reductive dissolution of Fe (hydr)oxides as well as the increase in soil pH towards neutral values, suggest that anoxic conditions could indeed lead to the abiotic release of DOC previously stabilized on the mineral matrix (Grybos et al. 2009). This was further supported by the significant correlation between DOC and Fe^{2+} concentrations in the topsoil (r = 0.639; p < 0.001; Fig. 10a). Continuous flooding also resulted in an increase in DOC contents, SUVA values and Fe^{2+} concentrations in the subsoil. This points to the mobility of DOC along the soil profile, not only as a consequence of the higher concentrations in the topsoil, but also due to a limited retention of aromatic constituents during passage through the reduced mineral horizons. Moreover, maintaining anoxic soil conditions for relatively long periods of time could result in an important transfer of pedogenic Fe from the topsoil to the subsoil, with important implications on C stabilization (Wissing et al. 2013; Sodano et al. 2016). Fe redox transformations, transport of soluble Fe^{2+}, and redistribution of pedogenetic Fe (hydr)oxides along the soil profile may have a profound, but still not well understood, influence on DOC cycling and C sink potential of paddy soils subjected to frequent changes in redox conditions (*c.f.* Kalbitz et al. 2013; Winkler et al., 2016).

Adoption of dry seeding and delayed flooding resulted in much lower DOC concentrations in the first part of the cropping season with respect to water seeding and continuous flooding. Oxic soil conditions present during this period probably favoured the rapid turnover of this labile organic C pool preventing its accumulation. Nonetheless, with the onset of flooding at tillering stage, the concentration of DOC and its aromatic character tended to increase suggesting an important release of soil-derived DOC in this water management too. This was consistent with the corresponding increase in pore-water Fe^{2+} concentrations observed in the later stages of the cropping season. Moreover, variations in Fe^{2+} concentrations in the dry seeded treatment explained 71% of the variability in DOC concentrations ($p < 0.001$), compared to only 41% in the water seeded treatment (Fig. 10a) supporting our hypothesis that DOC accumulated under the former water management was mainly soil-derived.

The release of Fe^{2+} in solution during field flooding was however, more limited and clearly slower in the dry with respect to water seeded treatment. In the former, the oxic soil conditions together with the warmer ambient temperatures during the first 25-35 DAS probably favoured the decomposition of the straw-derived C incorporated into the soil. This could have limited the availability of labile C once the fields were flooded, partially reducing the supply of electrons from organic matter degradation to Fe-reducing microorganisms. Moreover the lower pH values and slower decrease in Eh observed with the onset of field flooding in the dry with respect to the water seeded treatment, lends support to this interpretation. These observations suggest that whereas crop residue incorporation in proximity of field flooding (water seeded) could actually result in a positive feedback on DOC concentrations by stimulating the microbially-driven, reductive dissolution of Fe (hydr)oxides and the consequent release of soil-derived DOC, dry seeding could limit this effect. This was further corroborated by the generally higher DOC concentrations and maximum SUVA values observed under continuous flooding in the 2013 with respect to the 2012 cropping season as a consequence of the closer temporal proximity between residue incorporation and flooding in 2013.

In contrast to the other two water management practices, maintaining rice cropping under aerobic conditions by intermittent irrigation resulted in relatively low DOC contents throughout the soil profile with concentrations generally <10 mg C l^{-1}. Specific UV absorption values and Fe^{2+} concentrations were relatively low, never exceeding 2.25 l mg^{-1} m^{-1} and 1.0 mg Fe l^{-1}, respectively. These results suggest that maintaining oxic conditions not only enhanced the turnover, but also limited the release and mobility of DOC throughout the cropping season.

DOC export and transport from topsoil to subsoil

Water management practices may have an important effect on the hydrology of paddy soils (Sacco et al. 2012; Chiaradia et al. 2014; Zhao et al. 2015), and consequently on DOC fluxes. In fact, rice paddies may contribute significant amounts of DOC to surface waters with important impacts on catchment C budgets and downstream water quality in rice-dominated areas (Ruark et al. 2010). All three water management practices studied evidenced higher DOC concentrations in the outflow with respect to inflow water. However, for all treatments, cumulative DOC fluxes in the outflow were generally lower than DOC fluxes entering the rice paddies with inflow waters, and decreased drastically on going from continuous flooding (18-44 g C m^{-2}) to intermittent irrigation (2-4 g C m^{-2}). This suggests that outflow rather than DOC concentrations, mainly governed organic C exports with surface waters from the different water management practices. This is consistent with the findings of other studies regarding DOC exports from agricultural watersheds (Hernes et al. 2008) and rice fields (Ruark et al. 2010) in particular. Nonetheless, the slightly higher flow-weighted DOC concentrations in output with respect to input waters suggests that rice paddies could represent a net source of organic C to surface waters at field-scale. Although Krupa et al. (2012) reported an increase in the fraction of aromatic and high molecular weight moieties lost with outflow waters over the course of the growing season, we did not observe any differences in the quality of DOC neither between inflow and outflow waters, nor between outflow waters from the different water management practices. This suggests that enrichment of surface waters in aromatic components is strongly linked to soil processes occurring in the topsoil and their contribution will depend on flow through these horizons.

Leaching losses of DOC from paddy topsoils may represent a crucial component of the ecosystem C balance, although this is often overlooked. Very few studies have attempted to quantify these fluxes (Katoh et al. 2004; Maie et al. 2004), and even less have evaluated the influence of water management (Xu et al. 2013). Our results evidenced that the transport of DOC from the topsoil to the subsoil was dependent on the combination of hydrological flow regime and the resulting soil moisture conditions. The former was mainly responsible for the differences in measured fluxes between the two years within each water management. In fact, the different water fluxes we observed between cropping seasons was mainly attributed to the higher water table depth in 2013 with respect to 2012. Over a cropping season, as much as 32.6-51.1 g C m^{-2} were lost by percolation from the silty-loam textured topsoil under continuous flooding. This could represent an important input of organic C into the subsoil particularly in coarse textured paddy soils where the plough pan does not act as a transport barrier for DOC between topsoil and subsoil (*c.f.* Wissing et al. 2011). Large vertical fluxes of DOC in rice paddies may strongly contribute to the formation of stable SOC in the deeper mineral horizons resulting in an increase in C stocks, as already postulated for oxic soils (Kalbitz and Kaiser 2008). However, the interaction of DOC with soil minerals and its subsequent stabilization against microbial mineralization (Eusterhues et al. 2014) could largely depend on soil redox conditions. Moreover, a significant proportion of this C flux (40-45%) occurred during the first month of rice cropping. Considering the variations in SUVA values with time, the distribution of C percolation fluxes over the cropping season could strongly influence the source and chemical composition of DOC reaching the subsoil, and consequently its retention on mineral surfaces.

Total DOC percolation was reduced by about 25% with the adoption of dry seeding (17.9-45.9 g C m^{-2}), and by 90% with intermittent irrigation (3.7-4.2 g C m^{-2}). This was in accordance with the findings of Xu et al. (2013) who observed a 46% decrease in DOC leaching under non-flooded, controlled irrigation (6.3 g C m^{-2}) with respect to continuous irrigation (11.8 g C m^{-2}). The relatively high flow-weighted concentrations >20 mg C l^{-1} observed during field flooding suggest that soil processes that led to the elevated DOC concentrations in topsoils under anoxic conditions, can also be responsible for important inputs of organic C to the subsoils. Significantly lower flow-weighted DOC concentrations were observed during the first month of dry seeded rice cropping, and throughout the season where intermittent irrigation was adopted. These results confirmed that the differences in DOC percolation we observed among treatments were not exclusively due to different water flows.

Substrate availability for methane production

Since both the production and oxidation of CH_4 are known to be influenced by oxygen availability (Conrad, 2002; Ma et al. 2013), water management is one of the most important factors influencing net CH_4 emissions from paddy fields (Neue, 1997). With respect to continuous flooding, dry seeding, and particularly, intermittent irrigation resulted in important reductions in net CH_4 emissions throughout the cropping season. This was in line with the findings of various authors (Tyagi et al. 2010; Yang et al. 2012; Ma et al. 2013; Liu et al. 2014) who showed that frequent field drainage during the cropping season could effectively mitigate CH_4 emissions by reducing the production and also enhancing the oxidation of CH_4.

Dissolved organic C may represent the primary carbon source for CH_4 production, leading to a strong positive correlation between the seasonal pattern of DOC concentrations and CH_4 emissions, particularly in the root zone (Lu et al. 2000). In fact, we observed strong correlations between DOC concentrations in the topsoil and CH_4 fluxes in the fields managed under continuous flooding and dry seeding (r = 0.607 and 0.395, respectively; $p < 0.001$), but not for the intermittent irrigation treatment where CH_4 emissions were often absent (Fig. 10b). Our findings suggest that under continuous flooding, the presence of a more readily mineralizable, residue-derived DOC pool was probably linked to a greater substrate availability for methane production, particularly at the beginning of the cropping season (Watanabe et al. 1999; Katoh et al. 2005). We do not, however, have substantial evidence to confirm that any positive feedback of residue-derived C on the release of presumably, less labile, soil-derived DOC could have led to a corresponding increase in CH_4 production as reported by Yuan et al. (2014). Nonetheless, maintaining aerobic soil conditions at the beginning of the cropping season with dry seeding may have led to a preferential mineralization of the more labile constituents of the incorporated crop residues before the onset of flooding, consequently resulting in a lower amount of CH_4 emitted per unit DOC (Fig. 10b).

Conclusions

Understanding how water management practices influence DOC cycling during the rice cropping season can provide important insights into the functions of this labile SOC pool in paddy soils. Our results confirm that the typically high DOC concentrations observed in paddy soils (>10-20 mg l^{-1}) are strongly linked to the reducing conditions resulting from field flooding. Adopting water regimes that maintain the soil under anoxic conditions from most of the cropping season, not only enhance CH_4 emissions, but also lead to important DOC fluxes with surface and subsurface waters. In particular, we showed that vertical fluxes of

DOC could be rather consistent, and together with the enhanced mobility of Fe^{2+} under reducing conditions, could possibly have important implications on C inputs and accumulation in the subsoil. However, as for CH_4 emissions, these fluxes are strongly dependent on water management.

The cycling of DOC in paddy soils is intimately linked to Fe cycling. In fact, our results indicated that the presence of important amounts of labile, residue-derived organic C in correspondence with field flooding may result in a positive feedback on the abiotic release of soil-derived DOC by promoting the microbially-driven reductive dissolution of Fe (hydr)oxides present in the soil. Moreover, the progressive release of soil-derived DOC under anoxic conditions, probably responsible for the increase in aromatic character during the cropping season, indicated that water management can also influence DOC quality with important implications on the chemical composition of DOC reaching the subsoil.

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Table 1 Basic properties of the soil horizons in the site

Horizon	Depth (cm)	Soil colour	Sand (g kg^{-1})	Silt (g kg^{-1})	Clay (g kg^{-1})	Texture class[a]	pH_{H_2O}	pH_{KCl}	CEC[b] ($cmol_{(+)}$ kg^{-1})	OC[c] (g kg^{-1})	N_t[d] (g kg^{-1})	Fe_o[e] (g kg^{-1})	Fe_d[f] (g kg^{-1})	Fe_o/Fe_d	Mn_o[e] (g kg^{-1})	Mn_d[f] (g kg^{-1})	Bulk density (g cm^{-3})
Apg1	0–30	5Y4/1	405	477	118	L	5.9	4.4	10.2	9.5	0.83	3.55	9.40	0.38	0.07	0.08	1.44
Apg2	30–40	5Y4/1	387	513	100	SiL	6.6	5.0	11.1	7.1	0.66	3.11	10.18	0.31	0.10	0.13	1.47
ABg	40–55	5Y3/1	309	554	137	SiL	6.6	4.9	17.1	14.3	1.29	2.60	5.30	0.49	0.08	0.12	1.30
Ab1	55–70	10YR3/2	327	562	111	SiL	6.3	4.9	17.8	20.6	1.78	3.09	5.42	0.57	0.10	0.13	0.97
Ab2	70–90	1.25Y3.5/2	333	574	93	SiL	6.3	5.0	16.6	13.8	1.19	3.62	5.18	0.70	0.13	0.13	1.10
Bwgb	90–130	5Y5/1.5	279	558	163	SiL	6.5	4.6	11.0	2.6	0.19	6.81	30.53	0.22	0.28	0.53	1.51
CBgb	130–200	5Y5/2	155	652	193	SiL	6.7	4.3	17.8	1.0	0.10	3.29	13.90	0.24	0.12	0.18	n.d.
2C	>200	2.5Y5.5/2	445	488	67	SL	6.7	4.4	9.1	0.3	0.10	0.80	4.43	0.18	0.05	0.05	n.d.

n.d. not determined

[a] Texture: L, loam; SiL, silty loam; SL, sandy loam

[b] Cation exchange capacity

[c] Organic carbon

[d] Total nitrogen

[e] NH_4-oxalate-extractable Fe and Mn

[f] Dithionite-citrate-bicarbonate extractable Fe and Mn

Table 2 Mean DOC concentrations and specific UV absorbance (SUVA) values for inflow and outflow waters from the three water management practices.

	n	DOC (mg C l^{-1})	SUVA (l mg^{-1} m^{-1})
Inflow	56	5.1 b	2.10
Outflow WFL	88	7.0 a	1.87
Outflow DFL	67	6.3 a	2.04
Outflow DIR	128	6.4 a	2.20

Values represent the mean of *n* measurements over two cropping seasons. Different letters indicate a significant difference between inflow and outflow waters (One-way ANOVA, Bonferroni post-hoc test $p < 0.05$)

Table 3 Cumulative DOC fluxes and flow-weighted DOC concentrations in inflow, outflow and percolation waters over the two cropping seasons as a function of water management practices

	DOC flux (g C m^{-2})			Flow-weighted DOC (mg C l^{-1})		
	WFL	DFL	DIR	WFL	DFL	DIR
2012 cropping season						
Inflow[a]	46.3	40.5	4.8	4.8	4.7	4.6
Outflow[a]	44.3 a	35.6 a	2.4 b	6.4	5.6	5.8
Percolation[a]	51.1 a	45.9 a	3.7 b	20.8 a	25.2 a	12.1 b
0–30 DAS[c]	19.7 a	0.7 b	0.5 b	19.1 a	13.7 b	13.8 b
31–60 DAS	11.9 a	16.7 a	1.6 b	21.4 a	20.3 a	11.9 b
61–90 DAS	12.3 a	14.1 a	0.8 b	21.7 ab	28.3 a	12.0 b
91–120 DAS	7.2 b	14.5 a	0.7 c	23.6 a	30.6 a	10.9 b
2013 cropping season						
Inflow[b]	21.6	17.5	6.9	5.0	5.1	5.0
Outflow[b]	18.1 a	13.7 b	4.1 c	6.5	6.3	6.3
Percolation[b]	32.6 a	17.9 b	4.2 c	27.0 a	18.5 b	9.7 c
0–30 DAS[c]	14.6 a	0.4 b	0.1 b	32.8 a	1.8 b	1.4 b
31–60 DAS	5.8 a	2.8 b	2.1 b	26.5 a	15.5 b	14.4 b
61–90 DAS	7.0 a	8.4 a	1.1 b	20.3 a	24.0 a	8.1 b
91–120 DAS	4.1 a	5.7 a	0.7 b	30.8 a	32.7 a	7.4 b

Values represent the mean of outflow ($n = 2$) and percolation ($n = 4$) fluxes and respective flow-weighted DOC concentrations, while only single determinations were possible for inflow values. For each cropping season, different letters indicate a significant difference between treatments (One-way ANOVA, Bonferroni post-hoc test $p < 0.05$).

[a] Calculated over entire cropping period (between 15/05/12 and 28/09/12)

[b] Calculated over entire cropping period (between 28/05/13 and 15/10/13)

[c] 30-day cumulative data for percolation flows; DAS, days after seeding

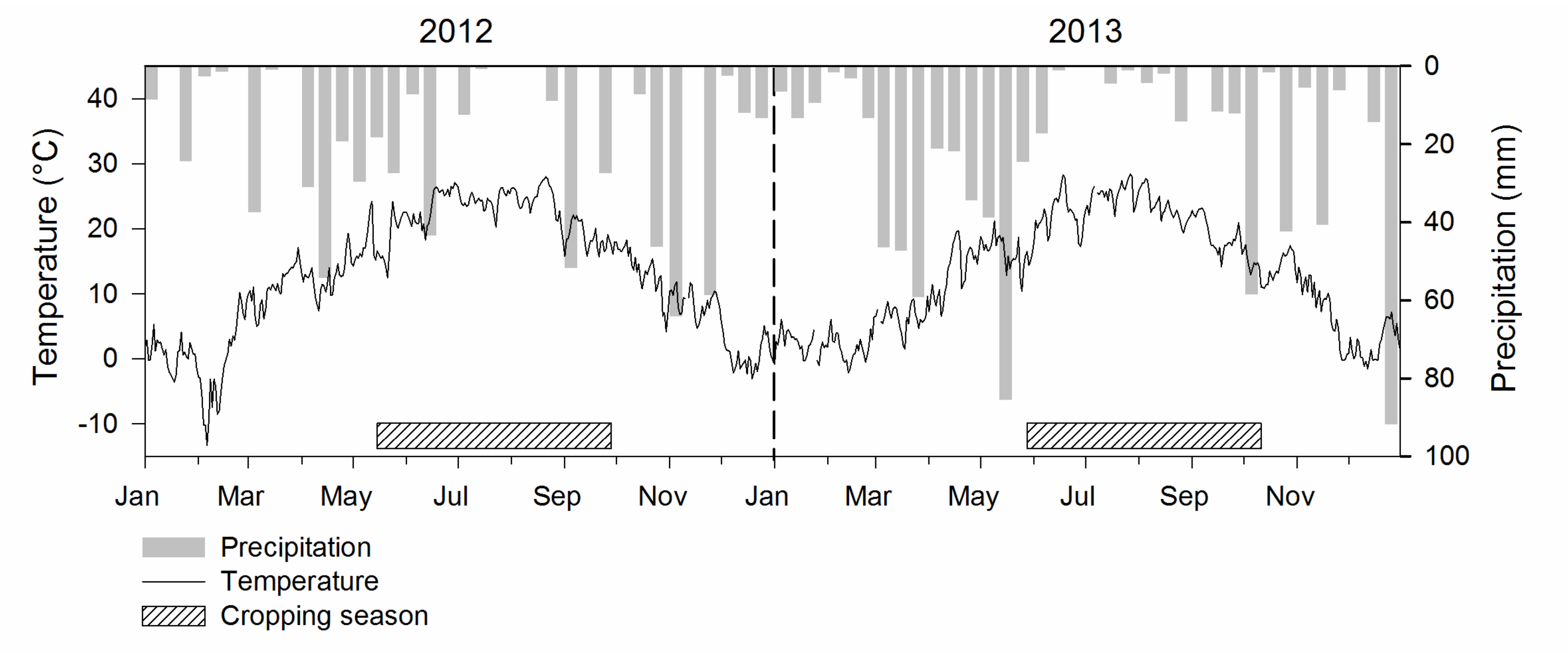

Fig. 1 Variations in mean daily air temperatures and cumulative precipitation (over 10 consecutive day periods) during the experimental period

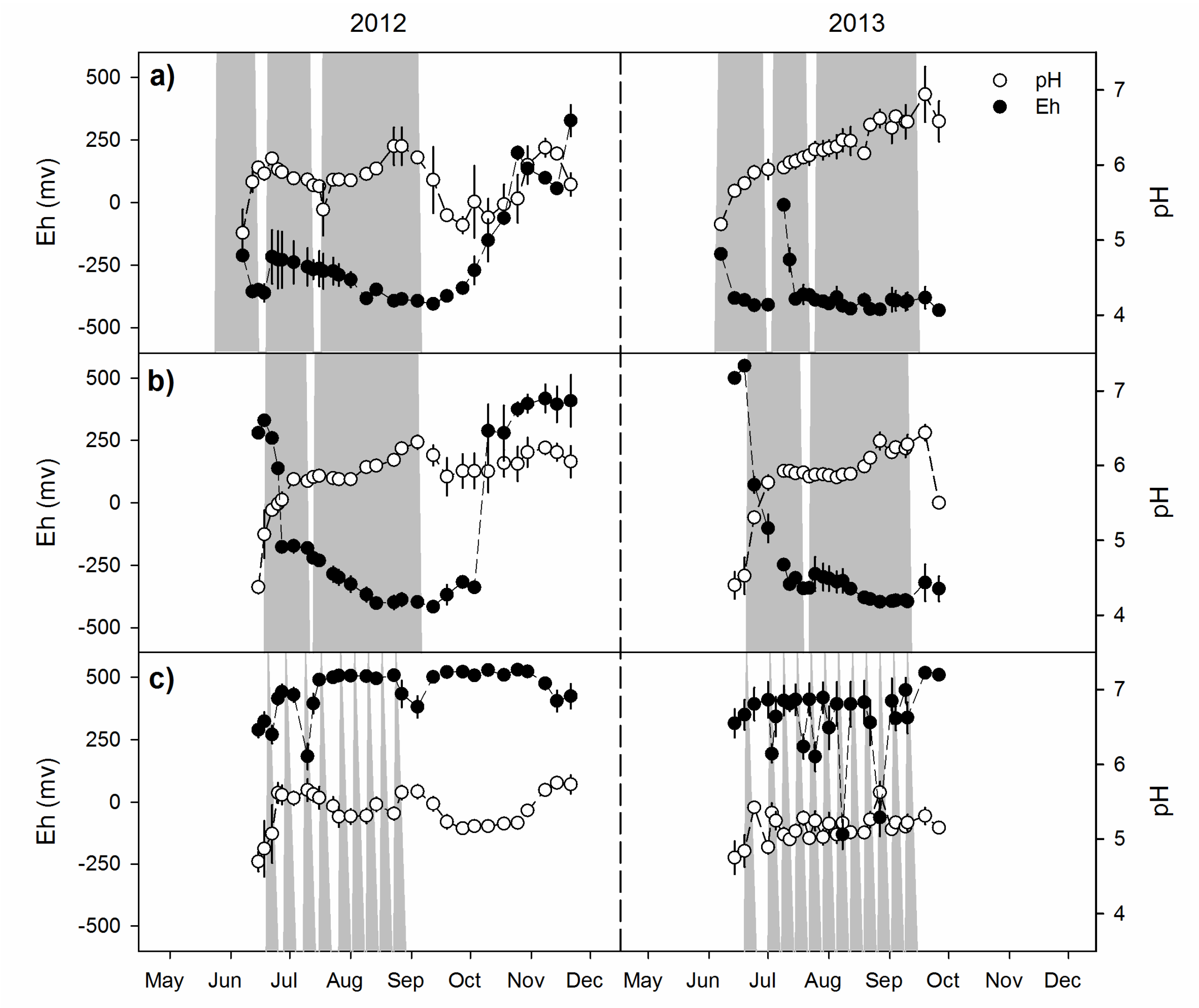

Fig. 2 Variations in topsoil pH (open symbols) and Eh (closed symbols) values over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Shaded areas represent the presence of flood water. Error bars represent the standard error of replicated measurements (n = 3)

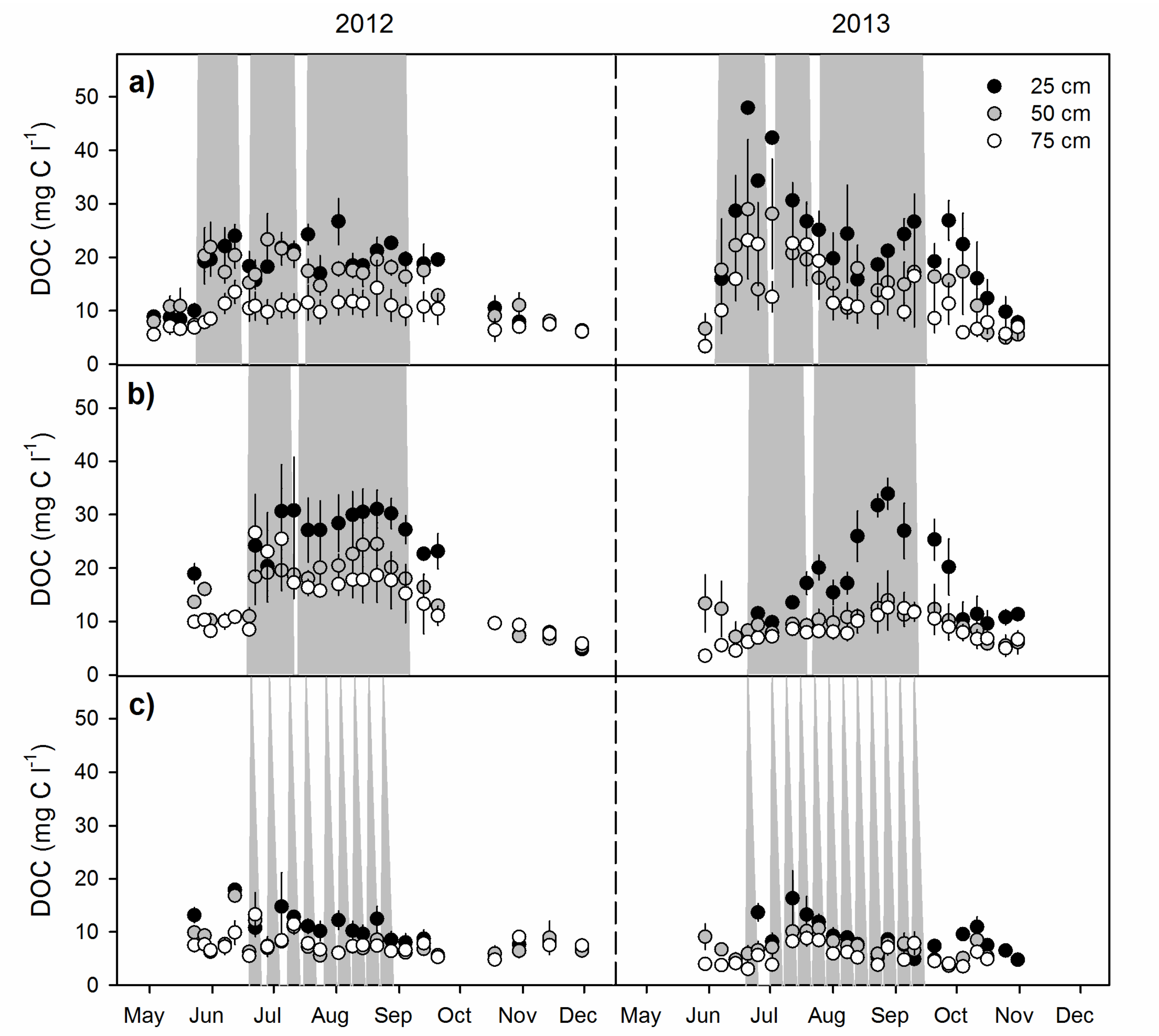

Fig. 3 Variations in DOC concentrations at different depths over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Shaded areas represent the presence of flood water. Error bars represent the standard error of replicated measurements (n = 4). The effects of water management, sampling date and depth, as well as water management × date, and water management × depth interactions, on DOC concentrations analysed by ANOVA for both years were all significant (p = 0.000)

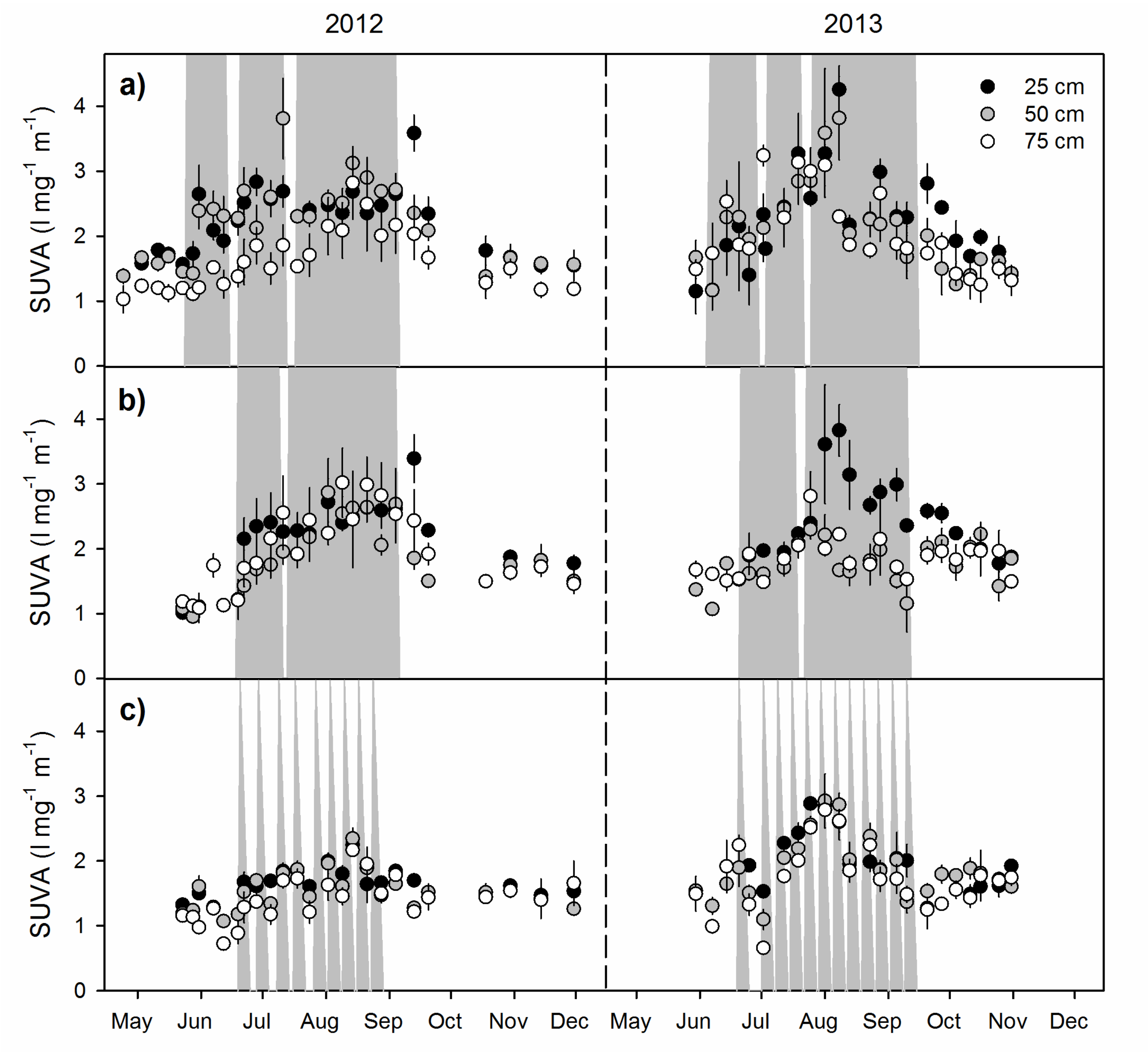

Fig. 4 Variations in soil solution specific UV absorbance (SUVA) values at different depths over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Shaded areas represent the presence of flood water. Error bars represent the standard error of replicated measurements (n = 4). The effects of water management, sampling date and depth, as well as water management × date, and water management × depth interactions, on SUVA analysed by ANOVA for both years were all significant (p = 0.000)

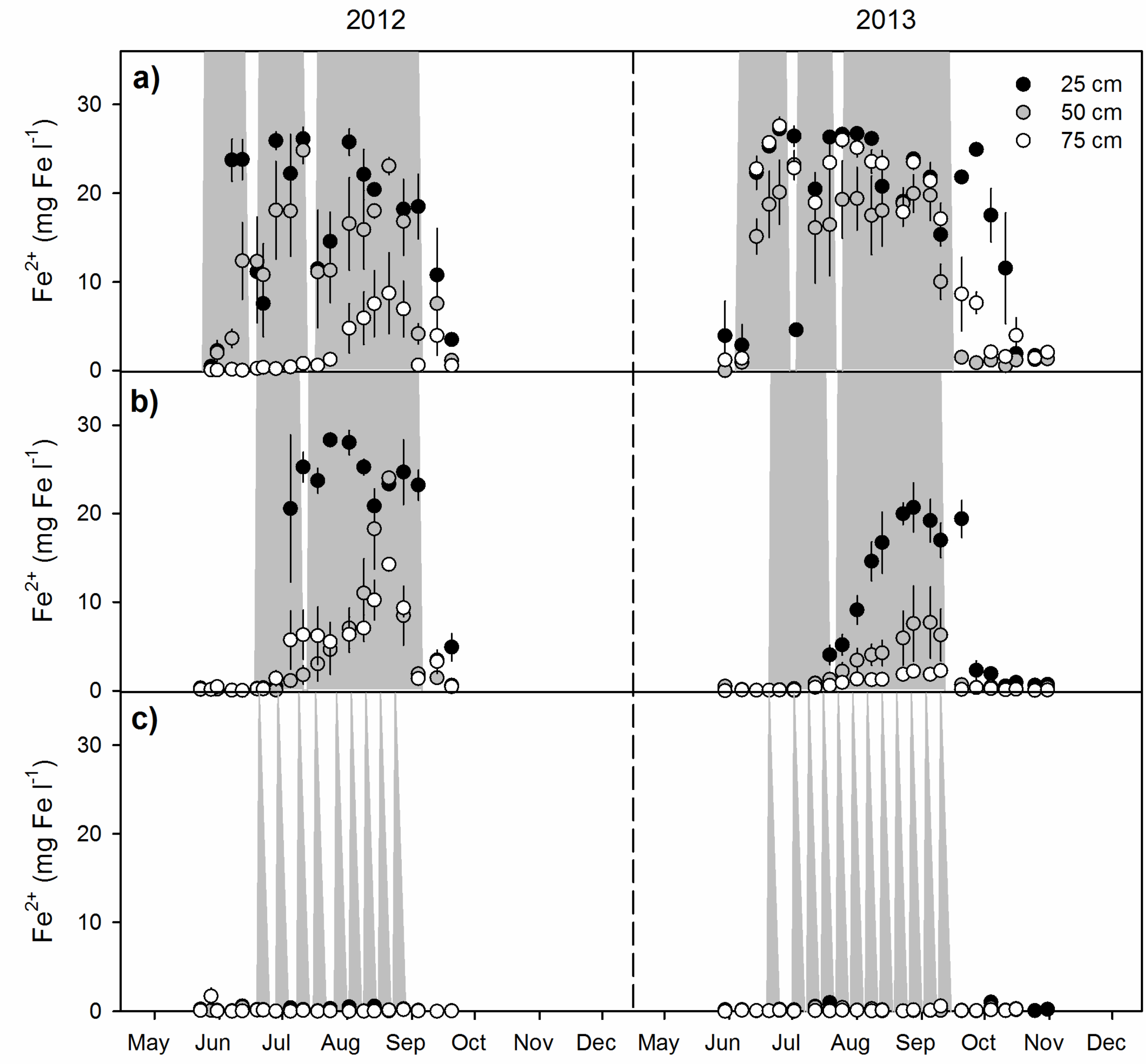

Fig. 5 Variations in soil solution Fe^{2+} concentrations at different depths over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Shaded areas represent the presence of flood water. Error bars represent the standard error of replicated measurements (n = 4). The effects of water management, sampling date and depth, as well as water management × date, and water management × depth interactions, on Fe^{2+} concentrations analysed by ANOVA for both years were all significant (p = 0.000)

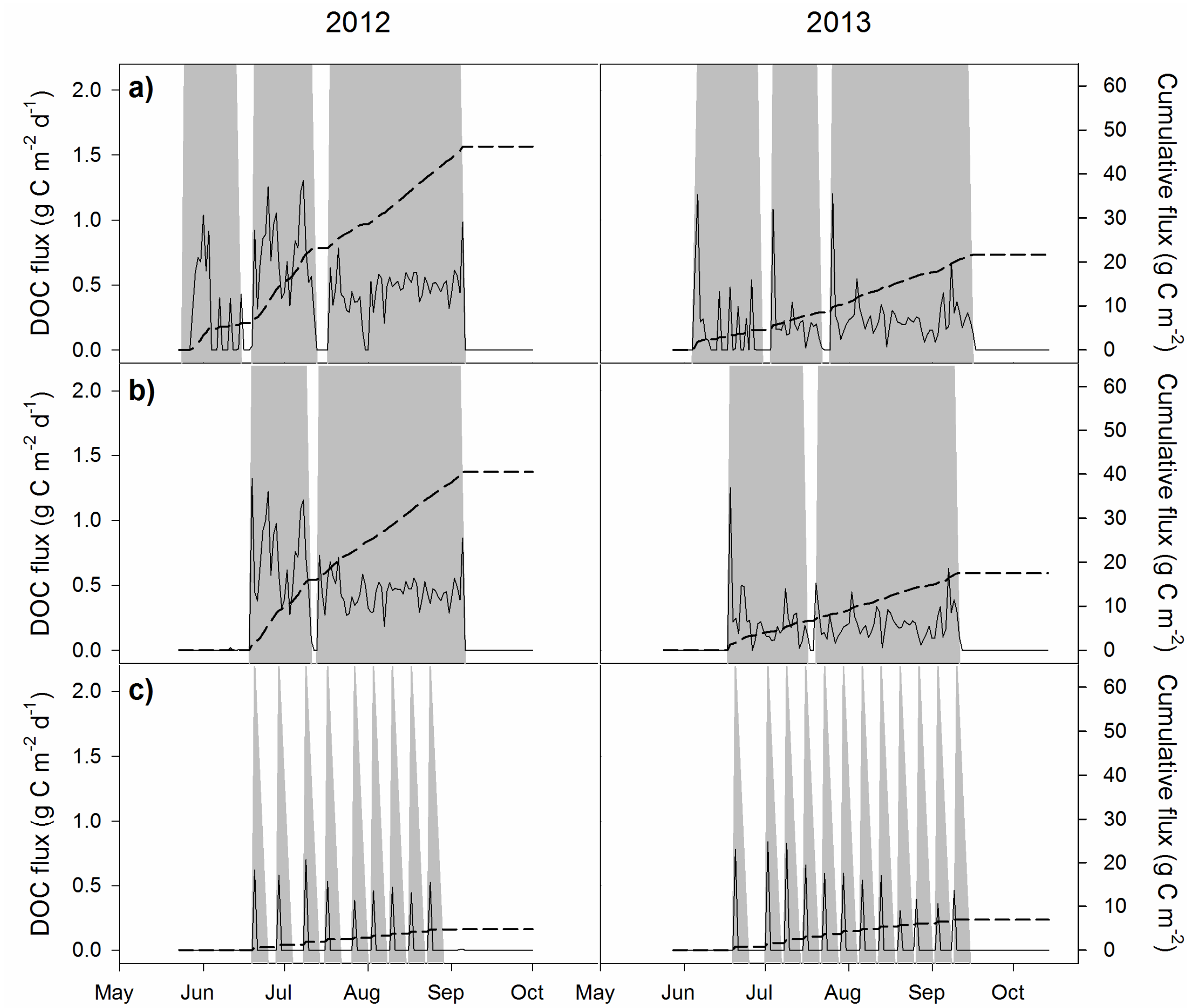

Fig. 6 Variations in estimated DOC inflow fluxes from supply canals over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Dashed line represents cumulative fluxes over the cropping season, while shaded areas represent the presence of flood water

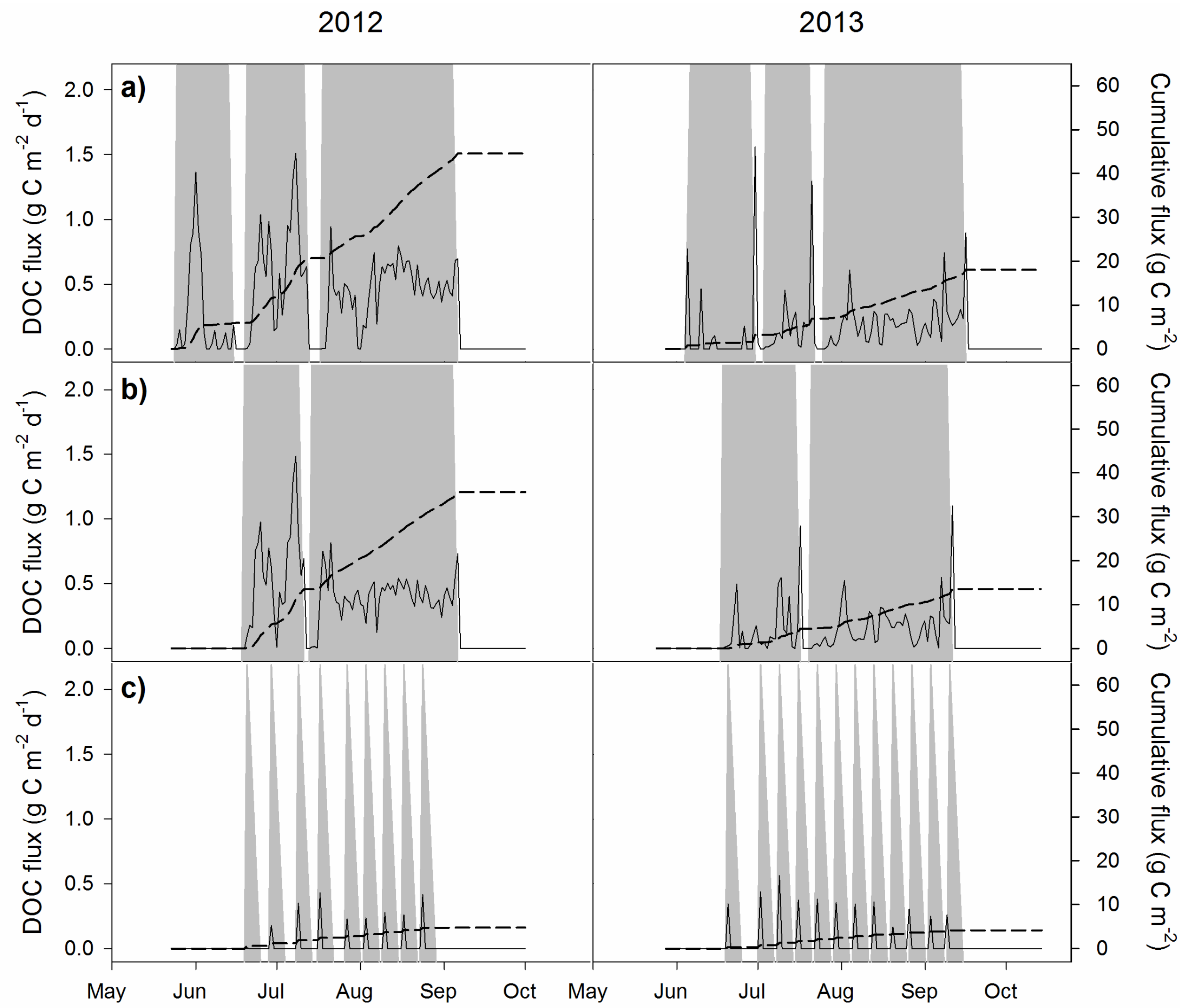

Fig. 7 Variations in estimated DOC outflow fluxes from drainage canals over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Dashed line represents cumulative fluxes over the cropping season, while shaded areas represent the presence of flood water

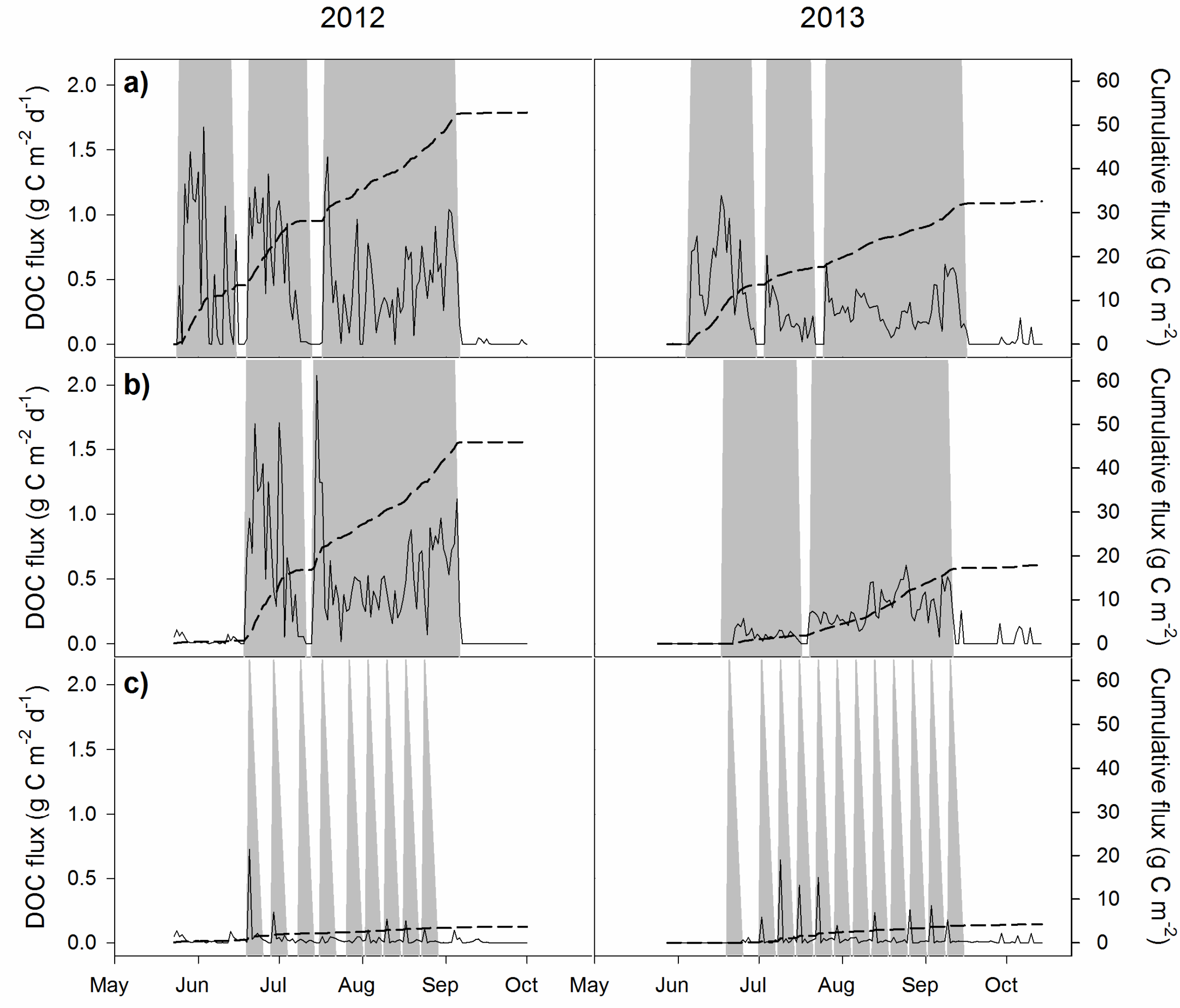

Fig. 8 Variations in estimated DOC percolation fluxes (at 25 cm) over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Dashed line represents cumulative fluxes over the cropping season, while shaded areas represent the presence of flood water

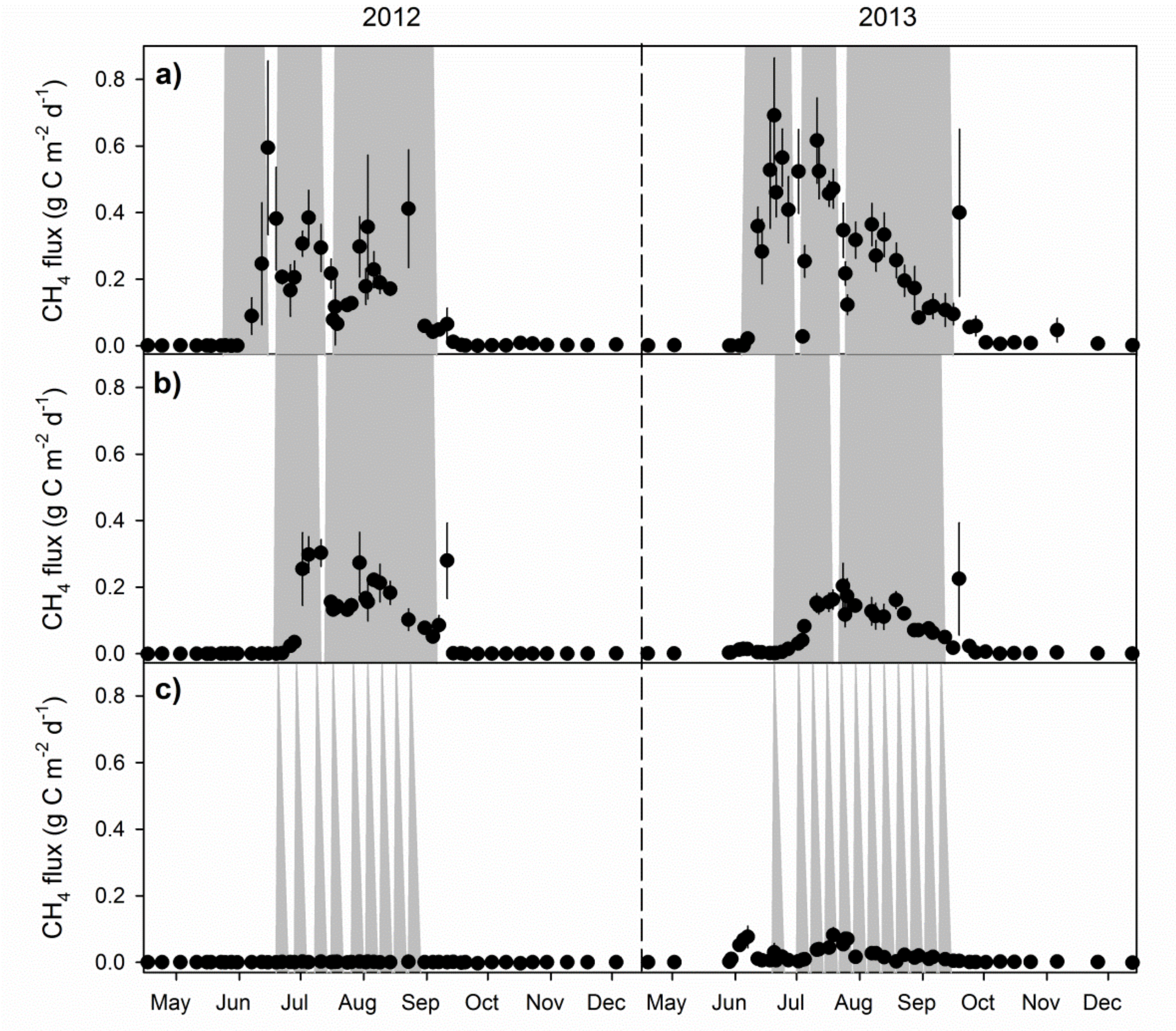

Fig. 9 Variations in net CH_4 emission fluxes over two rice cropping seasons as a function of water management practices involving (a) water seeding and continuous flooding (WFL), (b) dry seeding and flooding at tillering stage (DFL), and (c) dry seeding and intermittent irrigation (DIR). Shaded areas represent the presence of flood water. Error bars represent the standard error of replicated measurements (*n* = 4). The effects of water management and sampling date, as well as their interaction, on net CH_4 emission fluxes analysed by ANOVA for both years were all significant ($p = 0.000$)

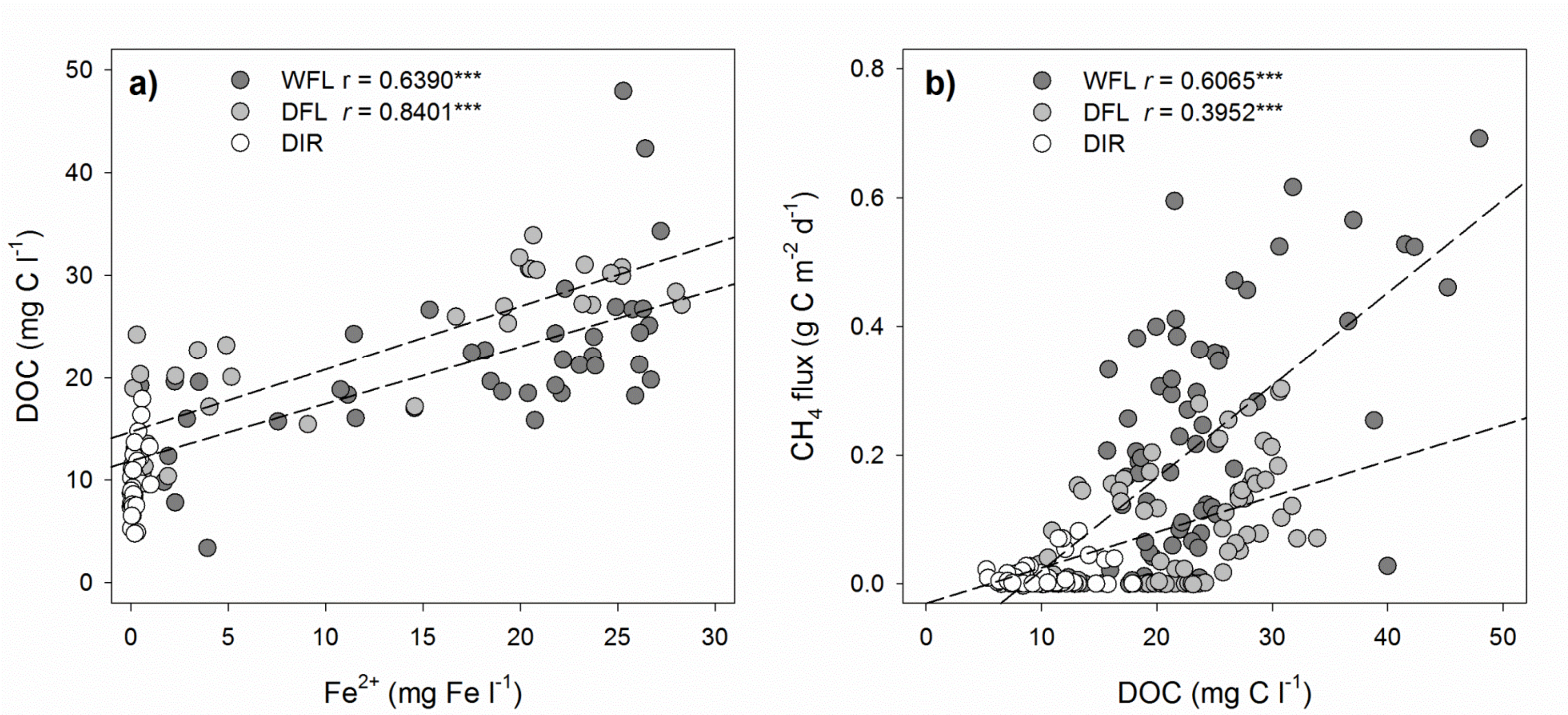

Fig. 10 Correlations between topsoil DOC concentrations, and (a) Fe^{2+} concentrations or (b) CH_4 fluxes for the three water management practices