Seasonal trends and environmental controls of methane emissions in a rice paddy field in Northern Italy

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Abstract

Rice paddy fields are one of the greatest anthropogenic sources of methane (CH$_4$), the third most important greenhouse gas after water vapour and carbon dioxide. In agricultural fields, CH$_4$ is usually measured with the closed chamber technique, resulting in discontinuous series of measurements performed over a limited area, that generally do not provide sufficient information on the short-term variation of the fluxes. On the contrary, aerodynamic techniques have been rarely applied for the measurement of CH$_4$ fluxes in rice paddy fields. The eddy covariance (EC) technique provides integrated continuous measurements over a large area and may increase our understanding of the underlying processes and diurnal and seasonal pattern of CH$_4$ emissions in this ecosystem.

For this purpose a Fast Methane Analyzer (Los Gatos Research Ltd.) was installed in an eddy-covariance field set-up in a rice paddy field in the Po Valley (Northern Italy). Methane fluxes were measured during the rice growing season, both with EC and with manually operated closed chambers. Methane fluxes were strongly influenced by the presence of the water table, with emissions peaking when it was above 10–12 cm. Further studies are required to evaluate if water table management could decrease CH$_4$ emissions. The development of rice plants and soil temperature were also responsible of the seasonal variation on the fluxes. The EC measured showed a diurnal cycle in the emissions, which was more relevant during the vegetative period, and with CH$_4$ emissions being higher in the late evening, possibly associated with higher water temperature. The comparison between both measurement techniques shows that greater fluxes are measured with the chambers, especially when higher fluxes are being produced, resulting in 30 % higher seasonal estimations with the chambers than with the EC (41.1 and 31.8 g CH$_4$ m$^{-2}$ measured with chambers and EC respectively). The differences may be a result of the combined effect of overestimation with the chambers, the possible underestimation by the EC technique and of not having considered the daily course of the fluxes for the calculation of seasonal emissions from chambers.
1 Introduction

Methane (CH$_4$) is the third most important greenhouse gas after water vapour and carbon dioxide. Atmospheric CH$_4$ concentration has been increasing during the last several hundred years due to changes in agricultural practices and other anthropogenic activities (Dlugokencky et al., 1994; Etheridge et al., 1998; Ferretti et al., 2005). Recent studies have shown that, if the effect of aerosols is also taken into account, the relative contribution of CH$_4$ to climate change is greater than what was previously estimated by the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report (AR4) (Shindell et al., 2009).

Rice paddy fields are one of the largest anthropogenic sources of CH$_4$. Irrigated rice fields are estimated to contribute between 6% and 8% (Cole et al., 1995) of the total methane emission emitted globally (Houghton et al., 1995) as they release large amounts of CH$_4$ and the land surface dedicated to rice cultivation is very large, mainly in Asia, but also in Mediterranean regions in Europe (IPCC, 2003). Italy is the largest rice producer in Europe (FAO, 2002) and this production is concentrated in the Po Valley (Ferrero, 2007), where this study took place.

Methane in rice paddy fields is emitted through different pathways: plant-mediated transport through the aerenchymal system of rice plants is responsible for 90% of the emission (Cicerone and Shetter, 1981; Holzapfel-Pschorn and Seiler, 1986; Schütz et al., 1989), 8% of CH$_4$ is released through bubbles and 2% comes from the diffusion through the water column. Field experiments have shown that there is a large variability on CH$_4$ emissions from rice fields, both spatially, with variability between different fields, and temporal, with seasonal and diurnal variation (Holzapfel-Pschorn and Seiler, 1986; Schfitz et al., 1989; Sass et al., 1991). This large spatio-temporal variability largely limits the possibility to produce robust estimates of yearly surface budgets. Further studies are therefore required to evaluate alternative methodologies that may guarantee the appropriate temporal and spatial data coverage and therefore reduce the uncertainty in the estimation of emissions and improve our understanding of the biogeochemical processes involved in CH$_4$ production.
In agricultural fields, CH$_4$ is usually measured with the closed chamber technique, resulting in discontinuous series of measurements performed over a limited area, that generally do not provide sufficient information on the short-term variation of the fluxes. Moreover, these samples are subject to uncertainties associated with the use of chambers (Mosier, 1990), which may interfere with the production and transport of the gas studied. However, closed chambers have the advantage of detecting low fluxes, of being easy to manipulate and of low cost. Therefore, this technique has commonly being used to estimate CH$_4$ emissions, and has already been used in rice paddy fields (Holzapfel-Pschorr and Seiler, 1986).

Alternatively, the aerodynamic technique of eddy covariance (EC) provides continuous measurements, without interfering in the processes of gas exchange between the sources and the atmosphere. This technique is commonly used for the estimation of CO$_2$ and H$_2$O and energy fluxes, but its use for the measurement of CH$_4$ fluxes is less common, as adequate analyzers have recently became available.

The EC technique provides integrated continuous measurements over a large area and may increase our understanding of the underlying processes and the seasonal and diurnal pattern of CH$_4$ emissions in a certain ecosystem. Some studies have already been carried out with this technique, showing that it is adequate for the estimation of CH$_4$ fluxes (Hendriks et al., 2008, 2009; Kroon et al., 2009; Long et al., 2010; Schrier-Uijl et al., 2010; Baldocchi et al., 2011; Detto et al., 2011; Herbst et al., 2011). However, the EC technique has rarely been used to measure CH$_4$ emissions from rice paddy fields (Detto et al., 2011).

Comparison of eddy covariance and chamber-based methods have previously been made for net ecosystem exchange of CO$_2$ (balance between respiratory and assimilatory processes) (Wang et al., 2010), pointing that further studies are required. Schrier-Uijl et al. (2010) compared CH$_4$ fluxes measured with both methods in a peat-land and concluded that fluxes were comparable when all the landscape elements involved in the EC flux were considered in the scaling up from chamber measurements. In this study we carried out a similar comparison, using eddy covariance and chamber-based
methods to measure CH$_4$ fluxes in a rice paddy field. The objectives of our study were to:

1. Compare the eddy covariance technique and closed-chamber-based method for estimating CH$_4$ fluxes in this ecosystem;

2. Identify the environmental drivers and the diurnal and seasonal patterns of CH$_4$ fluxes in a rice paddy field; and

3. Evaluate the differences in the CH$_4$ surface budgets produced with the two techniques and quantify the CH$_4$ emissions from a rice paddy field in northern Italy.

2 Materials and methods

2.1 Study site

The study site is located in an agricultural field located in the Po Valley, in Northern Italy, in the municipality of Torre Beretti and Castellaro (Pavia) (45°04′12.17″ N, 8°43′03.08″ E, 88 m a.s.l.). The site extends for 400 × 700 m and it is part of a farm which cultivates rice and corn for silage in 700 ha of irrigated land.

The study was carried out in 2009, when the site was cultivated with rice (Oryza sativa var. Selenio). Prior to initiation of the study, the site was cultivated with maize (Zea mais) in 2006 and with rice since 2007.

The soil is a Calcic Gleysol (FAO, 1998), with a loam to clay-loam texture. In 2009 the annual rainfall was 658 mm and the mean annual temperature 12.9°C. The field was flooded on day 104 (mid April), and a first sowing took place on day 107. The sowing was not successful so the soil was dried, tilled, and re-sowed at the end of April (day 120). Sowing was carried out in water with a centrifuge sowing machine. Then the water was removed to allow for the seeds to get to the soil and germinate. Once plants had germinated, the field was re-flooded (early June, day 160) and water
was kept during the rest of the growing season. A total of 131 \( (61 + 70) \) kg N ha\(^{-1} \) were applied as fertilizer in 2 different events, on days 91 and 183 (beginning of April and beginning of July), as N-P-K (30-0-30) and urea respectively. The standing water level fluctuated during the flooded periods due to the continuous water flow through the rice field, a typical management practice for this crop. At the beginning of September the water was removed from the field, and the rice was harvested on day 265 (end of September).

### 2.2 Chamber flux measurements

Manually operated closed chambers were used for the measurement of CH\(_4\) fluxes from the soil. In order to cover for spatial variability, the measured fluxes were calculated from the average of 8 different chambers distributed along the field. Stainless steel rings were inserted 5 cm into the soil at the beginning of the experiment. They were removed and reinstalled for the fertilization events and were then kept in place throughout the experimental period. The chambers consisted of a Plexiglass cylindrical structure (15 or 30 cm height) covered with a Teflon film (50 µm). These Plexiglass structures were fitted to the stainless steel rings, to avoid soil disturbance. The chamber surface was 0.11 m\(^2\) while the volume was modified during growing season, according to the growing of rice plants of each plot, by adding 15 or 30 cm height Plexiglas rings on top of those fitted to the stainless steel rings. The chambers were closed during the sampling period with Plexiglas lids. A syringe was fitted to the Plexiglas structure in order to remove the samples.

To estimate CH\(_4\) fluxes, 4 different samples were taken during the 60 to 90 min when the chambers were closed, the first one after chamber closure, second and third at regular intervals during chamber closure and the fourth at the end of the sampling period. 100 ml samples were removed from each chamber with a syringe, and were then transferred into 20 ml glass vials, flushing the sample through the vial with 2 needles. Temperature in the chamber headspace during all closure time was measured with an
electronic temperature sensor (Greisinger, GTH 175/MO) and recorded when samples were removed. Air samples were collected every 5–7 days in the periods when the rice was flooded, and every 2–4 weeks during the rest of the experimental period, from the 3 April until 9 December. Samples were always taken around 12 pm.

Methane concentration in the vials was then measured by gas chromatography (GC) with a Shimadzu GC 14B equipped with a packed column Porapak Q and a Flame Ionization Detector (FID). The GC was configured to allow for the simultaneous measurement of $N_2O$, so it was also equipped with an electron capture detector installed in line with the FID. The temperatures of the injector, oven and detector were 100, 40 and 340 °C respectively. Samples were automatically injected into the GC as reported in Leip (2000).

Methane fluxes were calculated from the rate of the change in the chambers headspace during the 60 to 90 min of closure. This was estimated as the slope of the linear regression between concentration (after corrections for temperature using the ideal gas law in order to compensate for the increases of temperature headspace during chamber closure) and time and from the ratio between chamber volume and soil surface area (MacKenzie et al., 1998). Only those chambers where there was a linear relation ($r^2 > 0.75$) for at least 3 of the sampling points were used for the calculation of the fluxes. Cumulative $CH_4$ fluxes measured with the chambers were estimated by linear interpolations between sampling dates.

### 2.3 Eddy covariance flux measurements

Methane fluxes were measured from the 9 April to 31 December 2009 using the EC technique (Baldocchi et al., 1988, 1996). The three components of the wind vector were measured by a Gill HS-100 ultrasonic research anemometer (GILL Instruments Limited, Hampshire, UK) positioned at a height of 2.2 m above soil surface. Methane mixing ratio was measured by a RMT-200 fast methane analyzer (FMA) from Los Gatos Research Ltd. In order to obtain a response time of 0.2 s, the FMA was operated in high flow mode by connecting the outlet of the analyzer to a dry scroll pump (Edwards XDS 9005).
In addition to the internal filter from the FMA, a second filter with the same pore size (2 µm) was placed at the sampling point close to the anemometer head in order to prevent dust, aerosols, insects and droplets from entering the tubing. Analogue outputs from the FMA were digitally converted, coupled with wind speed measurements and logged on a portable computer. Carbon dioxide and water vapour concentrations were measured by a close path infrared gas analyzer, (Li-6262, LI-COR Lincoln, NE, USA) with a response time of 0.2 s for CO\textsubscript{2} and 0.3 s for H\textsubscript{2}O. The EC set-up formed by the anemometer and CO\textsubscript{2}/H\textsubscript{2}O analyzer has been running since July 2006 and is further described in Rossini et al. (2010).

A three rotations scheme was applied to each turbulent averaging period following Mc Millen (1988) in order to place the anemometer into a streamwise coordinate system. Covariances between wind velocity components and concentrations were calculated with a time step of 30 min using a linear detrending algorithm (Gash and Culf, 1996). The time lag required to draw air from the sampling point to the analyzer was determined by maximizing the correlation between vertical wind speed and concentrations (Goulden et al., 1996). The average time lag for CH\textsubscript{4} was 1 s but in some short periods it increased because of the dust accumulated in the internal filter. Frequency response losses were corrected using empirical transfer functions, as described in Aubinet et al. (2000). Finally, a storage term was added to the calculated CH\textsubscript{4} fluxes for the determination of net ecosystem fluxes, calculated as difference between CH\textsubscript{4} concentrations in two consecutive half hour periods.

Methane fluxes have been corrected according to the Webb-Pearman-Leuning (WPL) theory to compensate for the air density fluctuation arising from heat and water vapour fluxes. Temperature fluctuations were assumed negligible, while fluctuations of water vapour were estimated with the frequency corrected water fluxes measured by the Li-6262. The attenuation of atmospheric water fluxes in the FMA set-up was estimated assuming that these fluxes undergo the same spectral attenuation of the WPL-uncorrected methane fluxes. We estimated the spectral attenuation for CH\textsubscript{4} and H\textsubscript{2}O flux by the empirical method described in Aubinet et
This method assumes that the heat flux measured by the anemometer is free from frequency losses. For this purpose the ratio between the cospectrum of heat flux and the cospectrum of a second scalar flux (as CH$_4$ flux) is used to estimate the transfer function that corrects the fluxes for the underestimation due to spectral attenuation.

A flux footprint analysis was carried out at the site by Rossini et al. (2010) for the EC measurements of CO$_2$ and water vapour fluxes. The study indicated that more than 80% of the measured scalar flux originates from the target rice field and is therefore representative of the study area.

Two tests were performed in order to evaluate the overall quality of eddy covariance fluxes: integral turbulence test and steady state test (Foken and Wichura, 1996). Results from both tests were combined in order to get an overall quality flag for each half-hour period. Three categories were established and data belonging to class 2 (steady state deviation >100% or integral turbulence characteristics >100%), were discarded.

Data were also filtered according to friction velocity ($u^*$) to avoid the possible underestimation of fluxes in stable atmospheric conditions. The critical $u^*$ threshold was set to 0.045 m s$^{-1}$ according to Rossini et al. (2010). In addition, data were filtered on the basis of the pressure inside the measurement cell of the FMA in order to exclude periods when filter clogging increased the lag time. The pressure threshold was set at 110 Torr in order to maintain the response time at 0.2 s. Finally data were smoothed using a 2 h moving window filter to reduce data inherent noise (Damm et al., 2010).

Data series have been gap-filled following the look-up table (LUT) method in accordance with Falge et al. (2001), and considering both the co-variation of fluxes with meteorological drivers and the mean diurnal variation. The LUT was created using environmental variables which showed the highest correlations with fluxes (soil and air temperature and depth of the water table) as well as some other considered relevant, such as radiation and rainfall.
2.4 Environmental variables

Meteorological variables were measured every 30 s and then averaged and stored as half-hour mean value. Photosynthetic photon flux density (PPFD) was measured by means of a quantum sensor (LI-190, LI-COR Inc.) and sunshine sensor (BF3, Delta T) and air temperature (Tair) was measured with a shielded thermo hygrometer (model RFT-2, UMS, Munich, Germany). Net radiation was measured by a radiometer (model CNR1, Kipp and Zonen; Delft, The Netherlands) at 3.5 m above ground and the heat flux into the soil by a heat flux plate (model HFP01, Hukseflux; Delft, The Netherlands) installed 4 cm below ground. Soil heat storage between soil surface and the heat flux plate sensor depth was estimated with a temperature profile (3.5, 7.5 and 15 cm) of UMS-Th2-h and assuming a volumetric heat capacity of $2.99 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ for wet soil (Hillel, 1982).

The depth of the soil water table was monitored with a Baro Diver (Schlumberger Water Services) and derived from the pressure at 110 cm below the soil surface minus the pressure at the soil surface. Soil water content was measured with a TDR (TRIME-EZ, IMKO) installed at a depth of 16 cm. Both measurements were recorded every 30 min.

2.5 Canopy structural parameters

Rice phenology was assessed during the development of the crop in 5 fixed sampling plots close to the EC flux tower. Rice phenology was evaluated according to the extended BBCH (Biologische Bundesanstalt, Bundessortenamt and Chemical industry) scale (Lancashire et al., 1991; Meier, 1997) based on Zadok et al. (1974) cereal code, on 5 plants from each sampling plot. The BBCH growth stages were grouped into three basic growth phases of the rice plant: vegetative (from germination to panicle initiation), reproductive (from panicle initiation to flowering) and ripening (from flowering to senescence). The dominant phenological phase at the five sampling plots was considered representative of the whole rice field.
The phenological phases were used to divide the temporal series of CH$_4$ fluxes into 5 data sets: before rice was sown (days 97 to 120), vegetative (days 121 to 165), reproductive (days 166 to 207), ripening (days 208 to 264) and after rice harvest (265 to 365).

2.6 Statistical analysis

Statistical analysis and data filtering were carried out with Statistica v8. Linear regression analyses ($P < 0.05$) were performed to determine relationships between CH$_4$ emissions with the measured environmental variables both with Statistica v8 and SigmaPlot 10.0. The statistical significance of the differences between the cumulative emissions measured with different techniques was tested by the analysis of variance (ANOVA, $P < 0.05$). Comparison of data obtained with both methods was also carried out by linear regressions (fluxes measured with chambers against average of fluxes measured with EC during the period when chamber measurements were taken) and by the Bland-Altman method (Altman and Bland, 1983).

3 Results

3.1 Environmental conditions and CH$_4$ fluxes from the rice field

During the experiment large variations on daily average air temperature were observed, with values ranging from 10 to 15°C in April, increasing up to 26°C in August and then decreasing until −7°C at the end of December (Fig. 1a). A similar pattern was observed in the daily average soil temperature (Fig. 1b), with minimum temperatures always above 1.5°C and maxima reaching 27°C. Soil temperatures are strictly coupled with air temperatures, except when major changes in the level of the water table are occurring (e.g. on day 104 the first flooding decreased soil temperature).

Soil was water logged (soil water content at about 60 %) during most of the observation period (Fig. 2a). Water table depth measurements started at the beginning of June (Fig. 2b). From that moment, the water table increased, reaching a maximum
of 21 cm in mid August (day 225). The water level started to decrease in coincidence with the second half of the ripening period, until early September when the soil was no longer submerged (day 250). Subsequent increases of water table depth were a consequence of intense rainfall and not of flooding.

Methane half-hour fluxes varied largely along the experimental period (Fig. 3). CH$_4$ emissions were very low (on average 0.23 µmol CH$_4$ m$^{-2}$ s$^{-1}$) until the end of May, with net CH$_4$ oxidation taking place at certain moments during this first period. When the field was flooded and the rice sown (day 120), emissions started to increase. The highest half-hourly emissions were measured in July and August, in the vegetative and ripening periods (maximums of 0.98 and 0.72 µmol CH$_4$ m$^{-2}$ s$^{-1}$ respectively). At the end of August emissions decreased and remained very low (between −0.02 and 0.12 µmol CH$_4$ m$^{-2}$ s$^{-1}$) during the rest of the year. Analysis of variance indicated statistically significant differences in the fluxes within the different stages of development of rice plants ($p < 0.001$).

As the amount of observations obtained with EC is much larger than with the chambers, all the studies of relationships between fluxes and environmental variables have been carried out with EC data.

Significant positive correlations were found between CH$_4$ fluxes and the depth of the water table ($r = 0.65$). Plotting the daily average depth of the water table against the daily average CH$_4$ flux (Fig. 4) we observed that fluxes were around zero when the depth of the water table was below 10 cm. Highest CH$_4$ fluxes (0.20–0.40 µmol CH$_4$ m$^{-2}$ s$^{-1}$) were only produced when the water level had risen above 12 cm.

Correlations between CH$_4$ fluxes and soil or air temperature were not significant when applied to the whole experimental period and neither when applied separately to periods with or without the crop. However, when the data set was partitioned in classes of day and night (based on associated measurements of light intensity (PPFD) being greater or less than 50 µmol m$^{-2}$ s$^{-1}$) and according to the plant development stages (i.e. vegetative, reproductive and ripening), high correlations were found between CH$_4$ fluxes and soil temperature.
Binning the data in 2 °C classes of soil temperature, strong positive correlations were found both for the day and night during the vegetative period ($r^2 = 0.99$ and $r^2 = 0.98$ respectively). Correlations were considerably lower during the reproductive period ($r^2 = 0.51$ and $r^2 = 0.68$ for day and night respectively) and high again in the ripening period ($r^2 = 0.87$ and $r^2 = 0.94$ for day and night respectively).

Eddy covariance fluxes averaged over a 2 weeks period showed a diurnal cycle in periods of high emissions (Fig. 5). During the vegetative period (be-week between 30 April and 14 May), the diurnal trend followed the temperature cycle with an increase of emissions between 9–10 a.m., maximum between 15–20 h and lower emissions during the night. During the reproductive and beginning of the ripening period the maximum emissions were reached earlier during the day (11–17 h) and decreased during the rest of the day. During the rest of the ripening period (be-weeks in the period from 29 July to 27 August) a similar diurnal cycle was observed but with two different peaks, one in the late evening and a second one around 23 h.

### 3.2 Comparison between chamber and eddy covariance measurements of CH$_4$

From the whole eddy covariance data series (7 April 2009–31 December 2009), high quality data were obtained for 31% of the experimental period. Long interruptions (>7 days) due to instrument failure were responsible of 40% of data gaps. Considering only periods when the system was properly running, after filtering for low turbulence and data spikes, 53% of the data were classified as of good quality.

For the same sampling period we obtained 23 measurements from the closed chambers. The comparison between the data sets obtained with the two techniques shows that both data series follow a similar temporal pattern (Fig. 3). However, we can also observe that fluxes measured with the chambers are on average higher than those measured with EC for the same period of the day.

The linear regression between the punctual data obtained with both measurement techniques ($\text{CH}_4\text{chmb} = 1.265 \times \text{CH}_4\text{EC} - 5.86 \times 10^{-3}, R^2 = 0.969$) indicates a good agreement between them. The value of the intercept is close to zero, indicating that
both methods are equally effective in detecting the shift from sink to source. The slope shows that fluxes measured with chambers were on average ~26% higher than those observed with EC. However, the high $R^2$ might be an effect of comparing very low off season fluxes with the high fluxes of the growing period.

To further compare the results of the two measurement techniques, the Bland-Altman test, which plots the average of the results obtained with the two methods against the difference between both of them, was carried out. When the test was applied on the whole data series, we observed that the differences between the results of the two methods (calculated as average ± 2*standard deviation) ranged between −0.06 and 0.16. When the analysis is performed separately on low fluxes (<0.02 µmol CH$_4$ m$^{-2}$ d$^{-1}$) differences between the 2 techniques ranged between −0.02 to 0.02, while for the higher fluxes these differences ranged between −0.02 to 0.18. This analysis shows that for low fluxes the differences between measurement techniques are limited, while for higher fluxes differences between the results obtained with the 2 methods increase linearly.

The comparison of the two measurement techniques has been extended to seasonal integrals (Fig. 6). For this purpose fluxes have been cumulated from 4 June 2009 (Day 155), as at this moment chamber data started to be regularly collected. A total of 31.7 g CH$_4$ m$^{-2}$ were measured with EC, while 41.1 g CH$_4$ m$^{-2}$ were measured with chambers for the same period (and 44.4 g CH$_4$ m$^{-2}$ if the correction for temperature increases inside the chamber is not applied, 39% higher than fluxes estimated with EC). If data from the beginning of EC measurements is considered, the cumulated CH$_4$ flux is 37.2 g CH$_4$ m$^{-2}$. Cumulative fluxes estimated from chamber measurements were therefore 30% higher than those from the eddy covariance.
4 Discussion

4.1 Seasonal variations of CH$_4$ fluxes from the rice field

Large variations in CH$_4$ fluxes were observed during the different stages of development of the rice crop. Gogoi et al. (2005) in rice cultivars in India, observed that CH$_4$ emissions were substantially influenced by crop phenology and growth, as they showed strong positive relationship with parameters related to the development of the canopy such as leaf number or leaf area index. In view of these results, the analysis of the environmental controls of methane emissions has been performed separately for these different stages of the crop development.

The net ecosystem CH$_4$ flux depends on the relative rates of CH$_4$ production and oxidation and therefore on the soil redox potential. At the investigated site the soil remains water logged during most of the year, due to its high clay content and as a result of either managed flooding or rainfall. Therefore, the conditions were favourable for methanogenesis during a large part of the experimental period, and favourable for CH$_4$ oxidation only in the spring before submersion. However, higher CH$_4$ fluxes were only produced at certain periods, when other environmental conditions were favourable (e.g. temperature) and in particular when rice plants were well developed. The relationship between CH$_4$ fluxes and water table depth (Fig. 4) shows that in this rice field, a minimum level of the water table (10–12 cm) is required to observe large emissions. The soil submersion creates the anaerobic conditions needed for the methanogenesis (Neue, 1993) and limits the possibility for CH$_4$ oxidation. Moreover, it favours the growth of rice plants, which are responsible for more than 90 % of the methane transport from the soil to the atmosphere (Inubushi et al., 1992).

The results reported in Fig. 4 support the opinion of Christensen et al. (2003) who suggested that the water table position operates like a general “on-off switch” for CH$_4$ emission. In ecosystems with relatively high water table, small fluctuations of the water level have only minor effects on CH$_4$ emissions. However, the reduction of the water table below a critical threshold could lead to a substantial reduction of CH$_4$ emissions.
Christensen et al. (2003) observed that for wetlands, once the water level was around 10 cm above the soil surface, other variables took over the variability on the emissions. The same threshold of 10 cm was observed for this rice paddy field. Above this threshold, small variations of the water table did not affect the emissions, which remained high anyway. Below this threshold, emissions were drastically reduced. However, in our experiment, the high water table coincided with the phenological stage in which rice plants have fully developed the aerenchyma and therefore were very effective in transporting CH$_4$ to the atmosphere. The apparent effect of the water table reported in Fig. 4 might therefore be due also to the close correlation between water level and plant development in rice paddy fields.

Similarly to what was observed by Zou et al. (2005) in rice paddies in China, these results suggest that the water table depth could be potentially used as a management option to control CH$_4$ emissions from rice fields, as lowering the water table might considerably reduce emissions. However, the reductions of the water table can also release CH$_4$ from pore water and result in large episodic bursts of CH$_4$ emission (Bubier and Moore, 1994). Further studies are therefore needed to develop optimal strategies for the management of the water table in order to control emissions of CH$_4$ and minimize any possible negative effects on crop yield.

Another important variable explaining CH$_4$ fluxes during the different stages of development of the plants was soil temperature. Positive relations between emission of CH$_4$ and temperature have also been reported by other authors (Pattey et al., 2006; Long et al., 2010; Schrier-Uijl et al., 2010). On the contrary Schutz et al. (1990) and Gogoi et al. (2005) did not find any positive correlation between CH$_4$ emission and temperature during the growing season, suggesting that the water table in the field, acted as an insulating body which kept the soil temperature fairly uniform.

In our experiment the relationships of methane emissions with soil temperature were especially important in the vegetative and ripening periods, when the water table was not that high. However, as in our experimental site ambient temperature oscillated much more than in the rice field studied by Gogoi et al. (2005), the water table could
not completely compensate the oscillations of temperature, resulting in a significant temperature control also during the reproductive period.

4.2 Diurnal variation of CH$_4$ fluxes

The occurrence of a diurnal cycle in CH$_4$ fluxes has been observed in previous studies in peatlands and submerged ecosystems (Suyker et al., 1996; Kim et al., 1998; Long et al., 2010). Miyata et al. (2000) and Tseng et al. (2010) in rice fields observed a diurnal variation of the fluxes with higher fluxes registered during the afternoon. Holzapfel-Pschorr and Seiler (1986) already observed a diurnal variation in CH$_4$ emissions in an Italian rice paddy field. Similarly to our results, they observed maximum amplitudes in the fluxes during the first half of the vegetation period. We observed this diurnal variation of the fluxes mainly during the first stages of development of the plants (vegetative period). Baldocchi et al. (2011) over a peatland pasture observed a diurnal variation of CH$_4$ fluxes, with emissions peaking at night. In their experiment they assumed that this was mainly due to cattle emitting CH$_4$ around the tower during night. However, they consider that a collapse of the nocturnal boundary could have also taken place and subsequently an extension of the flux footprint under stable stratification to areas where higher fluxes were registered. In studies carried out in ecosystems where a water table was not present, such as those made by Rinne et al. (2007) in a boreal forest in Finland, no diurnal cycle in CH$_4$ fluxes was observed. Therefore, the occurrence of a water table seems to be prerequisite to observe a clear diurnal cycle in emissions. The peak of CH$_4$ fluxes in the late evening, which is the time of the day when the water table reaches the highest temperatures, make us suppose that the environmental control of the diurnal cycle of emission is water temperature. We cannot confirm this hypothesis as the temperature of the water above the soil surface was not measured, and the available soil temperature is not strongly affected by daily variations in ambient temperature.

There are several possible mechanisms that may be responsible of the diurnal variation in CH$_4$ fluxes during the periods of high CH$_4$ production. The fact that the relations
between fluxes and soil temperature is evident only when data are separated for day and night suggests that processes influenced by light availability may interfere with CH$_4$ emissions. Nouchi et al. (1990) already observed that stomata are not responsible of the release of CH$_4$ from rice plants while Mariko et al. (1991) observed that the aerenchymal tissue of rice plant is indeed the most important path for the transport of CH$_4$ from the anoxic soil to the atmosphere. The effect of stomata control on diurnal variation of fluxes has therefore to be excluded.

Previous studies on rice cultivars have shown a strong positive correlation of the crop growth parameters like leaf number and leaf area index and the total CH$_4$ flux (Gogoi et al., 2005). Other studies report that a reduction in solar radiation results in a decrease of the emissions (Sass and Cicerone, 2002). Subsequently, Keppler et al. (2006) suggested that an explanation for the relationship between leaf biomass and solar radiation will be the “in situ” formation of CH$_4$ in the plants tissues, through an unknown process distinct from the widely accepted process requiring anoxic soil conditions. The type of measurements carried out in our study does not allow to differentiate the sources of CH$_4$.

Another process which may modulate the diurnal cycle of fluxes is the convective flow generated by pressure gradients in the plant and associated with air-leaf temperature and humidity gradients. Pressure gradients driven by diurnal variation in light availability may therefore produce variation on the emissions according to solar radiation (Dacey, 1981; Brix et al., 1992). As an additional process, it has also been shown that the CH$_4$ dissolved in the soil solution could be released to the atmosphere via transpiration (Nisbet et al., 2009) and thus contribute to the diurnal variation.

4.3 Comparison between chamber and eddy covariance measurements of CH$_4$

Chamber-based measurements are very sensitive, because of the large increase in gas concentration in the headspace (Denmead, 2008), but they are often criticised because of uncertainties due to pressure artefacts and temperature effects (Hutchinson and Livingston, 2002; Rochette and Eriksen-Hamel, 2008), discontinuity
of measurements and lack of spatial integration (Flechard et al., 2007). Despite these limitations the chamber technique is the most commonly used for measuring CH$_4$ fluxes from ecosystems. Lately, the number of studies of CH$_4$ fluxes with EC has increased, due to the recent availability of instruments able to measure CH$_4$ concentration at the sampling rates and response time required by this technique. EC offers the advantage of obtaining continuous data integrated over larger areas. However, recent studies have shown that the measurement of CH$_4$ fluxes may challenge the assumption of a horizontally homogeneous source or sink, and it has turned out to be much more complicated than the measurement of other fluxes such as carbon dioxide or water (Baldocchi et al., 2011). Nevertheless, it is expected that studies on CH$_4$ fluxes with EC will soon become more popular, and it is therefore relevant to compare the results obtained with the two different techniques.

Our comparisons of the two methods show an overestimation of fluxes when measured with chambers, similarly to the results reported by Bekku et al. (1995). The difference between the two techniques, as observed in the Blandt Altman test, is increasing at higher CH$_4$ fluxes. It is therefore likely that in systems with lower CH$_4$ emissions, both measurement techniques would lead to more consistent results.

One of the possible reasons for the higher CH$_4$ fluxes measured with the chambers may be the temperature increase during the closure of the chamber. Even if in the calculation of the fluxes the effect of temperature on the molar weight is taken into account, the possible increase of CH$_4$ release through plants due to the higher temperature inside the chamber cannot be accounted for.

Other possible reason for the mismatch of the observations is the non-homogenous surface cover or soil characteristics within the field. Chambers measure fluxes from a plot with optimal development of plants, while EC integrates fluxes from areas of the field where the vegetation might not be that well developed. To compensate for the spatial heterogeneity, Schrier-Uijl et al. (2010) suggested that the comparison of methods has to be done by weighting the emissions of different landscape elements. Wang et al. (2010) also pointed that the main reason for the disagreement between
both techniques might be the complex footprint covered by the EC and the spatial heterogeneity for the scaling up of chamber measurements.

The difference between the 26% bias observed in the regression of single observations and the 30% of cumulative fluxes is due to the linear interpolation of chamber fluxes (usually measured at noon) that ignores the diurnal variation of emission as observed with EC. Alternatively, cumulative emissions could be calculated with a model that accounts for the temperature dependence of fluxes, as proposed by Schrier-Ujil et al. (2010) for CO$_2$ and CH$_4$. In our experiment, we decided to adopt the linear interpolation since it is the method more commonly used for the integration of emissions over a certain measurement period. The differences we observed between the two techniques were however smaller than the 55.1% reported by Schrier-Ujil et al. (2010) when they did not take into account temperature and landscape heterogeneity. In our experiment we also observed that not considering the temperature increase inside the chamber would have resulted to an over-estimation of 39% in relation to the chambers (Fig. 6). Parkin (2008) observed that the sampling frequency had a great influence on the estimation of cumulative fluxes, and that as the time interval between sampling increased, the deviation in the estimated cumulative also increased.

Some authors have pointed out that the use of linear regressions to estimate fluxes from chamber concentrations could result in an underestimation of the fluxes and suggest the use of the slope intercept method (Kroon et al., 2008). This underestimation is caused by a decrease in the concentration gradient between the chamber and the soil atmosphere, due to the increased concentration in the chamber headspace. However, Schrier-Ujil et al. (2010), who compared the linear regression and the slope intercept methods for the calculation of the fluxes, observed 4% higher fluxes with the slope intercept method, but these differences were not significant. If this effect would have taken place in our chambers, even higher fluxes would have been estimated with the chambers.

Chambers measurements are prone to other possible sources of error, such as the possible inaccuracies derived from the analysis of CH$_4$ concentration by gas
chromatography, or the imperfect mixing in the chamber headspace (Liu and Si, 2009; Christiansen et al., 2011). Hutchinson et al. (2000) observed that the use of chambers alters the atmospheric mixing processes at the soil-atmosphere interface, resulting in either enhanced or suppressed gas exchange rates between −30% to +32% of the pre-deployment flux.

We think that the observed mismatch between the two measurement techniques is probably due to a combination of several issues explained above, resulting in a general over-estimation of the fluxes by the chambers combined with a potential underestimation of fluxes measured by EC.

5 Conclusions

A diurnal and a seasonal variation of CH$_4$ fluxes has been observed in this Italian rice paddy field. The seasonal variation was mainly caused by the presence of a water table, which above a certain threshold (10 cm) favoured the production of CH$_4$. Further studies should be carried out to assess if an adequate management of the water table could lead to a decrease in the emissions. The development of rice plants strongly influenced CH$_4$ emissions, possibly because CH$_4$ is mainly released through plant aerenchyma and once it is fully developed greater amounts of CH$_4$ are transported from the soil to the atmosphere. Temperature has been found to be other factor which strongly influenced the emissions, mainly during the vegetative and ripening periods. Several processes could be responsible of the diurnal pattern of the emissions, which was especially important during the vegetative period. This diurnal pattern in CH$_4$ fluxes seems to happen in systems where a water table is present, possibly as an effect of the increase of water temperature, as greater emissions take place in the evening.

The comparison between the data sets obtained with EC and chambers showed that both data series followed a similar temporal pattern. However, greater CH$_4$ fluxes were measured with chambers, and the differences between both techniques increased
when higher emissions were produced. Seasonal estimations with chambers resulted in 30% higher fluxes than with EC, as a consequence of the overestimation with the chambers, the possible underestimation by the EC technique and of not having considered the daily course of the fluxes for the calculation of seasonal emissions. Further studies on CH$_4$ fluxes with the EC technique, which provides greater information on the diurnal and seasonal variation of the fluxes, could be useful to develop strategies to reduce CH$_4$ production from rice paddy fields.

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Fig. 1. Seasonal trends of the daily average air (a) and soil (b) temperatures at depths of 50 and 30 cm.
Fig. 2. Daily average soil water content at 0–15 cm and 15–35 cm (a) and depth of the water table (b). Positive values indicate that the water table was above the soil surface.
Fig. 3. CH$_4$ fluxes derived from measurements with closed chambers (open triangles) and eddy covariance.
Fig. 4. Relationship between CH$_4$ fluxes and depth of the water table.
Fig. 5. Average daily variation during 2 weeks periods (with detail of CH$_4$ fluxes in periods with higher emissions). Data are binned by time of day and then averaged for 2 weeks periods. The standard deviations are calculated on data passing the quality test on turbulence intensity.
Fig. 6. Seasonal integrals of CH$_4$ fluxes measured with eddy covariance (during all the experimental period and from 4 June, day 155) and with chambers, with and without the temperature correction.