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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 a rice paddy field in the Po Valley (Northern Italy). Methane fluxes were measured during the rice growing season with both EC and manually operated closed chambers. Methane fluxes were strongly influenced by the height of the water table, with emissions peaking when it was above 10–12 cm. Soil temperature and the developmental stage of rice plants were also responsible of the seasonal variation on the fluxes. The measured EC fluxes 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 the two 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 31.7 g CH_4 m^{-2} measured with chambers and EC respectively) and even greater differences are found if shorter periods with high chamber sampling frequency are compared. The differences may be a result of the combined effect of overestimation with the chambers and of the possible underestimation by the EC technique.

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 global CH_4 emission (Houghton et al., 1995) as they have a high emission rate and occupy large areas, 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.

Field experiments in rice paddies have shown that there is a large spatio-temporal variability on CH_4 emissions that have to be accounted for in order to produce robust estimates of yearly budgets (Holzapfel-Pschorn and Seiler, 1986; Schfitz et al., 1989; Schutz et al., 1989; Sass et al., 1991). 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-Pschorn and Seiler, 1986). Alternatively, the aerodynamic technique of eddy covariance (EC) provides continuous measurements, without interfering with the processes of gas exchange between the sources and the atmosphere. This technique is commonly used for the estimation of CO_2 and H_2O and energy fluxes, but its use for the measurement of CH_4 fluxes is less common, as adequate analyzers have only recently became available.

The EC technique provides integrated continuous measurements over a large area and may increase our understanding of the underlying processes regulating 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 (Rinne et al., 2007; Hendriks et al., 2008; Hendriks et al., 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, so far there are few studies where the EC technique has been used to measure CH_4 emissions from rice paddy fields (Werle and Kormann, 2001; 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 as sources of error from the two techniques are not clearly understood. Schrier-Ujil 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. Werle and Kormann (2001) also performed a similar comparison in a rice paddy field, during a short campaign of one week, resulting in great differences between measurement techniques. In this study the comparison was carried out using eddy covariance and chamber-based methods to measure CH_4 fluxes in a rice paddy field during the growing season and the period after harvest.

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 seasonal 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 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. Chambers were placed in two groups of four at different sides of a small dike (1–2 m wide) where the eddy

covariance tower was installed, and each group was on average at 25 and 45 m from the EC tower (20 m between each group). Chambers within each of the groups were at a distance of 2–3 m. 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 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 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 period 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. Chambers were ususally closed for a maximum of 60 min, except at the beginning of the growing season, when closing period was increased to 90 min because both fluxes and temperature were very low. 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 a.m. (midday).

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 of CH_4 concentration in the chambers headspace during the closure time. 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 accounting for 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. When the last sampling point was not lin-

ear with the previous three the sampling point was rejected. 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; Baldocchi et al., 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 seconds, the FMA was operated in high flow mode by connecting the outlet of the analyzer to a dry scroll pump (Edwards XDS 35i). 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_2 and 0.3 s for H_2O. The EC set-up formed by the anemometer and CO_2/H_2O analyzer has been running since July 2006 and is further described in Rossini et al. (2010).

A three rotations scheme was applied to each 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_4 was 1 second 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_4 fluxes for the determination of net ecosystem fluxes, calculated as difference between CH_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_4 and H_2O flux by the empirical method described in Aubinet et al. (2000). 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 flux 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. We performed a similar footprint analysis for CH_4 fluxes using the analytical model described in Neftel et al. (2008). In order to evaluate the homogeneity of the source area, the rice paddy was split in four rectangular areas centred on the flux tower and having nearly the same area (80×180 m). We compared the average CH_4 flux coming from the area composed by 2 of the rectangular areas and the average flux from from the remaining two. The comparison was performed using the t-test (significance level of 5 %) on data collected during the period 10–23 July, when the daily pattern of meteorological conditions was steady. Flux averages were calculated using half-hourly data from 10:00 to 13:00 UTC in order to avoid biases due to changing meteorological conditions. Moreover half-hour fluxes were considered in the analysis only if the footprint contribution of the source area was higher than 80 %. The t-test showed that fluxes coming from the two areas were not different ($p = 0.06 - 0.08$) independently on the grouping of the rectangular areas.

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 deviation >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); air temperature (Tair) was measured with a shielded thermo hygrometer (model RFT-2, UMS, Munich, Germany). Net radiation was measured by a net radiometer (model CNR1, Kipp & Zonen; Delft, The Netherlands) installed 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 2.99×10^6 J m^{-3} K^{-1} for wet soil (Hillel, 1982). Soil water content was measured with a TDR (TRIME-EZ, IMKO) installed at a depth of 16 cm and 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.

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 (v. 8, StatSoft inc.). Linear regression analyses ($P < 0.05$) were performed to determine relationships between CH_4 emissions with the measured environmental variables. The statistical significance of the differences between the cumulative emissions measured with different techniques was tested by the analysis of variance (ANOVA, $P < 0.05$).
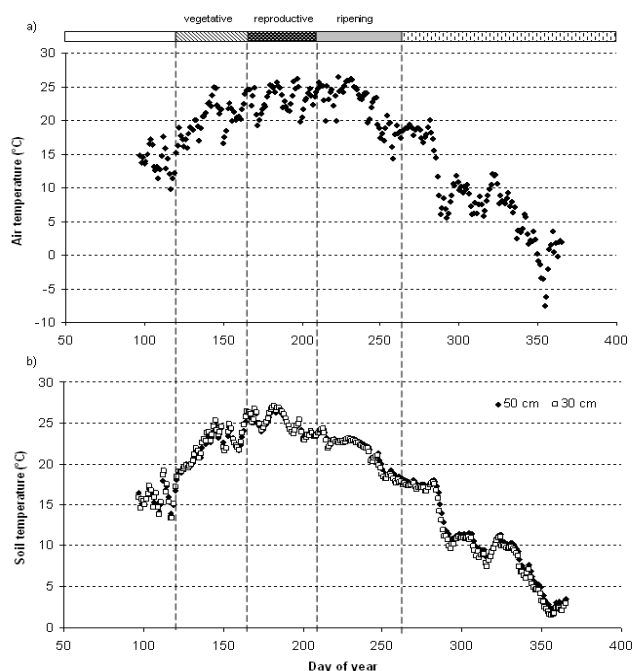
Fig. 1. Seasonal trends of the daily average air **(a)** and soil **(b)** temperatures at depths of 50 and 30 cm.

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.

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), by the Bland-Altman method (Altman and Bland, 1983) and comparing seasonal integrals during the periods when sufficient data coverage was available for both measurement techniques.

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,
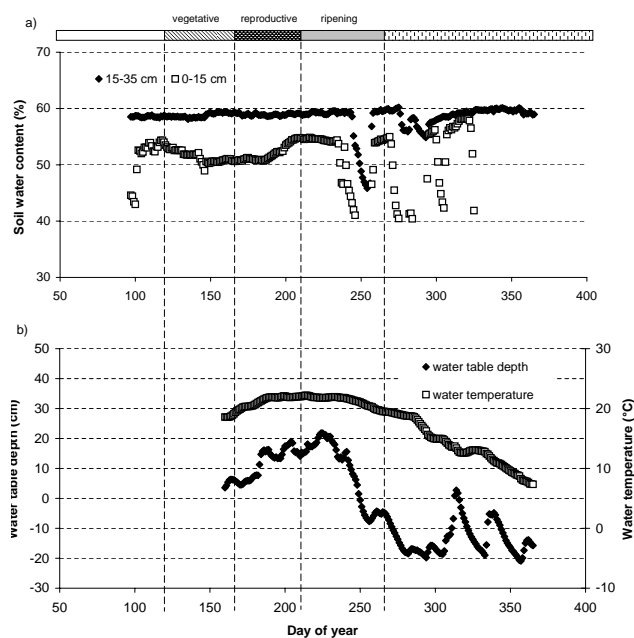
reaching a maximum of 21 cm in mid August (day 225). The water level started to decrease in coincidence with the second half of the ripening period, until early September when the soil was no longer submerged (day 250). Subsequent increases of water table depth were a consequence of intense rainfall 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, during the ripening period (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} vs^{-1}) till the end of the year. Analysis of variance indicated statistically significant differences in the fluxes within the different stages of development of rice plants ($p < 0.001$). Methane fluxes measured with chambers followed a similar pattern as those measured with eddy covariance. No significant differences ($p < 0.05$) were found between chambers placed at different sides of the dike.

Giving that the number of observations obtained with EC is much larger than with static chambers, the analysis of relationships between fluxes and environmental variables have been carried out exclusively with EC data.
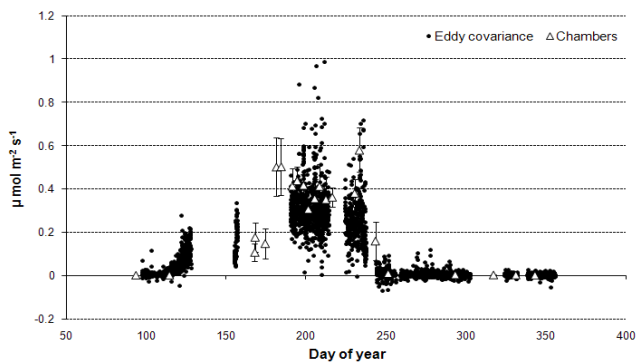
Fig. 3. CH$_4$ fluxes derived from measurements with closed chambers (open triangles) and eddy covariance.
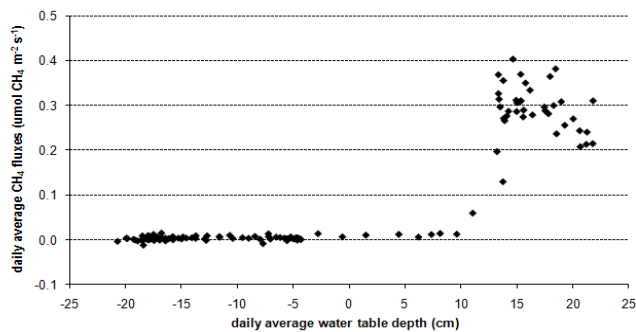

Fig. 4. Relationship between CH$_4$ fluxes and depth of the water table.

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 close to 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 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 lower than 50 μmol m^{-2} s^{-1}) and according to the plant development stages (ie. 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).
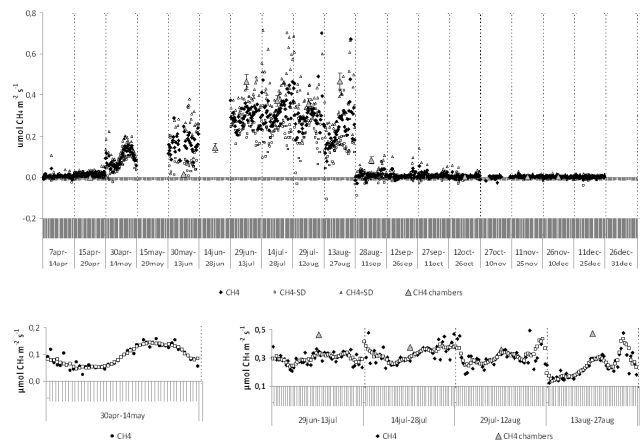

Fig. 5. Average daily variation during 2 weeks periods (with detail of CH$_4$ fluxes in periods with higher emissions). Data are binned by time of day and then averaged for 2 weeks periods. The standard deviations are calculated on data passing the quality test on turbulence intensity.

Eddy covariance fluxes averaged over a 2 weeks period showed a diurnal cycle in periods of high emissions (Fig. 5). During the vegetative period (bi-week between 30 April and 14 May), the diurnal trend followed the temperature cycle with an increase of emissions between 9-10am, 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.

The footprint analysis has shown that fluxes measured with the eddy covariance originate within the rice paddy and cover the area where the chambers were located (Rossini et al. 2010). In addition the analysis of the spatial distribution of emission in the footprint based on the methodology proposed by Neftel et al. (2008) demostrates that methane fluxes are homogeneously distributed in the rice field. Alltogether these results confirm the validity of the experimental setup and support the intercomparison of emissions retrieved with the two tecniques.
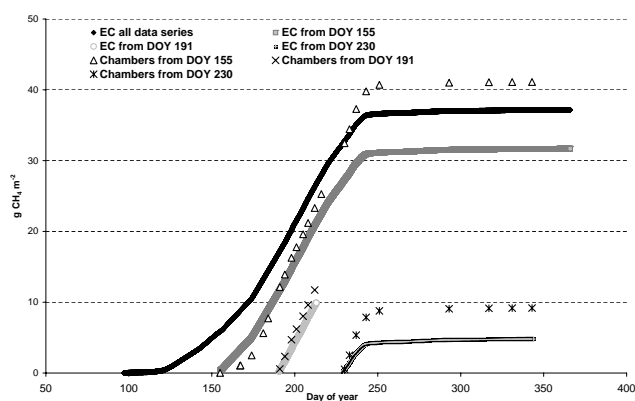
Fig. 6. Seasonal integrals of CH$_4$ fluxes measured with eddy covariance and with chambers (during all the experimental period, from DOY 155 and periods DOY 191-213 and DOY 230-244).

During the experimental 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 the two measurement techniques (CH$_4$ $_{chmb}$ = 1.265 CH$_4$ $_{EC}$ − 5.86 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 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 was 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 and on average null, 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 to 343), as from 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. This resulted in cumulative fluxes estimated from chamber measurements 30 % higher than those from the eddy covariance. Comparisons between measurement techniques over two intervals with no gaps in the eddy covariance series (day 191–213 and day 230–244) resulted in 18 and 91 % higher fluxes measured with chambers for the two periods, respectively (Fig. 6). If data from the beginning of EC measurements is considered, the cumulated CH$_4$ flux is 37.2 g CH$_4$ m^{-2}.

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. The magnitude of the fluxes is in good agreement with results obtained at other Italian rice paddy fields. Mean seasonal CH$_4$ emission rates reported in Butterbach-Bahl et al. (1997) were 11.4 mg CH$_4$ m^{-2} h^{-1} while mean daytime fluxes in Werle and Kormann (2001) were around 0.25 µmol m^{-2} s^{-1} (14.5 mg CH$_4$ m^{-2} h^{-1}), both similar to the mean CH$_4$ fluxes observed in our experiment during the rice growing season (11.36 mg CH$_4$ m^{-2} h^{-1}). Our results are also comparable with studies in other rice paddy fields in different parts of the globe (Simpson et al., 1995), ranging from 0.36 to 27.36 mg CH$_4$ m^{-2} h^{-1} in India (Parashar et al., 1991; Mitra, 1992) to 28.6 mg CH$_4$ m^{-2} h^{-1} in China (Wang et al., 1990).

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, we assume that the conditions were favourable for methanogenesis during a large part of the experimental period, and favourable for net CH$_4$ oxidation only in the spring before submersion. However, CH$_4$ oxidation in the surface of a flooded rice field may consume about 80 % of the gross CH$_4$ flux (Conrad and Rothfuss, 1991). The measured net flux is the result of simultaneous production and consumption processes, which 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; Butterbach-Bahl et al., 1997), 8 % of CH$_4$ is released through bubbles and 2 % comes from the diffusion through the water column. The methodologies applied in this study do not allow the differenciation of the underlaying processes.

Even if the soil was waterlogged during a large fraction of the observation time, high CH$_4$ fluxes were produced at specific 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 height 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 in wetlands, once the water level was aproximately 10 cm above the soil surface, other variables were responsible for the variability on the emissions. Even though our experiment was not specifically designed to elucidate the effect of the water table (other variables changed at the same time as the water table and for some of the water table ranges there is a lack of flux observations), a similar threshold of 10–12 cm as the limit for large CH_4 production was observed. 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 are 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 trigger large episodic bursts of CH_4 emission from soil pores (Bubier and Moore, 1994). The results from this experiment are not sufficient to explore this management option and 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 among other by (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, acts as an insulating body which keps 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 very high (below the 10 cm threshold in the vegetative and half of the ripening periods). 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.

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 methane emissions in the following sections has been performed separately for these different stages of the crop development.

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). Some other studies have already shown that there is diurnal variation on the fluxes in rice paddy fields, with higher fluxes observed during the afternoon (Simpson et al., 1995; Satpathy et al., 1997; Miyata et al., 2000; Tseng et al., 2010). Simpson et al. (1995) measured similar daily peak emissions as in our experiment ($8\,\mu g\,CH_4\,m^{-2}\,s^{-1}$ or $0.5\,\mu mol\,m^{-2}\,s^{-1}$, see Fig. 5). Holzapfel-Pschorn and Seiler (1986) and Werle and Kormann (2001) already observed a diurnal variation in CH_4 emissions in Italian rice paddy fields. Similarly to our results, they observed maximum amplitudes in the fluxes during the first stages of development of the plants (first half of the vegetative period). Different diurnal trends and environmental controls have been reported for peatland pastures. Baldocchi et al. (2011) observed a diurnal variation of CH_4 fluxes with emissions peaking at night probably due to the spatial heterogeneity of the sources (e.g. cattle emitting CH_4 around the tower during night) or to micrometeorological causes (e.g. collapse of the nocturnal boundary layer followed by an extension of the flux footprint under stable stratification to areas with higher fluxes).

In not submerged ecosystems, such as the boreal forest in Finland investigated by Rinne et al. (2007), 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 layer 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 observed soil temperature is marginally affected by daily variations in air temperature. However, in other studies where this daily cycle was observed, it was suggested that diurnal changes in CH_4 emission were only partially explained by temperature changes (Schutz et al., 1990) so other mechanisms might be responsible of the diurnal variation in CH_4 fluxes during the periods of high CH_4 emissions. 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 net 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. Frenzel et al. (1992) observed that rice plants also serve as a conduit for atmospheric O_2 into the rizosphere, resulting in decreased rates of CH_4 emission from the soil into the atmosphere (Holzapfel-Pschorn and Seiler, 1986). Following this observation, changes in the net CH_4 fluxes might be influenced by the efficiency in CH_4 oxidation in the rhizosphere (Frenzel et al., 1992).

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 emission, leaf biomass and solar radiation could 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.

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 the transpiration flux (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 with no alteration of the ecosystem microclimatology. 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 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) and Werle and Kormann, (2001). The difference between the two techniques, as shown by 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 the effect of temperature on the molar weight is taken into account in the calculation of the fluxes, the possible increase of CH_4 release through plants due to the increasing 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 homogeneusly developed. To compensate for the spatial heterogeneity, Schrier-Ujil 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 % difference of seasonally cumulated 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 can 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 this is the method more commonly used for the temporal integration of emissions. 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.

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. In our experiment even larger differences between measurement tecniques were observed during sub-periods when the series of EC data was continuous, up to 80 % higher for chamber CH_4 emissions, similarly to the values reported by Werle and Kormann (2001) who observed differences between 60 and 90 %.

Some authors have pointed out that the use of liner 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.

Similarly to what was observed in previous studies (Werle and Kormann, 2001) 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

Diurnal and seasonal variations of CH_4 fluxes were observed in an Italian rice paddy field. The seasonal variation seemed to be mainly triggered by the height of the water table, which above a certain threshold (10–12 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. Temperature has been found to be another factor which strongly influenced 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 first half of the vegetative period. Diurnal pattern in CH_4 fluxes with maxima in evening seems to happen in systems where a water table is present, possibly as an effect of the diurnal cycle of water temperature.

The comparison between the data sets obtained with EC and chambers showed that both data series followed a similar temporal pattern. However, CH_4 fluxes measured with chambers were larger, and the differences between techniques increased during periods of higher emissions. Estimation of seasonal cumulated emissions based on chamber measurements resulted in higher fluxes than with EC, as a consequence of the overestimation with the chambers or of the potential underestimation of ecosystem fluxes by the EC technique. Further studies based on the EC technique will provide detailed information on the dynamics and controls of the net ecosystem CH_4 flux, which will enhance the development of effective management strategies for the reduction of CH_4 emissions from rice paddy fields.

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