Chapter 7
Environmental Parameters Influencing the Methane Emissions in the Pantanal Floodplain, Brazil

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7.1 Introduction

Methane (CH_4) is a trace gas with an important role in both troposphere due to the reactions with the hydroxyl radical and the formation of organic radicals, and the stratosphere, because of its participation in the chlorine and water vapor chemistry. Methane is also an important greenhouse gas, with a relative contribution of about 20% for the global greenhouse effect (Wuebbles and Hayhoe 2002). Many works have evidenced that an increase of the methane concentration began around 1800 with the industrial era, and the consequent increase of human activities, including the utilization of fossil fuels, cattle raising and rice plantations (Blake and Rowland 1988; Stern and Kaufmann 1996; Dlugokencky et al. 1998; Etheridge et al. 1998). Presently, the CH_4 concentration is about 1,770 ppbv (part per billion by volume), but it presents a large inter-annual variation caused by eruptions, such as one of the Mt. Pinatubo, or by alterations of the wetlands emissions, mainly due to alterations in the precipitation and temperature regimes in the range between 30° and 90° N (Dlugokencky et al. 1996; Walter et al. 2001).

Global budget evaluations indicate that natural wetlands have a substantial contribution to tropospheric methane, estimated as $100\,\mathrm{Tg}\ CH_4\ y^{-1}$, or about 20% of the global emission (Wuebbles and Hayhoe 2002). Although most of the wetlands are located in the temperate region of the Northern Hemisphere (Lehner and Döll 2004), many experiments have pointed that the wetlands in the tropical region emit $66\,\mathrm{Tg}\ CH_4\ y^{-1}$, or 60% of the emissions from the natural wetlands (Bartlett and Harriss 1993). The emission of methane from the wetlands is influenced by many environmental factors, such as temperature, dissolved organic carbon (DOC), pH, oxyreduction potential (pO), water depth, and floating vegetation. Qualitative relations between the methane fluxes and the factors have been determined, but direct relations are more difficult to establish due to the complex mechanisms involved in

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the process, starting with the production in the sediment, which is followed by the transport though the water column and the subsequent liberation to the atmosphere. Many experiments have been performed in the tropical region, especially in the Amazonian wetland, showing that it is an important source of the global budget of atmospheric methane, with an emission range estimated from 1.73 to 21.0 Tg CH_4 y^{-1} for the whole Amazon basin (Devol et al. 1990; Bartlett et al. 1990; Melack et al. 2004).

Previous work in wetlands indicated that the transport of methane from the sediments to the water surface might occur by three main pathways, which are dependent on each ecosystem: (i) diffusion through the water column, (ii) ebullition from the sediments and (iii) transport through the plant stems (Bartlett et al. 1990; Devol et al. 1990; Keller and Stallard 1994; Bastviken et al. 2004). In Amazonia, the ebullition transport is very important, sometimes accounting for more than 60–70% of the total emission to the atmosphere, while the transport by plants is dependent on the plant type and how it covers the surface.

Present estimates of methane emission from tropical wetlands have an excessive dependence on data from Amazonia, with insufficient information of seasonal and spatial variation in the emission from other tropical wetlands, as evidenced by Smith et al. (2002). There are a few studies covering some important tropical and subtropical wetlands, which are not yet characterized.

One of the most important wetlands in Brazil is the Pantanal, which is covered by savanna-like vegetation and is flooded seasonally. Its total area is estimated about 138,183 km^2, with most of this area within Brazil, in the upper Paraguay River basin. Flooding in the region is clearly seasonal, with its maximum flooded area occurring at the end of March. Marani and Alvalá (2007) showed flux measurements for one year, and they identified the importance of the Pantanal floodplains as a source of methane to the atmosphere, with bubble fluxes constituting the major contribution to the general flux. This work presents a study of flux data obtained in five Pantanal sites during 2004 and 2005, and evaluates emissions from floodplains and lakes and their possible relationship with some environmental variables.

7.2 Methodology

7.2.1 Methane Flux

Methane fluxes were determined using the static chamber technique, described by Devol et al. (1988, 1990) and Bartlett et al. (1988). The chambers were covered with a thermal and reflective sheet to avoid temperature variations, had an area of 0.066 m^2 and a volume of 26 l. Inside the chamber, a small fan was installed to avoid any air stratification and was turned on at least 30 s before the sampling. The chambers were placed in the sampling site using a boat, with care to avoid perturbations in the water surface and surrounding vegetation. All samples were taken between 11:00 and 16:00 LT (local time), and they were done under conditions of almost no wind. Every 6 min, during 18 min, gas samples were removed through a septum with a 60 ml polyethylene syringe equipped with a 3-way polypropylene stopcock. To verify the linearity and possible perturbation in the chamber deployment, a sample was taken in the first minute after the chamber was placed. Six to eight locations were sampled for each site. Environmental variables that may affect the methane emissions were also measured: water depth, water and air temperatures, and pH.

The methane concentration of all samples was determined with a commercial gas chromatograph (Shimadzu, GC-14A), equipped with a flame ionization detector (FID), a 2.2 ml sample loop and two stainless steel columns that were optimized to perform methane analysis in the Ozone Laboratory at INPE, São José dos Campos, Brazil. The first column was packed with silica gel (2.5-m long and 1/8″ diameter) and it was used to remove the water vapor, CO_2 and others heavy organic compounds from the samples, in order to reduce the total retention time. The analysis column (3.0-m long and 1/8″ diameter) was packed with a zeolite 5 Å molecular sieve. The methane standard ($1{,}749.4 \pm 4.5$ ppbv) used for calibration was acquired from the Climate Monitoring and Diagnostic Laboratory of the National Oceanic and Atmospheric Administration (CMDL/NOAA).

For each syringe, three aliquots were analyzed with a relative precision of 0.7% or better. The minimum detectable methane flux was about 1 mg CH_4 m^{-2} d^{-1}. The methane flux was determined from the temporal variation of its mixing ratio inside the chamber during the sampling time, following the method of Schiller and Hastie (1994). The methane fluxes were considered diffusive, if the linear correlation between the mixing ratio change and the elapsed time showed a correlation coefficient (r^2) greater than 0.90 (Sass et al. 1992). A second criterion was that the initial concentration obtained by the linear regression (at time t=0) must be close to the measured environmental air concentration. If the flux did not follow the first criterion, and if an abrupt increase of the methane concentration did occur after the first sampling, the flux variation was interpreted as an ebullition. The rate of change of the methane mixing ratio was then determined by subtracting the environmental methane mixing ratio from the mixing ratios obtained at the end of the sampling time, divided by the enclosure time, as proposed by Cicerone et al. (1992) and Keller and Stallard (1994).

7.2.2 Site Location

The Pantanal is a hydrological complex plain constituting a large sedimentary basin, which is periodically flooded by the Paraguay River and its tributaries. Its altitude varies between 80 and 120 m, with a total area estimated 138,183 km^2, located mostly within Brazil, but with small areas in Paraguay and Bolivia. The Paraguay River and its tributaries carry continuously organic material and during the flood period, the water overflow spreads the sediments over the entire region. This organic material that is deposited in the lakes and in the floodplain is the most important source of nutrients for the methanogenic bacteria. The total area under flood

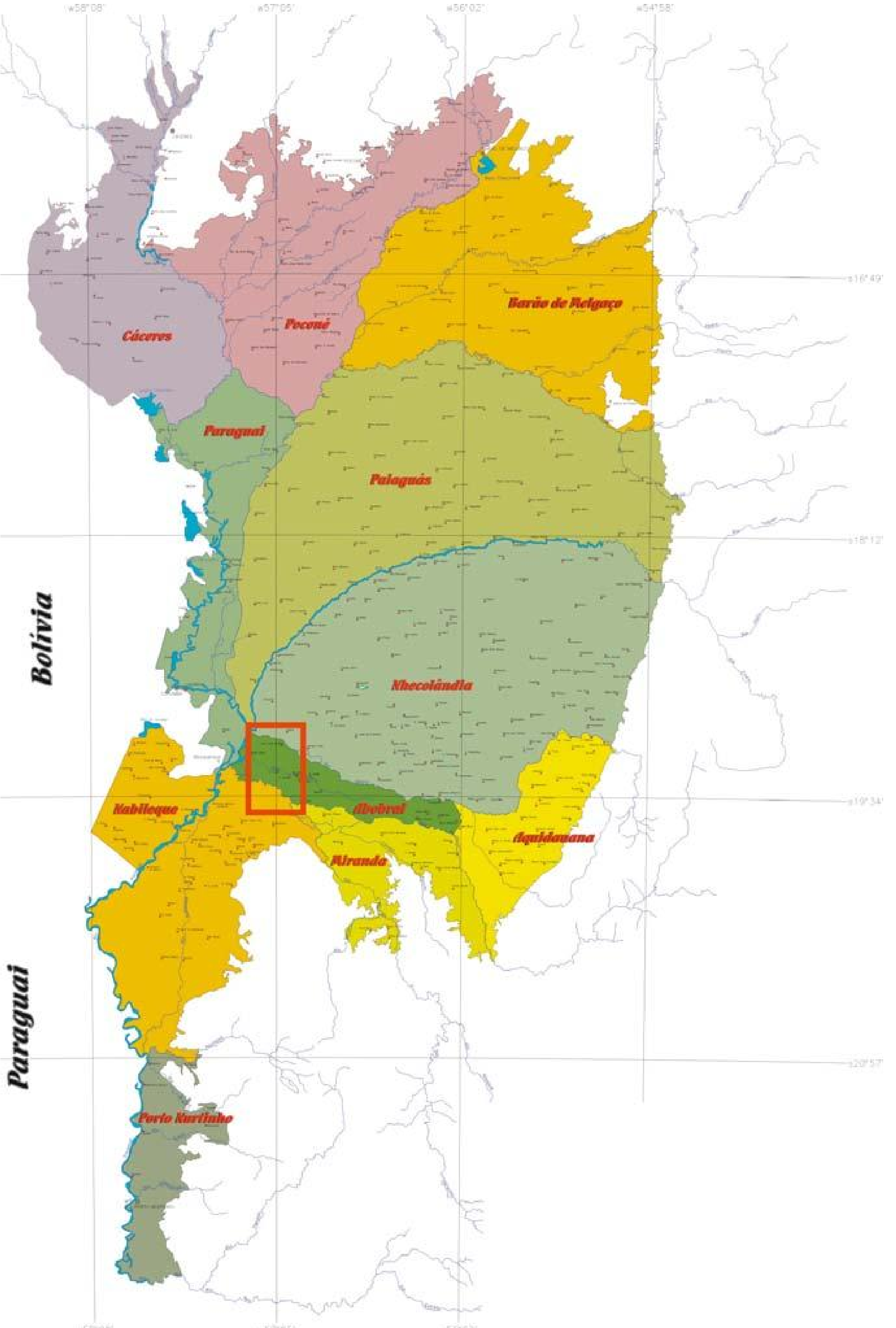

Fig. 7.1 The Brazilian Pantanal basin and its sub-division. The measurement was performed inside the rectangle in the Abobral region

conditions, including the floodplain, lakes, rivers, and channels that link lakes and rivers, was estimated by Hamilton et al. (2002) as 130,920 km^2, thus constituting the largest floodplain in South America. Using a 100-year data set of the Paraguay River level (from 1900 to 1999), Hamilton et al. (2002) also estimated an average flooded area of 34,880 km^2. The flooding of the region occurs after December, during the Southern Hemisphere summer, when the rain water that is falling on the riverhead of the basin since October reaches the region. The maximum flooded area occurs at the end of March. After April, up to the end of September, there are only a few rain episodes and the river level thus decreases to its lowest depth (Alvalá and Kirchhoff 2000). Normally, the period in which half of the maximum-flooded area stays flooded is of 172 days per year, and there is a delay of months between the summer rains and the flooding period, due to the slow passage of flood waters through the Pantanal plain.

The flux measurements were performed over water environments, consisting of open water and emergent macrophytes, at five sites near the Miranda River as shown in Fig. 7.1. Among these sites, three are considered floodplains: São João (19°24′S, 57°03′W), Baú (19°19′S, 57°03′W) and Arara Azul (19°19′S, 57°03′W); and two lakes: Mirante (19°23′S, 57°03′W) and Medalha (19°34′S, 57°00′W) where the water body is permanent, with less influence of the seasonal flooding. During the experiments, the Base de Estudos do Pantanal – BEP (19°34′S, 57°01′W), which belongs to the Universidade Federal do Mato Grosso do Sul, was used as the local logistic support. Hamilton et al. (2002) evaluated that permanent lakes and rivers in the Pantanal cover about 3,120 km^2, with small variation during the year. The remaining flooding areas of the Pantanal are characterized by vast plains subjected to seasonal flooding, mainly due to water overflow from the rivers, but also caused by local rain (Marani and Alvalá 2007). In general, these plains are shallow in comparison with the lakes and many of them dry completely during the dry season.

7.3 Results and Discussions

7.3.1 Overall Flux

Eight methane campaigns were performed during the years 2004 and 2005, thus resulting in the determination of 560 methane fluxes in two lakes and three floodplains of the Southern Pantanal Region. The overall average methane flux was 116.8±276.0 mg CH_4 m^{-2} d^{-1}, with the individual measurements varying from 1 to 2,187.0 mg CH_4 m^{-2} d^{-1}. Figure 7.2 presents the frequency distribution of all fluxes on a logarithmic scale. Although the fluxes to the atmosphere show skewness toward the smaller fluxes in the logarithmic scale, a Gaussian distribution follows at the 1% level. This skewness resulted from the relative higher number of diffusive fluxes (n=342, but with lower flux values), in contrast with the ebullitive fluxes (n=218, with higher flux values).

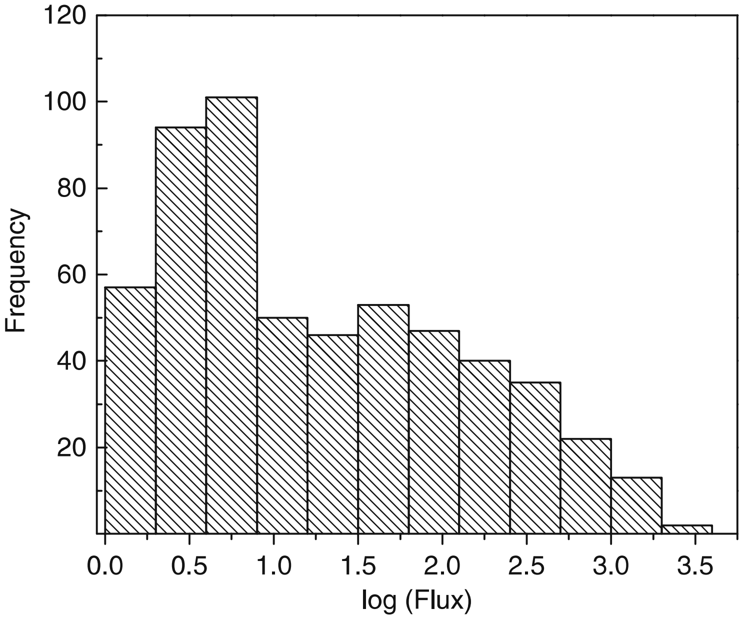

Fig. 7.2 Frequency distribution of all fluxes on a logarithmic scale

The Pantanal region was characterized by a drought during the years of the campaings, mainly in 2005, when the water maximum peak level in the Paraguai River was 3.29 m, while for the normal flooding condition, it ranges from 5.0 to 6.0 m (Embrapa 2006). In 2004, the maximum water level was 4.26 m, what characterizes a small flooding condition. This strong drought also contributed for lowering the depth of the lakes to 1.4 m in 2004, and to 0.9 m in 2005.These drought levels possibly influenced the organic matter distribution in the water.

The pH measured at 10 cm below the surface ranged from 6.4 to 9.8, and 90% of them fell in the range 6.5–7.7, which is the optimum range for the methane production by the methanogenic bacteria (Yang and Chang 1998). However, for this short range, relationships between fluxes and the pH are unlikely.

Marani and Alvalá (2007) observed differences of occurrence in the diffusive and in the ebullitive (bubbles) fluxes while considering lakes or floodplains, with a tendency of the higher occurrence of bubbles in the floodplains. While the diffusive fluxes were concentrated in the lower portion of the emission range (average: 13.1±20.7 mg CH_4 m^{-2} d^{-1}, median: 5.0 mg CH_4 m^{-2} d^{-1}), the ebullitive fluxes had higher values, with a greater dispersion (280.7±390.0 mg CH_4 m^{-2} d^{-1}, median: 128.5 mg CH_4 m^{-2} d^{-1}). This later result reflects the more intense nature of the emission, which occurred only in 39% of the measured fluxes. These higher bubble fluxes observed in the Pantanal floodplains reveal the importance of ebullitive fluxes in the emission of methane in the region when considering regional emission. Bubbling events are episodic, but when they occur, they dominate the methane release, thus resulting high average fluxes (Devol et al. 1990).

The fraction of occurrence of bubble events at different depth ranges for floodplains and for lakes is presented in Fig. 7.3. In the first ones, the bubble fluxes represented 51% of the occurrences, with a depth range from 0.1 to 1.4 m, while in the lakes they represented 27%, with a depth range from 0.1 to 3.5 m; also, in

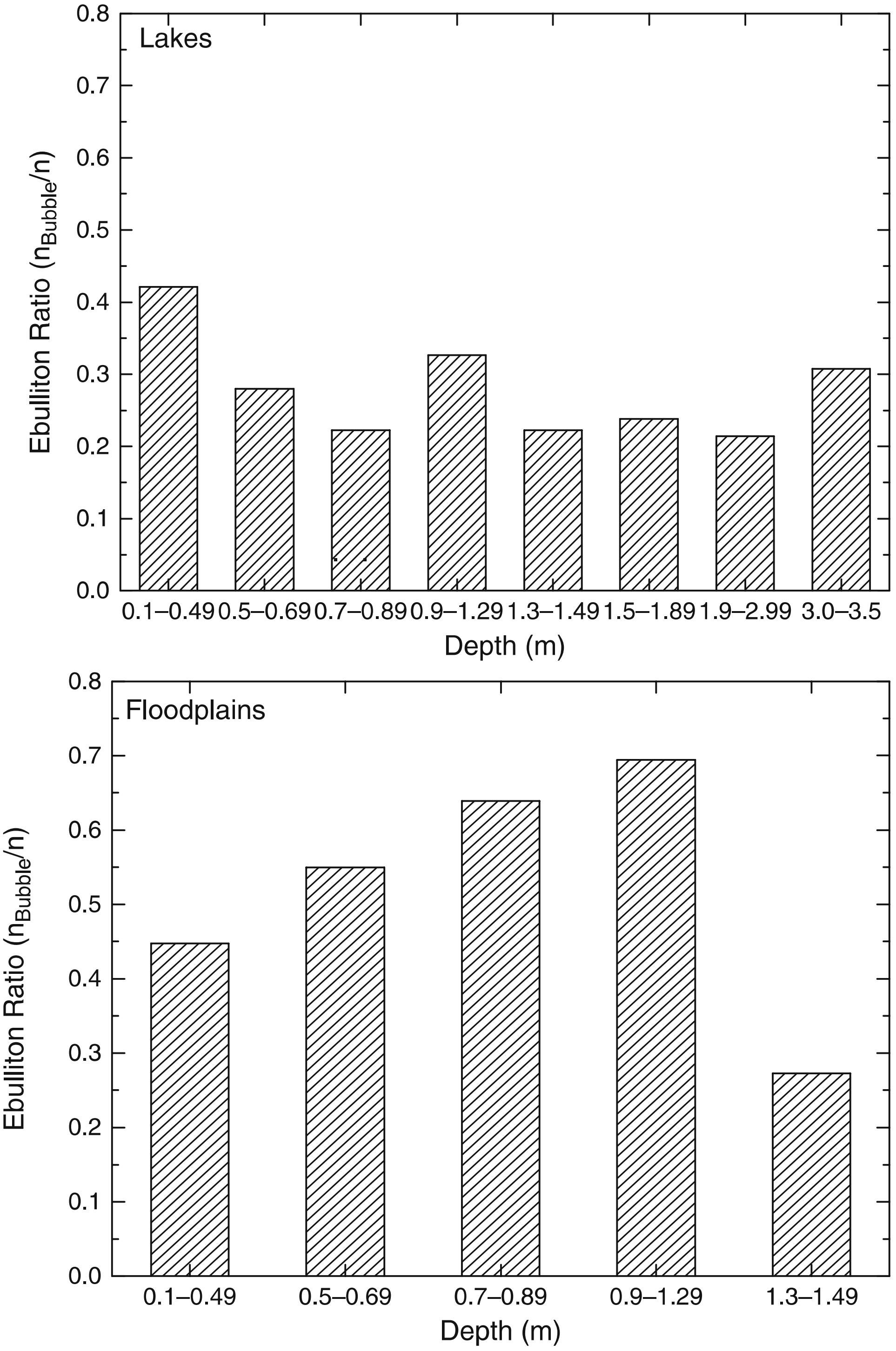

Fig. 7.3 Ratio of ebullition (i.e., fraction of fluxes measurements with detectable bubbles) at different depths to lakes and floodplains

the same range of depth (0.1–1.4 m), the relative number of ebullitive fluxes in the floodplains was higher than the one observed in the lakes.

In contrast, in Amazonia, the bubbling emission corresponded to up to 73% of the overall fluxes, with each one showing different contribution (Bartlett et al. 1990; Devol et al. 1990). Bastviken et al. (2004) observed that, in temperate lakes, there is no linear correlation between the frequency of occurrence of ebullitive fluxes and the depth; their frequency ranged from 25 to 80% of the measurements, depending on the water depth, with the higher values occurring in deep waters. Smith et al. (2002) verified that although the correlations of methane fluxes with a number of environmental variables are statistically significant, they are too weak to serve as a basis for either the prediction, or the analysis of emission mechanisms.

7.3.2 Seasonality

The seasonality of the emission rates during the wet and dry periods may be observed in Fig. 7.4, which presents the box plot diagrams for both the periods. For the average diffusive fluxes, a statistically difference (α=0.05) was observed between the wet (18.5±26.1 mg CH_4 m^{-2} d^{-1}) and the dry (9.5±15.1 mg CH_4 m^{-2} d^{-1}) periods, with greater fluxes during the wet periods, following increases in the water temperature and depth.

Although the correlation between the fluxes and the environmental parameters was low, the statistical difference observed between both periods shows some influence on the fluxes measured. The separation of the sites between floodplains and lakes showed that the variability with the depths was experienced mainly in the lakes. In general, the floodplains present a small slope, so that in the wet period, the depth increased about 0.5 m, while in the lakes, the depths increased more than one meter. In all floodplains, the influence of seasonality was observed mainly in their area, with a large decrease during the dry period, such that the São João site was completely dry in 2005.

Depth and temperature were altered from the wet to dry season in the lakes, but their flooded area had a small increase in the wet season. The results of this work, in some aspects, are different from those obtained in Amazonia by Bartlett et al. (1990) and Devol et al. (1990), since in the Pantanal, the diffusive fluxes, although lower in both periods, showed statistic differences between the wet and the dry periods, mostly in the floodplains. Following Keller and Stallard (1994), higher temperatures and input of substrates due to flooding in the wet period, could have influenced positively the diffusive fluxes, including some effects of depth.

The ebullitive fluxes did not show a statistically significant variation from wet (average: 281.6 ± 376.3 mg CH_4 m^{-2} d^{-1}) to dry (average: 277.2 ± 405.3 mg CH_4 m^{-2} d^{-1}) season; there was only an increase in the data dispersion in the dry season. During the dry period, were observed some higher fluxes, including the two highest ones. The separation of the ebullitive fluxes in the lakes and the floodplains components shows that the average fluxes were higher in the floodplains than in the lakes, with similar values in both periods, although the observed temperature and depth were statistically different for the wet and the dry seasons. This result may be associated with the buoyancy of the bubbles in the sediments, which is related to the depth, even if a correlation was not detected statistically. One indication of this is

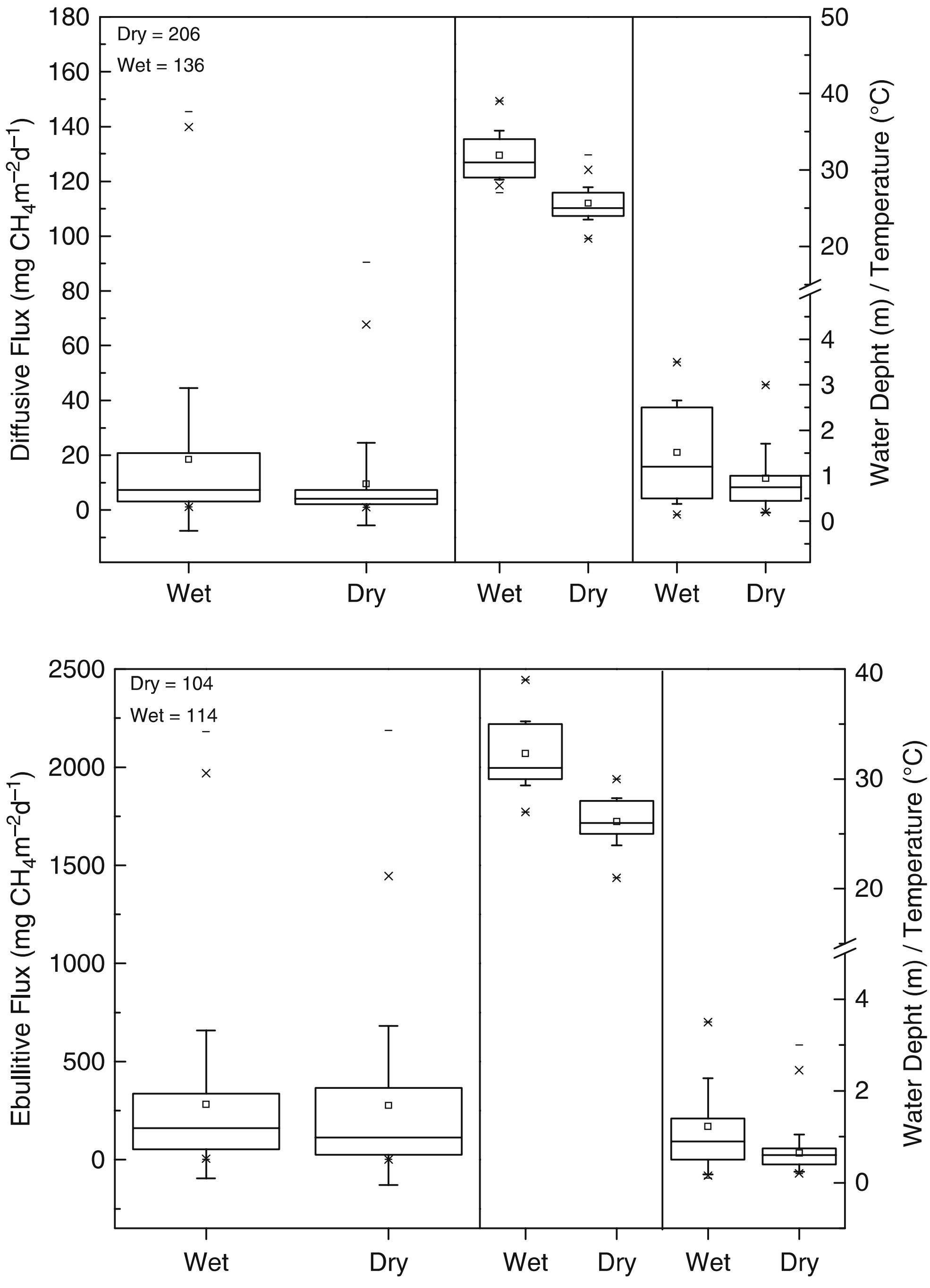

Fig. 7.4 Diffusive and ebullitive fluxes, water depth and water temperature in wet and dry seasons

that the average ebullitive flux for floodplains was 354.1 mg CH_4 m^{-2} d^{-1} (wet and dry seasons), while for lakes it was 134.3 mg CH_4 m^{-2} d^{-1}.

7.3.3 Vegetation Influence

To investigate the influence of vegetation on the methane fluxes, the diffusive and ebullitive fluxes collected over aquatic vegetation were considered separately.

Table 7.1 Diffusive and ebullitive fluxes in lakes and floodplains, separated by the presence of vegetation. Measured environmental variables are also presented

		Lakes		*Floodplains*	
		Vegetated (*n*=26)	*Open Water* (*n*=175)	*Vegetated* (*n*=55)	*Open Water* (*n*=86)
DIFFUSIVE	Flux, mgCH$_4$m^{-2}d^{-1}	12.3 ± 20.3	12.3 ± 16.0	22.6 ± 35.3	8.7 ± 13.9
	Depth, m	0,7 ± 0,3	1.6 ± 1.0	0,5 ± 0,3	0,5 ± 0,3
	Water Temperature, °C	26,8 ± 3,4	27.8 ± 3.8	29,3 ± 4,1	28,5 ± 4,4
	pH (*range*)	6.7–9.2	6.5–7.9	6.6–9.5	6.4–9.8
		Lakes		*Floodplains*	
		Vegetated (*n*=8)	*Open Water* (*n*=67)	*Vegetated* (*n*=60)	*Open Water* (*n*=83)
EBULLITIVE	Flux, mgCH$_4$m^{-2}d^{-1}	94.4 ± 94.2	139.1 ± 226.3	367.3 ± 457.5	348.7 ± 422.9
	Depth, m	0.7 ± 0.4	1.7 ± 1.1	0.6 ± 0.3	0.6 ± 0.3
	Water Temperature, °C	25.6 ± 4.6	26.6 ± 3.6	29.9 ± 4.5	29.1 ± 3.8
	pH (*range*)	6.9–7.8	6.6–7.8	6.5–9.5	6.4–9.6

A statistically significant difference (α=0.05) was observed only for the diffusive fluxes, with an average of 19.3 ± 31.5 mg CH_4 m^{-2} d^{-1} in vegetated waters (n=261) and 11.1 ± 15.4 mg CH_4 m^{-2} d^{-1} in open waters (n=81). The correlation among the fluxes and the measured variables (depth, water and air temperature), although positive, but were weak, ($r<0.4$ for all cases). Table 7.1 presents the fluxes divided in diffusive and ebullitive, for lakes and floodplains, with vegetated or open water. It shows that the vegetation influence was higher in the floodplains than in the lakes. In the floodplains, the methane diffusive flux reached an average of 22.6 ± 35.3 mg CH_4 m^{-2} d^{-1} in vegetated waters (n=55), while the average in open waters (n=86) was 8.7±13.9 mg CH_4 m^{-2} d^{-1}, thus revealing the importance of the vegetation in the methane transport in this environment.

As reported by Devol et al. (1988) and Christensen et al. (2003), the transport by the vegetation is effective when the roots are linked to the sediments, and it is also dependent on the density of the plants. In the Pantanal, the vegetation covers large extensions of the flooded areas, but in general, the vegetation is linked to the sediments mainly in the margins, where the depth is lower. The majority of the measurements in the lakes were performed in the central part, where the depth is sufficient to avoid the fixation of the roots to the sediments; so, the methane transport by vegetation was minimized. As the floodplains are shallower, the linking of the roots to the sediments is increased which facilitates the transport of methane by the stems. The comparison of the ebullitive fluxes of the open and vegetated areas did not show statistical significant differences, mainly due to the large variability observed in these fluxes.

The correlation analysis among the fluxes and the ambient variables (depth, water temperature and pH) showed that the correlations were weak ($r<0.4$) in all cases, although some of then had significant differences as seen above. The same correlations resulted from a Principal Component Analyses (PCA) of the data.

7.3.4 Regional Emission Estimates

The methane emission estimates are derived from the average fluxes and information about the flooded area. In spite of many questions about the relative contribution of the different transport mechanisms and the influence of the environmental variables about the Pantanal methane emission, this estimate may be a good indicator of the importance of the region to the global methane budget.

Hamilton et al. (2002) made estimates of flooding in the Pantanal region considering different flooding patterns. They estimated that the maximum flooding area is about 130,920 km^2, so that the Pantanal may represent the biggest flooding area in South America. From this area, about 3,120 km^2 represent open waters, like rivers and lakes, which have a small variation in their area during the year. They also estimated 172 days as the floodplain hydroperiod, which is defined as the time with the floodplain inundated above 50% of its maximum inundation area. Thus, the Pantanal has also the longest flooding period in South America.

One first crude regional estimate was determined from the average of all fluxes (116.8 mg CH_4 m^{-2} d^{-1}) and the average flooded area computed for both years (2004 and 2005), using the relation presented by Hamilton et al. (2002). This was worked out to be an emission of 1.37 Tg CH_4 y^{-1} for the whole Pantanal. Considering separately the diffusive and the ebullitive fluxes, the contributions are respectively 0.15 Tg CH_4 y^{-1} and 1.26 Tg CH_4 y^{-1}, with an annual emission of 1.41 Tg CH_4 y^{-1}. As the fluxes showed differences when they were stratified between the lakes and the floodplains, and as the vegetation increases the diffusive fluxes in the floodplains, a new evaluation may be obtained by considering the areas for the two habitats separately. Using the Hamilton et al. (2002) formulation, the floodplains area was estimated as 28,441 km^2, which leads to an emission of 1.95 Tg CH_4 y^{-1} from this environment. The lakes, with an annual flooded area of 3,120 km^2, caused an estimated methane emission of 0.25 Tg CH_4 y^{-1}. The total annual emission resulting from the sum of each component computed separately is 2.20 Tg CH_4 y^{-1}. A summary of these results is presented in Table 7.2.

For Amazonia, with measurements performed in different areas and flooding conditions, the estimates of the annual emission present a range from 2 to 21 TgCH_4 y^{-1}, which is a large range mainly due to the uncertain flooded area estimates (Bartlett et al. 1990). Based on many measurements performed in Amazonia and using remote sensing techniques, Melack et al. (2004) estimated the flooding area as 42,700 km^2, so that the revised annual methane emission from the Amazon basin was 1.73 Tg CH_4 y^{-1}. These authors also made an estimate for the Pantanal using measurements performed in Amazonian environments with savanna-like vegetation, which resulted in a mean methane flux of 95.2 mg CH_4 m^2 d^{-1}. This result is near the value obtained in this work (116.8 mg CH_4 m^2 d^{-1}) and higher than that one obtained by Smith et al. (2002) for the floodplains of the Orinoco River region (41.6 mg CH_4 m^2 d^{-1}). Melack et al. (2004) computed the flooded area using the long-term mean flooded area (34,800 km^2) estimated from Paraguay River stage records measured at Porto Ladário (from 1900 to 1999) by Hamilton et al. (2002); so, the annual emission was estimated as 3.32 Tg CH_4 y^{-1}. The results obtained above show that although there are several questions to clarify about the methane emissions from the Pantanal, this region is as important as Amazônia for the atmospheric methane balance.

Table 7.2 Annual emission of methane for each Pantanal habitat, with diffusive and ebullitive components and total flux (Tg CH_4 y^{-1})

	Diffusive	Ebullitive	Total
Pantanal (overall average area: 31,561 km^2)	–	–	1.37
Pantanal (overall average area: 31,561 km^2)	0.15	1.26	1.41
Lakes (average area: 3,120 km^2)	0.02	0.23	0.25
Floodplains (average area: 28,441 km^2)	0.04	1.91	1.95
Pantanal (lakes+floodplains)	0.06	2.14	2.20

7.4 Conclusions

Methane emission by ebullitive transport was detected only in about 40% of the measurements, but it contributed 90% to total methane release to the atmosphere in the southern Pantanal region, so confirming the early results presented by Marani and Alvalá (2007). Although a correlation between the fluxes and the environmental parameters was very weak, the diffusive transport events presented a statistically significant difference between the wet and dry seasons, however, the ebullitive fluxes did not present statistically significant differences between the wet and dry seasons, while the environmental parameters showed statistically significant differences between the two seasons. The severe drought that the region was subjected to during two years of the study may have influenced the flooding and the emission patterns. The methane emission estimates using different approximations, since a simplified general average flux, up to considering the diffusive, ebullitive and vegetation influences, resulted in methane release to atmosphere in the range of 1.4–2.2 Tg CH_4 y^{-1}, corresponding to about 2.2% of the global emission from natural wetlands. Thus, Pantanal may have the same potential of emission as Amazônia. Finally, additional areas of the Pantanal should be investigated to increase the confidence in the emission pattern obtained in this study.

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