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PRIMARY RESEARCH PAPER

Methane emissions from Mexican freshwater bodies: correlations with water pollution

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Abstract The literature concerning methane (CH_4) emissions from temperate and boreal lakes is extensive, but emissions from tropical and subtropical lakes have been less documented. In particular, methane emissions from Mexican lakes, which are often polluted by anthropogenic carbon and nutrient inputs, have not been reported previously. In this work, methane emissions from six Mexican lakes were measured, covering a broad range of organic inputs, trophic states, and climatic conditions. Methane emissions ranged from 5 to 5,000 mg CH_4 m^{-2} day^{-1}. Water samples from several depths in each lake were analyzed for correlation between water quality indicators and methane emissions. Trophic state and water quality indexes were most strongly correlated with methane fluxes. The global methane flux from Mexican freshwater lakes was estimated to be approximately 1.3 Tg CH_4 $year^{-1}$, which is about 20% of methane and 4.4% of total national greenhouse gas emissions. Data for untreated wastewater releases to the environment gave an emission factor of 0.19 kg CH_4 kg^{-1} of Biochemical Oxygen Demand, which is superior to that previously estimated by the IPCC for lake discharges. Thus, the large volume of untreated wastewater in Mexico implies higher methane emission than previously estimated.

Keywords Eutrophication · Methane emission · Trophic state index · Tropical lakes · Water quality

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Introduction

More than 3% of Earth's continental land surface (approximately 4.6 million km^2) comprises freshwater bodies (Downing et al., 2006) and it is well known that aquatic ecosystems are important sources of atmospheric methane (CH_4). Bastviken et al. (2011) estimated global freshwater methane emissions to be 103 Tg CH_4 annually (92 Tg CH_4 for lakes and reservoirs), while O'Connor et al. (2010) reported values ranging from 100 to 231 Tg CH_4. However, the magnitude of methane emissions from freshwater bodies in the context of other global natural and anthropogenic sources needs to be constrained (Chen & Prinn, 2006; Walter et al., 2007; Conrad et al., 2009).

CH_4 emissions from aquatic ecosystems are controlled by many factors, of which one of the most important is temperature (Bastviken et al., 2008). Indeed, methanogenesis is a mesophilic process with an optimum between 35 and 42°C (Schulz et al., 1997). Thus, lakes in tropical environments typically emit more CH_4 than those in temperate and boreal regions. In addition to data reported by Bastviken et al. (2011), Table 1 shows a selected list of CH_4 emissions previously reported for a range of lakes. According to these reports, lakes in the tropics emit up to nine times more CH_4 than temperate lakes, and up to 400 times more than boreal lakes. In addition, lakes located in tropical and subtropical regions are more prone to eutrophication (Lewis, 1996), which is known to promote CH_4 emissions (Huttunen et al., 2003; Pavel et al., 2009; Schrier-Uijl et al., 2011).

It has also been shown that high emissions of CH_4 are related to high inputs of organic material and nutrients (Tranvik et al., 2009). For instance, (i) Schrier-Uijl et al. (2011) found significant positive correlations between CH_4 emissions and concentration of total nitrogen (TN) and organic matter content of sediments, (ii) Bastviken et al. (2004) found positive correlations between CH_4 fluxes and total phosphorus combined with CH_4 concentration, and (iii) Juutinen et al. (2009) found that 3–37% of CH_4 fluxes could be explained by morphometric parameters, such as maximum depth and lake area, in combination with physicochemical parameters, such as TN or phosphorus. However, the impact of water pollution on greenhouse gas (GHG) emissions has been only partially studied and should be further investigated, particularly in subtropical and tropical environments.

Several factors make important to study subtropical and tropical lakes in Mexico. First, to the best of our knowledge, methane emissions from Mexican freshwater bodies have never been previously reported and are not included in the National Greenhouse Gas Inventory (SEMARNAT-INECC, 2012). Second, freshwater resources in Mexico are limited by moderate and non-homogenous rainfall throughout the country (i.e., normal precipitation = 760 mm; CNA, 2011, p. 22, Fig. G2.4) and are subject to increasing demand. Nevertheless, only 37 and 19% of urban and industrial wastewaters are

Table 1 CH_4 fluxes from lakes and reservoirs reported in the literature

Climate	Type	Flux ranges (mg CH_4 m^{-2} day^{-1})	Average flux (mg CH_4 m^{-2} day^{-1})	Reference
Tr	L	62.4 to 1,187.2	131.8	Bastviken et al. (2010)
Tr	L	1.0 to 1,179.0	122.0	Marani & Alvala (2007)
Tr	L	4,221.8 to 5,054.2	4,638.0	Verma et al. (2002)
Tr	L	–	374	Ortiz-Llorente & Alvarez-Cobelas (2012)
Tr	R	6.7 to 457.3	62.7	Kemenes et al. (2007)
Tr	R	−3026.0 to 5,763.2	84.0	dos Santos et al. (2006)
STr	L	–	1,272	Ortiz-Llorente & Alvarez-Cobelas (2012)
STr	L	6.7 to 71.3	23.3	Xing et al. (2005)
STr	R	0.1 to 2.8	2.8	Zheng et al. (2011)
T	L	0.0 to 1,733.9	192.0	Casper et al. (2000)
T	L	33.6 to 434.4	120.0	Schrier-Uijl et al. (2011)
T	L	1.9 to 1,505.6	70.1	Striegl & Michmerhuizen (1998)
T	L	0.0 to 720.0	5.8	Whitfield et al. (2011)
B	L	−0.1 to 10.8	0.8	Demarty et al. (2009)
B	L	0.2 to 0.9	0.4	Demarty et al. (2011)
B	L	0.3 to 19.0	3.8	Bellido et al. (2011)
B	L	1.0 to 2.7	1.9	Ojala et al. (2011)
B	L	−1.1 to 11.3	3.1	Zhu et al. (2010)
B	R	−0.2 to 27.7	0.3	Demarty et al. (2009)

L lake, *R* reservoir, *Tr* tropical, *STr* subtropical, *T* temperate, *B* boreal

treated, respectively (CNA, 2011, p. 73), which indicates that large amounts of untreated wastewater are released into aquatic ecosystems. Third, it was estimated that 88% of freshwater bodies was polluted (SEMARNAT, 2005, pp. 322, 326). Thus, Mexican lakes are both a critical resource and a potentially important source of atmospheric methane. Fourth, Mexico has a varied topography consisting of mountains with high elevations, deserts, low tropical coastal plains, and temperate high plateaus. Freshwater bodies (0.7% of the 1.97×10^6 km^2 territory) are therefore subject to varying climatic conditions, ranging from subtropical/temperate to tropical. A more detailed understanding of methane emissions from these contrasting climates may therefore be important and relevant on a broad geographical scale.

The objective of this study was to monitor methane emissions from Mexican freshwater bodies and to determine the impact of water pollution on these emissions. Particular emphasis was given to relationships between climate, water quality indicators, and methane emissions.

Materials and methods

Study sites, sampling stations, and sampling periods

Two tropical and four subtropical natural lakes or reservoirs were selected, covering a wide range of trophic states. The two tropical lakes were "Lago Olmeca" (LO) and "Lago Coyol" (LC), both located close to the urban area of the city of Veracruz (Veracruz State, Mexico). The four subtropical lakes were "Lago de Guadalupe" (LG) and "Lago El Llano" (LL), located in Mexico State close to Mexico City, and "Lago Zirahuen" (LZ) and "Lago Umecuaro" (LU), which are located in the Michoacan State. Table 2 shows the coordinates and main characteristics of these lakes.

Perimeter maps of the selected lakes are given in Fig. 1. LO is an almost circular and shallow reservoir that continually receives urban wastewater discharges, while LC is an oval shaped natural lake with no apparent wastewater discharge. Both LO and LC are at sea level, with tropical climate and an average annual air temperature of 25°C. LG is a dendritic reservoir located at 2,230 m above mean sea level (AMSL), which continually receives untreated wastewater discharges at 0.5 m^3 s^{-1}. LL is a nearly circular reservoir within the same drainage basin, located 26 km west of LG and at 2,840 m AMSL. This aquatic ecosystem is located in a protected area and receives water from an unpolluted tributary river and springs. Both LG and LL are located in the central region of Mexico, and have a subtropical climate of warm summers and mild winters with an average annual air temperature of 17°C. LZ is a circular natural lake at 2,080 m AMSL with no reported wastewater discharges, while LU is an elongated reservoir at 2,190 m AMSL, which receives low inputs of wastewater from surrounding areas. Both LZ and LU are characterized by subtropical climate with warm summers and mild winters, and an average annual air temperature of 18°C. The shape of the lakes was characterized by the shoreline development ratio, defined by Eq. 1 (Hutchinson, 1957) where L is the shoreline length (m) and A is the area of the lake (ha), both determined from the analysis of satellite imagery (Landsat-5 TM).

$$D_L = \frac{L}{2\sqrt{\pi A}} \quad (1)$$

Between two and seven monitoring and sampling stations (MSS) were established in each lake (Fig. 1; Table 2). When longitudinal zonation was clearly observed (LG, LL, and LU), MSS were selected in such a way, that the representative areas of the lakes were covered from the fluvial to the lacustrine zone. In those cases where no longitudinal zonation was observed (LO, LC, and LZ), the MSS were evenly distributed on a cross section of the lake (LC and LZ) or in randomly chosen locations (LO). Littoral zones were discarded during the selection of MSS, as they were changing over time in reservoirs, due to water level changes (LO, LG, LL, and LU). At each MSS, water samples were taken at 2-m interval from the water column's surface to the bottom; in those cases where depth was inferior to 2 m, only surface and bottom samples were taken. Water quality indicators and CH_4 fluxes were determined at least three times a year, between March 2009 and May 2010, i.e., during the three main characteristic seasons: cold, dry winter; warm, dry late spring to early summer; and warm, rainy late summer. Details of MSS locations, number of samples, and sampling dates are listed in Table 2. Aquatic plants were only found in LO, where *Eichhornia* sp. was covering 5–10% of the lake surface area; the LO areas covered with plants were not sampled.

Table 2 Lakes, dates, and MSS positions

Lake	Climate	Area (ha)	Dates[a]	MSS	Latitude	Longitude	Depth (m)	WS	FM
LO	Tropical	62	03/31/2009	LO1	19.1522	−96.1501	0.7	2	3
			10/28/2009	LO2	19.1488	−96.1500	1.6	2	2–3
			01/20/2010	LO3	19.1452	−96.1518	1.0	2	3
			05/22/2010	LO4	19.1438	−96.1557	1.2	2	3
LC	Tropical	4.5	03/30/2009	LC1	19.1620	−96.1466	3.2	3	2–3
			10/27/2009	LC2	19.1600	−96.1465	2.5	2	3
			05/25/2010	LC3	19.1585	−96.1464	3.2	3	3
LG	Subtropical	450	06/09/2009	LG1	19.6350	−99.2758	6.0	3	3
			09/24/2009	LG2	19.6232	−99.2791	6.0	3	2–3
			09/27/2009[b]	LG3	19.6274	−99.2686	19.0	8	2–3
			03/03/2010	LG4	19.6331	−99.2729	13.5	8	3
				LG5	19.6333	−99.2602	19.5	10	3
				LG6	19.6216	−99.2485	5.7	4	3
				LG7	19.6342	−99.2526	3.0	2	3
LL	Subtropical	6	09/29/2009	LL1	19.6582	−99.5071	13.0	6	3
			02/10/2010	LL2	19.6552	−99.5086	6.0	4	3
			04/03/2010						
LZ	Subtropical	859	07/02/2009	LZ1	19.4457	−101.7317	8.0	5	3
			12/15/2009	LZ2	19.4407	−101.7351	19.0	8	3
			04/26/2010	LZ3	19.4356	−101.7388	27.0	11	3
				LZ4	19.4311	−101.7424	32.0	13	2–3
				LZ5	19.4259	−101.7467	32.0	13	3
LU	Subtropical	131	07/03/2009	LU1	19.5281	−101.2525	2.5	2	3
			12/16/2009	LU2	19.5215	−101.2427	1.8	2	3
			04/27/2010	LU3	19.5180	−101.2334	1.0	1	2–3
						Total measurements		355	234

WS number of water samples analyzed, *FM* number of flux measurements

[a] Starting dates of sampling and monitoring at all MSS

[b] Measurement of night fluxes, no water sampling/analysis

CH_4 emissions

Most CH_4 emissions were measured in all lakes between 10:00 am and 06:00 pm. However, in order to assess potential diel variation, one nocturnal measurement of CH_4 emission was done in LG (between 02:00 and 08:00 am) on September 27, 2009. Fluxes were measured with the static chamber technique (St. Louis et al., 2000) following the minimum requirements stated by Rochette & Eriksen-Hamel (2008). The static chambers were cylindrical, with an open surface of 0.056 m^2 and headspace volume of 2.8×10^{-3} m^3. Static chambers were fully open at the bottom, to account for gas emissions by bubbling and diffusion, as commonly done before (Bastviken et al., 2004; DelSontro et al., 2011; Schubert et al., 2012). In addition to the standard chambers that were fully open at the bottom, some measurements in LG were done with modified static chambers including a polyethylene deflector to discard bubbles rising from beneath. Measurements performed with these modified chambers were considered to exclusively account for diffusive fluxes as previously done by DelSontro et al. (2010). Each static chamber was equipped with a sampling port from which headspace gas samples were taken every 30 min within a 4-h period, or every 10 min within a 1-h period, for the higher fluxes. Gas samples were taken in triplicate and stored in pre-vacuumed 25-ml serological vials closed with an aluminum cap and black butyl septum. Methane concentrations were

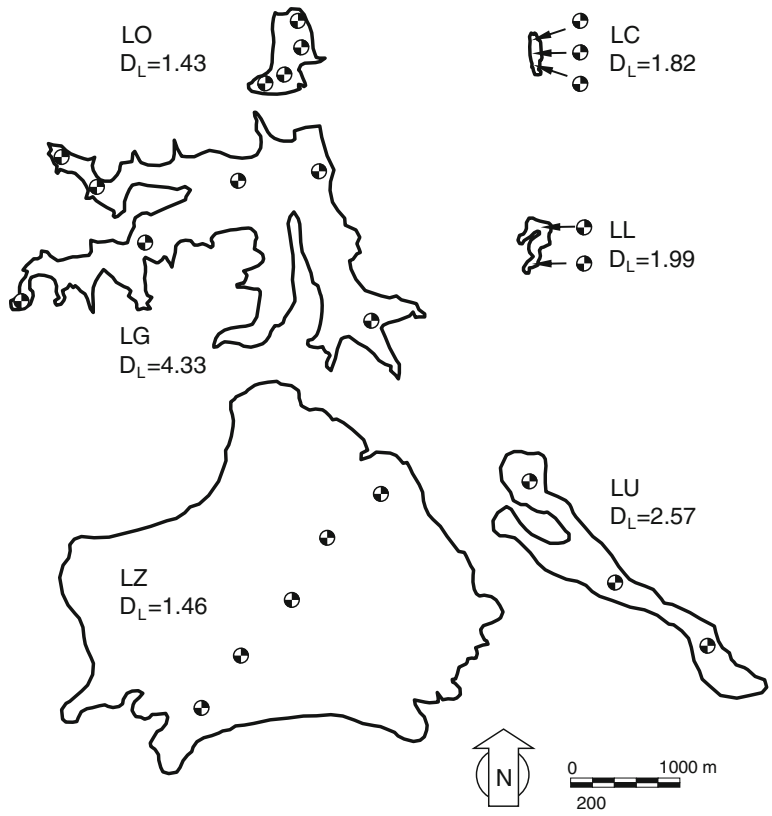

Fig. 1 *Perimeter maps* of the selected lakes and localization of monitoring stations (*black* and *white dots*)

determined between 8 and 48 h after sampling, via a gas chromatograph (Agilent Technology 4890D, Mexico) equipped with an FID detector and a packed Porapak-Q column. Methane standards were used before and after each sample set analyses. Methane fluxes (F, mg CH_4 m^{-2} day^{-1}) were determined from the slope of the CH_4 concentration increase against time of sampling ($\Delta C/\Delta t$, mg m^{-3} day^{-1}); where ΔC is the increase of CH_4 concentration in the static chamber headspace as measured by gas chromatography (mg m^{-3}). The area (A_{SC}, m^2) and the volume (V_{SC}, m^3) of the static chamber were taken into account as stipulated in Eq. 2 (Rolston, 1986). In Eq. 2, C was adjusted for pressure and temperature according to the ideal gas law.

$$F = \frac{\Delta C}{\Delta t} \cdot \frac{V_{SC}}{A_{SC}} \tag{2}$$

Two criteria were tested before data trends were analyzed (Duchemin et al., 1999): (i) that the initial concentration was nearly equal to ambient atmospheric concentration; and (ii) that the linear correlation coefficient (R^2) from the regression analysis was >0.90. Methane fluxes measured at each sampling date and each MSS were averaged to determine annual emissions. In LG, due to dendritic shape ($D_L = 4.33$) and in LL and LU, due to elongated shape, area weighted averages were used. In the other lakes, due to regular shape (D_L from 1.43 to 1.82) and the homogeneous MSS distribution on a cross section, unweighted averages were used. Methane fluxes at each sampling date were prorated over the corresponding time between sampling.

The potential national CH_4 emissions were related to wastewater discharges by the determination of an emission factor (EF). EF is defined as the amount of CH_4 produced from a given amount of Biochemical Oxygen Demand (BOD_5) as described in Eq. 3 (IPCC 2006, 6.2), where (i) B is the maximum methane production from a given amount of BOD_5 and (ii) MCF is a correction factor, defined as the extent to which the CH_4 producing capacity is accomplished.

$$EF = B \cdot MCF \tag{3}$$

Water quality analysis

In order to determine the impact of pollution of freshwater bodies on CH_4 emissions, this work focused almost exclusively on the water quality assessment, although CH_4 is mostly produced in sediments. Several reasons supported this choice. First, the objective of this work was to establish the impact of wastewater discharges on lakes. Second, as wastewater discharges are the main allochthonous carbon input in polluted lakes, water quality allows for the determination of a carbon mass balance, where sediments function as an intermediary between carbon inputs and CH_4 emissions. Finally, as it will be shown in the "Results" section, a partial characterization of sediments from one lake (LG) showed no correlation between sediments characteristics and CH_4 emissions. In situ water quality measurements included temperature, pH, and dissolved oxygen (DO), determined at different depths at each sampling site using a multiparametric probe (556 MPS, YSI, USA). Secchi disk depth (SD) was measured with a 0.2-m Secchi disk. Water samples for ex situ analyses were collected using a horizontal 2.2-l Van Dorn bottle (WILDCO, USA) at the same depths as in situ measurements. Water samples were handled according to standard methods (APHA, 1989). Nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), chemical oxygen demand (COD), BOD_5, chlorophyll "a" (Chl "a"), total solids (TS), and volatile solids (VS) were determined according to standard methods (APHA, 1989), whereas total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), and TN were measured using a total carbon and nitrogen analyzer (Shimadzu-Vcsn + TN1 module, Shimadzu, Mexico). Trophic state indexes (TSI) were used to determine cultural eutrophication. TSI were based on Secchi depth (TSI-SD), chlorophyll "a" (TSI-Chla), and orthophosphate (TSI-PO_4), all of which were calculated according to Carlson (1977). Global TSI was determined from the unweighted arithmetic mean of TSI-SD, TSI-Chla, and TSI-PO. Water quality indexes (WQI) were calculated with a weighted multiplicative function (Eq. 4) of parameter quality indexes (Q_i); where W_i is the weight of each quality index. Seven parameters were considered; pH, DO, TS, COD, BOD_5, PO_4^{3-} and NH_4^+. Q_i were obtained from the National Sanitary Foundation (www.water-research.net/watrqualindex) and W_i values were modified from Fernandez & Solano (2005); i.e., 0.14, 0.22, 0.07, 0.11, 0.21, 0.16, and 0.09 for pH, DO, TS, COD, BOD_5, PO_4^{3-}, and NH_4^+, respectively.

$$\mathrm{WQI} = \prod_{i=1}^{n} Q_i^{W_i} \tag{4}$$

Sediments analysis

In addition to water quality analysis and in order to establish the impact of sediment quality on CH_4 emissions, sediments from three MSS in LG were collected using a Petersen grab dredge. These samples were collected in February, May, and September 2008 together with independent CH_4 fluxes measurements in triplicate (not reported in Table 4 nor included in the overall analysis of this work). The MSS were located in the fluvial (LG 2), the transitional (LG 3) and the lacustrine (LG 5) zones. Sediments were analyzed for TOC, sulfate (SO_4^{2-}), total phosphorus (TP), TN, and dry weight. Simultaneously, CH_4 fluxes were measured in triplicate at the same MSS.

Data and statistical analyses

Results are presented as average (arithmetic mean) ± one standard deviation. Data were tested for normality using the Shapiro–Wilk test and, when necessary, log transformed prior to statistical analysis. TSI and WQI data were compared via one-way ANOVA followed by the Tukey–Kramer test. Multiple regression analysis was done in two ways. In a first method, parameters selected from a principal component analysis (PCA) were used in the multiple regression analysis. The second method added sequentially predictive variables and interactions between them to the model. P values of the model were used to evaluate the predictive variable. The least-squares method was used to derive the correlation between single parameters and CH_4 fluxes, after log transformation when necessary. The coefficient of variation (CV), defined as the standard deviation divided by the average, was used to determine the spatial and seasonal variation of CH_4 fluxes. First, variation in the CH_4 fluxes between the lakes was determined by the CV, comparing average CH_4 fluxes observed in each lake (all dates and all MSS). Second, spatial variation was determined, for a given lake, by comparing the average fluxes measured in each MSS

(all dates) and seasonal variation, for a given lake, was determined by comparing the average fluxes measured in each date (all MSS). Third, the variation of the static chamber technique was derived from the CV of replicated flux measurements. All statistical analyses were done with R language (R Core Team, 2012).

Results

Table 3 shows the mean water quality parameters of the six freshwater bodies. There was a large variation between the study sites. For example, the mean annual temperature ranged from 12.1 ± 4.0°C in LL (subtropical) to 32.8 ± 5.4°C in LC (tropical lake), with relatively small seasonal variations. Differences were also observed for parameters associated with anthropogenic carbon input: TOC ranged from 0.1 ± 0.0 (LZ) to 63.1 ± 61.9 mg l^{-1} (LO), TC from 6.9 ± 0.2 (LL) to 87.2 ± 64.7 mg l^{-1} (LO), and COD from 20.5 ± 1.2 (LU) to 245.9 ± 175.6 mg l^{-1} (LO). As a result of anthropogenic inputs, Chl "a" was also highly variable, ranging from 3.5 ± 1.8 (LZ) to 247.1 ± 105.6 mg m^{-3} (LO). NH_4^+ and PO_4^{3-} were found at different concentrations in all freshwater bodies, but NO_2^- and NO_3^- were not detected, suggesting either that nitrification (ammonium oxidation to nitrate) was inhibited or that denitrification (nitrate reduction to dinitrogen) was dominant. Table 4 shows the differences in TSI and WQI between the freshwater bodies. The selected ecosystems were mesotrophic to hypereutrophic, while WQI ranged from 20.1 ± 10.1 (LO) or "strongly polluted" to 63.5 ± 5.1 (LU) or of an "acceptable quality".

Table 4 also shows average methane emissions from the lakes. The mean CH_4 fluxes ranged from 5 (LZ) to 5,200 mg CH_4 m^{-2} day^{-1} (LO). In LG, methane emissions determined with static chambers equipped with a deflector, represented only 2–5% of the emissions determined with chambers with no deflector, suggesting that 95–98% of fluxes were ebullitive. Larger contribution of ebullition was observed in the fluvial zone. It should be noticed that in lakes where a continuous ebullition was observed (LO and LG), linear R^2 in CH_4 fluxes were lower and standard deviations were higher than in the other lakes (excluding LL). This could be explained by ebullition events. In LG, nighttime CH_4 emission was determined on September 27, 2009 and compared to daytime measurements, done on September 24–26, 2009. During daytime, CH_4 emission was 1,132 ± 1,558 and during nighttime, emission was 1,477 ± 1,102 mg CH_4 m^{-2} day^{-1}, statistical comparison resulted in no significant differences.

Table 3 Mean water quality parameters measured in the different water bodies ± standard deviation

Parameter	LO	LC	LG	LL	LZ	LU
SD (m)	0.16 ± 0.06	0.38 ± 0.03	1.21 ± 0.69	1.5 ± 0.56	5.00 ± 2.00	1.50 ± 0.55
pH	8.91 ± 0.79	8.87 ± 0.11	7.61 ± 0.65	5.60 ± 0.06	7.80 ± 0.27	6.30 ± 0.19
Temperature (°C)	28.39 ± 2.76	32.84 ± 5.41	16.28 ± 0.45	12.14 ± 4.04	21.05 ± 1.26	21.96 ± 0.01
DO (mg l^{-1})	6.70 ± 6.77	5.94 ± 2.25	2.78 ± 2.50	1.91 ± 0.26	8.00 ± 2.11	7.74 ± 0.12
TC (mg l^{-1})	87.21 ± 64.72	50.14 ± 4.75	37.55 ± 8.52	6.85 ± 0.19	13.85 ± 0.42	9.24 ± 0.26
IC (mg l^{-1})	44.91 ± 25.64	36.74 ± 6.25	30.52 ± 4.28	6.67 ± 0.21	13.74 ± 0.44	7.45 ± 0.03
TOC (mg l^{-1})	63.14 ± 61.86	13.40 ± 1.51	6.99 ± 4.93	1.44 ± 2.18	0.11 ± 0.02	1.66 ± 0.13
Chl a (mg m^{-3})	247.07 ± 105.60	89.47 ± 39.44	51.95 ± 28.77	6.85 ± 9.69	3.50 ± 1.75	50.3 ± 22.64
BOD_5 (mg l^{-1})	76.29 ± 81.97	34.87 ± 15.40	3.66 ± 0.74	1.50 ± 2.12	19.76 ± 4.32	13.65 ± 0.80
COD (mg l^{-1})	245.94 ± 175.57	70.08 ± 17.78	30.75 ± 25.93	34.72 ± 25.37	26.95 ± 1.78	20.48 ± 1.24
PO_4^{3-} (mg l^{-1})	1.58 ± 1.73	0.31 ± 0.04	0.35 ± 0.52	0.25 ± 0.11	0.01 ± 0.01	0.09 ± 0.01
NH_4^+ (mg l^{-1})	0.39 ± 0.47	0.30 ± 0.38	0.24 ± 0.01	0.19 ± 0.00	0.03 ± 0.00	0.10 ± 0.00
NO_3^- (mg l^{-1})	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
NO_2^- (mg l^{-1})	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
TN (mg l^{-1})	9.14 ± 9.45	2.51 ± 0.49	9.24 ± 2.88	0.28 ± 0.12	0.31 ± 0.01	0.45 ± 0.00
TS (mg l^{-1})	1,104 ± 1,376	367 ± 38	320 ± 188	129 ± 4	167 ± 94	267 ± 58
VS (mg l^{-1})	630 ± 629	121 ± 66	185 ± 152	122 ± 6	100 ± 0	133 ± 58

CH_4 fluxes showed large variations. Figure 2 shows the box and whiskers plot of the statistical dispersion of fluxes observed. LO, LG, and LL were the lakes with the largest variations. Both LO and LG are the lakes with higher amounts of wastewater discharges. Variations observed in these two lakes might be due to the combined effect of longitudinal zonation, water discharge, and seasonal dilution during the rainy season. In LL, no acceptable explanation was found, except possible sporadic ebullition events. This analysis was completed by determining the variation in CH_4 emission between lakes, and the spatial and seasonal variations. The lake to lake, spatial and seasonal variations were 188, 65, and 36%, respectively. Compared to a CV of 19%, for the static chamber technique, these variations were significant ($P < 0.05$).

Multiple regression analysis was performed to correlate CH_4 emission and water quality parameters. None was significant, except the correlation between CH_4 flux and WQI + SD, which was significant but the P values of both WQI and SD were not significant on their own. According to these results, single parameter correlations were sought. As previously mentioned, methanogenesis is a mesophilic process with an optimum temperature between 35 and 42°C. It was therefore expected that temperature would affect methane emissions, as previously reported. However, despite important temperature differences (Table 3), no correlation was found between temperature and methane emissions ($P = 0.44, R^2 = 0.15$), suggesting that water quality was the main factor controlling methane emissions. From all tested water quality parameters, a significant correlation was only observed between CH_4 emissions and TSI, WQI, SD, and TC (Fig. 3). These results indicate that most of single water quality indicators do not explain by themselves CH_4 emissions but on the contrary, global water quality indicators (TSI, WQI, and SD) correlated well with CH_4 emissions. Despite the latter, it should be pointed out that LO, being the most polluted lake selected, had an important statistical weight in that analysis. If excluded from the statistical regression analysis, P values increased and only TSI and SD remained significant (Fig. 3, inners). Excluding LO, it was also observed that PO_4^{3-} became significantly correlated with CH_4 emissions ($P = 0.011$, $R^2 = 0.91$). This analysis showed the importance of large parameters ranges for correlation purposes.

To further explore the impact of the range of water quality indicators on correlations with methane emissions, a theoretical analysis was conducted that consisted of determining simulated P values for correlations of CH_4 fluxes versus TSI, for several TSI ranges. The analysis used random TSI values within a specified range; for each TSI, a theoretical CH_4 flux was randomly generated in Microsoft Excel, based on the experimental correlation (Fig. 3a), assuming a normal distribution and taking into account the standard error of flux (Standard Error of the Regression, SER, Eq. 5).

$$\mathrm{Log}(F) = \mathrm{NORM.INV(RANDOM)}(), 0.07693 \cdot \mathrm{TSI} - 3.658,\ \mathrm{SER}) \quad (5)$$

The result of the analysis (see Fig. 4) shows that p decreases significantly when the TSI range increases, or when the number of TSI and CH_4 flux independent measurements increases. These results confirm that the range of measurement parameters is a key factor in establishing a correlation between these parameters and CH_4 fluxes.

As mentioned, LG was also tested for sediments characteristics, together with independent CH_4 fluxes measurements. No significant differences were found

Table 4 Average TSI and WQI observed in the six lakes

Lake	TSI	Classification	WQI	CH_4 fluxes (mg CH_4 m^{-2} day^{-1})
LO	89.7 ± 11.0 (A)	Hypereutrophic	20.1 ± 10.1 (C)	5,247.3 ± 4,825.4 (E, F)
LC	83.2 ± 0.5 (A, B)	Hypereutrophic	35.6 ± 12.9 (C)	390.0 ± 89.0 (E, F)
LG	87.4 ± 7.4 (A)	Hypereutrophic	36.0 ± 16.3 (C)	932.8 ± 673.5 (F)
LL	80.7 ± 2.3 (A, B)	Hypereutrophic	62.0 ± 17.0 (C, D)	114.1 ± 188.5 (E, G)
LZ	57.4 ± 2.3 (B)	Mesotrophic	57.7 ± 5.5 (C, D)	4.9 ± 0.8 (G)
LU	66.2 ± 3.0 (B)	Eutrophic	63.1 ± 5.1 (D)	57.8 ± 12.2 (F, G)

Letters in parentheses are Tukey–Kramer test results; values with the same capital letter are not significantly different ($P < 0.05$)

in TOC, TN, total phosphorus, and sulfate concentrations in LG sediments, throughout the monitoring periods. The overall averages of TN, phosphorus, and sulfate in the sediments were 3.64 ± 1.20 g N kg^{-1} dry weight, 1.40 ± 0.30 g P kg^{-1} dry weight, and 0.94 ± 0.28 g SO_4^{2-} kg^{-1} dry weight, respectively. The average TOC content in sediment samples of all MSS was 73.3 ± 18 g kg^{-1} dry weight. The highest TOC value was found in the lacustrine zone (LG5, 97.1 ± 8.2 g kg^{-1} dry weight), while the minimum was found in the fluvial zone (LG2, 21.3 ± 6.2 g kg^{-1} dry weight). In the transitional zone (LG3), TOC concentration was 36.1 ± 7.6 g kg^{-1} dry weight. CH_4 fluxes measured at the same dates in these MSS were 3,700 ± 234 mg CH_4 m^{-2} day^{-1} in the fluvial zone, 1,858 ± 188 mg CH_4 m^{-2} day^{-1} in the transitional zone and 178 ± 119 mg CH_4 m^{-2} day^{-1} in the lacustrine zone (data not included in Table 4). No significant correlation was found between sediments characteristics and CH_4 fluxes, as larger TOC concentrations in LG sediments were found where lower CH_4 emissions were measured and vice versa. These results suggest that rather than concentration, quality of the organic carbon (i.e., degradability) might play a prevailing role in CH_4 production.

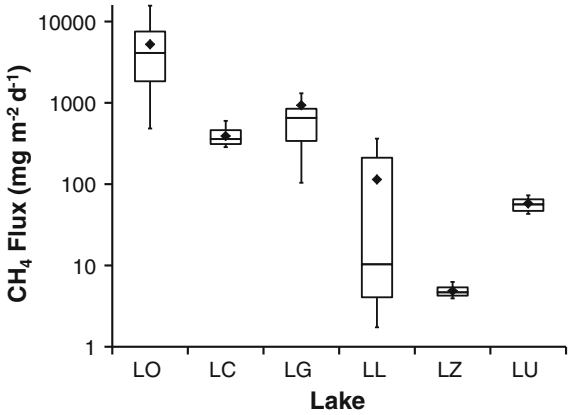

Fig. 2 Statistical distribution of the CH_4 fluxes. The *boxers* include the median standard deviations (Q2) and the quartile range (IRQ = Q3 − Q1; where Q denotes quartiles). The *whiskers* show minimum and maximum data and the diamonds show averages

Discussion

CH_4 emissions from tropical lakes (LO and LC, Table 4) were within the ranges reported by DelSontro et al. (2011) (<100–10,000 mg CH_4 m^{-2} day^{-1}), Bastviken et al. (2010) (62–1,187 mg CH_4 m^{-2} day^{-1}), and Marani

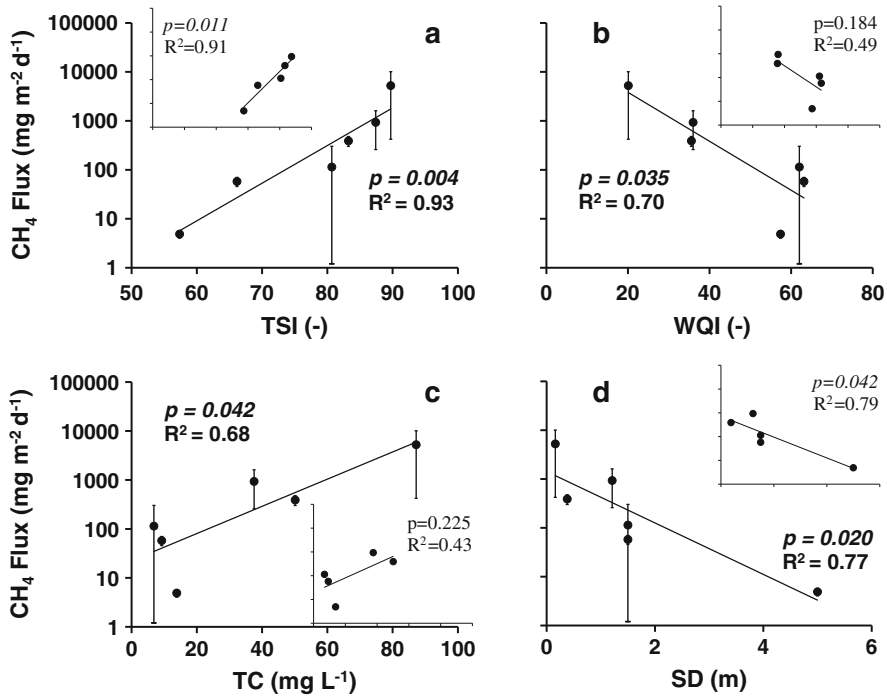

Fig. 3 Correlations between methane emissions from freshwater bodies and water quality indicators; TSI (**a**), WQI (**b**), TC (**c**), and SD (**d**). *Straight lines* represent the best correlation found; $F = 2.19 \times 10^{-4}\ e^{(0.177\ TSI)}$ (**a**), $F = 38{,}268\ e^{(-0.115\ WQI)}$ (**b**), $F = 22.40\ e^{(0.063\ TC)}$ (**c**), and $F = 1{,}427\ e^{(-1.213\ SD)}$ (**d**). *Inners figures* show same analysis, excluding LO

& Alvala (2007) (1–2,184 mg CH_4 m^{-2} day^{-1}). Similarly, CH_4 emissions observed in the subtropical water bodies were similar to those reported by Xing et al. (2004) (5.8–1,080 mg CH_4 m^{-2} day^{-1}) and within the range of fluxes reported for subtropical and temperate lakes (Table 1). As previously mentioned, in LG, 95–98% of total CH_4 emissions occurred through ebullition. The relative importance of the ebullitive flux was superior to those previously reported for temperate lakes and reservoirs; i.e., 63 ± 33% in 15 lakes as reported by Bastviken et al. (2004) and 56% as reported by Sobek et al. (2012). However, the ebullition contribution was similar to values reported by DelSontro et al. (2011) for a large tropical reservoir and by Casper et al. (2000) for a temperate lake. In LG, larger ebullition contributions were observed in the fluvial zone, in accordance to previous reports showing that minor depths favor ebullition (Bastviken et al., 2004; DelSontro et al., 2011).

In this work, with the exception of a single nighttime measurement in LG, all measurements of CH_4 emissions correspond to daytime, the latter is a common strategy reported in the literature. However, some authors have reported diel variation of CH_4 emissions, without reaching a consensus. For instance, Zheng et al. (2011) and Duan et al. (2005) found higher fluxes during daytime, while Xing et al. (2004) found no correlation between fluxes and solar irradiance and Bolpagni et al. (2007) and Crill et al. (1988) found higher CH_4 emissions during nighttime. It should be mentioned that Bolpagni et al. (2007) also observed major CH_4 emissions during daytime, in presence of aquatic plants. Chanton et al. (1993) as well as Dacey & Klug (1979) and Bastviken et al. (2010) have also shown results suggesting that daytime increase in CH_4 emissions is probably related to aquatic plants. In the present work, no significant difference was observed in LG between nighttime and daytime measurements and CH_4 emissions were determined in absence of aquatic plants. This suggests that daytime measurements presented here can be extrapolated to daily emission as often considered in the literature.

CH_4 emissions were characterized by a CV of 188, 65, and 36% for lake to lake, spatial and seasonal variations, respectively. These results show that variations within a lake (both spatial and seasonal) where lower than variation between lakes. This is contradictory to what previously found by Bastviken et al. (2010), but can be easily explained by the fact that in the present work, lakes were specially selected to cover a wide range of different conditions, which was not the case of Bastviken et al. (2010). The results also suggest that spatial variations were more important than seasonal variations. This was observed in all lakes, which was probably due to several factors, such as depth profiles, inputs of wastewater discharges, and/or lake morphometry.

Establishing correlations between environmental parameters and methane emissions is an essential step in estimating global emissions from aquatic ecosystems. Several authors have sought correlations between pollution indicators and methane emissions. As previously mentioned, Schrier-Uijl et al. (2011), Bastviken et al. (2004), and Juutinen et al. (2009) reported correlations between methane emissions and nutrient/carbon inputs. Yvon-Durocher et al. (2011) found a positive correlation between CH_4 fluxes and gross primary production. Several other studies, however, have failed to correlate water characteristics with CH_4 emissions, or showed statistically significant effects but without an obvious phenomenological relationship. There are several potential reasons why it is apparently difficult to correlate ecological indicators with CH_4 emissions. Despite the complexities of methane cycling processes and the temporal and spatial variability of methane emissions (Ortiz-Llorente & Alvarez-Cobelas, 2012), most previous works compared emissions measured in one or several ecosystems, but within a limited range of water quality indicators. In contrast, the present work determined

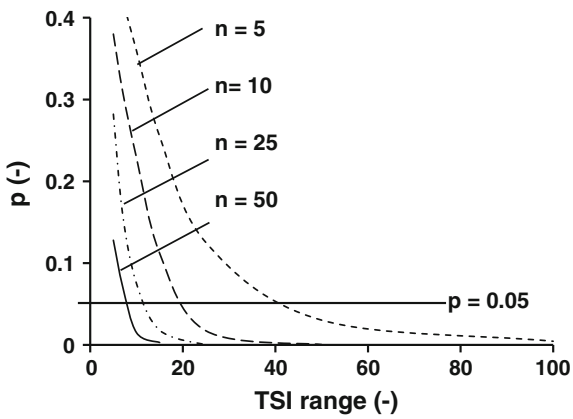

Fig. 4 *P* values of correlations between methane emissions and TSI, versus TSI range, for several independent measurements (*n*)

Table 5 Calculated emissions from superficial water bodies in Mexico

WQI range[a]	85–100	70–84	50–69	30–49	0–29
WQI average	92.5	77	59.5	39.5	14.5
Area of superficial water bodies (%)[a]	6	20	51	16	6
Area of superficial water bodies (km^2)[b]	415	1,382	3,524	1,106	415
Estimated CH_4 flux (mg m^{-2} day^{-1})	0.9	5.5	40.8	407.4	7,221.9
CH_4 emission (Tg CH_4 $year^{-1}$)	0.1×10^{-3}	2.8×10^{-3}	52.5×10^{-3}	164.4×10^{-3}	1.09
CH_4 emission (Tg CO_2eq $year^{-1}$)[c]	3.5×10^{-3}	68.8×10^{-3}	1.31	4.11	27.32
Total CH_4 emission (Tg CO_2 eq $year^{-1}$)[2]					32.82

[a] SEMARNAT (2003)

[b] Total area covered by water bodies in Mexico is 6,910 km^2 (Alcocer & Bernal-Brooks, 2010)

[c] Using a Global Warming Potential of 25 (100 years GWP time horizon) for CH_4 (IPCC, 2007, p. 33)

methane emissions from freshwater bodies with a large variation of water quality indicators; i.e., ratio of the standard deviations to the average from 18% (pH) to 168% (TOC).

The latter was confirmed by Fig. 4, which showed how large parameter range is a key feature for establishing correlations. Results also showed that most of single water quality indicators failed to explain by themselves CH_4 emissions as global water quality indicators do. Indeed, of the water quality parameters examined, TSI best described CH_4 emissions. The TSI parameter includes SD, PO_4^{3-}, and Chl "a", which are indirect indicators of allochthonous organic matter and nutrient inputs. These parameters have two possible effects on lakes: organic matter and nutrient inputs stimulate microbial activity, thereby consuming DO within the water column; moreover, they promote primary production and autochthonous organic carbon production, both of which are favorable for methanogens (Lampert & Sommer, 1997; Barrera & Wong, 2007).

From the results obtained, CH_4 emission was estimated for all Mexican lakes and reservoirs, and the impact of water pollution on CH_4 emissions was determined. Fluxes from the Mexican lake and reservoir system were estimated from the relationship shown in Fig. 3b, using previously reported WQI values (SEMARNAT, 2003, p. 146). These fluxes were then related to the extent of superficial water bodies in Mexico (Alcocer & Bernal-Brooks, 2010). From that analysis, it was estimated that Mexican lakes and reservoirs in combination emit 1.3 ± 0.4 Tg CH_4 $year^{-1}$ or 33 ± 11 Tg CO_2-equivalent $year^{-1}$ (Table 5), which represents about 4.4 ± 1.4% of the total national GHG budget (747 Tg CO_2 equivalent $year^{-1}$) or 19.7 ± 6.3% of the national methane budget (SEMARNAT-INECC, 2012, p. 239). Emissions from highly polluted freshwater bodies (WQI < 30), which represent 6% of the Mexican freshwater bodies, would represent about 83% of total emissions from lakes and reservoirs.

According to CNA (2011, p. 73), about 7 Tg of BOD_5 in untreated wastewater is released every year, ending up in superficial waters. It can therefore be estimated that, for each kg BOD_5 released to the environment, 0.19 ± 0.06 kg of CH_4 is emitted by freshwater bodies. This EF (Eq. 3), when divided by a maximum methane capacity (B) of 0.6 kg CH_4 kg^{-1} BOD, gives a methane correction factor (MCF) of 0.30 ± 0.09 (Eq. 3). The calculated MCF is similar to those suggested by the IPCC for poorly managed or overloaded aerobic treatment plants and for anaerobic shallow lagoons, but is higher than MCF reported for lake discharges (IPCC, 2006, 6.3). It should be pointed out that this estimation does not take into account that only part of the released BOD_5 reaches freshwater bodies; nor that the calculation used data from different sources, and is thus potentially subject to error. However, this is a clear indication that high level of pollution (WQI < 30) might result in a greater contribution to methane emissions than previously thought.

Conclusions

Significant correlations were found between water quality indicators and methane emissions, with WQI

being the most strongly correlated with methane emissions. From the correlations established and from the overall WQI previously reported for Mexican lakes and reservoirs, annual methane emissions from freshwater bodies in Mexico were estimated at 1.3 ± 0.4 Tg CH_4 or 33 ± 11 Tg CO_2-equivalent. The results also suggest that the 6% most polluted Mexican aquatic ecosystems would contribute to approximately 77% of the total methane emissions from lakes and reservoirs. The EF of the lakes was also larger than the one estimated previously by the IPCC for lake discharges. Thus, the large volume of untreated wastewater in Mexico results in higher methane emission than previously estimated. As temperature was not a key factor in methane emissions, the results presented here are potentially applicable to other subtropical and tropical regions of the world, with high amounts of BOD_5 released in the environment. On a national scale, these results underline the importance of reducing untreated wastewater discharges, particularly to lakes that are already highly polluted. It is also concluded that methane emissions from freshwater bodies represent a relevant fraction of total national greenhouse gas budget, and should therefore be included in the national emissions inventory.

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