



## Ecosystem maturity modulates greenhouse gases fluxes from artificial lakes

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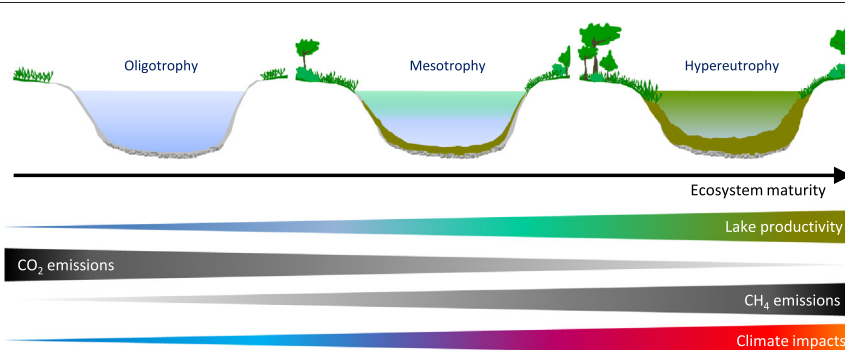
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### HIGHLIGHTS

- C cycling variability and its variability in artificial lakes have been overlooked.
- We quantified gas fluxes in 11 gravel pit lakes across a gradient of ecosystem maturity.
- Lakes ranged from heterotrophic to autotrophic as maturity increased.
- Eutrophication turns lakes as CO<sub>2</sub>-sinks.
- CH<sub>4</sub> emissions and associated climate impacts increased with ecosystem maturity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Lentic ecosystems play a major role in the global carbon cycling but the understanding of the environmental determinants of lake metabolism is still limited, notably in small artificial lakes. Here the effects of environmental conditions on lake metabolism and CO<sub>2</sub> and CH<sub>4</sub> emissions were quantified in 11 small artificial gravel pit lakes covering a gradient of ecosystem maturity, ranging from young oligotrophic to older, hypereutrophic lakes. The diffusive fluxes of CO<sub>2</sub> and CH<sub>4</sub> ranged from  $-30.10$  to  $37.78$  mmol m<sup>-2</sup> d<sup>-1</sup> and from  $3.05$  to  $25.45$  mmol m<sup>-2</sup> d<sup>-1</sup> across gravel pit lakes, respectively. Nutrients and chlorophyll *a* concentrations were negatively correlated with CO<sub>2</sub> concentrations and emissions but positively correlated with CH<sub>4</sub> concentrations and emissions from lakes. These findings indicate that, as they mature, gravel pit lakes switch from heterotrophic to autotrophic-based metabolism and hence turn into CO<sub>2</sub>-sinks. In contrast, the emission of CH<sub>4</sub> increased along the maturity gradient. As a result, eutrophication occurring during ecosystem maturity increased net emissions in terms of climate impact (CO<sub>2</sub> equivalent) due to the higher contribution of CH<sub>4</sub> emissions. Overall, mean CO<sub>2</sub> equivalent emission was  $7.9$  g m<sup>-2</sup> d<sup>-1</sup>, a value 3.7 and 4.7 times higher than values previously reported in temperate lakes and reservoirs, respectively. While previous studies reported that lakes represent emitters of C to the atmosphere, this study highlights that eutrophication may reverse lake contribution to global C budgets. However, this finding is to be balanced with the fact that eutrophication also increased CH<sub>4</sub> emissions and hence,

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enhanced the potential impact of these ecosystems on climate. Implementing mitigation strategies for maintaining intermediate levels of maturity is therefore needed to limit the impacts of small artificial waterbodies on climate. This could be facilitated by their small size and should be planned at the earliest stages of artificial lake construction.

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## 1. Introduction

Due to the large amounts of terrestrial C that they transport, process and store, inland waters are an active component of the global carbon (C) cycle thus potentially affect global climate (Cole et al., 2007; Tranvik et al., 2009). During the last decade, a myriad of studies has focused on quantifying CO<sub>2</sub> (e.g., Battin et al., 2009; Raymond et al., 2013) and CH<sub>4</sub> (e.g., Bastviken et al., 2011) emissions from inland waters. In particular, lentic inland ecosystems including lakes appeared to be globally significant emitters of CO<sub>2</sub> and CH<sub>4</sub> to the atmosphere (e.g., Bastviken et al., 2011; Deemer et al., 2016; DelSontro et al., 2018a, 2018b; Holgerson and Raymond, 2016) justifying their inclusion in IPCC guidelines for national and global inventories of greenhouse gases (GHG) (IPCC, 2019). Nonetheless, current estimates of C emissions from lentic ecosystems are based on extrapolations of average emission rates to global lake surface area. These estimates vary considerably, ranging from 0.38 to 0.81 Pg C yr<sup>-1</sup> (e.g., Cole et al., 2007; DelSontro et al., 2018a, 2018b; Holgerson and Raymond, 2016; Tranvik et al., 2009), highlighting the existence of large uncertainties for global estimates that was likely driven by a lack of knowledge of the mechanisms driving emission rate variability (e.g., DelSontro et al., 2018a, 2018b).

Eutrophication is a paramount environmental concern worldwide (Carpenter et al., 1999; Jeppesen et al., 2012), but its role as a driver of the direction and magnitude of GHG flux from/to lentic ecosystems remains unclear. The role of lakes as sources or sinks of C is highly dependent on the balance between primary production and ecosystem respiration (e.g., Cole et al., 2000; Jeppesen et al., 2016; Prairie et al., 2002). Lakes with high loading of organic C tend to be net heterotrophic ecosystems and act as significant sources of C to the atmosphere through respiration (e.g., Andersson and Sobek, 2006; Hanson et al., 2003; Laas et al., 2012). However, the relative importance of organic C load and associated heterotrophic respiration may be offset by a high CO<sub>2</sub> uptake by primary producers, especially in lakes with high total phosphorus (TP) concentrations since it is known that TP regulated primary productivity (e.g., Davidson et al., 2015; Laas et al., 2012; Yang et al., 2019). In some eutrophic lakes, high CO<sub>2</sub> uptake by primary producers can turn lakes into net autotrophic ecosystems and hence CO<sub>2</sub> sinks (Kosten et al., 2010; Pacheco et al., 2014; Roland et al., 2010). Yet, this holds for a small proportion of lakes while most of them are predominant sources of C. This is because the loading of allochthonous organic C generally greatly exceeds autochthonous primary production (e.g., Bastviken et al., 2011; Cole et al., 2000, 1994; Deemer et al., 2016). The projected increase in lakes eutrophication (e.g., Beaulieu et al., 2019) may therefore reverse the global contribution of lakes to global C budget (Pacheco et al., 2014). While high primary productivity may decrease CO<sub>2</sub> emissions from lakes, it may act oppositely by promoting CH<sub>4</sub> emissions, providing labile substrate for methanogenic bacteria and promoting C-rich and oxygen-poor environment (e.g., Sepulveda-Jauregui et al., 2018; Vachon et al., 2020; West et al., 2016, 2012; Yang et al., 2019). This suggests that eutrophication may lead to a decrease in emissions of C from lakes in the form of CO<sub>2</sub> but, at the same time, to an increase in emissions of C in the form of CH<sub>4</sub>. This is an important consideration because CH<sub>4</sub> in the atmosphere is up to 34 times more potent as greenhouse gas (GHG) than CO<sub>2</sub> over a 100-year time scale (IPCC, 2013) and its individual contribution to total radiative forcing range between 71.8 and 77.8% when considering aquatic waterbodies (DelSontro et al., 2018a). This indicates that the effects of eutrophication

on CH<sub>4</sub> emissions can deeply influence lake contribution to global warming.

The relationships between eutrophication, CO<sub>2</sub> autotrophy and CH<sub>4</sub> emissions are, however, highly context-dependant (Deemer et al., 2016; DelSontro et al., 2018a; Ollivier et al., 2019). For instance, DelSontro et al. (2018a, 2018b) reported that TP enrichment decreased CO<sub>2</sub> emissions in medium to large-size lakes while it increased emissions in small lakes. In addition, chlorophyll *a* was positively associated to CH<sub>4</sub> emissions, though the strength of this effect was stronger for larger ecosystems (DelSontro et al., 2018a, 2018b). This suggests that the extent to which eutrophication influences greenhouse gas emissions may be dependent on lake morphometry and highlights the high contribution of small lakes to global C emissions from lentic ecosystems. While they are particularly prone to eutrophication (e.g., Ollivier et al., 2019; Wetzel, 2001) and extremely abundant worldwide (e.g., Cael et al., 2017; Verpoorter et al., 2014), small, shallow and artificial lakes remain overlooked compared to natural and large ecosystems (e.g., Peacock et al., 2019; van Bergen et al., 2019; Webb et al., 2019). For instance, C fluxes from gravel pit lakes, artificially formed when gravel pits are excavated at or below the water table (Mollema and Antonellini, 2016), have not been documented yet. Gravel pits lakes are extremely abundant across the globe (Mollema and Antonellini, 2016), notably because more than 890 million tons of gravel are produced globally per year (USGS, 2017). Gravel pit lakes are usually small (1–100 ha), shallow (2–12 m maximal depth) and distributed in regional clusters experiencing similar climatic conditions. They represent interesting model ecosystems for disentangling the effects of eutrophication on C emissions in small lentic ecosystems. In particular, as they age (defined here as the time since the end of excavation), gravel pit lakes tend to switch from oligotrophic to hypereutrophic waterbodies due to increased nutrients concentrations, lake productivity and the sedimentation of detritus including autochthonous material (Kattner et al., 2000; Mollema and Antonellini, 2016; Zhao et al., 2016). This represents a maturation process (Vitousek and Reiners, 1975) that may be promoted in gravel pit lakes by their disconnection to the rest of the river network and the importance of terrestrial inputs in their functioning (Alp et al., 2016). For instance, Zhao et al. (2016) reported a large range of lake productivity (e.g. chlorophyll-*a* concentration ranging from 0.9 to 58.8 mg l<sup>-1</sup>) in gravel pit lakes. Maturation of these artificial ecosystems is multifaceted process that includes an increased amount of nutrient in the systems (eutrophication), a change in animal communities, an increased ripisylve along the shore as trees grow and a higher intensity of human activities as ecosystems become older (Zhao et al., 2016). Because of their high environmental heterogeneity, gravel pit lakes represent a unique model system to examine the impact of eutrophication on C cycling, while controlling other factors such as climate variability given their very restricted geographical distribution.

In the present study, the effects of eutrophication on gas metabolism and emissions were quantified in 11 gravel pit lakes across a large range of ecosystem maturity to identify the environmental factors driving lakes as C-source or sink. In particular, gravel pit lakes were predicted to shift from net CO<sub>2</sub> sources to net CO<sub>2</sub> sinks as they mature, mainly due to the increased CO<sub>2</sub> uptake by primary producers. Nonetheless, increased CH<sub>4</sub> emissions as primary production and nutrient contents increased were predicted. The impacts of gas fluxes from gravel pit lakes on climate were also estimated and were predicted to be dependent on the balance between CO<sub>2</sub> and CH<sub>4</sub> fluxes and hence, between heterotrophic benthic and the autotrophic water layer metabolism. In

addition, and to provide a broader perspective to these results, the values of gas fluxes measured in the present study were compared to values reported in the literature in other temperate lentic ecosystems.

## 2. Materials and methods

### 2.1. Study sites

The study area was located in the Garonne floodplain (south-west of Toulouse, France) that contains more than 1522 ha of gravel pit lakes (Saplaïroles et al., 2007). The study was conducted in an area with a large quantity of gravel pit lakes with varying environmental conditions (Alp et al., 2016; Jackson et al., 2017; Zhao et al., 2016). From mid-September to mid-October 2017, 11 gravel pit lakes were selected to cover a gradient of ecosystem maturity based on their age that ranged from 12 to 55 years (Fig.1). Several abiotic and biotic environmental variables were assessed once at three locations within each lake (Table 1). Specifically, a portable multiparameter probe (EXO2, YSI Incorporated, Ohio, USA) was used to determine the depth profiles of temperature, pH, turbidity and conductivity. Nine important physicochemical variables including variables related to eutrophication (e.g. total phosphorus, total nitrogen, ammonium, phosphate) were measured according to national standards (NF EN ISO 10304-1, 1339; AFNOR NF EN ISO 14911) with water sampled at 1 m depth. Sediments were sampled with an Ekman dredge, sieved, homogenized, and stored in a cooler. Grain size distribution, ash free dry mass and concentrations in organic carbon, TN, TP were subsequently measured (LDA26, Valence, France). Water clarity (Secchi depth) was measured using a Secchi-disk.

Chlorophyll *a* (chl<sub>a</sub>) and Cyanobacteria concentrations were measured directly in the surface water (0.5 m depth) via fluorescence using a portable fluorescence photometer (AlgaeTorch, BBE-Moldaenke, Kiel, Germany). Specifically, the AlgaeTorch measures the fluorescence of algae cells in the water by exciting the algae pigments by 6 coloured LEDs of different wavelengths (i.e., 470, 525 and 610 nm) to obtain a fluorescence spectrum. In parallel, turbidity was determined by measuring the reflection at a wavelength of 700 nm which allows simultaneous turbidity correction during chlorophyll measurement. A standardised zooplankton sample was collected at the water surface in all lakes using a 250 µm mesh net. Samples were sieved and fixed in 100 mL 70% ethanol. In the laboratory, a 10 mL sub-samples was taken and debris removed from the sample that was oven-dried (60 °C for 72 h) and weighted to the nearest mg to estimate zooplankton density (mg.L<sup>-1</sup>). The average value of each variable across the three replicates in each lake was used for subsequent analyses. Additionally, aerial pictures and geographic information system (GIS) analyses were used to calculate the area, the perimeter and the percentage of area covered by riparian vegetation (10-metre buffer around each lake), urbanization and other gravel pit lake dredging (5-km buffer) (Zhao et al., 2016). Lake depth and volume were determined using bathymetry analyses.

### 2.2. Ecosystem maturity gradient

The lakes covered a large range of environmental conditions associated to ecosystem maturity (Table 1), including productivity (e.g., chl<sub>a</sub> ranging from 2.5 to 48.2 µg L<sup>-1</sup>) and water nutrient content (e.g., TP

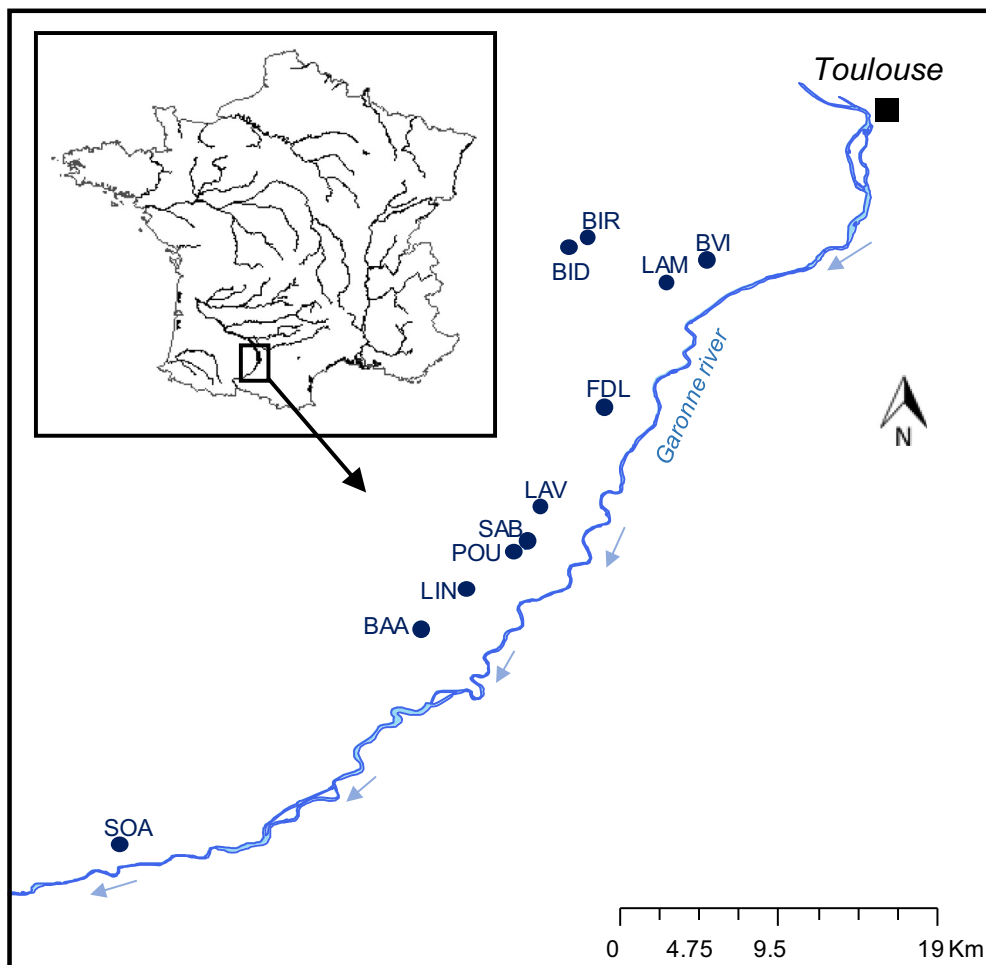


Fig. 1. Map of the 11 gravel pit lakes in the Garonne floodplain (south-west of Toulouse, France).

**Table 1**  
Environmental characteristics (minimum, mean and maximum values) of the 11 studied gravel pit lakes.

	Full names	Short names	Min	Mean	Max	
Hydromorphology	Age (years)	AGE <sup>c,d</sup>	12.0	26.9	55.0	
	Surface (ha)	SUR <sup>c</sup>	1.8	13.7	21.2	
	Perimeter (km)	PER	0.57	2.27	4.55	
	Mean depth (m)	mDE	1.20	2.38	3.60	
	Maximal depth (m)	maxDE <sup>c</sup>	1.90	4.03	6.90	
	Volume (m <sup>3</sup> )	VOL	2.5 × 10 <sup>4</sup>	2.7 × 10 <sup>5</sup>	7.4 × 10 <sup>5</sup>	
	Slope (%) <sup>a</sup>	SLO	26.7	46.9	93.3	
	Shoreline development <sup>b</sup>	SLD <sup>c</sup>	2.06	3.05	5.04	
	Urban area (%)	UrA <sup>c,d</sup>	5.3	17.3	47.3	
	Gravel pit area (%)	GrA	0.30	1.91	3.54	
	Riparian vegetation area (%)	RiA	8.5	47.8	87.3	
	Forest area (%)	FoA	0.5	28.1	56.6	
	Water quality	Specific conductance (μs.cm <sup>-1</sup> )	Cond	247.9	367.1	619.3
		Temperature (°C)	Temp <sup>c</sup>	18.0	19.0	20.3
pH		pH	7.95	8.28	8.78	
Secchi depth (m)		Secc	0.25	0.84	1.60	
Turbidity (FTU)		Turb	4.0	11.6	25.4	
Total phosphorus (μg.L <sup>-1</sup> )		TP <sup>c,d</sup>	28.8	59.6	115.9	
Phosphate (P-PO <sub>4</sub> <sup>3-</sup> μg.L <sup>-1</sup> )		PP04	4.7	16.0	76.6	
Total nitrogen (mg.L <sup>-1</sup> )		TN <sup>c,d</sup>	0.48	1.28	3.11	
Nitrates (N-NO <sub>3</sub> <sup>-</sup> mg.L <sup>-1</sup> )		NN03	<0.11	0.20	0.98	
Ammonium (N-NH <sub>4</sub> <sup>+</sup> mg.L <sup>-1</sup> )		NNH4	0.08	0.10	0.17	
Nitrite (N- NO <sub>2</sub> <sup>-</sup> μg.L <sup>-1</sup> )		NN02	<3.0	3.5	16.0	
Sulphate (mg.L <sup>-1</sup> )		SO4	25.0	52.3	139.0	
Dissolved organic carbon (mg C.L <sup>-1</sup> )		DOC	2.0	4.3	17.5	
Total organic carbon (mg C.L <sup>-1</sup> )		TOC	1.70	4.28	9.50	
Dissolved oxygen (mg.L <sup>-1</sup> )		DO	8.1	10.1	12.9	
Dissolved oxygen at saturation (%)		DOsat	86.3	108.8	140.3	
Total chlorophyll (μg chl-a L <sup>-1</sup> )		Chl <sub>a</sub> <sup>c</sup>	2.5	17.3	48.2	
Cyanobacteria (μg chl-a L <sup>-1</sup> )		Cya	2.1	8.8	248.2	
Zooplankton biomass (mg/m <sup>3</sup> )		Zoo	48.2	34.3	764.1	
Sediment		Grain size distribution (%)				
	Clay (<2 μm)	Cla	0.3	2.8	5.5	
	Silt (2–50 μm)	Sil	2.4	52.1	83.3	
	Sand (>50 μm)	San	13.6	45.1	97.3	
	Ash free dry mass (%)	AFDM	85.4	94.6	98.6	
	Total organic carbon (g C. Kg <sub>DM</sub> <sup>-1</sup> )	TOCsed <sup>c,e</sup>	1.1	15.7	73.3	
	Kjeldahl nitrogen (g N.Kg <sub>DM</sub> <sup>-1</sup> )	N <sub>sed</sub> <sup>c,d</sup>	0.10	1.72	5.66	
	Phosphorus (mg P.Kg <sub>DM</sub> <sup>-1</sup> )	P <sub>sed</sub> <sup>c</sup>	0.35	0.62	1.07	
	C:N	C:N <sub>sed</sub>	4.1	8.8	14.4	

<sup>a</sup> SLO = (maxDE / Distance from banks) × 100.

<sup>b</sup> SLD = PER / (2√πSUR) according to Hutchinson (1957).

<sup>c</sup> Variables included in partial least squares models.

<sup>d</sup> Log-transformed variables.

<sup>e</sup> Inverse transformation.

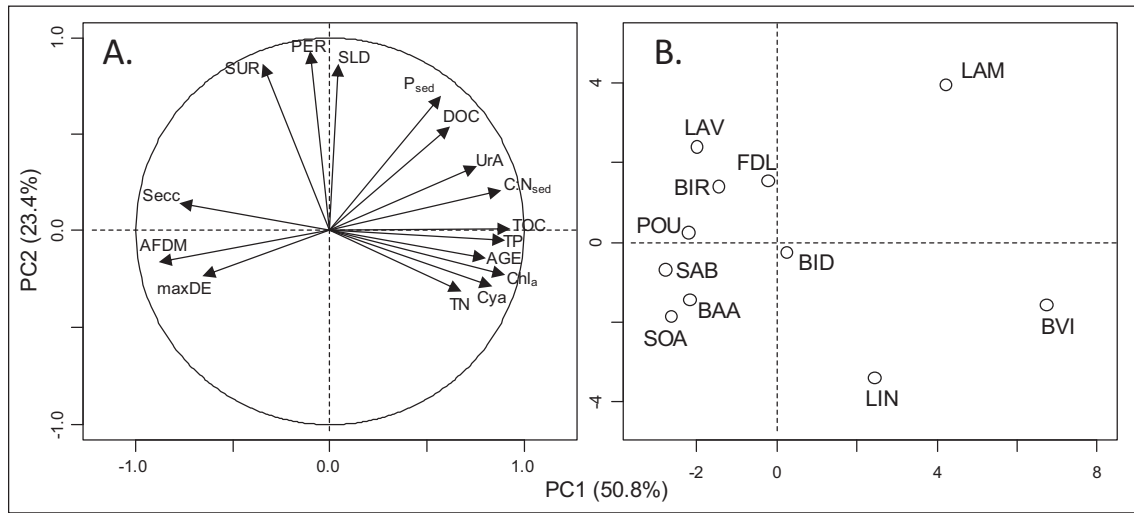
ranging from 28.8 to 115.9 μg L<sup>-1</sup>). The lakes were distributed along a gradient of ecosystem maturity defined using a principal component analyses (PCA) based on environmental conditions in the lakes. The first two dimensions of the PCA accounted for 74.2% of the total inertia (Fig. 2). The main variables positively correlated with PC1 (50.8%) were the concentrations of chl<sub>a</sub>, of nutrients in water and in sediments, lake age and the level of urbanization (see details in Supplementary material, Table A1). The content of mineral matter in sediment, the Secchi depth and the maximal depth were negatively correlated with PC1. Therefore, PC1 axis was used to represent the multifaceted characteristics of ecosystem maturity and the distribution of studied lakes along a maturity gradient based on their rank from the youngest unproductive lake (rank 1; SAB) to the oldest highly productive lake (rank 11, BVI). The main variables positively correlated with PC2 (23.4%) were related to lake hydromorphology including perimeter, surface and shoreline development. The second component discriminated smaller and circular lakes (e.g., LIN, BVI) from larger lakes with more complex shape (e.g. LAM, LAV).

## 2.3. Gas concentrations and fluxes

### 2.3.1. Dissolved gas concentrations and metabolic balances

Depth profiles of dissolved methane (CH<sub>4</sub>), dioxide carbon (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) concentrations were measured once at three locations

within lakes (i.e., at littoral area, center and deepest area) for capturing the heterogeneity of lakes. In particular, CH<sub>4</sub> and CO<sub>2</sub> concentrations were measured using submersible gas sensors (Mini CH<sub>4</sub><sup>TM</sup>, Mini CO<sub>2</sub><sup>TM</sup>, ProOceanus, Nova Scotia, Canada) operating through diffusion of dissolved gases from liquids through a supported semi-permeable membrane to a non-dispersive infrared detector (NDIR). Dissolved O<sub>2</sub> concentrations were measured using a portable multiparameter probe (EXO2, YSI Incorporated, Ohio, USA). Dissolved gas concentrations were measured during 15 min every 0.5 m depth. In addition, temperature, pressure, and humidity of the internal gas were determined to correct the gas concentration measurement. The solubility coefficients of Weiss (1974) and Yamamoto et al. (1976) were then used to calculate the dissolved concentrations of CO<sub>2</sub> and CH<sub>4</sub>, respectively. Because there was no significant variation on gas concentrations across depth (*P*-value > 0.05), the entire profiles were used to calculate the water column gas concentration (average of 0.5-m interval profiles values) for each replicate. The mean surface concentrations were then expressed as a concentration differential (Δgas in μM) from elevation and temperature corrected saturation values (named hereafter 'departures from saturation'). Gas saturation was calculated using atmospheric concentrations of 407.8 ppm for CO<sub>2</sub> and 1869 ppb for CH<sub>4</sub> (Source: WMO Global Atmosphere Watch). The average value of dissolved gas concentrations and metabolic balance using the three replicate in each lake was used for subsequent analyses.



**Fig. 2.** Environmental characteristics of the 11 studied lakes: (A) correlation circle for the environmental variables (only significant variables were included,  $P$ -value  $< 0.05$ ), and (B) factorial plane of the lakes on the PCA.

### 2.3.2. Atmospheric gas emissions

Atmospheric gas emissions were determined for  $\text{CO}_2$  and  $\text{CH}_4$ .  $\text{CO}_2$  flux across air-water interface were estimated using two floating chambers (FC; volume: 47 L; area:  $0.24 \text{ m}^2$ ; water penetration: 6 cm). The FC were covered with reflective alumina tape to minimize internal heating. The FC were equipped with a vent on the top to equalize the air pressure in the chamber with the atmospheric pressure before starting the measurements and with a floating structure (PVC tube  $\varnothing 90 \text{ cm}$ ).  $\text{CO}_2$  concentrations within the FC were measured continuously using a non-dispersive infrared (NDIR) spectroscopy logger (ELG  $\text{CO}_2$ , SenseAir, Delsbo, Sweden) (details in Bastviken et al. (2015)). For each lake, the two FC were deployed three times from the center of lake. The FC were left drifting during measurement to avoid creation of artificial turbulence. Each deployment was run over about 15 min after an equilibration period with opened vent for 5 min. Before starting new deployment, the chamber was lifted, vented for 5 min, and then replaced on the water. Diffusive  $\text{CO}_2$  flux at the air-water interface ( $\text{mmol m}^{-2}\text{-day}^{-1}$ ) were calculated according to:

$$F_{\text{CO}_2} = S \cdot t \cdot V_{\text{FC}} (V_m \times A) \quad (1)$$

where  $S$  is the slope of the linear regression of gas concentration in the chamber versus time ( $\text{ppm} \cdot \text{min}^{-1}$ ),  $t$  is a conversion factor of minutes into days ( $1440 \text{ min d}^{-1}$ ),  $V_{\text{FC}}$  is the volume of the chamber,  $V_m$  is the gas molar volume at ambient temperature and pressure and  $A$  is the area of the chamber. Fluxes derived from chamber deployments were kept only when the linear regression exhibited  $R^2 > 0.8$  and a significant slope ( $P$ -value  $< 0.05$ ).

Then, gas exchange coefficients for  $\text{CO}_2$  ( $k_{\text{CO}_2}$ ) expressed in  $\text{m d}^{-1}$  were derived from concomitant measurements of gas flux and partial pressure in air ( $p\text{CO}_{2a}$ ) and in surface water ( $p\text{CO}_{2w}$ ) expressed in atmosphere following:

$$k_{\text{CO}_2} = \frac{F_{\text{CO}_2}}{K_o \cdot (p\text{CO}_{2w} - p\text{CO}_{2a})} \quad (2)$$

where  $K_o$  is the solubility of  $\text{CO}_2$  in water expressed in  $\text{mole l}^{-1} \text{atm}^{-1}$  at surface water temperature of given lake (Weiss, 1974).

The  $k_{\text{CO}_2}$  was normalized to a Schmidt number of 600 at  $20^\circ \text{C}$  according to Jähne et al. (1987):

$$k_{600 \text{ CO}_2} = k_{\text{CO}_2} \left( \frac{600}{Sc_{\text{CO}_2, T}} \right)^{-n} \quad (3)$$

where  $Sc_{\text{CO}_2, T}$  is the Schmidt number for  $\text{CO}_2$  at a given temperature.  $N = 2/3$  was used for wind speed at  $10 \text{ m} < 3.7 \text{ m s}^{-1}$  (Jähne et al., 1987).

Then,  $k_{600 \text{ CO}_2}$  in a given lake was used to extrapolate the gas exchange coefficient for  $\text{CH}_4$  as follows:

$$k_{\text{CH}_4} = \frac{k_{600 \text{ CO}_2}}{(600/Sc_{\text{CH}_4, T})^{-n}} \quad (4)$$

The diffusive flux of  $\text{CH}_4$  at the air-water interface was then computed following the equation proposed by Cole and Caraco (1998):

$$F_{\text{CH}_4} = k_{\text{CH}_4} (C_w - C_{eq}) \quad (5)$$

where  $F_{\text{CH}_4}$  is the flux at the air-water interface for  $\text{CH}_4$  ( $\text{mmol m}^{-2}\text{-day}^{-1}$ ),  $k_{\text{CH}_4}$  is the gas exchange coefficient ( $\text{m day}^{-1}$ ),  $C_w$  is the concentration of  $\text{CH}_4$  in water ( $\text{mmol m}^{-3}$ ), and  $C_{eq}$  is the theoretical concentration of  $\text{CH}_4$  in water if the water phase was in equilibrium with the atmosphere ( $\text{mmol m}^{-3}$ ).

To integrate the contributions of both  $\text{CO}_2$  and  $\text{CH}_4$  fluxes in total GHG emissions from the 11 gravel pit lakes, the emission terms were expressed in C and  $\text{CO}_2$  equivalent ( $\text{CO}_{2eq}$ ). For this purpose, diffusive fluxes were previously converted into  $\text{g m}^{-2} \text{d}^{-1}$  and a global warming potential for  $\text{CH}_4$  of 34 was taken assuming a period of 100 years and no carbon feedback loop (IPCC, 2013).

### 2.3.3. Benthic gas fluxes

An optically clear acrylic benthic chamber mounted on a stainless steel frame was used for estimating benthic fluxes of  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$ . The chamber was configured to have 10 cm of chamber walls buried inside the sediment. The chamber was equipped at the top with a data logger of dissolved oxygen concentration and temperature (hobo U26, onset), a stirrer, three non-return check valves and a PVC tubing (6 mm outer diameter, 4 mm inner diameter) inserted through cable glands. The stirrer (5–7 rpm) was mounted at approximately 15 cm above the sediment and was used for mixing chamber water during the deployment. The two non-return valves placed at the corners of the chamber allowed the water to drain into the chamber during the immersion. The small non-return valve in the center allowed water to

enter inside the chamber during water sampling. Deployments usually started between 08:30 and 09:30 AM by slowly lowering the chamber to the sediment on a rope tethered to a float from a small boat. The chamber was placed at approximately 4 m from the shoreline. During the incubation, approx. 1 m of water remained over the chamber. The incubation period was 5–6 h during which oxygen concentrations and temperature were recorded every 5 min and water was sampled every 20 min. Water samples were collected using 50 mL syringes with three-way stopcocks connected to the end of the PVC tubing equipped with a luer-lock syringe valve. 15 mL of water was injected into pre-evacuated 21 mL-serum bottles previously filled with 6 g of NaCl (final saturation concentration) to inhibit microbial activity before analysis (Bastviken et al., 2011). Then, a headspace was created at the lab, and CO<sub>2</sub> and CH<sub>4</sub> concentrations in the headspace were measured by GC–MS (gas chromatograph CompactGC, GASTM, Global Analyser Solutions equipped with GS-Carbon plot column (Agilent), coupled to mass spectrometer detector in ionisation mode ISQ, THERMO) after desorption (simultaneous autosampler-desorber TriPlus 300, Thermo). The benthic flux ( $F_{sed}$ ) for each gas was then calculated as follows:

$$F_{sed, gas} = \frac{S \times V_{BC} \times t}{A_{BC}} \quad (6)$$

where  $S$  is the slope of the linear regression of dissolved gas concentration in the benthic chamber versus time ( $\mu\text{mol m}^{-3} \text{h}^{-1}$ ),  $t$  is a conversion factor of hours into days ( $24 \text{ h d}^{-1}$ ),  $V_{BC}$  is the volume of water in the benthic chamber ( $0.0405 \text{ m}^3$ ) and  $A_{BC}$  is the surface area of the sediment enclosed in the chamber ( $0.2025 \text{ m}^2$ ). Fluxes derived from chamber deployments were kept only for linear regression with  $R^2 > 0.8$  and a significant slope.

#### 2.4. Comparisons with existing emission data

A literature survey of studies quantifying CO<sub>2</sub> and CH<sub>4</sub> diffusive emissions from temperate lentic ecosystems was performed. A total of 31 references (see details in Supplementary Material Table A2) were collected and a total of 1026 emissions estimates obtained. Only summer-autumn measurements were considered to allow comparison with the present study. For some references, values provided were expressed in CH<sub>4</sub>-C or CO<sub>2</sub>-C. These values were converted using 1.34 and 3.66 conversion factors, respectively. All CO<sub>2</sub>-equivalent values (expressed in  $\text{g CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ ) presented in this study were calculated using the global warming potentials (GWPs) of CH<sub>4</sub> at the 100 year (1  $\text{g CH}_4 = 34 \text{ g CO}_2$ ) time-scales (IPCC, 2013).

#### 2.5. Statistical analyses

The relationships between dissolved gas concentrations, gas emissions and environmental gradients defined according the coordinates of sites on the PCA axes were examined using Spearman's rank correlation coefficient. Partial least-squares (PLS) regressions (Abdi, 2003) were then performed to identify environmental variables significantly associated to gas concentrations and emissions. Cross-validation was used for selecting the optimal number of components that minimize the prediction errors (RMSE). The variable importance in projection (VIP) coefficients were calculated to classify the predictors according to their explanatory power of the dependent variable. Predictors with VIP larger than 1 are the most relevant for explaining the dependent variable (Eriksson et al., 1999; Tenenhaus, 1998). Then, specific relationships between gas concentrations and environmental variables were examined using linear models. For all parametric analyses, normal distribution and homoscedasticity were checked. All statistical analyses were performed using R software (R Development Core Team, 2008) using FactoMineR (Lê et al., 2008) and PLS (Mevik and Wehrens, 2007) packages.

**Table 2** Gas concentrations (mean  $\pm$  SD) and fluxes at the interfaces surface water/air (mean  $\pm$  SD), and sediment/water for the 11 gravel pit lakes. Lakes are ordered according to level of maturity from the youngest to the oldest lake. For  $k_{CO_2}$  the number in brackets indicates the number of measurements with floating chambers used for calculating  $k$ . n.s. indicates invalidated data because models were not significant or  $R^2 < 0.80$ .  $\Delta_{gas}$  indicates the departures from saturation.

Lakes	SAB	POU	BAA	LAV	SOA	BID	BIR	FDL	LIN	LAM	BVI
Gas concentrations ( $\mu\text{M}$ )											
CO <sub>2</sub>	39.9 $\pm$ 6.0	26.9 $\pm$ 7.1	20.1 $\pm$ 3.8	25.3 $\pm$ 7.1	17.4 $\pm$ 1.6	15.2 $\pm$ 3.6	8.7 $\pm$ 1.8	11.6 $\pm$ 0.9	5.2 $\pm$ 0.8	18.6 $\pm$ 3.3	11.7 $\pm$ 1.2
$\Delta\text{CO}_2$	23.5 $\pm$ 5.3	10.4 $\pm$ 0.7	3.7 $\pm$ 6.1	8.9 $\pm$ 0.1	0.9 $\pm$ 2.2	-1.3 $\pm$ 2.3	-7.7 $\pm$ 1.1	-4.8 $\pm$ 1.5	-11.2 $\pm$ 0.2	2.1 $\pm$ 1.9	-4.8 $\pm$ 1.4
CH <sub>4</sub>	2.6 $\pm$ 0.6	4.2 $\pm$ 1.0	2.8 $\pm$ 0.6	4.4 $\pm$ 0.3	2.0 $\pm$ 0.2	2.9 $\pm$ 0.5	4.3 $\pm$ 1.3	3.6 $\pm$ 0.4	3.2 $\pm$ 0.7	4.0 $\pm$ 1.2	4.0 $\pm$ 0.7
$\Delta\text{CH}_4$	2.0 $\pm$ 0.5	4.1 $\pm$ 1.0	3.1 $\pm$ 0.4	4.8 $\pm$ 0.9	2.2 $\pm$ 0.5	2.5 $\pm$ 0.4	3.3 $\pm$ 1.4	4.1 $\pm$ 1.2	2.6 $\pm$ 0.8	3.5 $\pm$ 2.3	4.2 $\pm$ 1.5
CH <sub>4</sub> :CO <sub>2</sub>	0.07 $\pm$ 0.005	0.18 $\pm$ 0.12	0.14 $\pm$ 0.05	0.18 $\pm$ 0.05	0.11 $\pm$ 0.003	0.20 $\pm$ 0.07	0.51 $\pm$ 0.03	0.31 $\pm$ 0.007	0.68 $\pm$ 0.16	0.25 $\pm$ 0.08	0.31 $\pm$ 0.04
O <sub>2</sub>	259.7 $\pm$ 8.6	325.6 $\pm$ 50.2	275.2 $\pm$ 13.0	359.4 $\pm$ 80.9	323.5 $\pm$ 61.5	395.0 $\pm$ 7.1	309.0 $\pm$ 3.0	327.7 $\pm$ 61.6	403.1 $\pm$ 33.9	312.2 $\pm$ 12.1	310.2 $\pm$ 16.7
$\Delta\text{O}_2$	-19.9 $\pm$ 1.7	141.2 $\pm$ 19.1	2.9 $\pm$ 12.9	30.6 $\pm$ 1.0	0.6 $\pm$ 10.1	122.7 $\pm$ 7.1	36.7 $\pm$ 3.0	96.8 $\pm$ 3.0	125.5 $\pm$ 26.5	30.1 $\pm$ 25.8	37.8 $\pm$ 16.7
Gas exchange coefficient ( $\text{m d}^{-1}$ )											
$k_{CO_2}$	1.5 $\pm$ 0.3(4)	3.4 $\pm$ 1.7(5)	6.4 $\pm$ 0.6(3)	1.3 $\pm$ 0.3(4)	10.4 $\pm$ 0.8(3)	5.6 $\pm$ 1.2(3)	4.0 $\pm$ 1.2(4)	4.5 $\pm$ 1.5(5)	2.1 $\pm$ 1.0(6)	8.6 $\pm$ 1.5(5)	5.0 $\pm$ 3.0(5)
$k_{CH_4}$	1.6 $\pm$ 0.3	3.4 $\pm$ 1.6	6.3 $\pm$ 0.6	1.2 $\pm$ 0.3	10.3 $\pm$ 0.8	5.5 $\pm$ 1.1	3.9 $\pm$ 1.3	4.5 $\pm$ 1.5	2.1 $\pm$ 1.0	8.6 $\pm$ 1.5	5.1 $\pm$ 3.1
Atmospheric emissions ( $\text{mmol m}^{-2} \text{ d}^{-1}$ )											
$F_{CO_2}$	37.8 $\pm$ 8.0	35.3 $\pm$ 19.8	20.8 $\pm$ 2.7	12.2 $\pm$ 3.2	9.2 $\pm$ 1.5	-8.1 $\pm$ 1.8	-30.1 $\pm$ 8.4	-21.5 $\pm$ 5.7	-24.2 $\pm$ 10.9	-18.2 $\pm$ 4.7	-25.5 $\pm$ 12.6
$F_{CH_4}$	3.0 $\pm$ 1.3	12.4 $\pm$ 1.9	15.7 $\pm$ 0.5	5.4 $\pm$ 0.1	16.0 $\pm$ 1.4	16.5 $\pm$ 0.5	15.6 $\pm$ 4.1	19.4 $\pm$ 4.6	6.8 $\pm$ 1.4	23.6 $\pm$ 8.1	25.4 $\pm$ 3.6
Benthic fluxes ( $\text{mmol m}^{-2} \text{ d}^{-1}$ )											
$F_{sed, CO_2}$	-28.4	n.s.	n.s.	-93.8	21.2	n.s.	n.s.	-29.8	n.s.	-47.5	26.4
$F_{sed, CO_2}$	154.3	122.9	228.0	144.1	n.s.	n.s.	-33.6	22.1	33.7	n.s.	-54.4
$F_{sed, CH_4}$	n.s.	n.s.	n.s.	178.7	n.s.	n.s.	140.8	n.s.	n.s.	n.s.	n.s.

### 3. Results

#### 3.1. Metabolic balance and gas emissions

Dissolved gas concentrations in the water column varied moderately among the studied lakes, ranging from 259.7 to 403.1  $\mu\text{M}$  for  $\text{O}_2$ , from 5.2 and 39.9  $\mu\text{M}$  for  $\text{CO}_2$  and from 1.97 to 4.42  $\mu\text{M}$  for  $\text{CH}_4$  (Table 2).  $\text{CH}_4$ : $\text{CO}_2$  molar ratio ranged from 0.07 to 0.68 among lakes (mean  $\pm$  SD:  $0.27 \pm 0.18$ ) suggesting predominance of aerobic respiration in the water column and/or strong methanotrophic activities. Five mature lakes were oversaturated with  $\text{O}_2$  and undersaturated with  $\text{CO}_2$  suggesting an epilimnetic net autotrophy (Fig. 3A). The least mature lake was undersaturated with  $\text{O}_2$  and oversaturated with  $\text{CO}_2$  suggesting net heterotrophy of water column (Fig. 3A). The other lakes were oversaturated with both  $\text{O}_2$  and  $\text{CO}_2$ . The five lakes exhibiting net autotrophy of water column were  $\text{CO}_2$  sinks (Fig. 3B). The others lakes were  $\text{CO}_2$  sources. All lakes were  $\text{CH}_4$  sources with a relatively broad range of saturation levels (2.0–4.8  $\mu\text{M}$ ; Fig. 3B). The least mature lake showed highest departure from saturation for  $\text{CO}_2$  but lowest for  $\text{CH}_4$ .  $\text{CO}_2$  and  $\text{CH}_4$  emission fluxes ranged from  $-30.10$  to  $37.78$   $\text{mmol m}^{-2} \text{d}^{-1}$  and from  $3.05$  to  $25.45$   $\text{mmol m}^{-2} \text{d}^{-1}$ , respectively (Table 2). Except for one lake, the fluxes mirrored the patterns obtained by the departure from saturation (Fig. 3). Five lakes were sinks of  $\text{CO}_2$  but sources of  $\text{CH}_4$ . The six other lakes were sources of both  $\text{CO}_2$  and  $\text{CH}_4$ . Total net emissions ranged from  $-0.21$  to  $0.60$   $\text{g C m}^{-2} \text{d}^{-1}$  (Fig. 4) and from  $2.6$  to  $12.8$   $\text{g CO}_{2\text{eq}} \text{m}^{-2} \text{d}^{-1}$ . The net emissions fluxes were negatively correlated with the gradient of ecosystem maturity when expressed in C equivalents ( $\rho = -0.85$ ,  $P = 0.002$ ), but positively correlated when expressed in  $\text{CO}_2$ -equivalents ( $\rho = 0.61$ ,  $P = 0.052$ ).

#### 3.2. Coupling benthic-pelagic metabolism

Benthic gas fluxes were successfully computed on six and eight lakes for  $\text{O}_2$  and  $\text{CO}_2$ , respectively (Table 2). They ranged from  $-93.8$  to  $26.4$   $\text{mmol m}^{-2} \text{d}^{-1}$  for  $\text{O}_2$  and from  $-54.4$  to  $228.0$   $\text{mmol m}^{-2} \text{d}^{-1}$  for  $\text{CO}_2$ . Except for two lakes that exhibited benthic primary production (BVI, SOA), most of lakes exhibited benthic fluxes suggesting sediment respiration ( $\text{O}_2$  consumption,  $\text{CO}_2$  release).  $\text{CH}_4$  fluxes from sediment were successfully computed only for two lakes exhibiting methanogenesis (BIR:  $140.8$   $\text{mmol m}^{-2} \text{d}^{-1}$  and LAV  $178.7$   $\text{mmol m}^{-2} \text{d}^{-1}$ ), while in the other lakes models were not significant or  $R^2 < 0.80$ . Six lakes showed benthic-pelagic metabolism coupling, i.e. atmospheric emissions of  $\text{CO}_2$  by lakes exhibiting sediment respiration and

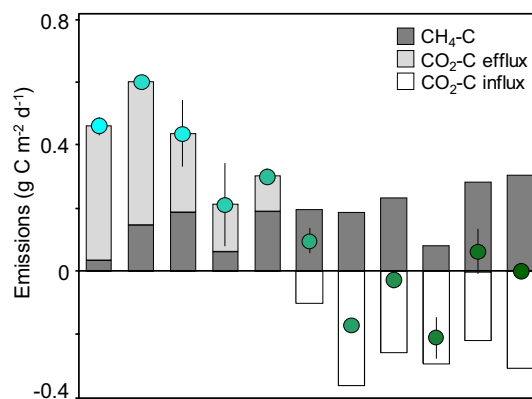


Fig. 4. Total emission fluxes expressed in  $\text{g C m}^{-2} \text{d}^{-1}$  (mean  $\pm$  SD) in the 11 studied gravel pit lakes. Dots represent the mean total emission fluxes and are filled based on the level of ecosystem maturity. Bar plots represent the relative contribution of  $\text{CH}_4$  and  $\text{CO}_2$  fluxes into net total emission fluxes.

conversely influx of  $\text{CO}_2$  at the air-water interface by lakes exhibiting benthic primary production. Uncoupling between benthic and surface metabolism was observed in two lakes exhibiting a net autotrophy of the water column.  $\sim 15\%$  of  $\text{CO}_2$  and only  $\sim 7\%$  of  $\text{CH}_4$  produced in sediments were emitted to the atmosphere.

#### 3.3. Environmental drivers of gas concentrations and emission

$\text{CO}_2$  concentrations and emissions decreased significantly along the gradient of ecosystem maturity ( $\rho = -0.83$ ,  $P = 0.003$ ;  $\rho = -0.74$ ,  $P = 0.013$ ; respectively) whereas  $\text{CH}_4$  emissions and the  $\text{CH}_4$ : $\text{CO}_2$  molar ratio significantly increased ( $\rho = 0.73$ ,  $P = 0.01$ ;  $\rho = 0.78$ ;  $P = 0.007$ ; respectively). Variability in  $\text{CO}_2$  and  $\text{CH}_4$  concentrations and fluxes were overall well explained by the model (Table 3,  $R^2$  of 0.56 for  $\text{CO}_2$ , 0.59 for  $\text{CH}_4$ , 0.61 for  $F_{\text{CO}_2}$ , 0.87 for  $F_{\text{CH}_4}$ ). Atmospheric gas emissions had overall the same explanatory variables than dissolved gas concentration. The most influential variables (VIP > 1.0) for  $\text{CO}_2$  concentrations and emissions were *chl a* and DOC concentrations, lake depth, nutrient concentrations in the water (TP, TN), urbanization level and TOC contents in sediments (Fig. 5). In particular,  $\text{CO}_2$  concentrations and emissions decreased with increased values of *chl a*, nutrients, DOC and TOC concentrations and urbanization. Conversely, deeper lakes exhibited higher  $\text{CO}_2$  concentrations and emissions.

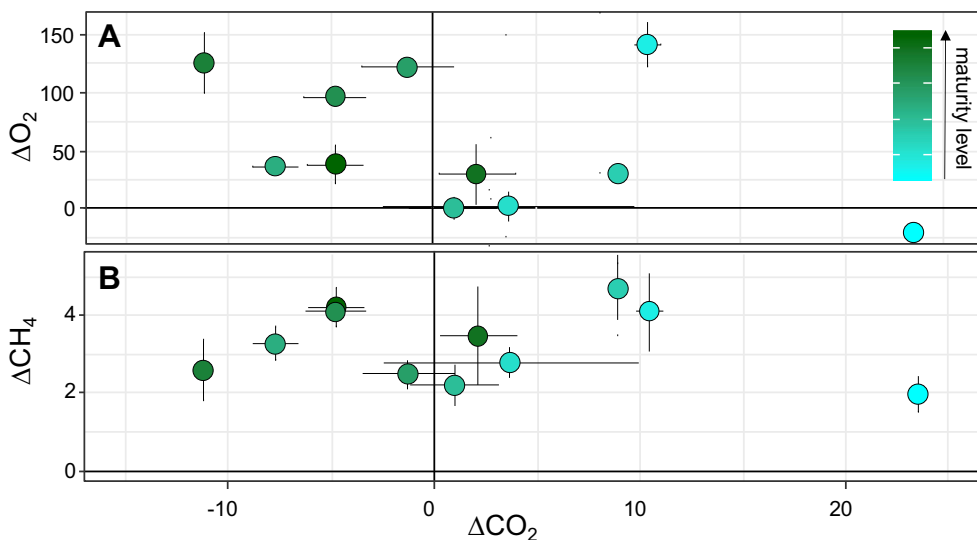


Fig. 3. Relationship between (A)  $\text{CO}_2$  and  $\text{O}_2$  departure from saturation (mean  $\pm$  SD) and (B)  $\text{CO}_2$  and  $\text{CH}_4$  departure from saturation ( $\mu\text{M}$ ) in the studied gravel pit lakes. Dots are filled based on the level of ecosystem maturity.

**Table 3**

Loadings of the PLS analyses explaining the variability in gas concentrations (CO<sub>2</sub>, CH<sub>4</sub>) and emissions (F<sub>CO2</sub>, F<sub>CH4</sub>) among gravel pit lakes. Coefficients (Coef.) and loadings (Load.) are provided only for parameters with VIP > 0.7. Highly influential variables (VIP > 1.0) and loadings values >0.3 are displayed in bold. n.a. represents 'not analyzed'. Parameter names are provided in the Table 1.

Y	CO <sub>2</sub>			F <sub>CO2</sub>			CH <sub>4</sub> (μM)			F <sub>CH4</sub>		
Components	1			1			1			2		
r <sup>2</sup> Y	0.56			0.61			0.59			0.87		
Parameter	VIP	Coef.	Load.	VIP	Coef.	Load.	VIP	Coef.	Load.	VIP	Coef.	Load.
Chla	<b>1.55</b>	-1.378	<b>-0.42</b>	<b>1.36</b>	-3.320	<b>-0.37</b>	<0.7			<b>1.21</b>	0.779	<b>-0.51</b>
CH <sub>4</sub>	<0.7			<0.7			n.a.			n.a.		
DOC <sup>b</sup>	<b>1.52</b>	1.345	<b>0.41</b>	<b>1.74</b>	4.231	<b>0.47</b>	0.81	-0.067	-0.23	0.74	-0.476	-0.23
F <sub>sedCO2</sub>	<b>1.04</b>	0.923	0.28	<0.7			n.a.			n.a.		
maxDE	<b>1.34</b>	1.184	<b>0.36</b>	<b>1.40</b>	3.406	<b>0.37</b>	<b>1.11</b>	-0.092	<b>-0.32</b>	<b>1.29</b>	-0.835	<b>-0.32</b>
N <sub>sed</sub> <sup>a</sup>	<0.7			<0.7			<b>1.04</b>	0.086	<b>0.30</b>	<b>1.05</b>	0.678	<b>0.30</b>
P <sub>sed</sub>	<0.7			<0.7			<b>1.58</b>	0.130	<b>0.46</b>	0.73	0.440	0.25
SLD	<0.7			<0.7			0.99	0.083	0.29	<0.7		
SUR	0.72	0.635	0.19	<0.7			0.74	0.061	0.21	<0.7		
Temp	<0.7			<0.7			<b>1.26</b>	0.104	<b>0.36</b>	<0.7		
TN <sup>a</sup>	<b>1.10</b>	-0.975	-0.29	<b>1.08</b>	-2.627	-0.29	<0.7			<0.7		
TOC <sub>sed</sub> <sup>b</sup>	<b>1.18</b>	1.045	<b>0.32</b>	<b>1.13</b>	2.757	<b>0.30</b>	<b>1.49</b>	-0.123	<b>-0.43</b>	<b>1.60</b>	-1.028	<b>-0.43</b>
TP <sup>a</sup>	<b>1.26</b>	-1.115	<b>-0.34</b>	<b>1.26</b>	-3.069	<b>-0.34</b>	<0.7			0.75	0.481	<b>-0.51</b>
UrA <sup>a</sup>	<b>1.17</b>	-1.034	<b>-0.31</b>	<b>1.44</b>	-3.495	<b>-0.38</b>	<b>1.02</b>	0.084	0.29	<b>1.79</b>	1.156	0.29

<sup>a</sup> Log-transformed variables.

<sup>b</sup> Inverse transformation.

Additionally, positive relationship between CO<sub>2</sub> concentrations in the water column and CO<sub>2</sub> fluxes from sediments was detected. CH<sub>4</sub> concentrations and emissions exhibited opposite relationships with environmental parameters than those described for CO<sub>2</sub> concentrations and emissions. In particular, CH<sub>4</sub> concentrations and emissions increased with nutrient and TOC contents in sediments and urbanization but decreased with lake depth (Fig. 5). Additionally, atmospheric CH<sub>4</sub> emissions increased with the concentrations in chl<sub>a</sub>.

### 3.4. Comparison of emissions with other temperate lentic ecosystems

A comparison with values reported in the literature about GHG emissions in other freshwater (natural and artificial) ecosystems in temperate climate was performed (see details in Supplementary material, Table A2). This comparison revealed that the studied gravel pit lakes generally emitted more CO<sub>2</sub>-equivalent (supported by higher CH<sub>4</sub> emission contribution) than natural ecosystems such as lakes and ponds. In particular, CO<sub>2</sub>-equivalent emissions from the studied gravel pit lakes were about 3.7 times and 1.5 times higher than emissions from natural lakes and ponds belonging to the same climatic zone (Fig. 6), respectively. CH<sub>4</sub> and CO<sub>2</sub>-equivalent emissions from gravel pit lakes were overall similar to emissions reported for other temperate small artificial-waterbodies such as urban and farm ponds (CH<sub>4</sub>: 195 mg m<sup>-2</sup> d<sup>-1</sup>; CO<sub>2</sub>eq: 7.8 g m<sup>-2</sup> d<sup>-1</sup>, in average).

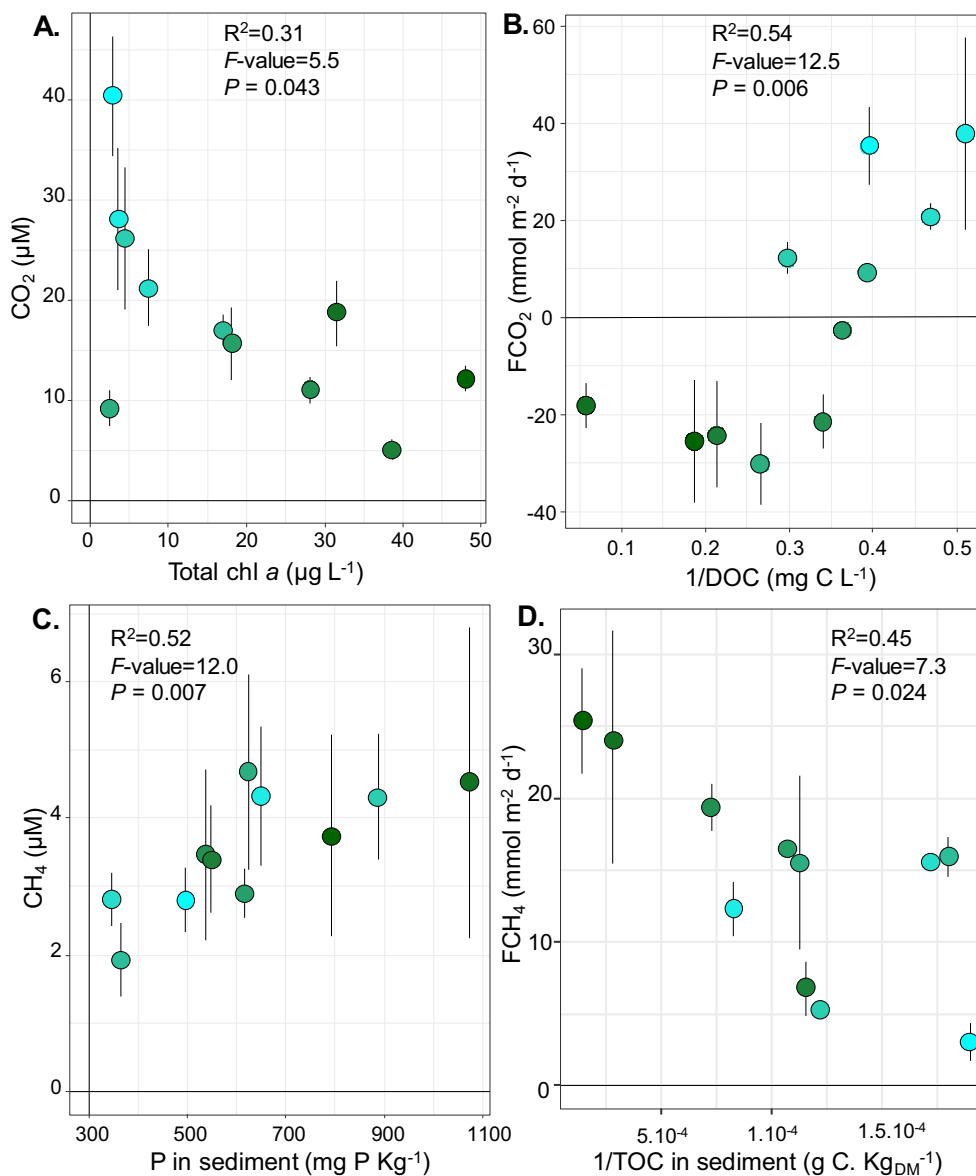
## 4. Discussion

### 4.1. Switching from heterotrophy to autotrophy when increases ecosystem maturity

Eutrophication of aquatic ecosystems is key facet of future ecosystem changes (Beaulieu et al., 2019) and its consequences on C cycling in aquatic ecosystems remains unclear, and this is particularly true for small, artificial lakes. In the present study, lake productivity (i.e. eutrophication) increased quickly after artificial lake construction, with some lakes being hypereutrophic after 26 years (Carlson, 1977; Wetzel, 2001). This gradient of ecosystem maturity was accelerated by human activities as suggested by the positive correlation between variables related to lake productivity (e.g., TP concentrations), lake age and urbanization level. Consistently with previous studies, increased chlorophyll *a* concentration (likely due to increased nutrient loadings) was

negatively correlated with CO<sub>2</sub> concentrations and emissions from lakes (e.g., Li et al., 2015; Pacheco et al., 2014). As they mature, lakes shifted from heterotrophic to autotrophic-based metabolism due to the CO<sub>2</sub> uptake by primary producers. As they turned into a CO<sub>2</sub> sink, more C buried in lake sediments, as suggested by the negative relationships between the total organic C contents in sediments and both CO<sub>2</sub> concentrations and efflux. As observed previously, eutrophication may reverse lake contribution to global C budget (Pacheco et al., 2014), in particular in the small ecosystems. Nonetheless, this finding contrasts with some studies reporting that small lakes globally strong emitters of CO<sub>2</sub> (e.g., Holgerson and Raymond, 2016), especially when eutrophic (DelSontro et al., 2018a; Ollivier et al., 2019). The extent to which eutrophication affects the direction and magnitude of CO<sub>2</sub> emissions from lakes is likely dependent on the balance between the rates of primary productivity and the input of terrestrial C, substrate of heterotrophic respiration. Here, the young gravel pit lakes exhibited high CO<sub>2</sub> concentrations and emissions probably because, even in small quantities (average DOC concentrations <3 mg L<sup>-1</sup>), allochthonous C subsidies exceeded autochthonous C-CO<sub>2</sub> consumption limited by low nutrient concentrations (as already described for many oligotrophic lakes, e.g., Biddanda et al., 2001; Del Giorgio et al., 1997; Depew et al., 2006). Furthermore, a coupling between sediment respiration and CO<sub>2</sub> concentrations in water column of young lakes was observed, likely promoted by the shallow depth of the lakes. This suggests that sediment respiration may be a major driver of CO<sub>2</sub> oversaturation in young gravel pit lakes (Kortelainen et al., 2006). Conversely, eutrophication led to an uncoupling between benthic heterotrophic metabolism and water column autotrophy suggesting that CO<sub>2</sub> uptake by primary producers offset the CO<sub>2</sub> efflux from sediments. The overweight of primary producers' CO<sub>2</sub> uptake over ecosystem respiration is likely favored by low inputs of terrestrial materials to gravel pit lakes. Indeed, even if DOC concentrations increased in concert with primary productivity along the maturity gradient, they remained overall low among gravel pit lakes (<6 mg L<sup>-1</sup>, except for one lake, LAM, with DOC = 17.5 mg L<sup>-1</sup>). Several studies reported that switching from net autotrophy to net heterotrophy occurred at DOC concentrations higher than 6–10 mg L<sup>-1</sup> (e.g., Andersson and Sobek, 2006; Hanson et al., 2003; Prairie et al., 2002). Consequently, it is likely that here, increase in DOC concentrations was not enough for maintaining heterotrophy along the maturity gradient.



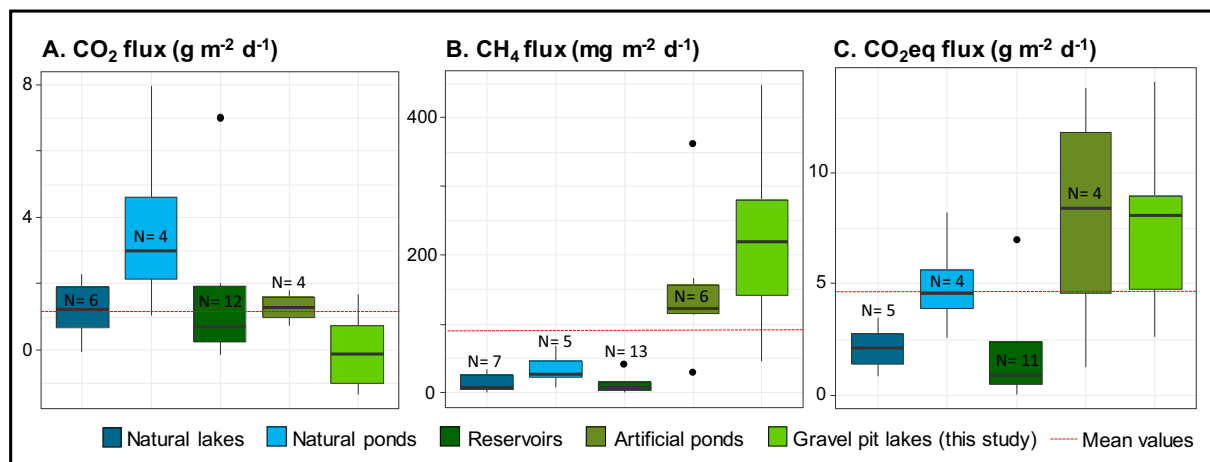


**Fig. 5.** Relationship between  $\text{CO}_2$  or  $\text{CH}_4$  dissolved concentrations in the water column and emissions with the most influential environmental variables according to the PLS analyses. (A)  $\text{CO}_2$  concentrations ( $\mu\text{M}$ ) and concentrations in chl *a* ( $\mu\text{g L}^{-1}$ ); (B)  $\text{CO}_2$  emissions ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) and DOC concentrations ( $\text{mg C L}^{-1}$ ); (C)  $\text{CH}_4$  concentrations ( $\mu\text{M}$ ) and P content in sediments ( $\text{mg P Kg}^{-1}$ ); (D)  $\text{CH}_4$  emissions ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) and TOC content in sediments ( $\text{g C Kg}^{-1}$ ). Dots are filled based on the level of ecosystem maturity.

#### 4.2. Eutrophication increases $\text{CH}_4$ emissions

In contrast with  $\text{CO}_2$  fluxes, atmospheric  $\text{CH}_4$  fluxes exhibited positive relationships with nutrients (TP, TN) and organic material contents in sediments, and DOC and chlorophyll *a* concentrations in water, suggesting that eutrophication promoted  $\text{CH}_4$  emissions. Conversely,  $\text{CH}_4$  fluxes were negatively correlated with lake depth. This could reflect that higher depth leads to higher potential oxidation capacity of  $\text{CH}_4$  produced in the sediments before reaching the atmosphere (e.g., Bastviken et al., 2004). Yet, this could also be explained by the accumulation of organic matter in the water and in the sediments through sinking, resulting in a reduced water depth, along the ecosystem maturation (e.g., Staehr et al., 2010). In particular, highly productive autotrophic systems produce substantial organic detritus since about 15–35% of dead phytoplankton settles to sediments (Baines and Pace, 1994). This accumulation of easily degradable phytoplankton-derived organic substrate (e.g., West et al., 2016, 2012) tends to promote C-rich and oxygen-depleted environment favouring  $\text{CH}_4$

production (e.g., Bastviken et al., 2004; DelSontro et al., 2018a, 2018b; Borrel et al., 2011; Sepulveda-Jauregui et al., 2018; West et al., 2012). Additionally, a positive correlation between the  $\text{CH}_4$  concentration and nutrient contents (notably TP) in sediments of gravel pit lakes was found. The link between  $\text{CH}_4$  production and nutrient content in sediments has been paid less attention. Here, the positive relationship could merely reflect enhanced primary production in pelagic waters, since TP content in sediments increased with lake productivity. Enhanced TP content in sediments may in turn fuel methanogenesis of accumulated organic C by methanogenic archaea (e.g., Adhya et al., 1998; Alphenaar et al., 1993).  $\text{CH}_4$  benthic fluxes could not be successfully measured in most lakes, even those exhibiting high  $\text{CH}_4$  concentrations in the water column. That is likely due to methodological biases associated with the benthic chambers (e.g., short incubation time,  $\text{CH}_4$  oxidation occurring at the sediment water-interface inside the benthic chamber). Nonetheless and consistently with several studies, most of the  $\text{CH}_4$  produced in sediments (~93% based on the two lakes with successful measurement of benthic methanogenesis) was oxidized before reaching the



**Fig. 6.** Estimated flux of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CO}_2\text{-eq}$  across various temperate lentic ecosystems. Values are mean flux extracted from different studies (see Supplementary material, Table A2) and from the present study (gravel pit lakes). The lines within the boxes represent median fluxes. Artificial ponds include farm, urban and storm water ponds. Mean values (red dotted line) were  $1.16 \text{ g m}^{-2} \text{ d}^{-1}$ ,  $89.75 \text{ mg m}^{-2} \text{ d}^{-1}$  and  $4.67 \text{ g m}^{-2} \text{ d}^{-1}$  for  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CO}_2\text{-eq}$  fluxes, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

atmosphere (e.g., Bastviken et al., 2003; Yang et al., 2019). This oxidation was likely promoted by well-oxygenated water of the gravel pit lakes. Despite this, the small part of  $\text{CH}_4$  escaping oxidation outweighed the primary producers'  $\text{CO}_2$  uptake along the maturation gradient. This stronger contribution of  $\text{CH}_4$  emissions is particularly since  $\text{CH}_4$  has a global warming potential (GWP) approximately 34 times higher than that of  $\text{CO}_2$  (IPCC, 2013). As a result, while the lakes turned into a  $\text{CO}_2$ -sink as they matured, the increased  $\text{CH}_4$  emissions due to eutrophication led to the increase of atmospheric C flux when expressed in  $\text{CO}_2$  equivalents. Furthermore, these measurements of  $\text{CH}_4$  emissions are probably underestimated because ebullition was not measured, despite being an important  $\text{CH}_4$  efflux mechanism in shallow and eutrophic lakes (Bastviken et al., 2004; DelSontro et al., 2016; Huttunen et al., 2003; McGinnis et al., 2006). Moreover, lateral  $\text{CH}_4$  transport (DelSontro et al., 2018b; Fernández et al., 2016) or  $\text{CH}_4$  production in the oxic water layers by cyanobacteria (Bižić et al., 2020; Günthel et al., 2020), or within anaerobic microniches associated to suspended particles (Bianchi et al., 1992; Grossart et al., 2011) or through methylphosphonate metabolism by planktonic microbes (Khatun et al., 2019; Wang et al., 2017) cannot be excluded (Peeters et al., 2019). Yet, the balance between autotrophy (mainly in water column) and respiration (mainly in sediment), both influenced by maturity, seems clearly determine the total flux of GHG from gravel pit lakes.

#### 4.3. Perspectives

This study provides first insights on autumn emissions in gravel pit lakes and highlights the importance of  $\text{CH}_4$  emissions from mature ecosystems. In particular, gravel pit lakes studied here, similarly to others man-made small ecosystems (e.g., farm and urban ponds), generally emitted more  $\text{CO}_2$ -equivalent (supported by higher  $\text{CH}_4$  emission contribution) than lakes, ponds and reservoirs ecosystems. This is probably because these small and shallow artificial ecosystems tend to be highly productive (e.g., Ortiz-Llorente and Alvarez-Cobelas, 2012; Webb et al., 2019) and hence, exhibit frequent phytoplankton and cyanobacteria blooms that may fuels  $\text{CH}_4$  production rates (e.g., Günthel et al., 2020; West et al., 2016). Since gravel pit lakes are made in terrestrial ecosystems (considered as C sinks), GHG emissions, in particular the  $\text{CH}_4$  ones, can be considered as a direct consequence of the construction of the waterbody (concept of net emissions, Prairie et al., 2018). Considering their potential high number in the landscape of many countries, small artificial waterbodies should be integrated in the future estimates of regional and global C emissions from inland waters. The present study included a limited number ( $n = 11$ ) of gravel pit lakes

and a more complete survey is still needed to fully estimate their contribution. This is particularly important to quantify annual emissions of gravel pit lakes since it is likely that benthic and epilimnetic metabolisms as well as resulting gas flux vary between seasons and years (e.g., Jeppesen et al., 2016; Laas et al., 2012). In particular, considering that the magnitude of sediment respiration and the epilimnetic metabolism are strongly regulated by primary production, one might expect a switch from net autotrophy to net heterotrophy during the winter season due to a reduced phytoplankton growth (Marshall and Peters, 1989). A long-term survey is therefore needed to fully characterize the dynamics of GHG fluxes and the extent to which gravel pit lakes are C sink or sources over time. It would be also interesting to assess the organic C stored in sediments that can potentially be considered as an offset to net C emissions (Prairie et al., 2018). Finally, a crucial avenue of research is to identify the extent to which the switch from heterotrophy to autotrophy is regulated by biotic interactions and the structure of food webs (e.g., Atwood et al., 2013; Cole et al., 2000; Davidson et al., 2015). A previous study on the same gravel pit lakes showed changes in fish communities from an initial biomass of pioneer and predator species (e.g., European perch) in young lakes to higher biomass of cyprinids species in mature and eutrophic lake (Zhao et al., 2016), probably driven by fishery management. Changes in fish community composition (including planktivorous fishes) along the maturation gradient may strongly control the zooplankton community, which, as primary consumers of phytoplankton, might have an effect on primary productivity (e.g., Carpenter et al., 1999). Here, zooplankton biomass exhibited no significant changes along the maturity gradient. However, a lack of complete survey cannot rule out changes in species composition or abundance along the maturity gradient. It is likely that both controls (i.e., by food web and eutrophication) exert here in concert and that the increased primary production due to eutrophication is accelerated in lakes where the biomass of predatory fish is reduced. Further researches will be needed to disentangle the relative importance of both controls.

#### 5. Conclusion

This study demonstrated that eutrophication increased  $\text{CO}_2$  sequestration in small and shallow lakes by increasing the relative importance of primary productivity compared to ecosystem respiration. Nevertheless, eutrophication also increased net GHG emissions in terms of climate impact by providing labile organic matter for enhanced  $\text{CH}_4$  production. Consequently, gravel pit lakes turned into  $\text{CO}_2$ -sinks along the ecosystem maturity gradient but also into hotspots of  $\text{CH}_4$

emissions. Additionally, since CH<sub>4</sub> emissions increased as gravel pit lake mature, mitigation strategies are urgently needed to maintain intermediate levels of eutrophication by limiting nutrient inputs, using biomanipulation or removing sediments. By providing a first insight into the biogeochemical functioning of gravel pit lakes, this study confirms recent evidences on the important role of small artificial waterbodies on global C cycling. Further studies are therefore needed to assess the GHG emissions and their environmental drivers in small artificial ecosystems in order to accurately estimate their global contribution to C budgets.

### CRedit authorship contribution statement

**Fanny Colas:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Jean-Marc Baudoin:** Conceptualization, Project administration, Funding acquisition, Writing – review & editing. **Patricia Bonin:** Methodology, Investigation, Resources, Writing – review & editing. **Léa Cabrol:** Methodology, Investigation, Resources, Writing – review & editing. **Martin Daufresne:** Project administration. **Rémy Lassus:** Investigation, Resources. **Julien Cucherousset:** Supervision, Conceptualization, Resources, Investigation, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

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### References

- Abdi, H., 2003. Partial least square regression (PLS regression). *Encyclopedia for Research Methods for the Social Sciences*. vol. 6, pp. 792–795.
- Adhya, T.K., Pattanaik, P., Satpathy, S.N., Kumaraswamy, S., Sethunathan, N., 1998. Influence of phosphorus application on methane emission and production in flooded paddy soils. *Soil Biol. Biochem.* 30, 177–181.
- Alp, M., Cucherousset, J., Buoro, M., Lecerf, A., 2016. Phenological response of a key ecosystem function to biological invasion. *Ecol. Lett.* 19, 519–527.
- Alphenaar, P.A., Sleyster, R., De Reuver, P., Ligthart, G.-J., Lettinga, G., 1993. Phosphorus requirement in high-rate anaerobic wastewater treatment. *Water Res.* 27, 749–756.
- Andersson, E., Sobek, S., 2006. Comparison of a mass balance and an ecosystem model approach when evaluating the carbon cycling in a lake ecosystem. *Ambio* 476–483.
- Atwood, T.B., Hammill, E., Greig, H.S., Kratina, P., Shurin, J.B., Srivastava, D.S., Richardson, J.S., 2013. Predator-induced reduction of freshwater carbon dioxide emissions. *Nat. Geosci.* 6, 191–194.
- Baines, S.B., Pace, M.L., 1994. Relationships between suspended particulate matter and sinking flux along a trophic gradient and implications for the fate of planktonic primary production. *Can. J. Fish. Aquat. Sci.* 51, 25–36. <https://doi.org/10.1139/f94-005>.
- Bastviken, D., Ejlertsson, J., Sundh, I., Tranvik, L., 2003. Methane as a source of carbon and energy for lake pelagic food webs. *Ecology* 84, 969–981. [https://doi.org/10.1890/0012-9658\(2003\)084\[0969:MAASOC\]2.0.CO;2](https://doi.org/10.1890/0012-9658(2003)084[0969:MAASOC]2.0.CO;2).
- Bastviken, D., Cole, J., Pace, M., Tranvik, L., 2004. Methane emissions from lakes: dependence of lake characteristics, two regional assessments, and a global estimate. *Glob. Biogeochem. Cycles* 18, GB4009. <https://doi.org/10.1029/2004GB002238>.

- Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater methane emissions offset the continental carbon sink. *Science* 331, 50.
- Bastviken, D., Sundgren, I., Natchimuthu, S., Reyier, H., Galfalk, M., 2015. Cost-efficient approaches to measure carbon dioxide (CO<sub>2</sub>) fluxes and concentrations in terrestrial and aquatic environments using mini loggers. *Biogeosciences* 12, 3849–3859.
- Battin, T.J., Luysaert, S., Kaplan, L.A., Aufdenkampe, A.K., Richter, A., Tranvik, L.J., 2009. The boundless carbon cycle. *Nat. Geosci.* 2, 598–600.
- Beaulieu, J.J., DelSontro, T., Downing, J.A., 2019. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. *Nat. Commun.* 10, 1375. <https://doi.org/10.1038/s41467-019-09100-5>.
- Bianchi, M., Marty, D., Teyssie, J.-L., Fowler, S., 1992. Strictly aerobic and anaerobic bacteria associated with sinking particulate matter and zooplankton fecal pellets. *Mar. Ecol. Prog. Ser.* 88, 55–60. <https://doi.org/10.3354/meps088055>.
- Biddanda, B., Ogdahl, M., Cotner, J., 2001. Dominance of bacterial metabolism in oligotrophic relative to eutrophic waters. *Limnol. Oceanogr.* 46, 730–739.
- Bižič, M., Klintzsch, T., Ionescu, D., Hindiyeh, M.Y., Günthel, M., Muro-Pastor, A.M., Eckert, W., Ulrich, T., Keppler, F., Grossart, H.-P., 2020. Aquatic and terrestrial cyanobacteria produce methane. *Sci. Adv.* 6, eaax5343.
- Borrel, G., Jézéquel, D., Biderre-Petit, C., Morel-Desrosiers, N., Morel, J.-P., Peyret, P., Fonty, G., Lehours, A.-C., 2011. Production and consumption of methane in freshwater lake ecosystems. *Res. Microbiol.* 162, 832–847.
- Cael, B.B., Heathcote, A.J., Seekell, D.A., 2017. The volume and mean depth of Earth's lakes. *Geophys. Res. Lett.* 44, 209–218. <https://doi.org/10.1002/2016GL071378>.
- Carlson, R.E., 1977. A trophic state index for lakes. *Limnol. Oceanogr.* 22, 361–369. <https://doi.org/10.4319/lo.1977.22.2.0361>.
- Carpenter, S.R., Kitchell, J.F., Cole, J.J., Pace, M.L., 1999. Predicting responses of chlorophyll and primary production to changes in phosphorus, grazing, and dissolved organic carbon (reply to comment by Nürnberg). *Limnol. Oceanogr.* 44, 1179–1182.
- Cole, J.J., Caraco, N.F., 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF<sub>6</sub>. *Limnol. Oceanogr.* 43, 647–656.
- Cole, J.J., Caraco, N.F., Kling, G.W., Kratz, T.K., 1994. Carbon dioxide supersaturation in the surface waters of lakes. *Science* 265, 1568–1570.
- Cole, J.J., Pace, M.L., Carpenter, S.R., Kitchell, J.F., 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnol. Oceanogr.* 45, 1718–1730.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., 2007. Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems* 10, 172–185.
- Davidson, T.A., Audet, J., Svenning, J.-C., Lauridsen, T.L., Søndergaard, M., Landkildehus, F., Larsen, S.E., Jeppesen, E., 2015. Eutrophication effects on greenhouse gas fluxes from shallow-lake mesocosms override those of climate warming. *Glob. Change Biol.* 21, 4449–4463. <https://doi.org/10.1111/gcb.13062>.
- Deemer, B.R., Harrison, J.A., Li, S., Beaulieu, J.J., DelSontro, T., Barros, N., Bezerra-Neto, J.F., Powers, S.M., dos Santos, M.A., Vonk, J.A., 2016. Greenhouse gas emissions from reservoir water surfaces: a new global synthesis. *BioScience* 66, 949–964. <https://doi.org/10.1093/biosci/biw117>.
- Del Giorgio, P.A., Cole, J.J., Cimleris, A., 1997. Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. *Nature* 385, 148–151.
- DelSontro, T., Boutet, L., St-Pierre, A., del Giorgio, P.A., Prairie, Y.T., 2016. Methane ebullition and diffusion from northern ponds and lakes regulated by the interaction between temperature and system productivity: productivity regulates methane lake flux. *Limnol. Oceanogr.* 61, S62–S77. <https://doi.org/10.1002/lno.10335>.
- DelSontro, T., Beaulieu, J.J., Downing, J.A., 2018a. Greenhouse gas emissions from lakes and impoundments: upscaling in the face of global change: GHG emissions from lakes and impoundments. *Limnol. Oceanogr.* 63, 64–75. <https://doi.org/10.1002/lol2.10073>.
- DelSontro, T., del Giorgio, P.A., Prairie, Y.T., 2018b. No longer a paradox: the interaction between physical transport and biological processes explains the spatial distribution of surface water methane within and across lakes. *Ecosystems* 21, 1073–1087. <https://doi.org/10.1007/s10021-017-0205-1>.
- Depew, D., Smith, R., Guildford, S., 2006. Production and respiration in Lake Erie Plankton Communities. *J. Great Lakes Res.* 32, 817. [https://doi.org/10.3394/0380-1330\(2006\)32\[817:PARILE\]2.0.CO;2](https://doi.org/10.3394/0380-1330(2006)32[817:PARILE]2.0.CO;2).
- Eriksson, L., Johansson, E., Kettaneh-Wold, N., Wold, S., 1999. Introduction to Multi- and Megavariate Data Analysis Using Projection Methods (PCA and PLS). *Umetrics, Umea, Sweden*.
- Fernández, J.E., Peeters, F., Hofmann, H., 2016. On the methane paradox: transport from shallow water zones rather than in situ methanogenesis is the major source of CH<sub>4</sub> in the open surface water of lakes. *J. Geophys. Res. Biogeosci.* 121, 2717–2726.
- Grossart, H.-P., Frindt, K., Dziallas, C., Eckert, W., Tang, K.W., 2011. Microbial methane production in oxygenated water column of an oligotrophic lake. *Proc. Natl. Acad. Sci.* 108, 19657–19661.
- Günthel, M., Klawonn, I., Woodhouse, J., Bižič, M., Ionescu, D., Ganzert, L., Kümmel, S., Nijenhuis, I., Zoccarato, L., Grossart, H., Tang, K.W., 2020. Photosynthesis-driven methane production in oxic lake water as an important contributor to methane emission. *Limnol. Oceanogr.* 65, 11557. <https://doi.org/10.1002/lno.11557>.
- Hanson, P.C., Bade, D.L., Carpenter, S.R., Kratz, T.K., 2003. Lake metabolism: relationships with dissolved organic carbon and phosphorus. *Limnol. Oceanogr.* 48, 1112–1119.
- Holgerson, M.A., Raymond, P.A., 2016. Large contribution to inland water CO<sub>2</sub> and CH<sub>4</sub> emissions from very small ponds. *Nat. Geosci.* 9, 222–226. <https://doi.org/10.1038/ngeo2654>.
- Hutchinson, G.E., 1957. Concluding remarks. *Cold Spring Harb. Symp. Quant. Biol.* 22, 415–427.
- Huttunen, J.T., Alm, J., Liikainen, A., Juutinen, S., Larmola, T., Hammar, T., Silvola, J., Martikainen, P.J., 2003. Fluxes of methane, carbon dioxide and nitrous oxide in boreal

- lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions. *Chemosphere* 52, 609–621. [https://doi.org/10.1016/S0045-6535\(03\)00243-1](https://doi.org/10.1016/S0045-6535(03)00243-1).
- IPCC, 2013. *Climate change 2013: the physical science basis*. In: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P.M. (Eds.), Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- IPCC, 2019. *2006 IPCC Guidelines for National Greenhouse Gas Inventories (2006 IPCC Guidelines)*.
- Jackson, M.C., Evangelista, C., Zhao, T., Lecerf, A., Britton, J.R., Cucherousset, J., 2017. Between-lake variation in the trophic ecology of an invasive crayfish. *Freshw. Biol.* 62, 1501–1510.
- Jähne, B., Münnich, K.O., Börsinger, R., Dutzi, A., Huber, W., Libner, P., 1987. On the parameters influencing air-water gas exchange. *J. Geophys. Res. Oceans* 92, 1937–1949.
- Jeppesen, E., Søndergaard, M., Lauridsen, T.L., Davidson, T.A., Liu, Z., Mazzeo, N., Trochine, C., Özkan, K., Jensen, H.S., Trolle, D., Starling, F., Lazzaro, X., Johansson, L.S., Bjerring, R., Liboriussen, L., Larsen, S.E., Landkildehus, F., Egemose, S., Meerhoff, M., 2012. Chapter 6 - biomanipulation as a restoration tool to combat eutrophication: recent advances and future challenges. In: Woodward, G., Jacob, U., O’Gorman, E.J. (Eds.), *Advances in Ecological Research, Global Change in Multispecies Systems Part 2*. Academic Press, pp. 411–488 <https://doi.org/10.1016/B978-0-12-398315-2.00006-5>.
- Jeppesen, E., Trolle, D., Davidson, T.A., Bjerring, R., Søndergaard, M., Johansson, L.S., Lauridsen, T.L., Nielsen, A., Larsen, S.E., Meerhoff, M., 2016. Major changes in CO<sub>2</sub> efflux when shallow lakes shift from a turbid to a clear water state. *Hydrobiologia* 778, 33–44.
- Kattner, E., Schwarz, D., Maier, G., 2000. Eutrophication of gravel pit lakes which are situated in close vicinity to the river Donau: water and nutrient transport. *Limnologia* 30, 261–270. [https://doi.org/10.1016/S0075-9511\(00\)80057-2](https://doi.org/10.1016/S0075-9511(00)80057-2).
- Khatun, S., Iwata, T., Kojima, H., Fukui, M., Aoki, T., Mochizuki, S., Naito, A., Kobayashi, A., Uzawa, R., 2019. Aerobic methane production by planktonic microbes in lakes. *Sci. Total Environ.* 696, 133916. <https://doi.org/10.1016/j.scitotenv.2019.133916>.
- Kortelainen, P., Rantakari, M., Huttunen, J.T., Mattsson, T., Alm, J., Juutinen, S., Larmola, T., Silvola, J., Martikainen, P.J., 2006. Sediment respiration and lake trophic state are important predictors of large CO<sub>2</sub> evasion from small boreal lakes. *Glob. Chang. Biol.* 12, 1554–1567.
- Kosten, S., Roland, F., Da Motta Marques, D.M.L., Van Nes, E.H., Mazzeo, N., Sternberg, L. da S.L., Scheffer, M., Cole, J.J., 2010. Climate-dependent CO<sub>2</sub> emissions from lakes: climate-dependent CO<sub>2</sub> emissions. *Global Biogeochemical Cycles* 24. <https://doi.org/10.1029/2009GB003618> (n/a-n/a).
- Laas, A., Noges, P., Koiv, T., Noges, T., 2012. High-frequency metabolism study in a large and shallow temperate lake reveals seasonal switching between net autotrophy and net heterotrophy. *Hydrobiologia* 694, 57–74.
- Lê, S., Josse, J., Husson, F., 2008. FactoMineR: an R package for multivariate analysis. *J. Stat. Softw.* 25, 1–18.
- Li, S., Zhang, Q., Bush, R.T., Sullivan, L.A., 2015. Methane and CO<sub>2</sub> emissions from China’s hydroelectric reservoirs: a new quantitative synthesis. *Environ. Sci. Pollut. Res.* 22, 5325–5339. <https://doi.org/10.1007/s11356-015-4083-9>.
- Marshall, C.T., Peters, R.H., 1989. General patterns in the seasonal development of chlorophyll a for temperate lakes. *Limnol. Oceanogr.* 34, 856–867. <https://doi.org/10.4319/lo.1989.34.5.0856>.
- McGinnis, D.F., Greinert, J., Artemov, Y., Beaubien, S.E., Wüest, A., 2006. Fate of rising methane bubbles in stratified waters: how much methane reaches the atmosphere? *J. Geophys. Res.* 111, C09007. <https://doi.org/10.1029/2005JC003183>.
- Mevik, B.H., Wehrens, R., 2007. The pls package: principal component and partial least squares regression in R. *J. Stat. Softw.* 18, 1–24.
- Mollema, P.N., Antonellini, M., 2016. Water and (bio)chemical cycling in gravel pit lakes: a review and outlook. *Earth Sci. Rev.* 159, 247–270. <https://doi.org/10.1016/j.earscirev.2016.05.006>.
- Ober, J.A., 2017. Mineral commodity summaries 2017 (Report), Mineral Commodity Summaries. Reston, VA. <https://doi.org/10.3133/70180197>.
- Ollivier, Q.R., Maher, D.T., Pitfield, C., Macreadie, P.I., 2019. Punching above their weight: large release of greenhouse gases from small agricultural dams. *Glob. Chang. Biol.* 25, 721–732. <https://doi.org/10.1111/gcb.14477>.
- Ortiz-Llorente, M.J., Alvarez-Cobelas, M., 2012. Comparison of biogenic methane emissions from unmanaged estuaries, lakes, oceans, rivers and wetlands. *Atmos. Environ.* 59, 328–337. <https://doi.org/10.1016/j.atmosenv.2012.05.031>.
- Pacheco, F., Roland, F., Downing, J., 2014. Eutrophication reverses whole-lake carbon budgets. *Inland Waters* 4, 41–48. <https://doi.org/10.5268/IW-4.1.614>.
- Peacock, M., Audet, J., Jordan, S., Smeds, J., Wallin, M.B., 2019. Greenhouse gas emissions from urban ponds are driven by nutrient status and hydrology. *Ecosphere* 10, e02643. <https://doi.org/10.1002/ecs2.2643>.
- Peeters, F., Encinas Fernandez, J., Hofmann, H., 2019. Sediment fluxes rather than oxalic methanogenesis explain diffusive CH<sub>4</sub> emissions from lakes and reservoirs. *Sci. Rep.* 9, 243. <https://doi.org/10.1038/s41598-018-36530-w>.
- Prairie, Y.T., Bird, D.F., Cole, J.J., 2002. The summer metabolic balance in the epilimnion of southeastern Quebec lakes. *Limnol. Oceanogr.* 47, 316–321.
- Prairie, Y.T., Alm, J., Beaulieu, J., Barros, N., Battin, T., Cole, J., del Giorgio, P., DelSontro, T., Guérin, F., Harby, A., Harrison, J., Mercier-Blais, S., Serça, D., Sobek, S., Vachon, D., 2018. Greenhouse gas emissions from freshwater reservoirs: what does the atmosphere see? *Ecosystems* 21, 1058–1071. <https://doi.org/10.1007/s10021-017-0198-9>.
- R Development Core Team, 2008. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.
- Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., 2013. Global carbon dioxide emissions from inland waters. *Nature* 503, 355.
- Roland, F., Vidal, L.O., Pacheco, F.S., Barros, N.O., Assireu, A., Ometto, J.P., Cimleris, A.C., Cole, J.J., 2010. Variability of carbon dioxide flux from tropical (Cerrado) hydroelectric reservoirs. *Aquat. Sci.* 72, 283–293.
- Saplaioles, M., Desprats, J.F., Delpont, G., Bourguignon, A., 2007. Evaluation de l’impact sur la ressource en eaux souterraines de l’exploitation de granulats dans le milieu alluvionnaire de la Garonne (31) (Rapport final No. BRGM/RP-55673-FR).
- Sepúlveda-Jauregui, A., Hoyos-Santillan, J., Martínez-Cruz, K., Walter Anthony, K.M., Casper, P., Belmonte-Izquierdo, Y., Thalasso, F., 2018. Eutrophication exacerbates the impact of climate warming on lake methane emission. *Sci. Total Environ.* 636, 411–419. <https://doi.org/10.1016/j.scitotenv.2018.04.283>.
- Staehr, P.A., Sand-Jensen, K., Raun, A.L., Nilsson, B., Kidmose, J., 2010. Drivers of metabolism and net heterotrophy in contrasting lakes. *Limnol. Oceanogr.* 55, 817–830.
- Tenenhaus, M., 1998. *La régression PLS: théorie et pratique* (Editions technip).
- Tranvik, L.J., Downing, J.A., Cotner, J.B., Loiselle, S.A., Striegl, R.G., Ballatore, T.J., Dillon, P., Finlay, K., Fortino, K., Knoll, L.B., 2009. Lakes and reservoirs as regulators of carbon cycling and climate. *Limnol. Oceanogr.* 54, 2298–2314.
- Vachon, D., Langenegger, T., Donis, D., Beaubien, S.E., McGinnis, D.F., 2020. Methane emission offsets carbon dioxide uptake in a small productive lake. *Limnol. Oceanogr.* 65, 10161. <https://doi.org/10.1002/lol2.10161>.
- van Bergen, T.J.H.M., Barros, N., Mendonça, R., Aben, R.C.H., Althuisen, I.H.J., Huszar, V., Lamers, L.P.M., Lürling, M., Roland, F., Kosten, S., 2019. Seasonal and diel variation in greenhouse gas emissions from an urban pond and its major drivers. *Limnol. Oceanogr.* 64, 2129–2139. <https://doi.org/10.1002/lno.11173>.
- Verpoorter, C., Kutser, T., Seekell, D.A., Tranvik, L.J., 2014. A global inventory of lakes based on high-resolution satellite imagery. *Geophys. Res. Lett.* 41, 6396–6402. <https://doi.org/10.1002/2014GL060641>.
- Vitousek, P.M., Reiners, W.A., 1975. Ecosystem succession and nutrient retention: a hypothesis. *BioScience* 25, 376–381.
- Wang, Q., Dore, J.E., McDermott, T.R., 2017. Methylphosphonate metabolism by *Pseudomonas* sp. populations contributes to the methane oversaturation paradox in an oxalic freshwater lake. *Environ. Microbiol.* 19, 2366–2378.
- Webb, J.R., Leavitt, P.R., Simpson, G.L., Baulch, H.M., Haig, H.A., Hodder, K.R., Finlay, K., 2019. Regulation of carbon dioxide and methane in small agricultural reservoirs: optimizing potential for greenhouse gas uptake. *Biogeosciences* 16, 4211–4227. <https://doi.org/10.5194/bg-16-4211-2019>.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2, 203–215. [https://doi.org/10.1016/0304-4203\(74\)90015-2](https://doi.org/10.1016/0304-4203(74)90015-2).
- West, W.E., Coloso, J.J., Jones, S.E., 2012. Effects of algal and terrestrial carbon on methane production rates and methanogen community structure in a temperate lake sediment. *Freshw. Biol.* 57, 949–955. <https://doi.org/10.1111/j.1365-2427.2012.02755.x>.
- West, W.E., Creamer, K.P., Jones, S.E., 2016. Productivity and depth regulate lake contributions to atmospheric methane. *Limnol. Oceanogr.* 61, S51–S61. <https://doi.org/10.2307/26628562>.
- Wetzel, R.G., 2001. *Limnology: Lake and River Ecosystems*. Gulf Professional Publishing.
- Yamamoto, S., Alcauskas, J.B., Crozier, T.E., 1976. Solubility of methane in distilled water and seawater. *J. Chem. Eng. Data* 21, 78–80.
- Yang, Y., Chen, J., Tong, T., Li, B., He, T., Liu, Y., Xie, S., 2019. Eutrophication influences methanotrophic activity, abundance and community structure in freshwater lakes. *Sci. Total Environ.* 662, 863–872.
- Zhao, T., Grenouillet, G., Pool, T., Tudesque, L., Cucherousset, J., 2016. Environmental determinants of fish community structure in gravel pit lakes. *Ecol. Freshw. Fish* 25, 412–421.