Science of the Total Environment 610–611 (2018) 342–355

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Effects of agricultural land use on fluvial carbon dioxide, methane and nitrous oxide concentrations in a large European river, the Meuse (Belgium)

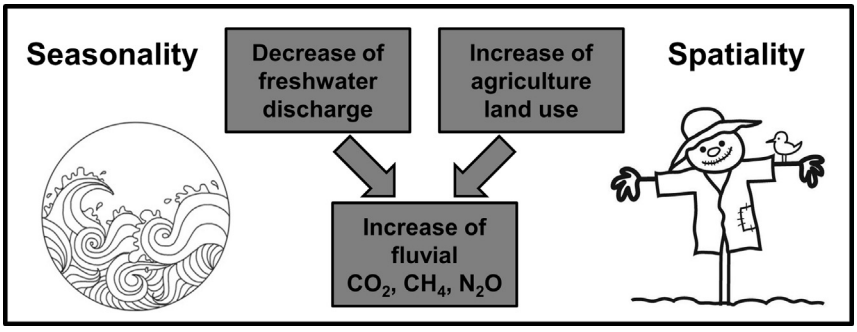
A.V. Borges [a,*], F. Darchambeau [a,1], T. Lambert [a,2], S. Bouillon [b], C. Morana [b], S. Brouyère [c], V. Hakoun [c,3], A. Jurado [c], H.-C. Tseng [a], J.-P. Descy [a], F.A.E. Roland [a]

[a] Chemical Oceanography Unit, University of Liège, Liège, Belgium
[b] Department of Earth and Environmental Sciences, KU Leuven, Leuven, Belgium
[c] Hydrogeology and Environmental Geology, University of Liège, Liège, Belgium

HIGHLIGHTS

- Large data-set of CO_2, CH_4, and N_2O in the surface waters of the Meuse River
- Highest fluvial CO_2, CH_4, and N_2O concentrations during low water
- Highest fluvial CO_2, CH_4 and N_2O concentrations in agriculture dominated catchments

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 July 2017
Received in revised form 4 August 2017
Accepted 5 August 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Meuse river
Carbon dioxide
Methane
Nitrous oxide
Land use
Agriculture

ABSTRACT

We report a data-set of CO_2, CH_4, and N_2O concentrations in the surface waters of the Meuse river network in Belgium, obtained during four surveys covering 50 stations (summer 2013 and late winter 2013, 2014 and 2015), from yearly cycles in four rivers of variable size and catchment land cover, and from 111 groundwater samples. Surface waters of the Meuse river network were over-saturated in CO_2, CH_4, N_2O with respect to atmospheric equilibrium, acting as sources of these greenhouse gases to the atmosphere, although the dissolved gases also showed marked seasonal and spatial variations. Seasonal variations were related to changes in freshwater discharge following the hydrological cycle, with highest concentrations of CO_2, CH_4, N_2O during low water owing to a longer water residence time and lower currents (i.e. lower gas transfer velocities), both contributing to the accumulation of gases in the water column, combined with higher temperatures favourable to microbial processes. Inter-annual differences of discharge also led to differences in CH_4 and N_2O that were higher in years with prolonged low water periods. Spatial variations were mostly due to differences in land cover over the catchments, with systems dominated by agriculture (croplands and pastures) having higher CO_2, CH_4, N_2O levels than forested systems. This seemed to be related to higher levels of dissolved and particulate organic matter, as well as dissolved inorganic nitrogen in agriculture dominated systems compared to forested ones. Groundwater had very low CH_4 concentrations in the shallow and unconfined aquifers (mostly fractured limestones) of the

* Corresponding author.
E-mail address: alberto.borges@ulg.ac.be (A.V. Borges).
[1] Present address: Direction générale opérationnelle Agriculture, Ressources naturelles et Environnement, Service Publique de Wallonie, Belgium.
[2] Present address: University of Lausanne, Institute of Earth Surface Dynamics, Lausanne, Switzerland.
[3] Present address: Spanish National Research Council, Madrid, Spain.

http://dx.doi.org/10.1016/j.scitotenv.2017.08.047

Meuse basin, hence, should not contribute significantly to the high CH_4 levels in surface riverine waters. Owing to high dissolved concentrations, groundwater could potentially transfer important quantities of CO_2 and N_2O to surface waters of the Meuse basin, although this hypothesis remains to be tested.

1. Introduction

Inland waters are important players in the global budgets of long-lived green-house gases (GHGs), acting as vigorous sources to the atmosphere of carbon dioxide (CO_2) (Raymond et al., 2013; Lauerwald et al., 2015; Borges et al., 2015a), methane (CH_4) (Bastviken et al., 2011; Borges et al., 2015a; Stanley et al., 2016), and nitrous oxide (N_2O) (Seitzinger and Kroeze, 1998; Hu et al., 2016). The largest fraction of global CO_2 and CH_4 emissions from riverine networks occurs at tropical and sub-tropical latitudes (Bloom et al., 2010; Raymond et al., 2013; Lauerwald et al., 2015; Borges et al., 2015b) that are in general more pristine than their temperate counter-parts. Conversely, the largest fraction of global N_2O emissions from riverine networks is assumed to occur in human impacted temperate rivers (Seitzinger and Kroeze, 1998; Hu et al., 2016).

In pristine river networks, CO_2 and CH_4 emissions are driven by in-stream production related to the degradation of terrestrial organic matter (Cole and Caraco, 2001; Richey et al., 2002), as well as lateral inputs from groundwater and/or wetlands (Abril et al., 2014; Borges et al., 2015a, 2015b). Pristine rivers are usually nitrogen poor and seem to be low sources or even sinks of N_2O, related to sediment denitrification that removes N_2O from the water column (Richey et al., 1988; Baulch et al., 2011; Borges et al., 2015a).

In strongly human influenced rivers typically located in Europe, North America, Asia and Australia, the CO_2, CH_4 and N_2O dynamics are modified in several ways. Organic matter inputs from wastewater enhance organic matter degradation and the production of CO_2 and CH_4 (Abril et al., 2000; Garnier et al., 2013; Marwick et al., 2014); effluents from wastewater treatment plants are enriched in CO_2 and CH_4 that are degassed within the river network (Alshboul et al., 2016). In extreme cases of wastewater pollution, anoxic conditions will lead to low N_2O levels due to denitrification (Rajkumar et al., 2008), but in oxic conditions nitrification fuelled by NH_4^+ inputs from wastewater leads to N_2O production (Garnier et al., 2009; Yu et al., 2013; Marwick et al., 2014). Impoundments increase water residence time that favour organic matter sedimentation and CH_4 production (Maeck et al., 2013; Crawford et al., 2016). Increased water residence time and water transparency due to impoundments can lead to low CO_2 levels related to enhanced primary production (Crawford et al., 2016). Agriculture can enhance mobilisation of labile soil organic matter (Wilson and Xenopoulos, 2009; Graeber et al., 2012, 2015; Lambert et al., 2017) and potentially enhance organic matter degradation and the production of CO_2 and CH_4 in rivers, although this has been seldom investigated (Bodmer et al., 2016). Leaching of nitrogen from artificial fertilizers from agricultural soils leads to enhanced in-stream N_2O production, presumably related to enhanced denitrification (Beaulieu et al., 2011). Enhanced nutrient inputs will fuel primary production leading to low CO_2 and high CH_4 concentrations, the latter related to enhanced organic matter delivery to sediments (Crawford et al., 2016). Other human impacts that affect carbon and nitrogen cycling in river networks that can potentially influence cycling of GHGs are river bank stabilization and floodplain drainage that disrupt the river-wetland connectivity that is important for CO_2 and CH_4 dynamics in rivers (Abril et al., 2014; Teodoru et al., 2015; Borges et al., 2015a, 2015b; Sieczko et al., 2016).

The introduction of invasive animal species such as the zebra mussel (*Dreissena polymorpha*) in US rivers and lakes (Caraco et al., 1997; Evans et al., 2011) and the Asian clam (*Corbicula* spp.) in European rivers, including the Meuse (Descy et al., 2003; Pigneur et al., 2014) led to major changes in phytoplankton dynamics, with potential but undocumented effects on GHGs fluxes. Several alien aquatic plants have been reported in European inland waters (Hussner, 2012), some with high production and biomass (Hussner, 2009); invasive floating macrophytes such as the water hyacinth (*Eichhornia crassipes*) have been documented to increase CO_2 and CH_4 levels in tropical rivers (Koné et al., 2009, 2010), but this remains undocumented in temperate rivers.

We report a dataset of CO_2, CH_4, and N_2O concentrations in the surface waters of the Meuse river network in Belgium, obtained during four surveys of 50 stations (summer 2013 and late winter 2013, 2014 and 2015), and from yearly monitoring at four rivers of variable catchment size and land cover (Table 1). The aim of this study is to describe the temporal and spatial variability of CO_2, CH_4, and N_2O concentrations and to check if the spatial variability can be related to catchment land use. The Meuse is a large European river (total length 885 km, catchment of ~34,550 km^2, average annual discharge of 10 $km^3\ yr^{-1}$) that rises in eastern France and flows through Belgium and The Netherlands before discharging into the North Sea in conjunction with the Rhine. It is densely populated (~7 10^6 inhabitants, ~200 inhabitants km^{-2}) and has experienced numerous impacts from human activities since the 19th century such as river bank stabilization, and eutrophication related to nutrient leaching from croplands and waste water from cities (Descy et al., 2009). Throughout the catchment, there has been a large conversion of forests to agriculture and pastures, as well as urbanization. In the Meuse basin situated in Belgium (Wallonia) about 34% of the catchment is covered on average by croplands, 15% by pastures, 37% by forests, and 13% by urban areas; major cities along water courses are Charleroi (205,000 inhabitants), Liège (196,000 inhabitants), Namur (110,000 inhabitants), and Verviers (57,000 inhabitants). Nowadays, about 96% of the wastewater from urban agglomerations in Wallonia is collected, while 84% is effectively treated in wastewater treatment plants, meaning that only 20% of domestic wastewater is delivered untreated directly into streams and rivers.

2. Material and methods

Four surveys of 50 stations (Fig. 1) were carried out (08-01-13 to 15-04-13; 12-07-13 to 31-07-13; 18-02-14 to 27-03-14; 03-02-15 to 12-03-15) covering 35 sub-basins. The duration of each survey was different because sampling on some occasions was not possible mainly due to bad weather conditions (snow or heavy rains), in particular during

Table 1
Characteristics of four rivers in the Meuse basin that were monitored from February 2011 to February 2013 (July 2014 for the Meuse station). Catchment surface and fresh-water discharge correspond to values upstream of sampling point (Fig. 1) and not the values of the whole river basin.

	Meuse	Ourthe	Geer	Colonster
Catchment (km^2)	16,672	1837	115	19
Fresh-water discharge[a] ($m^3\ s^{-1}$)	207	41	0.5	n.d.
Channel width (m)	110	50	8	1
Land cover				
Urban (%)	8.5	6.3	25.8	28.0
Croplands (%)	32.5	28.2	74.2	0.0
Pasture (%)	21.8	20.7	0.0	6.4
Forest (%)	34.9	43.3	0.0	65.6
Grassland (%)	2.0	1.3	0.0	0.0
Wetlands (%)	0.0	0.2	0.0	0.0

[a] Average 2011–2014.

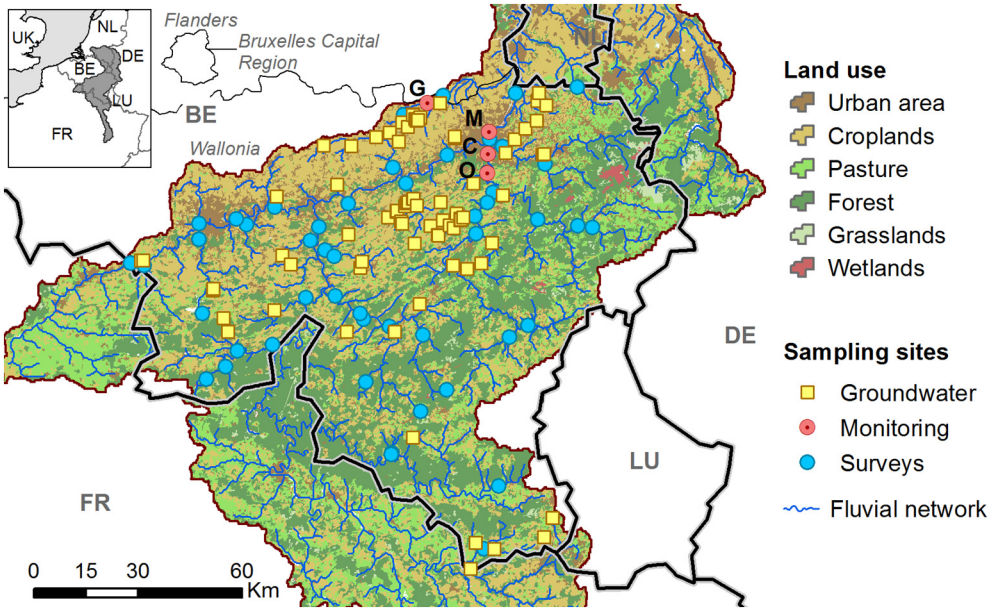


Fig. 1. Sampling stations and land cover in the Meuse basin in Wallonia (Belgium). Survey stations (n = 50, blue dots) were sampled on four occasions (summer 2013 and in late winter 2013, 2014 and 2015), four fixed stations (purple dots; C: Colonster stream; O: Ourthe river; M: Meuse river; G: Geer river) were sampled every 1–2 weeks from February 2011 to February 2013 (July 2014 for the Meuse), groundwater sites (n = 111, green square) were sampled from 2014 to 2016. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

late winter 2013. Four fixed stations were monitored at weekly intervals during rising-high-declining water period and every two weeks during low water at four rivers (Table 1), from 07-02-11 to 28-02-13 for the Ourthe, Geer and Colonster rivers, and from 07-02-11 to 03-07-14 for the Meuse river. Groundwater was sampled at 111 stations from 15-09-14 to 26-10-16.

CH_4 and N_2O were sampled at all stations, and the partial pressure of CO_2 (pCO_2) was measured during the last three spatial surveys, and during the last year of monitoring of the Meuse river. Sampling was carried out in surface waters from the shore or from bridges using a 1.7 L Niskin bottle (General Oceanics) for dissolved gases, and a polyethylene bucket (5 L) for other variables. Samples for CH_4 and N_2O were transferred with tubing from the Niskin bottle to 50 ml borosilicate serum bottles that were poisoned with a saturated solution of $HgCl_2$ (100 μl), sealed with a butyl stopper and crimped with an aluminum cap. Four polypropylene syringes of 60 ml for measurements of pCO_2 were also filled from the Niskin bottle. River water was stored in a polyethylene 2 L bottle for further processing in the laboratory. Water temperature, specific conductivity, pH and dissolved oxygen were measured with a multiprobe (YSI ProPlus). Groundwater samples were collected in a similar fashion, with pumps from piezometers, after stabilization of the water temperature and electrical conductivity monitored with a portable probe.

The concentrations of dissolved CH_4 and N_2O were measured with the head-space equilibration technique (Weiss, 1981) and a gas chromatograph fitted with a flame ionisation detector and an electron capture detector (SRI 8610C) calibrated with CH_4:CO_2:N_2O:N_2 mixtures (Air Liquide Belgium) of 1, 10 and 30 ppm CH_4 and of 0.2, 2.0 and 6.0 ppm N_2O. The pCO_2 was measured with an infra-red gas analyser (Li-Cor Li-840) within minutes after sampling, with head-space equilibration technique (Abril et al., 2015) by creating a headspace with ambient air in the polypropylene syringes (1:1 ratio of air and water). The Li-840 was calibrated with a suite of CO_2:N_2 mixtures (Air Liquide Belgium) with mixing ratios of 388, 813, 3788 and 8300 ppm CO_2. The reproducibility of measurements was ±2.0, ±3.9, and ±3.2% for pCO_2, CH_4, and N_2O, respectively.

Water was filtered on Macherey-Nagel 47 mm diameter GF-5 filters for the determination of chlorophyll-a (Chl-a) concentration that were stored frozen (−20 °C). Total suspended matter (TSM) was determined after filtration of water on pre-weighted and pre-combusted (4 h at 500 °C) Whatman GF/F 47 mm diameter filters. Samples for particulate organic carbon (POC) were filtered on pre-combusted (4 h at 500 °C) Whatman GF/F 25 mm diameter filters. The filtrate was further filtered on polyethersulfone syringe filters (0.2 μm porosity) for samples to determine dissolved organic carbon (DOC) that were stored in 40 ml borosilicate vials with polytetrafluoroethylene (PTFE) coated septa and poisoned with 50 μL of H_3PO_4 (85%), and for samples to determine inorganic nutrients (NO_3^-, NO_2^- and NH_4^+) that were stored frozen (−20 °C) in 50 ml polypropylene vials.

Chl-a concentration was analysed by high performance liquid chromatography on acetone (90%) extracts, according to Descy et al. (2005), using a Waters system equipped with a Waters 996 photo-diode array detector. POC concentration was determined with elemental analyser - isotope ratio mass spectrometer (EA-IRMS, ThermoFinnigan Flash HT and Delta V Advantage). DOC concentration was determined with a wet oxidation total organic carbon analyser (IO Analytical Aurora 1030 W) coupled with an EA-IRMS (ThermoFinnigan DeltaV Advantage). NO_3^- and NO_2^- were determined with the sulfanilamide colorimetric with the vanadium reduction method (APHA, 1998), and NH_4^+ with the dichloroisocyanurate-salicylate-nitroprussiate colorimetric method (SCA, 1981).

Data on land cover were retrieved from the CORINE land cover dataset (EEA, 2014) using the geographic information system software ArcGis® (10.3.1).

The georeferenced and timestamped data-set is available in a Supplemental File.

3. Results and discussion

Minimal temperatures were observed in late winter and maximal values in mid-summer in the Meuse, Ourthe, Geer and Colonster rivers, during the annual monitorings of 2011 and 2012 (Fig. 2, Table 1).

The seasonal amplitude of water temperature was lower in the Colonster stream (~14 °C), a small system under forest canopy than in the large Meuse main-stem (~23 °C). Chl-a concentrations were minimal in the forested Colonster stream; high Chl-a concentrations in the Meuse (up to 80 μg L^{-1}) were observed during the spring diatom bloom. The average Chl-a in the Meuse from early March to late September was ~20 μg L^{-1} in 2011, but was ~40 μg L^{-1} for the same period of

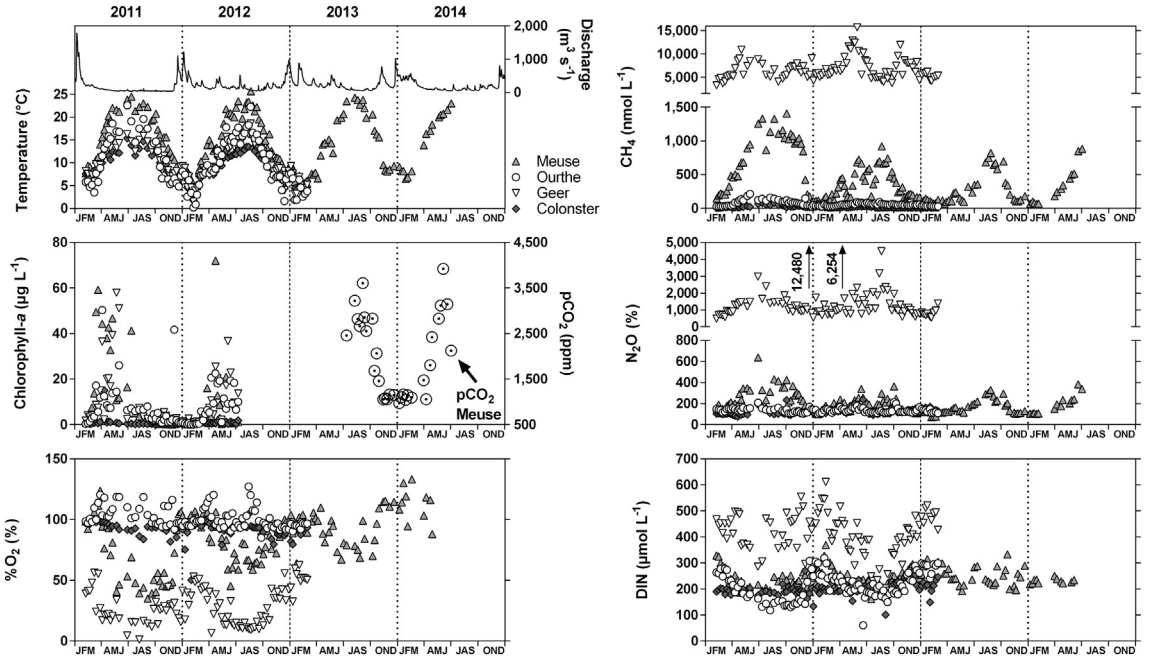


Fig. 2. Evolution in four rivers (Meuse, Ourthe, Geer and Colonster) of freshwater discharge ($m^3\ s^{-1}$, Meuse only), water temperature (°C), Chlorophyll-a ($\mu g\ L^{-1}$), partial pressure of CO_2 (pCO_2, ppm, Meuse only), oxygen saturation level ($\%O_2$, %), dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%), and dissolved inorganic nitrogen (DIN, µmol L^{-1}).

the year in 2000 (Descy et al., 2002), and ~42 µg L^{-1} in 1984 (Descy et al., 1987). The Chl-a peaked in spring in 2010–2011, and strongly declined in summer, contrary most observations made before the 2000s, when phytoplankton also developed throughout summer and autumn (Everbecq et al., 2001). These changes most probably reflect the effect of population growth of invasive benthic filter-feeders such as the zebra mussel (*Dreissena polymorpha*), the quagga mussel (*Dreissena rostriformis*) and the Asian clam (*Corbicula* spp.) (Descy et al., 2003; Pigneur et al., 2014; Marescaux et al., 2015). Surface waters were close to saturation regarding dissolved oxygen in the forested Colonster stream (average $\%O_2$ = 92%) and in the Ourthe (average $\%O_2$ = 101%), distinctly under-saturated in the Geer river (average $\%O_2$ = 29%) and the Meuse (average $\%O_2$ = 86%) (Table 2). Minimal $\%O_2$ values were observed in summer in both the Meuse and the Geer rivers, coinciding with maximal values of pCO_2 in the Meuse. This is consistent with the summer time maximum of bacterial biomass and production in the Meuse (Servais, 1989). CH_4 concentrations were well above the value at equilibrium with the atmosphere (~2 nmol L^{-1}), and were highest in the Geer river (average 6709 nmol L^{-1}) followed by the Meuse (average 422 nmol L^{-1}) and lowest in the Colonster river (average 20 nmol L^{-1}), and the Ourthe (average 66 nmol L^{-1}) (Table 2). Similarly, N_2O saturation levels were well above equilibrium (100%), and were distinctly higher in the Geer river (average 1406%, i.e. 168 nmol L^{-1}) than in the Colonster river (average 127%, i.e. 16 nmol L^{-1}), followed by the

Table 2
Average ± standard deviation (minimum;maximum) of water temperature (temp., °C), total suspended matter (TSM, mg L^{-1}), chlorophyll-a (Chl-a, µg L^{-1}), particulate organic carbon (POC, mg L^{-1}), dissolved organic carbon (DOC, mg L^{-1}), dissolved inorganic nitrogen (DIN, µmol L^{-1}), oxygen saturation level ($\%O_2$, %), partial pressure of CO_2 (pCO_2, ppm), CH_4 concentration (nmol L^{-1}), N_2O saturation level (%) in surface waters from seasonal (bi)weekly monitoring at four fixed stations (February 2011 to February 2013 (July 2014 for the Meuse station)), from four spatial surveys at 50 stations (summer 2013 and late winter 2013, 2014 and 2015) and 111 stations in groundwater of the Meuse basin in Wallonia (Belgium).

	Water temp. (°C)	TSM (mg L^{-1})	Chl-a (µg L^{-1})	POC (mg L^{-1})	DOC (mg L^{-1})	DIN (µmol L^{-1})	$\%O_2$ (%)	pCO_2 (ppm)	CH_4 (nmol L^{-1})	N_2O (%)
Seasonal monitoring stations (river)										
Meuse	14.4 ± 6.1 (2.6;25.7)	12.7 ± 17.1 (1.7;130.0)	9.6 ± 15.0 (0.1;59.2)	1.4 ± 0.6 (0.7;3.2)	3.2 ± 0.7 (1.9;4.8)	242 ± 36 (161;369)	85.7 ± 22.8 (34.9;139.0)	2004 ± 912 (971;3921)	422 ± 339 (62;1407)	197 ± 88 (72;637)
Ourthe	10.2 ± 5.4 (0.2;22.6)	11.0 ± 16.9 (0.3;139.2)	7.8 ± 9.4 (0.1;50.3)			214 ± 54 (61;319)	101.1 ± 8.5 (85.0;127.2)		66 ± 37 (25;213)	136 ± 22 (100;214)
Geer	10.2 ± 3.8 (1.5;18.6)	29.6 ± 28.4 (7.4;187.2)	8.8 ± 12.2 (0.6;58.0)			404 ± 90 (172;611)	28.9 ± 15.0 (1.2;62.5)		6709 ± 2249 (3275;15,709)	1406 ± 1390 (492;12,480)
Colonster	9.4 ± 3.0 (1.7;16.1)	7.7 ± 7.4 (1.0;41.2)	0.8 ± 1.9 (0.1;15.0)			202 ± 26 (101;270)	92.1 ± 6.5 (50.2;104.6)		20 ± 15 (4;77)	127 ± 30 (76;238)
Spatial surveys (river)										
08-01/15-04-13	5.7 ± 2.0 (0.7;10.8)	18.6 ± 24.3 (0.2;147.5)		1.6 ± 1.4 (0.3;6.8)	2.5 ± 1.3 (0.9;6.6)	291 ± 123 (59;585)	102.7 ± 12.5 (58.4;161.9)		207 ± 439 (7;2827)	170 ± 139 (78;923)
12-07/31-07-13	18.1 ± 3.1 (13.3;25.9)	6.7 ± 4.3 (1.7;20.8)		1.0 ± 0.5 (0.4;2.7)	2.7 ± 0.9 (1.2;4.8)	230 ± 97 (35;555)	90.4 ± 19.6 (39.4;127.8)	2292 ± 2037 (176;10,033)	556 ± 955 (26;4594)	370 ± 457 (91;2757)
18-02/27-03-14	8.0 ± 1.1 (5.5;9.9)	7.6 ± 11.2 (0.2;64.5)		1.1 ± 1.0 (0.3;5.2)	2.3 ± 0.9 (1.0;5.4)	264 ± 110 (50;493)	111.4 ± 14.1 (72.7;141.8)	1281 ± 1450 (34;8151)	246 ± 493 (13;2602)	179 ± 152 (77;730)
03-02/12-03-15	5.6 ± 1.1 (3.2;7.5)	20.4 ± 29.7 (0.2;111.2)		1.9 ± 1.7 (0.3;6.7)	1.7 ± 1.0 (0.2;4.3)	266 ± 116 (36;580)	108.0 ± 9.8 (74.0;125.0)	1281 ± 1140 (444;6815)	267 ± 604 (15;3533)	180 ± 129 (86;672)
Groundwater										
	11.6 ± 1.9 (8.68;23.0)					526 ± 406 (0;2592)	54.7 ± 23.7 (1.8;97.4)	20,297 ± 13,420 (1769;100,514)	44 ± 166 (0;1064)	7027 ± 10,016 (11; 418,920)

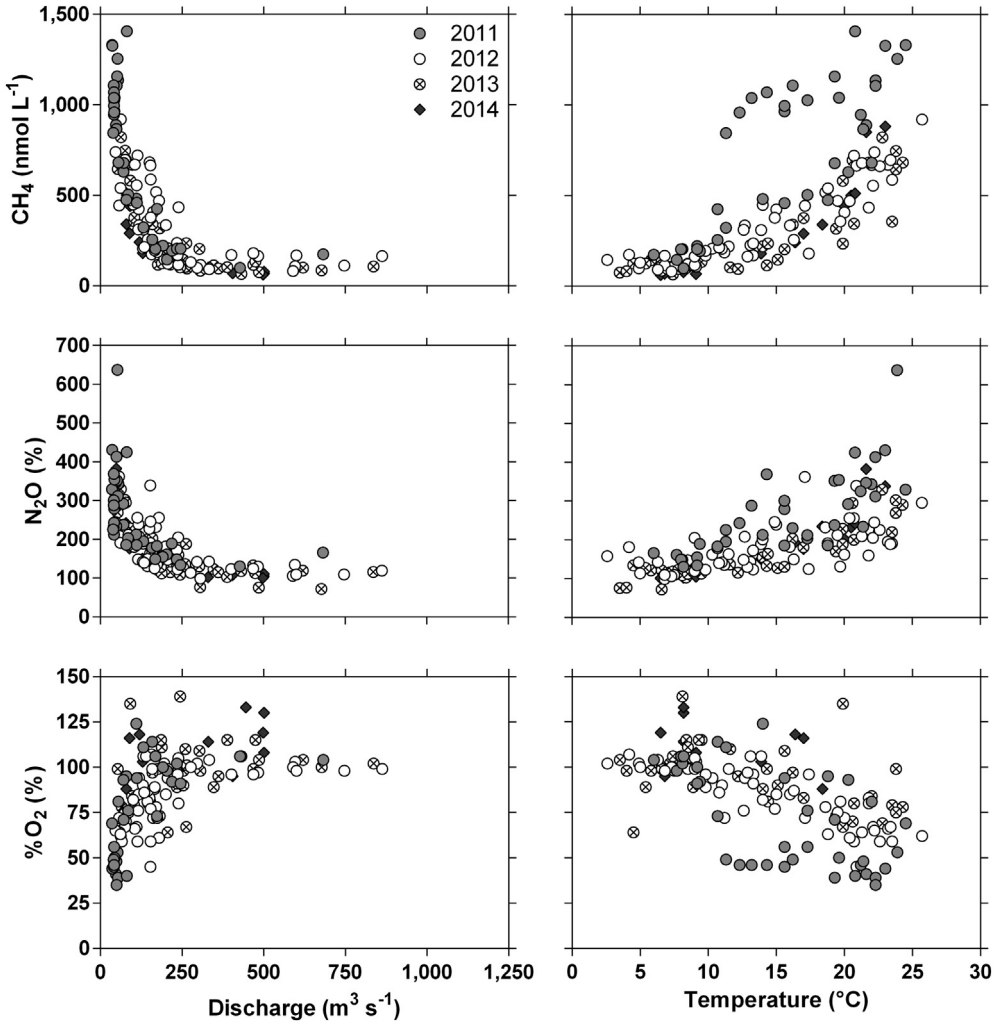


Fig. 3. Dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%), oxygen saturation level ($\%O_2$, %) versus freshwater discharge ($m^3\ s^{-1}$) and water temperature (°C) in the Meuse river in 2011, 2012, 2013 and 2014.

Meuse (average 197%, i.e. 20 nmol L^{-1}) and the Ourthe (average 136%, i.e. 17 nmol L^{-1}) (Table 2). The N_2O pattern was consistent with much the higher dissolved inorganic nitrogen (DIN) values in the Geer river (average 404 μmol L^{-1}) than in the Colonster stream (average 202 μmol L^{-1}) (Table 2). The lowest values of O_2, and highest values of CH_4, N_2O and DIN in the Geer were most probably related to its small size and discharge (leading to high water residence time), as well as the dominance of cropland on its catchment (Table 1).

The seasonal cycles of O_2, CH_4 and N_2O were relatively similar in the four rivers (albeit the seasonal amplitudes are very different), with minimal $\%O_2$ and maximal CH_4 and N_2O in summer coinciding with the highest temperatures (Fig. 2). This would suggest an enhancement of microbial activity in summer related to temperature, as suggested by the positive relationship in the Meuse with temperature of CH_4 and N_2O, and the negative relationship with temperature of $\%O_2$ (Fig. 3).

Similarly, the pCO_2 in the Meuse was positively related to temperature and to a specific fraction of the dissolved organic matter (DOM) pool (C6) (Fig. 4) that characterizes in-stream microbially produced compounds (Lambert et al., 2017). Bodmer et al. (2016) showed a similar correlation between pCO_2 and DOM composition across a spatial

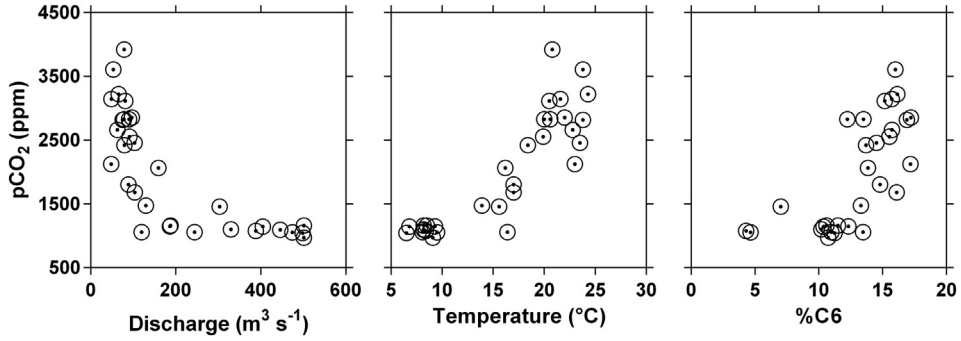


Fig. 4. Partial pressure of CO_2 (pCO_2, ppm) versus freshwater discharge ($m^3\ s^{-1}$), water temperature (°C), and the C6 component of dissolved organic matter in the Meuse river in 2013 and 2014. The C6 component is derived from a parallel factor analysis of excitation–emission matrices of dissolved organic matter from a parallel study (Lambert et al., 2017).

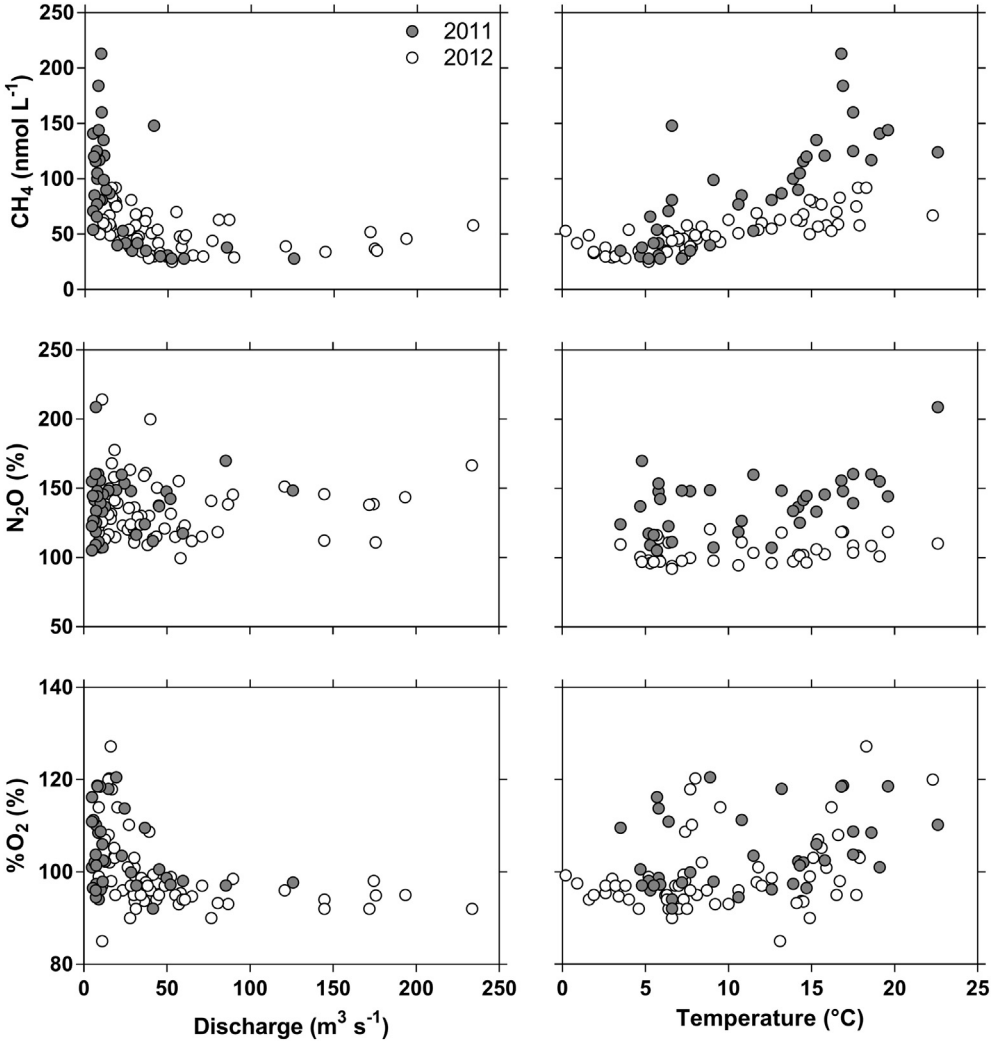


Fig. 5. Dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%), oxygen saturation level (%O_2, %) versus freshwater discharge (m^3 s^{-1}) and water temperature in the Ourthe river in 2011 and 2012.

gradient of different rivers, while here we show a correlation between those same quantities at a single site but across seasons. The summertime lowering of O_2 in the water column should lead to a lower O_2 penetration in sediments, enhancing reducing and anoxic conditions in sediments favourable to CH_4 and N_2O production. Finally, the decrease of freshwater discharge in summer leads to an increase of the water residence time, enhancing an accumulation of CH_4, N_2O and CO_2 in the water, as well as decreasing the loss of these gases to the atmosphere due to the decrease the gas transfer velocity (Raymond et al., 2012). While the increase of CH_4, N_2O and CO_2 with the lowering of freshwater discharge could also be interpreted as resulting from the increase in groundwater inputs, this would not explain the CH_4 distribution, since groundwater in the Meuse basin was characterized by very low CH_4 concentrations (see hereafter). A second yearly maximum of CH_4 occurs in the Geer basin in late autumn (November) that could be related to agricultural activities such as fertilisation of cropland with manure.

In the Meuse river, the CH_4 concentration was distinctly higher in 2011 (yearly maximum of 1407 nmol L^{-1}) than the other three following years (yearly maximum ranging between 822 and 920 nmol L^{-1}). The low water period was longer and the average discharge was

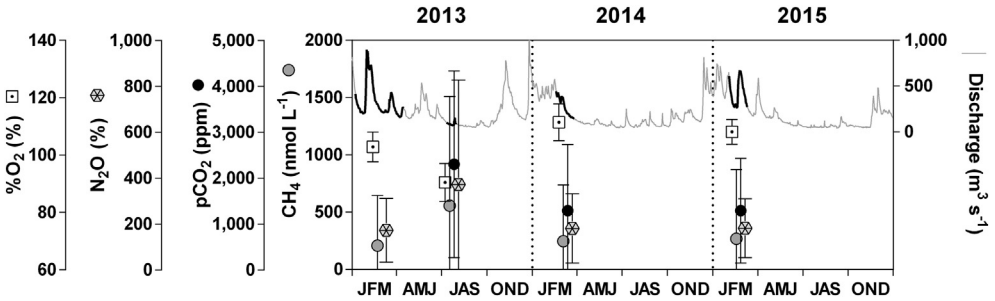


Fig. 6. Freshwater discharge (m^3 s^{-1}, Meuse only) from 2013 to 2015, and average partial pressure of CO_2 (pCO_2, ppm), oxygen saturation level (%O_2, %), dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%) from the spatial surveys in the Meuse basin. The thick line in the discharge plot indicates the duration of the survey. Data points were spread horizontally for clarity, but all variables were sampled simultaneously.

lower in 2011 compared to the other years, with average discharge from early April to late October of 54 $m^3\ s^{-1}$ in 2011 compared to 148, 156 and 94 $m^3\ s^{-1}$ in 2012, 2013 and 2014, respectively. Also, the minimum daily discharge was lower in 2011 (31 $m^3\ s^{-1}$) compared to the other years (range 45–51 $m^3\ s^{-1}$). The CH_4 concentrations in the Meuse were negatively correlated to discharge (Fig. 3), with the highest CH_4 values in 2011 associated to the lowest discharge values. We hypothesize that the lower discharge and longer residence time likely promoted CH_4 accumulation in the water leading to higher CH_4 in the 2011 compared to the other years at similar temperatures for values between 10 and 25 °C (Fig. 3). N_2O and $\%O_2$ in the Meuse river showed consistent patterns with the one of CH_4 (Fig. 3) with higher N_2O and lower $\%O_2$ in 2011 in particular at low discharge values, and deviations at similar temperatures compared to the other years. Although data are only available in 2011 and 2012, CH_4 shows similar patterns in the Ourthe river (Fig. 5), although less obvious for N_2O. However, the $\%O_2$ patterns in the Ourthe were different from the Meuse river, with values well above saturation in summer, in particular at low discharge values. This most probably reflects the effect of primary production from aquatic plants (mostly *Ranunculus fluitans*) and filamentous green algae such as *Cladophora glomerata* that reach maximum development in summer, combined to lower water levels and lower water residence time due to lower discharge, both promoting the accumulation of O_2 in the water column.

The basin-wide average of O_2 and GHGs obtained during the four basin surveys showed similar seasonal variations as those described above for the four "monitoring" sites (Fig. 2), with highest pCO_2, CH_4 and N_2O values in summer and lowest in winter mirrored by the $\%O_2$ variations (Fig. 6, Table 2). Despite the different duration of each of the four sampling surveys, mainly due to bad weather conditions that slowed down sampling on some occasions, the average values of pCO_2, CH_4 and N_2O from the three late winter surveys were very similar (Fig. 6, Table 2). The analysis of the whole dataset ("monitoring" and "survey" merged) suggests a control of both spatial and seasonal variations of CO_2, CH_4 and N_2O by microbial processing, as indicated by the negative relationships between GHGs and O_2 (Fig. 7), with the most extreme values observed in the Geer river.

CH_4 and N_2O were not significantly correlated to NO_3^- and to DOC (not shown), so that the dynamics of these two gases in the Meuse river network did not fit the conceptual model of Schade et al. (2016) developed from data in New Hampshire streams, whereby the CH_4 and N_2O were both positively correlated to DOC, while negatively and positively related to NO_3^-, respectively. In the global meta-analysis of riverine CH_4 by Stanley et al. (2016) there were also no significant correlations between CH_4 and DOC or NO_3^-. However, in the Meuse river network, CH_4 was positively linearly correlated to NH_4^+ (not shown, $r^2 = 0.81$, $p < 0.0001$, $n = 648$), and N_2O was positively linearly correlated to NO_2^- (not shown, $r^2 = 0.72$, $p < 0.0001$, $n = 647$) and NH_4^+ (not shown, $r^2 = 0.62$, $p < 0.0001$, $n = 646$) (excluding the two highest N_2O values). A correlation between N_2O and NO_2^- has also been shown in English and Welsh rivers by Dong et al. (2005), while a correlation of N_2O and NH_4^+ has also been shown in the Shanghai river network (Yu et al., 2013). It is unclear if such correlations imply a direct causality or if they are spurious resulting indirectly from a common driver such as O_2 variability, as NO_2^- ($r^2 = 0.60$, $p < 0.0001$, $n = 648$) and NH_4^+ ($r^2 = 0.63$, $p < 0.0001$, $n = 647$) were also correlated to $\%O_2$ (not shown), as N_2O and CH_4 (Fig. 6).

Groundwater can be a source of GHGs to riverine systems in particular in lower order streams and headwaters (Johnson et al., 2008; Hotchkiss et al., 2015). The comparison of CO_2 and CH_4 in groundwater and riverine waters of the Meuse basin (Fig. 8) shows that part of the CO_2 in riverine waters could come from groundwater where the average pCO_2 value (20,297 ppm, Table 2) was distinctly higher than in river waters (1684 ppm), and in both cases above atmospheric equilibrium (~400 ppm).

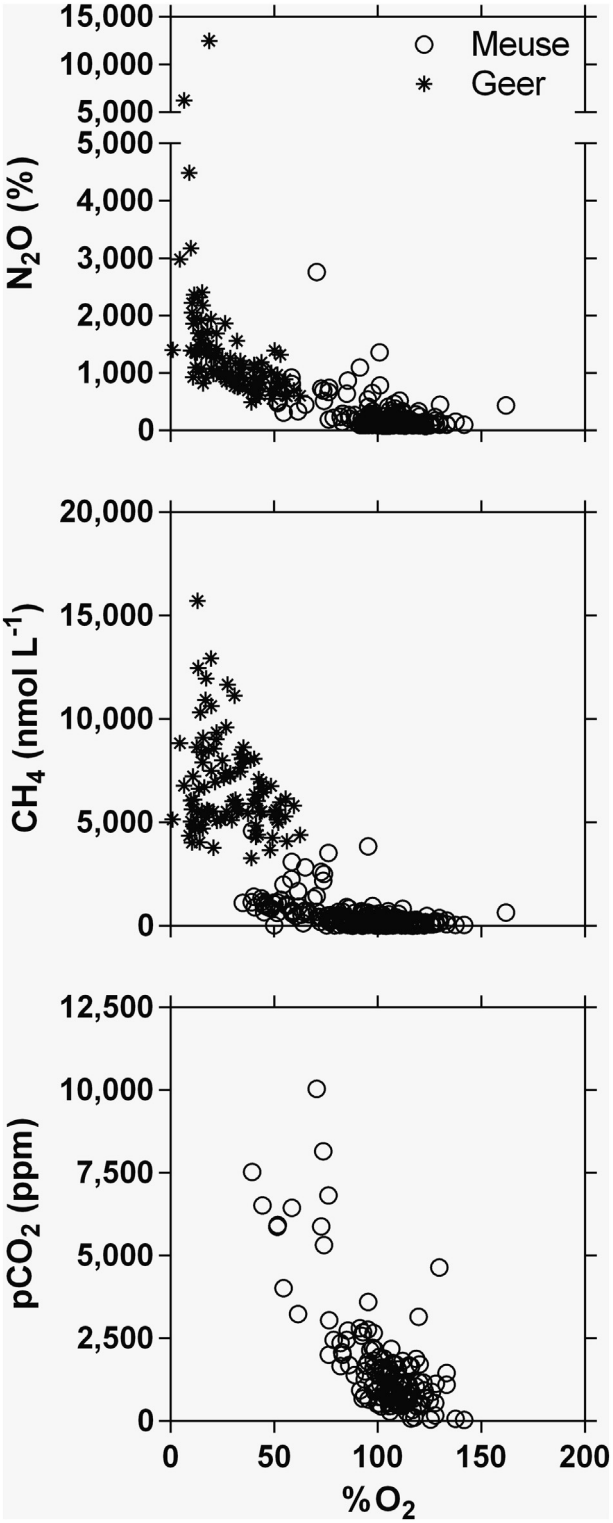


Fig. 7. N_2O saturation level (%), dissolved CH_4 concentration (nmol L^{-1}), and partial pressure of CO_2 (pCO_2, ppm) versus oxygen saturation level ($\%O_2$, %) for all of the data gathered from fixed station monitoring and spatial surveys in the Meuse basin from 2011 to 2015. Data from the Geer (star) are separated from the other rivers for the basin referred to as "Meuse" (circles).

The opposite was observed for CH_4 with a lower average value in groundwater (44 nmol L^{-1}, Table 2) than in surface waters (360 nmol L^{-1}). This would then suggest that the CH_4 in river waters in the Meuse basin were produced in-stream or in riparian areas but not discharged through groundwater. Since pCO_2 and CH_4 in riverine

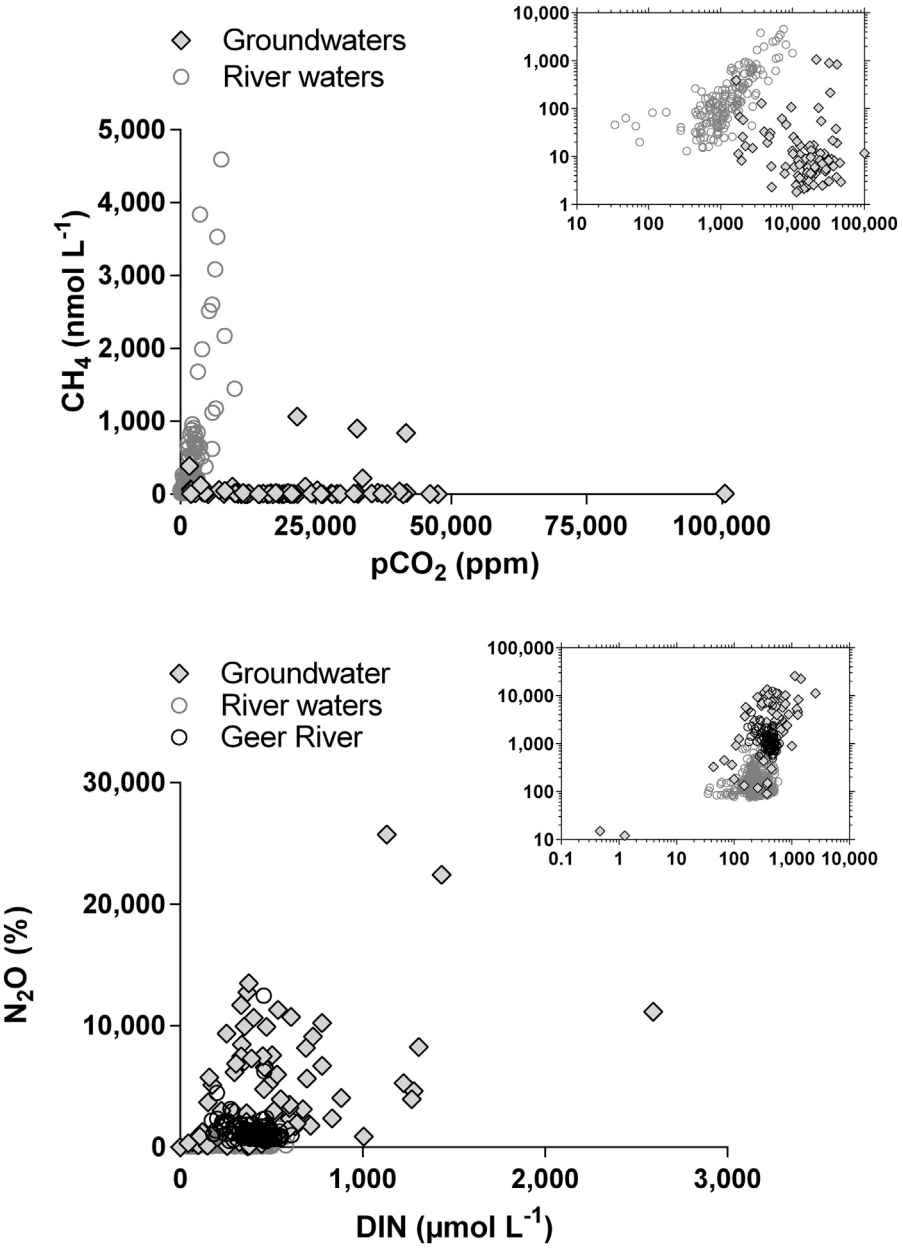


Fig. 8. Dissolved CH_4 concentration (nmol L^{-1}) versus partial pressure of CO_2 (pCO_2, ppm), and N_2O saturation level (%) versus dissolved inorganic nitrogen (DIN, µmol L^{-1}) in groundwater (diamonds) and surface riverine waters (from all of the data gathered from fixed station monitoring and spatial surveys) in the Meuse basin from 2011 to 2015. Data from the Geer (dark circles) are separated from the other rivers for the basin referred to as "Meuse" (light circles). Data of pCO_2 are unavailable for the Geer.

waters were positively correlated ($r^2 = 0.60$, $p < 0.0001$, $n = 180$) this would suggest that most of the CO_2 in riverine waters might also have resulted from in-stream production. Extremely high N_2O values were observed in groundwater (maximum 418,920% or 37,060 nmol L^{-1}) that are among the highest reported in groundwater (Jurado et al., 2017). This is probably related to a strong contamination of groundwater in Belgium by NO_3^- from use of artificial fertilizers (e.g. Orban et al., 2010; Hakoun et al., 2017). Further, oxic conditions prevail in groundwater of the shallow (1–100 m) and unconfined sampled aquifers (mostly fractured limestone aquifers) that dominate in Wallonia. The $\%O_2$ values in the sampled groundwater stations ranged between 1.8 and 97.4%, and averaged 55.1% (Table 2). Due to general oxic conditions, the removal of NO_3^- by denitrification is likely to be low in groundwater in Wallonia. These oxic conditions also explain the low CH_4 concentrations in the Meuse groundwater (Table 2). The average of DIN was higher in groundwater (526 µmol L^{-1}, Table 2) than in surface waters (266 µmol L^{-1}), as well as N_2O, 70,027 and 183%, respectively. Hence, part of N_2O in rivers could come from groundwater in the Meuse basin, although the actual fraction remains to be quantified.

The spatial variations in surface riverine waters were in part related to the stream/river size, with a decreasing pattern of CO_2 and CH_4 with Strahler order mirrored by an increase of O_2 (Fig. 9). Such a pattern has been previously reported for CO_2 in US rivers (Butman and Raymond, 2011), and might be interpreted as resulting from decreasing input of CO_2 rich groundwater with increasing Strahler order (Hotchkiss et al., 2015). However, this is inconsistent with the decreasing pattern of CH_4 with Strahler order since groundwater in the Meuse basin has low CH_4 concentrations (Fig. 8). There was an increasing pattern of TSM and POC with Strahler order, while other variables such as DOC and DIN showed no discernible patterns with Strahler order.

Besides the size of streams and rivers, the catchment characteristics, such as lithology and land cover, control water composition and biogeochemical processes (e.g. Kempe, 1984; Meybeck, 1987). TSM, POC, DOC and DIN were positively related to the fraction of agriculture cover of

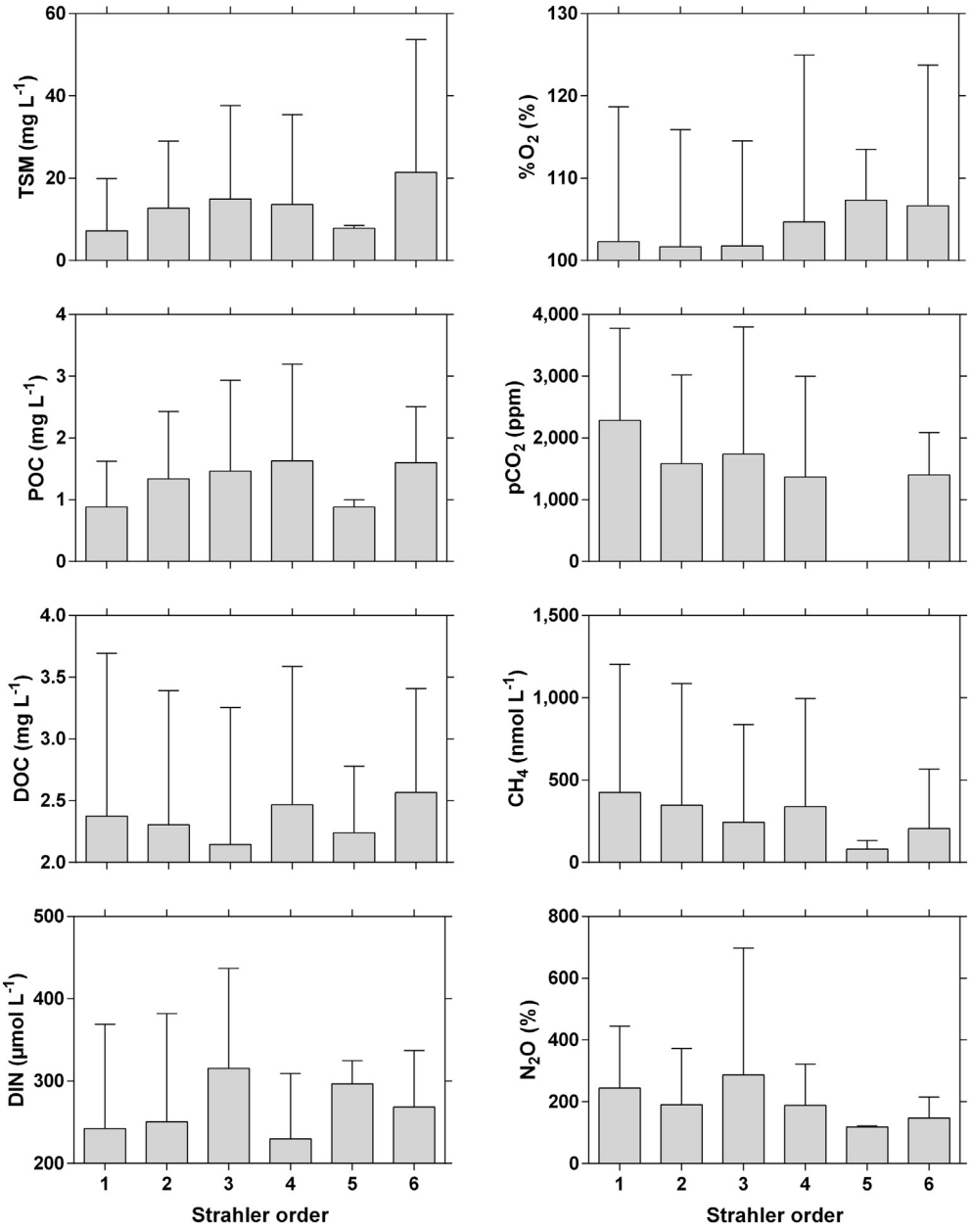


Fig. 9. Average and standard deviation of total suspended matter (TSM, mg L^{-1}), particulate organic carbon (POC, mg L^{-1}), dissolved organic carbon (DOC, mg L^{-1}), dissolved inorganic nitrogen (DIN, µmol L^{-1}), oxygen saturation level (%O_2, %), partial pressure of CO_2 (pCO_2, ppm), dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%) as a function of Strahler order from the four spatial surveys in the Meuse basin (summer 2013 and in late winter 2013, 2014 and 2015).

the catchment (Fig. 10), whereby agriculture cover is the sum of cropland and pasture, with an overall dominance in the data-set of cropland that represented on average 33% of the cover over studied catchments, while pastures represented 19%. TSM, POC/DOC and DIN patterns reflect the delivery of nutrients, particulate organic matter and DOM to fluvial systems from agricultural catchments. A parallel study showed the increasing fraction of agriculture cover of the catchment also affected the quality of DOM delivered to the rivers that tended to be more labile (Lambert et al., 2017), in agreement with a similar study in German rivers (Bodmer et al., 2016). The delivery of more labile DOM is consistent with the decrease of O_2 and increase of pCO_2 and CH_4 with the increasing fraction of agriculture cover due to enhanced in-stream microbial activity. The parallel increase of N_2O could result from both the increase of DIN and decrease of O_2, as the yield of N_2O production from nitrification or denitrification is highest at low O_2 levels (Codispoti and Christensen, 1985). An increased delivery of dissolved organic nitrogen to rivers from agricultural catchments has been also been reported (Graeber et al., 2012) although not measured during the present study.

Forest was the main catchment land cover substituting agriculture when the latter was a less prominent land use type (Supplemental Fig. 1). The comparison of catchments mainly occupied (>60%) by forest and by agriculture also showed the importance of agriculture on the catchment in generating GHGs in the river network (Fig. 11).

Catchments dominated by agriculture compared to those dominated by forest were characterized by higher TSM, POC, DOC, consequently by higher pCO_2 and CH_4, and lower %O_2, and by higher DIN, consequently by higher N_2O (Fig. 11). This conclusion is different from the study of Butman and Raymond (2011) that showed higher CO_2 values associated to forested watersheds across the US. This difference might be due to cross-correlations of land cover with altitude and precipitation that also affect CO_2 in the large scale study across the US compared to our much smaller scale regional study. Our results converge with those of

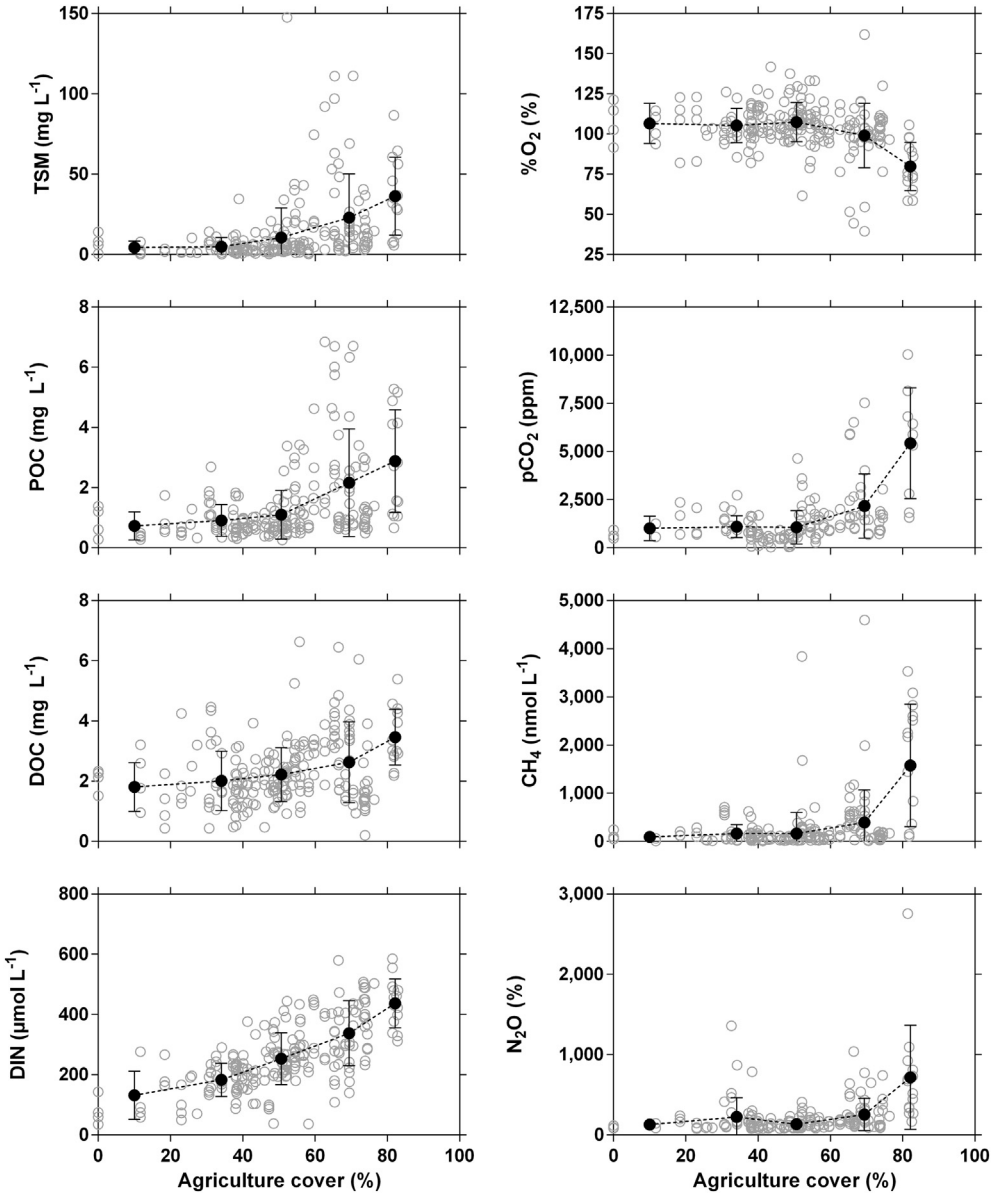


Fig. 10. Total suspended matter (TSM, mg L^{-1}), particulate organic carbon (POC, mg L^{-1}), dissolved organic carbon (DOC, mg L^{-1}), dissolved inorganic nitrogen (DIN, µmol L^{-1}), oxygen saturation level (%O_2, %), partial pressure of CO_2 (pCO_2, ppm), dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%) as a function of the agriculture (cropland and pastures) land cover over the catchment from the four spatial surveys in the Meuse basin (summer 2013 and in late winter 2013, 2014 and 2015). Light circles indicate the individual stations, the dark circles indicate the average and standard deviation of data-bins every 20% of agriculture cover.

Bodmer et al. (2016) that also showed an increase of CO_2 in agriculture impacted streams in Germany compared to forested ones, but not for CH_4. Urban areas occupied on average 9% of the land cover in the sampled sub-catchments but there were no significant correlations between sampled variables and urban area cover (not shown). Large cities can lead to an increase of fluvial GHGs, as shown for CH_4 in the Seine River in response to effluent inputs from the city of Paris (Garnier et al., 2013). However, such effects are very local and large scale spatial variations of fluvial GHGs seem to be related to variations of the more dominant land cover such as agriculture and forest. Furthermore, about 80% of domestic wastewater from urban agglomerations in Wallonia is nowadays collected and processed in wastewater treatment plants.

Finally, in order to further characterize human-impacted river networks compared to relatively pristine ones, and also to compare temperate and tropical rivers we compared CH_4 and N_2O in the Meuse with our own data-sets obtained in the Congo and Zambezi rivers (Borges et al., 2015a; Teodoru et al., 2015) (Fig. 12). At moderate and high O_2 levels (%O_2 > 50%), the CH_4 in the Meuse basin was lower (average 203 nmol L^{-1}) than in the Congo and Zambezi (average 351 and 325 nmol L^{-1}, respectively), owing to higher temperatures and organic matter inputs typical of tropical rivers. However, the Geer River, highly impacted by agriculture and with a high water residence time owing its impounded nature, was characterized by much higher CH_4 average concentrations (6709 nmol L^{-1}) than the Congo and the Zambezi (3073 and 4440 nmol L^{-1}, respectively) within the same %O_2 range (5–60%). The highest CH_4 concentrations were observed in the wetlands of the Congo (up to 56,240 nmol L^{-1}) where nearly anoxic conditions were observed in surface waters (Fig. 11). At low O_2 values (%O_2 < 50%), the N_2O distribution is radically different, with values close to or below saturation in the Congo and Zambezi (100 and 69%, respectively) in these DIN poor systems (average ~15 µmol L^{-1} for both rivers), due to low pressure of agriculture (that is not based anyway on artificial fertilizers) in these two near pristine systems. On the

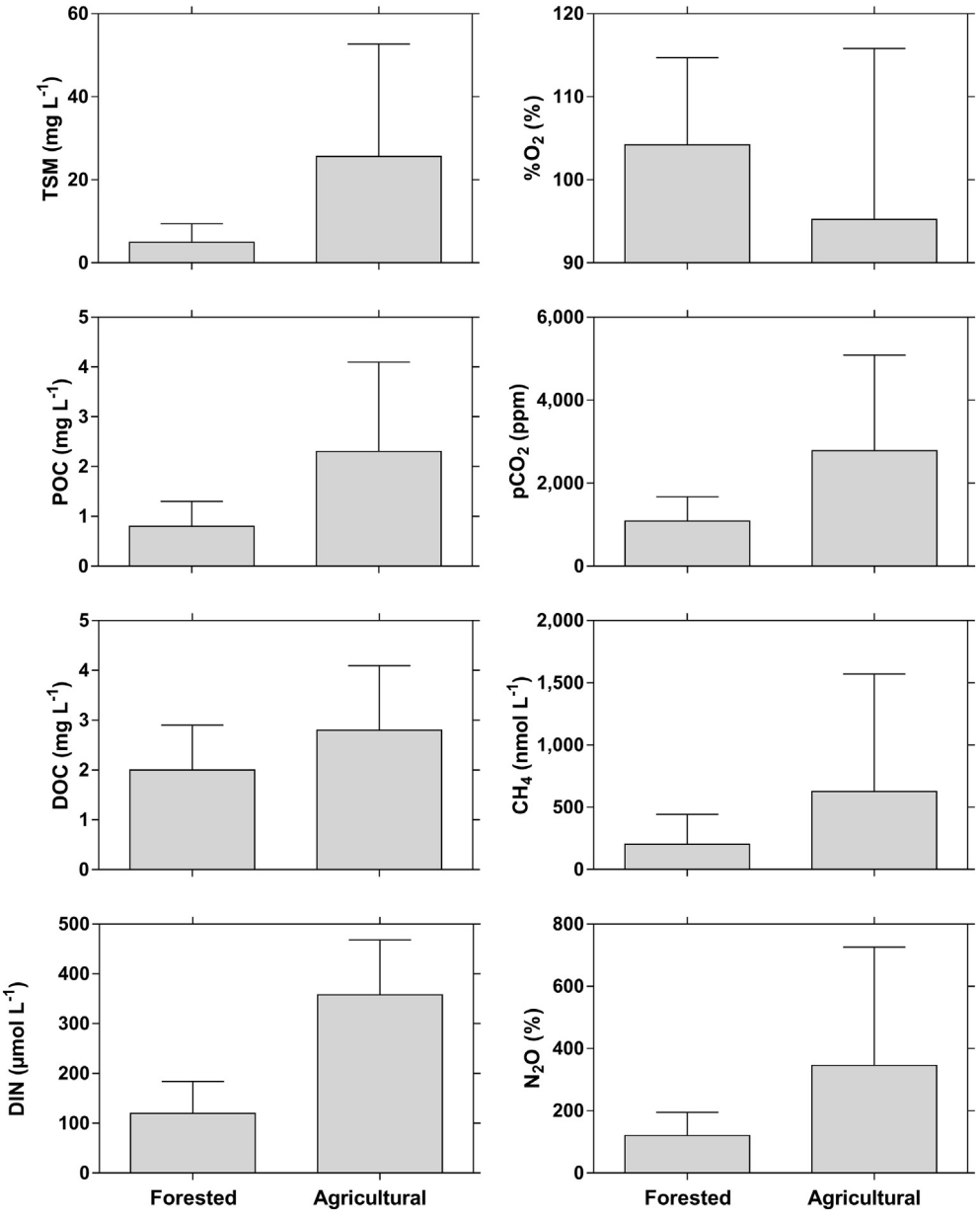


Fig. 11. Average and standard deviation of total suspended matter (TSM, mg L^{-1}), particulate organic carbon (POC, mg L^{-1}), dissolved organic carbon (DOC, mg L^{-1}), dissolved inorganic nitrogen (DIN, μmol L^{-1}), oxygen saturation level (%O_2, %), partial pressure of CO_2 (pCO_2, ppm), dissolved CH_4 concentration (nmol L^{-1}), N_2O saturation level (%) for river basins dominated by forest (>60% of cover) and by agriculture (cropland and pastures) (>60% of cover).

contrary, the N_2O levels strongly increase in the Meuse basin owing to much higher DIN values (average 265 μmol L^{-1}), in particular in the Geer (Fig.10, Table 2), due leaching from agricultural soils strongly impacted by the use of artificial fertilizers (Hakoun et al., 2017).

4. Conclusions

A recent synthesis on the sensitivity of river ecosystem processes to environmental stressors (von Schiller et al., 2017) did not list GHG emissions among the riverine processes, although these are known to be important in global budgets. The present study showed that surface waters of the rivers and streams of Meuse river network were oversaturated in CO_2, CH_4, N_2O with respect to atmospheric equilibrium, which should lead to an emission of these GHGs to the atmosphere, although not quantified in the present study. This study also adds to others that show that GHG emissions from inland waters are sensitive to human modifications of hydrology and catchment land use. Cropland and pasture cover about 40% of the Earth's ice-free surface area (Foley et al., 2005). Here, we show that the concentrations of dissolved CO_2, CH_4 and N_2O in rivers – and hence, their emissions, increased with fraction of agriculture on the catchment owing to a larger delivery of DIN and organic matter. Agriculture (livestock and rice cultivation) contributes globally to about 57% of total anthropogenic CH_4 emissions (Saunois et al., 2016). Here, we show that rivers can be an additional source of CH_4 related to agricultural practise (croplands and pastures) that has not been previously accounted, although already acknowledged for N_2O (Yu et al., 2013). Unlike impounded rivers such as the Mississippi where low CO_2 values have been reported due to planktonic primary production (Crawford et al., 2016), the Meuse was characterized by CO_2 oversaturation that increased in summer. This difference might result from the occurrence of invasive benthic filter feeders (mussels and clams) that exert a strong top-down control on phytoplankton development that is nowadays confined to early spring in the Meuse. Comparison with pristine tropical rivers showed that the use of artificial

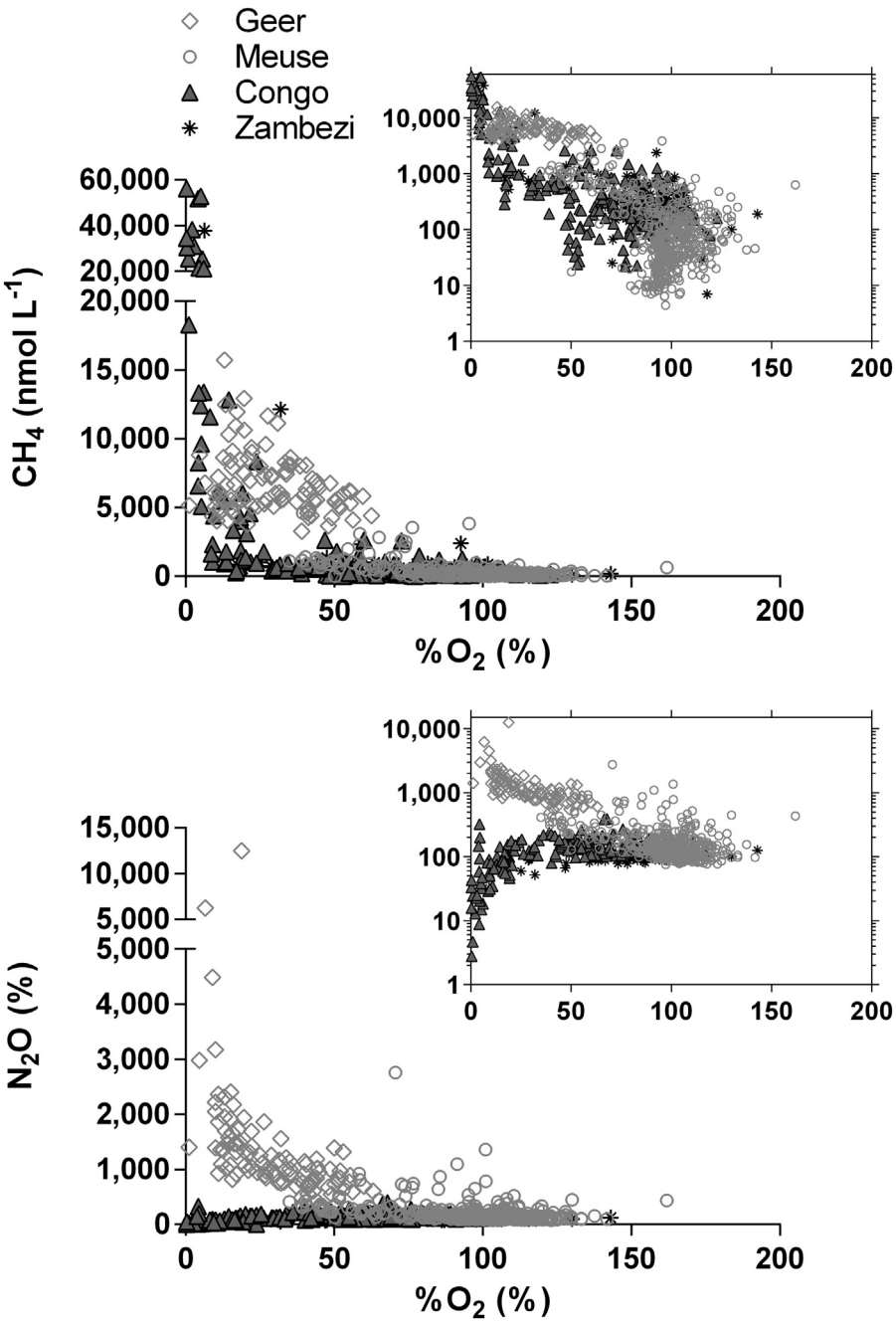


Fig. 12. Dissolved CH_4 concentration (nmol L^{-1}) and N_2O saturation level (%) versus partial pressure of CO_2 (pCO_2, ppm), and versus oxygen saturation level ($\%O_2$, %) from for all of the data gathered from fixed station monitoring and spatial surveys in the Meuse basin from 2011 to 2015 and in the Congo (triangles) and Zambezi (stars) rivers (Borges et al., 2015a; Teodoru et al., 2015). Data from the Geer (light grey diamonds) are separated from the other rivers for the basin referred to as "Meuse" (light grey circles). Data of pCO_2 are unavailable for the Geer.

fertilizers on the catchments strongly enhanced N_2O production, while DIN poor pristine systems tended to be sinks of N_2O at low O_2 levels, probably owing to sediment denitrification.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.08.047.

Acknowledgements

This is a contribution to the WAL-H2O-GHG project funded by the Walloon Institute of Sustainable Development and the Fonds National de la Recherche Scientifique (FNRS) (project n X.3007.17). We thank Aurore Beulen, Jonathan Reichling, Stephane Hoornaert, Marc-Vincent Commarieu, Jérôme Harlay, Sandro Petrovic and Bruno Leporcq for help in sampling and analytical support, the DGO2 (Direction Générale Opérationnelle de la Mobilité et des Voies hydrauliques) of the Service Public de Wallonie (SPW) for providing freshwater discharge data, the DGO3 (Direction Générale Opérationnelle Agriculture, Ressources naturelles et Environnement) and the Institut Scientifique de Service Public and for help during the groundwater samplings, and three anonymous reviewers for helpful comments on a previous version of the manuscript. VH acknowledges funding from the European Commission through the Marie Skłodowska-Curie International Training Network Advocate (Project No. 265063). AJ gratefully acknowledges the financial support from the University of Liège and the European Commission through the Marie Skłodowska-Curie BeIPD-COFUND postdoctoral fellowship programme (2015-2017 fellows from FP7-MSCA-COFUND, 600405). AVB is a senior research associate at the FNRS.

References

Abril, G., Etcheber, H., Borges, A.V., Frankignoulle, M., 2000. Excess atmospheric carbon dioxide transported by rivers into the Scheldt Estuary. C.R. Acad. Sci., Ser. IIa: Sci. Terre Planets 330, 761–768.

Abril, G., Martinez, J.-M., Artigas, L.F., Moreira-Turcq, P., Benedetti, M.F., Vidal, L., Meziane, T., Kim, J.-H., Bernardes, M.C., Savoye, N., Deborde, J., Albéric, P., Souza, M.F.L., Souza, E.L., Roland, F., 2014. Amazon River carbon dioxide outgassing fuelled by wetlands. Nature 505, 395–398.

Abril, G., Bouillon, S., Darchambeau, F., Teodoru, C.R., Marwick, T.R., Tamooh, F., Omengo, F.O., Geeraert, N., Deirmendjian, L., Polsenaere, P., Borges, A.V., 2015. Technical note: large overestimation of pCO_2 calculated from pH and alkalinity in acidic, organic-rich freshwaters. Biogeosciences 12, 67–78.

Alshboul, Z., Encinas-Fernandéz, J., Hofmann, H., Lorke, A., 2016. Export of dissolved methane and carbon dioxide with effluents from municipal wastewater treatment plants. Environ. Sci. Technol. 50, 5555–5563.

APHA, 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association.

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.

Baulch, H.M., Schiff, S.L., Maranger, R., Dillon, P.J., 2011. Nitrogen enrichment and the emission of nitrous oxide from streams. Glob. Biogeochem. Cycles 25, GB4013. http://dx.doi.org/10.1029/2011GB004047.

Beaulieu, J.J., Tank, J.L., Hamilton, S.K., Wollheim, W.M., Hall Jr., R.O., Mulholland, P.J., Peterson, B.J., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Dodds, W.K., Grimm, N.B., Johnson, S.L., McDowell, W.H., Poole, G.C., Valett, H.M., Arango, C.P., Bernot, M.J., Burgin, A.J., Crenshaw, C.L., Helton, A.M., Johnson, L.T., O'Brien, J.M., Potter, J.D., Sheibley, R.W., Sobota, D.J., Thomas, S.M., 2011. Nitrous oxide emission from denitrification in stream and river networks. Proc. Natl. Acad. Sci. U. S. A. 108, 214–219.

Bloom, A.A., Palmer, P.I., Fraser, A., Reay, D.S., Frankenberg, C., 2010. Large-scale controls of methanogenesis inferred from methane and gravity spaceborne data. Science 327, 322–325.

Bodmer, P., Heinz, M., Pusch, M., Singer, G., Premke, K., 2016. Carbon dynamics and their link to dissolved organic matter quality across contrasting stream ecosystems. Sci. Total Environ. 553, 574–586.

Borges, A.V., Darchambeau, F., Teodoru, C.R., Marwick, T.R., Tamooh, F., Geeraert, N., Omengo, F.O., Guérin, F., Lambert, T., Morana, C., Okuku, E., Bouillon, S., 2015a. Globally significant greenhouse gas emissions from African inland waters. Nat. Geosci. 8, 637–642.

Borges, A.V., Abril, G., Darchambeau, F., Teodoru, C.R., Deborde, J., Vidal, L.O., Lambert, T., Bouillon, S., 2015b. Divergent biophysical controls of aquatic CO_2 and CH4 in the World's two largest rivers. Sci Rep 5:15614. http://dx.doi.org/10.1038/srep15614.

Butman, D., Raymond, P.A., 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. Nat. Geosci. 4, 839–842.

Caraco, N.F., Cole, J.J., Raymond, P.A., Strayer, D.L., Pace, M.L., Findlay, S.E.G., Fischer, D.T., 1997. Zebra mussel invasion in a large, turbid river: phytoplankton response to increased grazing. Ecology 78, 588–602.

Codispoti, L.A., Christensen, J.P., 1985. Nitirification, denitrification and nitroux oxide cycling in the Eastern tropical South Pacific Ocean. Mar. Chem. 16, 277–300.

Cole, J.J., Caraco, N.F., 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Mar. Freshw. Res. 52, 101–110.

Crawford, J.T., Loken, L.C., Stanley, E.H., Stets, E.G., Dornblaser, M.M., Striegl, R.G., 2016. Basin scale controls on CO_2 and CH_4 emissions from the upper Mississippi River. Geophys. Res. Lett. 43, 1973–1979.

Descy, J.-P., Servais, P., Smitz, J.S., Billen, G., Everbecq, E., 1987. Phytoplankton biomass and production in the river meuse (Belgium). Water Res. 21, 1557–1566.

Descy, J.-P., Leporcq, B., Viroux, L., François, C., Servais, P., 2002. Phytoplankton production, exudation and bacterial reassimilation in the River Meuse (Belgium). J. Plankton Res. 24, 161–166.

Descy, J.-P., Everbecq, E., Gosselain, V., Viroux, L., Smitz, J.S., 2003. Modelling the impact of benthic filter-feeders on the composition and biomass of river plankton. Freshw. Biol. 48, 404–417.

Descy, J.-P., Hardy, M.-A., Sténuite, S., Pirlot, S., Leporcq, B., Kimirei, I., Sekadende, B., Mwaitega, S.R., Sinyenza, D., 2005. Phytoplankton pigments and community composition in Lake Tanganyika. Freshw. Biol. 50, 668–684.

Descy, J.-P., Patrick, K., Everbecq, E., Verniers, G., Usseglio-Polatera, P., Gérard, P., Viroux, L., Beisel, J.-N., Smitz, J., 2009. Continental Atlantic Rivers. In: Tockner, Klement, Uehlinger, Urs, Robinson, Christopher T. (Eds.), Rivers of Europe. Academic Press, London, pp. 151–198.

Dong, L.F., Nedwell, D.B., Colbeck, I., Finch, J., 2005. Nitrous oxide emission from some English and Welsh rivers and estuaries. Water Air Soil Pollut. Focus 4, 127–134.

EEA, 2014. European Environmental Agency, Corine Land Cover 2006 raster data. Retrieved from. http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster-3.

Evans, M.A., Fahnenstiel, G., Scavia, D., 2011. Incidental oligotrophication of North American Great Lakes. Environ. Sci. Technol. 45, 3297–3303.

Everbecq, E., Gosselain, V., Viroux, L., Descy, J.-P., 2001. Potamon: a dynamic model for predicting phytoplankton composition and biomass in lowland rivers. Water Res. 35, 901–912.

Foley, J., DeFries, R., Asner, C., Barford, G., Bonan, S.R., Carpenter, F.S., Chapin, M.T., Coe, G.C., Daly, H.K., Gibbs, J.H., Helkowski, T., Hollaway, E.A., Howard, C.J., Kucharik, C., Monfreda, C., Patz, A., Prentice, I.C., Ramankutty, N., Snyder, P.K., 2005. Global consequences of land use. Science 309, 570–574.

Garnier, J., Billen, G., Vilain, G., Martinez, A., Silvestre, M., Mounier, E., Toche, F., 2009. Nitrous oxide (N_2O) in the Seine river and basin: observations and budgets. Agric. Agric. Ecosyst. Environ. 133, 223–233.

Garnier, J., Vilain, G., Silvestre, M., Billen, G., Jehanno, S., Poirier, D., Martinez, A., Decuq, C., Cellier, P., Abril, G., 2013. Budget of methane emissions from soils, livestock and the river network at the regional scale of the Seine basin (France). Biogeochemistry 116, 199–214.

Graeber, D., Gelbrecht, J., Pusch, M.T., Anlanger, C., von Schiller, D., 2012. Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. Sci. Total Environ. 438, 435–446.

Graeber, D., Boëchat, I.G., Encina-Montoya, F., Esse, C., Gelbrecht, J., Goyenola, G., Gücker, B., Heinz, M., Kronvang, B., Meerhoff, M., Nimptsch, J., Pusch, M.T., Silva, R.C., von Schiller, D., Zwirnmann, E., 2015. Global effects of agriculture on fluvial dissolved organic matter. Sci Rep 5:16328. http://dx.doi.org/10.1038/srep16328.

Hakoun, V., Orban, P., Dassargues, A., Brouyère, S., 2017. Factors controlling spatial and temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer, Belgium). Environ. Pollut. 223, 185–199.

Hotchkiss, E.R., Hall Jr., R.O., Sponseller, R.A., Butman, D., Klaminder, J., Laudon, H., Rosvall, M., Karlsson, J., 2015. Sources of and processes controlling CO_2 emissions change with the size of streams and rivers. Nat. Geosci. 8, 696–699.

Hu, M., Chen, D., Dahlgren, R.A., 2016. Modeling nitrous oxide emission from rivers: a global assessment. Glob. Chang. Biol. 22, 3566–3582.

Hussner, A., 2009. Growth and photosynthesis of four invasive aquatic plant species in Europe. Weed Res. 49, 506–515.

Hussner, A., 2012. Alien aquatic plant species in European countries. Weed Res. 52, 297–306.

Johnson, M.S., Lehmann, J., Riha, S.J., Krusche, A.V., Richey, J.E., Ometto, J.P.H.B., Couto, E.G., 2008. CO_2 efflux from Amazonian headwater streams represents a significant fate for deep soil respiration. Geophys. Res. Lett. 35, L17401. http://dx.doi.org/10.1029/2008GL034619.

Jurado, A., Borges, A.V., Brouyère, S., 2017. Dynamics and emissions of N_2O in groundwater: a review. Sci. Total Environ. 584–585, 207–218.

Kempe, S., 1984. Sinks of the anthropogenically enhanced carbon cycle in surface fresh waters. J. Geophys. Res. 89, 4657–4676.

Koné, Y.J.M., Abril, G., Kouadio, K.N., Delille, B., Borges, A.V., 2009. Seasonal variability of carbon dioxide in the rivers and lagoons of Ivory Coast (West Africa). Estuar. Coasts 32, 246–260.

Koné, Y.J.M., Abril, G., Delille, B., Borges, A.V., 2010. Seasonal variability of methane in the rivers and lagoons of Ivory Coast (West Africa). Biogeochemistry 100, 21–37.

Lambert, T., Bouillon, S., Darchambeau, F., Morana, C., Roland, F., Descy, J.-P., Borges, A.V., 2017. Effects of human land use on the terrestrial and aquatic sources of fluvial organic matter in a temperate river basin (The Meuse River, Belgium) (submitted).

Lauerwald, R., Laruelle, G.G., Hartmann, J., Ciais, P., Regnier, P.A.G., 2015. Spatial patterns in CO_2 evasion from the global river network. Glob. Biogeochem. Cycles 29, 534–554.

Maeck, A., Delsontro, T., McGinnis, D.F., Fischer, H., Flury, S., Schmidt, M., Fietzek, P., Lorke, A., 2013. Sediment trapping by dams creates methane emission hot spots. Environ. Sci. Technol. 47, 8130–8137.

Marescaux, J., Boets, P., Lorquet, J., Sablon, R., Van Doninck, K., Beisel, J.-N., 2015. Sympatric *Dreissena* species in the Meuse River: towards a dominance shift from zebra to quagga mussels. Aquat. Invasions 10, 287–298.

Marwick, T.R., Tamooh, F., Ogwoka, B., Teodoru, C., Borges, A.V., Darchambeau, F., Bouillon, S., 2014. Dynamic seasonal nitrogen cycling in response to anthropogenic N loading in a tropical catchment, Athi–Galana–Sabaki River, Kenya. Biogeosciences 11, 1–18.

Meybeck, M., 1987. Global chemical weathering of surficial rocks estimated from river dissolved loads. Am. J. Sci. 287, 401–428.

Orban, P., Brouyère, S., Batlle-Aguilar, J., Couturier, J., Goderniaux, P., Leroy, M., Maloszewski, P., Dassargues, A., 2010. Regional transport modelling for nitrate trend assessment and forecasting in a chalk aquifer. J. Contam. Hydrol. 118, 79–93.

Pigneur, L.M., Falisse, E., Roland, K., Everbecq, E., Deliège, J.F., Smitz, J.S., Doninck, K., Descy, J.P., 2014. Impact of invasive Asian clams, *Corbicula* spp., on a large river ecosystem. Freshw. Biol. 59, 573–583.

Rajkumar, A.N., Barnes, J., Ramesh, R., Purvaja, R., Upstill-Goddard, R.C., 2008. Methane and nitrous oxide fluxes in the polluted Adyar River and estuary, SE India. Mar. Pollut. Bull. 56, 2043–2051.

Raymond, P.A., Zappa, C.J., Butman, D., Bott, T.L., Potter, C., Mulholland, P., Laursen, A.E., McDowell, W.H., Newbold, D., 2012. Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. Limnol. Oceanogr. Fluids Environ. 2, 41–53.

Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Dürr, H., Meybeck, M., Ciais, P., Guth, P., 2013. Global carbon dioxide emissions from inland waters. Nature 503, 355–359.

Richey, J.E., Devol, A.H., Wofy, S.C., Victoria, R., Riberio, M.N.G., 1988. Biogenic gases and the oxidation and reduction of carbon in Amazon River and floodplain waters. Limnol. Oceanogr. 33, 551–561.

Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., Hess, L., 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. Nature 416, 617–620.

Saunois, M., Bousquet, P., Poulter, B., Peregon, A., Ciais, P., Canadell, J.G., Dlugokencky, E.J., Etiope, G., Bastviken, D., Houweling, S., Janssens-Maenhout, G., Tubiello, F.N., Castaldi, S., Jackson, R.B., Alexe, M., Arora, V.K., Beerling, D.J., Bergamaschi, P., Blake, D.R., Brailsford, G., Brovkin, V., Bruhwiler, L., Crevoisier, C., Crill, P., Kovey, K., Curry, C., Frankenberg, C., Gedney, N., Höglund-Isaksson, L., Ishizawa, M., Ito, A., Joos, F., Kim, H.-S., Kleinen, T., Krummel, P., Lamarque, J.-F., Langenfelds, R., Locatelli, R., Machida, T., Maksyutov, S., McDonald, K.C., Marshall, J., Melton, J.R., Morino, I., Naik, V., O'Doherty, S., Parmentier, F.-J.W., Patra, P.K., Peng, C., Peng, S., Peters, G., Pison, I., Prigent, C., Prinn, R., Ramonet, M., Riley, W.J., Saito, M., Sanyini, M., Schroeder, R., Simpson, I.J., Spahni, R., Steele, P., Takizawa, A., Thornton, B.F., Tian, H., Tohjima, Y., Viovy, N., Voulgarakis, A., van Weele, M., van der Werf, G., Weiss, R., Wiedinmyer, C., Wilton, D.J., Wiltshire, A., Worthy, D., Wunch, D.B., Xu, X., Yoshida, Y., Zhang, B., Zhang, Z., Zhu, Q., 2016. The global methane budget. Earth Syst. Sci. Data 8, 697–751.

Schade, J.D., Bailio, J., McDowell, W.H., 2016. Greenhouse gas flux from headwater streams in New Hampshire, USA: patterns and drivers. Limnol. Oceanogr. 61, S165–S174.

von Schiller, D., Acuña, V., Aristi, I., Arroita, M., Basaguren, A., Bellin, A., Boyero, L., Butturini, A., Ginebreda, A., Kalogianni, E., Larrañaga, A., Majone, B., Martínez, A., Monroy, S., Muñoz, I., Paunović, M., Pereda, O., Petrovic, M., Pozo, J., Rodríguez-Mozaz, S., Rivas, D., Sabater, S., Sabater, F., Skoulikidis, N., Solagaistua, L., Vardakas, L., Elosegi, A., 2017. River ecosystem processes: a synthesis of approaches, criteria of use and sensitivity to environmental stressors. Sci. Total Environ. 596–597, 465–480.

Seitzinger, S.P., Kroeze, C., 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Glob. Biogeochem. Cycles 12, 93–113.

Servais, P., 1989. Bacterioplankton biomass and production in the river Meuse (Belgium). Hydrobiologia 174, 99–110.

Sieczko, A.K., Demeter, K., Singer, G.A., Tritthart, M., Preiner, S., Mayr, M., Meisterl, K., Peduzzi, P., 2016. Aquatic methane dynamics in a human-impacted river-floodplain of the Danube. Limnol. Oceanogr. 61, S175–S187.

Standing committee of Analysts, 1981. Ammonia in waters. Methods for the Examination of Waters and Associated Materials (16 pp.).

Stanley, E.H., Casson, N.J., Christel, S.T., Crawford, J.T., Loken, L.C., Oliver, S.K., 2016. The ecology of methane in streams and rivers: patterns, controls, and global significance. Ecol. Monogr. 86, 146–171.

Teodoru, C.R., Nyoni, F.C., Borges, A.V., Darchambeau, F., Nyambe, I., Bouillon, S., 2015. Dynamics of greenhouse gases (CO_2, CH_4, N_2O) along the Zambezi River and major tributaries, and their importance in the riverine carbon budget. Biogeosciences 12, 2431–2453.

Weiss, R.F., 1981. Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography. J. Chromatogr. Sci. 19, 611–616.

Wilson, H.F., Xenopoulos, M.A., 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nat. Geosci. 2, 37–41.

Yu, Z., Deng, H., Wang, D., Ye, M., Tan, Y., Li, Y., Chen, Z., Xu, S., 2013. Nitrous oxide emissions in the Shanghai river network: implications for the effects of urban sewage and IPCC methodology. Glob. Chang. Biol. 19, 2999–3010.