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

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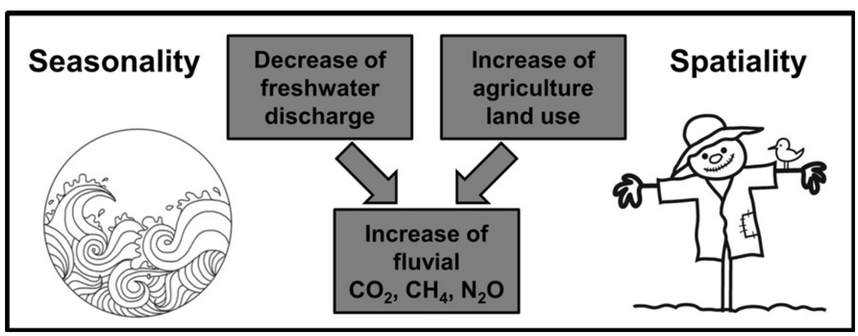
HIGHLIGHTS

- 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



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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

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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.