

# CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O dynamics in Belgian rivers across a gradient of anthropogenic disturbance

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Two rivers and two streams close to the city of Liège in Belgium (Meuse, Ourthe, Geer and Blanc Gravier) were sampled to describe the dynamics of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O (for the first time in Belgium for freshwaters). The four systems were chosen to cover a gradient of size (stream to river) and of human influence (mainly forested to mainly agricultural watersheds). The study covers the period from February 2011 to March 2013 with weekly sampling in surface waters. The variables were very contrasted in the four systems, the Geer showing a strong enrichment in nitrogen NH<sub>4</sub><sup>+</sup> et NO<sub>2</sub><sup>-</sup>) and phosphorous in relation to the other three systems. The O<sub>2</sub> concentrations were much lower, and the concentration of CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub> were much higher in the Geer than in other three systems. The concentrations in CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub> were higher in the Ourthe than in the Meuse and than in the Blanc Gravier. Marked seasonal variations were observed in the 4 systems. In general the concentration of CH<sub>4</sub>, N<sub>2</sub>O and pCO<sub>2</sub> were higher in summer than in winter. This is related on one hand to the increase of temperature in summer that stimulates bacterial activity. Also in summer, the availability of organic matter for bacterial activity is higher after the spring phytoplankton blooms and also from allochthonous inputs from the watersheds. The increase of temperature and bacterial consumption of O<sub>2</sub> in the water column leads to a lesser O<sub>2</sub> penetration in the sediments that could stimulate benthic anaerobic processes among which methanogenesis and denitrification, leading to an increase of CH<sub>4</sub> and N<sub>2</sub>O in the water column. Also, the production of N<sub>2</sub>O by denitrification strongly increases at low O<sub>2</sub>. During low water, the increase of residence time of the water mass and the decrease of current (decrease of degasing) allow an accumulation of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O in the water column. On the contrary during high water, dilution and increase of current (increase of degasing) lead to a decrease of concentrations. The four systems were over-saturated in CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub>, excepted during spring phytoplankton blooms when an under-saturation of CO<sub>2</sub> was observed in the Ourthe. Hence, the four systems were sources of CH<sub>4</sub>, N<sub>2</sub>O and CO<sub>2</sub> to the atmosphere. Diffusive CO<sub>2</sub> fluxes varied from 24 to 607 mol m<sup>-2</sup> yr<sup>-1</sup> (Ourthe and Geer, respectively). Diffusive CH<sub>4</sub> fluxes varied from 28 to 8199 mmol m<sup>-2</sup> an<sup>-1</sup> (Blanc Gravier and Geer, respectively). Diffusive N<sub>2</sub>O fluxes varied from 2 to 201 mmol m<sup>-2</sup> an<sup>-1</sup> (Ourthe and Geer, respectively).

	Forest (%)	Grassland (%)	Cropland (%)	Catchment (km <sup>2</sup> )	Pop. density (habit. km <sup>-2</sup> )
Meuse	64	14	22	36000	255
Ourthe	47	32	21	1837	71
Geer	<1	7	93	463	194
Blanc Gravier	~100	~0	~0	~20	~0

