Dynamics of greenhouse gases in the river-groundwater interface in gaining river stretch (Triffoy catchment, Belgium)

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Abstract

This study investigates the occurrence of greenhouse gases (GHGs) and the role of groundwater as an indirect pathway of GHG emissions into surface waters in a gaining stretch of the Triffoy River agricultural catchment (Belgium). To this end, nitrous oxide (N2O), methane (CH4) and carbon dioxide (CO2) concentrations, the stable isotopes of nitrate and major ions were monitored in river and groundwater during 8 months. Results indicated that groundwater was strongly oversaturated in N2O and CO2 with respect to atmospheric equilibrium (50.1 vs. 0.55 µg/L for N2O and 14,569 vs. 400 ppm for CO2), but only marginally for CH4 (0.45 vs. 0.056 µg/L), suggesting that groundwater can be a source of these GHGs to the atmosphere. Nitrification seemed to be the main process for the accumulation of N2O in groundwater. Oxidation conditions prevailing in the aquifer were not prone to the accumulation of CH4. In fact, the emissions of CH4 from the river were one to two orders of magnitude higher than the inputs from groundwater, meaning that CH4 emissions from the river were due to CH4 in-situ production in river-bed or riparian zone sediments. For CO2 and N2O, average emissions from groundwater were $1.5 \times 10^5$ kg CO2 Ha$^{-1}$ y$^{-1}$ and 207.1 kg N2O Ha$^{-1}$ y$^{-1}$, respectively. Groundwater is probably an important source of N2O and CO2 in gaining streams but when the measures are scaled at catchment scale, these fluxes are probably relatively modest. Nevertheless, their quantification would better constrain nitrogen and carbon budgets in natural systems.

Keywords: Greenhouse gases, indirect emissions, river-groundwater interface, gaining stream, field scale, Belgium
1. Introduction

Anthropogenic application of organic and inorganic fertilisers of nitrogen (N) in agricultural landscapes and livestock wastes have a negative impact on groundwater resources quality due to leaching of N species into aquifers (Glavan et al., 2017). Agricultural practices represented up to one third of anthropogenic emissions of greenhouse gases (GHGs) (Gilbert, 2012), such as nitrous oxide (N₂O), methane (CH₄) and carbon dioxide (CO₂), which all contribute to climate change and N₂O to stratospheric ozone destruction (IPCC, 2014). Therefore, aquifers below agricultural landscapes can be an indirect source of GHG emissions to the atmosphere because groundwater is generally oversaturated in these GHGs with respect to atmospheric equilibrium (Bell et al., 2017; Jurado et al., 2018; McAleer et al., 2017).

Dynamics of GHGs in groundwater are complex because their occurrence depends on the geochemical conditions (e.g., nitrate NO₃⁻, ammonium NH₄⁺, dissolved oxygen DO, organic carbon OC, bicarbonate HCO₃⁻, pH, among others) that control nitrogen (N) and carbon (C) cycles (Nikolenko et al., 2018; Jahangir et al., 2013). Denitrification is considered to be the main process of NO₃⁻ attenuation under anaerobic conditions in groundwater but N₂O is an intermediate product (Rivett et al., 2008). When NO₃⁻ is non-limiting and at intermediate DO concentrations, N₂O is not reduced to N₂ and it can accumulate in shallow groundwater (Deurer et al., 2008). Nitrification also contributes to the N₂O production in groundwater, in which case N₂O is a byproduct that can be produced during the oxidation of nitrite (NO₂⁻) to NO₃⁻ (e.g., Vilain et al., 2012). In addition, hydrogeological parameters (e.g., groundwater table, rainfall periods and aquifer permeability) also play a major role on the dynamics of N₂O in groundwater (Jahangir et al., 2013). For instance, Deurer et al. (2008) suggested that during high-intensity precipitation events, denitrification might be inhibited in the Fuhrberger Feld aquifer (Germany) by the transport of DO with the infiltrating water. This situation promoted variable geochemical conditions leading to “cold” and “hot” spots of N₂O in near surface...
groundwater. Concerning C species, the presence of CH$_4$ in shallow groundwater is associated with strongly anaerobic environments such as wetlands and landfills and comes from a biogenic origin (Bell et al., 2017). For example, Cheung et al. (2010) reported that dissolved CH$_4$ in shallow groundwater of Alberta (Canada) was of biogenic origin via CO$_2$ reduction. Likewise, CO$_2$ is also produced and consumed by several processes in groundwater, such as plant root respiration, oxidation of organic matter and the precipitation and dissolution of carbonate minerals (Wang et al., 2015).

Several studies have assessed the indirect GHG emissions in aquifers below agricultural landscapes (Hasegawa et al., 2000; Jahangir et al., 2012; McAleer et al., 2017; Minamikawa et al., 2010; Vilain et al., 2012; von der Heide et al., 2009) but the contribution of groundwater as a source of GHGs via surface water bodies such as streams and rivers has received less attention. Groundwater discharge to river (base flow) has been recognized as a potential pathway of N$_2$O into streams and rivers, which generally are net sources of N$_2$O in N rich environments (Beaulieu et al., 2012; Fox et al., 2014, Gardner et al., 2016; Werner et al., 2012) but can be sinks of N$_2$O in N and DO poor environments (Borges et al. 2015; 2018). Groundwater has also been recognised as an important source of CO$_2$ in riverine systems (Worral and Lancaster, 2005), especially in small streams and headwaters (Hotchkiss et al., 2015, Johnson et al., 2008). Recently, Borges et al. (2018) have reported that surface waters of the Meuse River network (Belgium) act as a source of CO$_2$, CH$_4$ and N$_2$O to the atmosphere. The authors pointed out that the extremely high concentrations of N$_2$O and CO$_2$ in groundwater might indicate that part of these GHGs could come from groundwater in the Meuse basin, although the actual fraction remains to be quantified.

To date, studies that have simultaneously quantified the contribution of groundwater as a potential source of N$_2$O, CH$_4$ and CO$_2$ in rivers are scarce. Moreover, several authors have recently stated that groundwater-surface water interactions and groundwater hydrology
require further analysis to better estimate the contribution of GHGs dissolved in groundwater into atmospheric fluxes at a local scale (Hinshaw and Dahlgren, 2016; Jurado et al., 2018; Vidon and Serchan, 2016). The objectives of this study are to (1) investigate the occurrence and examine the sources of GHGs in the river-groundwater interface and (2) evaluate the contribution of indirect GHG emissions from groundwater into surface waters. To this end, GHGs, major and minor ions and stable isotopes were sampled over 8 months in a small river catchment (Triffoy) located in the Walloon Region (Belgium).

2. Materials and methods

2.1 Study area

The Triffoy River catchment, with an area of 30.31 km², is in the natural region of Condroz in Wallonia (Belgium) (Fig. 1). It is an agricultural catchment where land use is dominated by cropland (48%) and grassland (38%). The remaining territory is occupied by urban areas (7%), forests (6%) and natural environments (1%). There are no industries in the whole catchment but NO₃⁻ concentrations can exceed the limit of good status during winter due to leaching of agricultural soil NO₃⁻ residue by infiltrating water (Brouyère et al., 2015; 2017). The climate is oceanic temperate, with an average annual rainfall of 900 mm and an average annual temperature of 10 °C.

The Triffoy River intersects geological formations of Palaeozoic age, from Devonian to Carboniferous (Briers et al., 2016a). It flows through a Carboniferous limestone syncline located between two Frasnian-Famennian sandstone crests. At the base of Carboniferous limestone, the Hastarien shales constitute impermeable hydrogeological barriers separating the Carboniferous limestone aquifer from the Famennian sandstone aquifer. The sandstone aquifer is limited in extension and capacity. In contrast, the Carboniferous limestone aquifer is
an important groundwater reservoir that belongs to one of the most productive groundwater bodies of Wallonia (RWM21, Fig.1). The limestone aquifer is exploited by two water catchments: Jamagne (2,600,000 m³ y⁻¹) and the Compagnie Intercommunale Liégeoise des Eaux (CILE, 700,000 m³ y⁻¹).

Previous studies carried out in this basin reported two different types of river-groundwater interactions (Briers et al., 2016b): (i) gaining streams where water level is higher in the groundwater, feeding river and helping to maintain its base flow and (2) losing streams where river water recharges the aquifer. The stretch of river monitored in this study is a gaining stream (Fig. 1) and therefore it is suitable to quantify the groundwater contribution to GHGs emissions from rivers. On average, it was estimated that 92% of the Triffoy River baseflow comes from groundwater recharge (Briers et al., 2016c).

A river segment of 2 Km (from Jamagne to State river sampling locations, Fig.1) was monitored over 8 months using river gauging and pressiometric and temperature probes installed in piezometers and in the river (MPZ river sampling location, Fig. 1). The monitoring network for the analysis of GHGs is composed by 3 river sampling locations (Jamagne, MPZ and State) and 7 groundwater observation points: 5 shallow piezometers (MP-4, MP2-3, MP2-6, MP3-3 and MP3-6) and two springs (S1 and S2). The location of these points and the characteristics of the piezometers are summarized in Figure A and Table A (supplementary material).

### 2.2 Groundwater and river sampling

A total of six field campaigns were carried out from October 2016 to May 2017 (October (C1) and December (C2) 2016 and January (C3), February (C4), March (C5) and May (C6) 2017). Forty samples were collected from groundwater and 18 from the Triffoy River at different locations (Fig. 1). Before sampling, the piezometers were purged by pumping three
well volumes to remove the stagnant water and samples were collected when field parameters were stabilised. Temperature (°C), electrical conductivity (EC, μS/cm), pH and DO (mg/L) were measured with a portable multi-probe (YSI 556 MPS) within a flow-through cell. Samples were stored in a field refrigerator and taken to the laboratory at the end of the sampling day.

Groundwater samples were collected through tubing avoiding any contact with the atmosphere. Sampling in surface waters was carried out using a 1.7 L Niskin bottle (General Oceanics). Samples for CH₄ and N₂O were transferred with tubing from the Niskin bottle to 50 ml borosilicate serum bottles that were poisoned with a saturated solution of HgCl₂ (200 μl), sealed with a butyl stopper and crimped with an aluminum cap. Four polypropylene syringes of 60 ml for measurements of pCO₂ were filled from each sampling point. For the general chemistry (major and minor ions), groundwater samples were collected in polypropylene bottles of 180 mL for major and minor ions and 125 mL for metals (iron (Fe) and manganese (Mn)). Metal samples were filtered through a 0.45 μm polyethersulphone and micro-quartz fibre filter and acidified with 1 mL of HCl 12N for sample preservation. Samples for NO₃⁻ isotopes were collected in polypropylene bottle of 60 mL and filtered through 0.22 μm nylon filter. Samples to determine dissolved organic carbon (DOC) were filtered through 0.22 μm nylon filter and stored in 40 ml borosilicate vials with polytetrafluoroethylene (PTFE) coated septa and poisoned with 100 μL of H₃PO₄ (85%).

2.3 Analytical methods

The dissolved concentrations of N₂O and CH₄ were analysed with the headspace equilibration technique (25 mL of N₂ headspace in 50 mL serum bottles) and measured by gas chromatography (GC) fitted with electron capture detection (ECD, SRI 8610C) for N₂O and flame ionization detection (FID) for CH₄. The SRI 8610C GC-ECD-FID was calibrated with certified CH₄:CO₂:N₂O:N₂ mixtures (Air Liquide Belgium) of 0.2, 2 and 6 ppm N₂O and of 1,
10 and 30 ppm CH₄. The pCO₂ was measured in the field using an infrared gas analyser (Li-Cor Li-840) a few minutes after sampling by creating a headspace with ambient air in the polypropylene syringes (1:1 ratio of air and water) (Abril et al., 2015). The Li-840 was calibrated with a suite of CO₂:N₂ mixtures (Air Liquide Belgium) with mixing ratios of 388, 813, 3,788, 8,300 and 19,150 ppm CO₂. The reproducibility of the measurements was ±3.2%, ±3.9% and ±2.0% for N₂O, CH₄ and pCO₂, respectively. Major ions (Na⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻ and NO₃⁻) and minor ions (NO₂⁻ and NH₄⁺) were measured by ion chromatography via a specific ion exchange resin and a conductivity detector. Calcium (Ca²⁺) concentrations and alkalinity were obtained by potentiometric titration in the laboratory. Fe and Mn concentrations were obtained by atomic absorption spectrometry. Nitrogen (δ¹⁵NNO₃) and oxygen (δ¹⁸ONO₃) isotope analyses of NO₃⁻ were determined by a mass DELTA V plus spectrometer plus a GasBench II from Thermo using the denitrifier method that convert all sampled NO₃⁻ to N₂O (Sigman et al., 2001; Casciotti et al., 2002). The notation was expressed in terms of delta (δ) per mil (‰) relative to the international standards for the environmental isotopes (V-SMOW for δ¹⁸O and AIR-N₂ for δ¹⁵N of NO₃⁻). The reproducibility of NO₃⁻ isotope samples was ±0.4‰ for δ¹⁵N and ±1.6‰ for δ¹⁸O of NO₃⁻. The NO₃⁻ isotope results represent the mean value of true double measurements of each sample. 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).

2.4 Indirect greenhouse gas emissions from groundwater

The indirect GHG emissions from groundwater to the river (E_GHG-Gw) were evaluated using hydrogeological data and the dissolved concentrations of GHGs measured in the groundwater as follows:

\[
E_{GHG-Gw} = \frac{Q_{dis} \times \left[ C_{GHG-Gw} - C_{GHG-Eq} \right]}{A} \tag{1}
\]
where $Q_{dis}$ is groundwater discharge into the Triffoy River (m$^3$ d$^{-1}$), $C_{\text{GHG-Gw}}$ is the measured concentration of a given GHG in groundwater observation points (µg/L), $C_{\text{GHG-Eq}}$ is the GHGs air-equilibrated water concentration and $A$ is the area of the river between the upstream and the downstream river sampling locations (0.51 Ha). Groundwater discharge into the Triffoy River ($Q_{dis}$) was estimated by the difference in stream flow rate between the upstream (Jamagne, $Q_{in}$) and the downstream (State, $Q_{out}$) river sampling locations (Fig. 1). Note that groundwater was considered the only recharge source of the river because baseflow conditions prevailed during all the monitoring period. Hence, Eq. (1) represents the maximal flux of GHGs from groundwater to the river.

The fluxes of GHGs from groundwater to the river (Eq. (1)) were compared with those from the river surface to the atmosphere ($E_{\text{GHG-Riv}}$). The latter were computed according to:

$$E_{\text{GHG-Riv}} = k \times \Delta G = k \times \left[ C_{\text{GHG-Riv}} - C_{\text{GHG-Eq}} \right]$$

(2)

where $k$ is the gas transfer velocity and $\Delta G$ is the air-water gradient ($\Delta$) of a given gas ($G$). The air water gradient is difference between the measured concentration of a given GHG in river water ($C_{\text{GHG-Riv}}$, µg/L) and the GHG air-equilibrated water concentration ($C_{\text{GHG-Eq}}$, µg/L). $k$ was calculated from the gas transfer velocity normalised to a Schmidt number of 600 ($k_{600}$) with the Schmidt numbers of N$_2$O, CH$_4$ and CO$_2$, computed from in-situ water temperature according to Wanniknhof (1992). $k_{600}$ (cm h$^{-1}$) was computed with the parameterisation of Raymond et al. (2012) as a function of stream velocity ($v$ in m s$^{-1}$) and slope of the river channel ($S$ is 0.0135, unitless):

$$k_{600} = 2.02 + 2841 \times v \times S$$

(3)

This parameterisation was derived from a compilation of gas tracer experiments in small to medium sized rivers and streams, and is then adequate to compute $k_{600}$ in the Triffoy River.
Note that the fluxes computed using Eq. (1) and Eq. (2) should be similar if groundwater is the only source of GHGs to the river (i.e., there are no processes that consumed or produced these GHGs in the river-groundwater interface).

Finally, the indirect groundwater N$_2$O emissions were also estimated at catchment scale using the Intergovernmental Panel on Climate Change methodology (IPCC, 2006) as follows:

$$E_{N_2O-GW} = 0.3\text{N}_\text{Leach} \times \text{EF}_{gw} = 0.3\text{N}_\text{Leach} \times \frac{c_{N_2O-N}}{c_{NO_3-N}}$$

This method considers that 30% of fertiliser and manure N applied to soils in agricultural areas is leached to groundwater (NLeach). The EF$_{gw}$ is the emission factor from groundwater and it is defined as the mass ratio of the dissolved concentrations of N$_2$O (cN$_2$O−N) and NO$_3$− (cNO$_3$−−N) in groundwater.

3. Results and discussion

3.1 Climatic conditions, water levels and groundwater discharge

Data regarding weather conditions and water levels help to understand the water dynamics in the river-groundwater interface. Figure 2 shows rainfall (mm), temperature (°C) and water levels (in meters above the sea level, m.a.s.l.) from December 2016 to May 2017. Total rainfall was 311 mm from October 2016 to May 2017. This value is low compared to the average monthly precipitation for the period 2012-2015 (311 mm vs. 561.4 mm; Table B, supplementary material). All sampled months, except March, presented a lower amount of precipitation than the previous years. The driest months were April 2017 and December 2016 with total precipitations of 15.7 mm and 21.4 mm, respectively (Fig. 2a). In December 2016, the amount of precipitation was 5 times lower than the average monthly precipitation for 2012-2015 (21.4 mm vs. 98.4 mm). Conversely, November was a relatively wet month with
60 mm of precipitation. During the studied period, daily air temperature ranged from -9°C (January 2017) to 19.6°C (March 2017) with an average value of 4.5°C (Fig. 2b). Diurnal air temperature variation turned out to be large. In contrast, the temperatures of river water and, especially, of groundwater were more constant. Groundwater temperatures ranged from 7.9°C to 9°C with an average temperature of 8.2°C. River water temperatures varied from 2.3°C to 12.8°C with an average temperature of 7.9°C, which was similar to the average groundwater temperature.

Figure 2c shows the evolution of water levels (m.a.s.l.) in the river (MPZ sampling location) and in groundwater (piezometers MP-4, MP2-6 and MP3-6). River and groundwater levels were relatively constant during the sampling period. Water levels slightly increased from January to March 2017 after rain events and progressively decreased due to scarce rain occurred in April and May. It is also important to point out that river water level was always lower than those of groundwater, indicating a continuous groundwater discharge to the river. This observation is also supported by temperature measured in the river because it followed the same pattern than groundwater temperature although it was also partly influenced by air temperature (Fig. 2b).

As pointed out before, groundwater was considered the only source of recharge to the Triffoy River (i.e., 100% groundwater) and the contribution of runoff was likely to be insignificant due to the scarce rain events occurred during the sampling period (Fig. 2a). The average groundwater discharge for the sampling period was 5,870±1,310 m³ d⁻¹ and it was higher during the colder months (January and March, being 7,450 m³ d⁻¹ and 7,040 m³ d⁻¹) compared to the most temperate ones (May 2017 being 3,840 m³ d⁻¹).

### 3.2 Hydrochemistry of the Triffoy River basin

#### 3.2.1 General hydrochemistry
Understanding the interactions between groundwater and surface water is a key issue to quantify the contribution of groundwater as an indirect source of GHGs via rivers, especially in gaining rivers where groundwater is the main source of river recharge. Figure 3 shows the average concentrations for major ions, metals, redox indicators and GHGs in the Triffoy River versus the average concentrations in the aquifer from October 2016 to May 2017. It can be observed that major ions presented similar concentrations in the river and in the aquifer, indicating that groundwater clearly controlled the chemical composition of the Triffoy River.

The hydrochemical conditions of groundwater and river water are described using the in-situ parameters measured in the field and major ions (Table 1 and Fig. 4). Groundwater pH values ranged from 7 to 7.8 (average is 7.4±0.2). River pH values were slightly higher than those from groundwater with an average value of 8.0±0.2. Average EC values were similar in groundwater and river water being 673±35 μS/cm and 665±53 μS/cm, respectively. Groundwater concentrations of DO and DOC displayed lower values than river water (Table 1, Fig. 3). Averages DO and DOC concentrations were 4.8±1 mg/L and 0.94±0.47 mg/L in groundwater and 9.2±1.1 mg/L and 1.4±0.70 mg/L in the river.

Major ion compositions showed that groundwater and river water were of Ca-(Mg)-HCO₃ type accounting for all sampling campaigns (see Fig. B of the supplementary material). The range and average concentrations and standard deviations for bicarbonate (HCO₃⁻), Ca²⁺, Mg²⁺ and NO₃⁻ for the groundwater observation points and the three river locations are shown in Table 1. Note that NH₄⁺ concentrations are not included because they were below detection limit. The concentrations of these tracers did not present large variation neither spatially nor temporally in groundwater and river water samples (Fig. 4 and Table C of the supplementary material). For instance, average NO₃⁻ concentrations ranged from 18.6 mg/L to 22.4 mg/L and average HCO₃⁻ concentrations ranged from 353.3 mg/L to 361.7 mg/L in groundwater (Table C of the supplementary material).
3.2.2 Occurrence of greenhouse gases

Average GHG concentrations in groundwater and river water are summarized in Table 1. Groundwater was largely oversaturated in N\textsubscript{2}O and pCO\textsubscript{2} whilst only slightly oversaturated in CH\textsubscript{4} compared with the atmospheric equilibration concentrations (0.55 µg/L for N\textsubscript{2}O, 400 ppm for CO\textsubscript{2} and 0.056 µg/L for CH\textsubscript{4}). N\textsubscript{2}O concentrations ranged from 26 µg/L to 87.6 µg/L (average concentration of 50.1±16.7 µg/L), CH\textsubscript{4} concentrations ranged from 0.01 µg/L to 4.8 µg/L (average concentration of 0.45±0.89 µg/L) and pCO\textsubscript{2} values varied from 8,285 to 21,897 ppm (average of 14,569±3,843 ppm). Average N\textsubscript{2}O concentrations in groundwater were higher in temperate months (October 2016 and May 2017 being 55.2 µg/L and 54.1 µg/L, respectively) than in winter months (minimum average concentration was 46.1 µg/L in January 2017) (Table C of the supplementary material). Average pCO\textsubscript{2} concentrations were constant from October 2016 to February 2017 (around 14,200 ppm) and the highest value was detected in May 2017 (15,402 ppm) (Table C of supplementary material).

Average GHG concentrations in river water were 10±6.3 µg/L for N\textsubscript{2}O, 6.9±16.6 µg/L for CH\textsubscript{4} and 3,168±1,253 ppm for pCO\textsubscript{2}. The concentrations of N\textsubscript{2}O and pCO\textsubscript{2} in groundwater were systematically higher than those found in river water (Fig. 3 and Fig. 4b and 4d). On the contrary, dissolved CH\textsubscript{4} concentrations were lower in groundwater than in the river (average concentrations were 0.45±0.89 µg/L vs. 6.9±16.6 µg/L, respectively). This observation shows that groundwater was not a source of CH\textsubscript{4}, as also concluded by Borges et al. (2018) based on large scale analysis in the Meuse basin in Wallonia.

3.2.3 Stable isotopes

Figure 5 shows δ\textsuperscript{15}N\textsubscript{NO\textsubscript{3}} – δ\textsuperscript{18}O\textsubscript{NO\textsubscript{3}} compositions for the groundwater (black dots) and river samples (grey dots) and boxes representing the isotopic compositions of possible NO\textsubscript{3}⁻ sources (Kendall, 1998, Mayer, 2005). The isotopic compositions for δ\textsuperscript{15}N\textsubscript{NO\textsubscript{3}} varied from +4.9‰ to +7.3‰ (average composition +6‰±0.57) for groundwater samples and from
+6.2‰ to +9.9‰ (average composition +7.5‰±0.85) for river samples. The isotopic compositions for δ\(^{18}\)ONO\(_3\) ranged from +1.1‰ to +6.8‰ (average composition +2.9‰±1.7) for groundwater samples and from +1.9‰ to +6.9‰ (average composition +3.3‰±1.5) for river samples. All groundwater and river samples agreed with the isotopic values of organic N from soil and/or the lightest values of δ\(^{15}\)NNO\(_3\) coming from manure or sewage water.

3.3 Processes that produce and/or consume greenhouse gases in groundwater

Nitrous oxide

The occurrence of N\(_2\)O depends on geochemical conditions prevailing in groundwater. Oxic conditions observed in groundwater might indicate that N\(_2\)O resulted from nitrification rather than denitrification since the latter is generally associated with low concentrations of DO. The positive correlation between NO\(_3^-\) and N\(_2\)O (r=0.62, Fig. C1 of the supplementary material) also suggests that nitrification was the main process for the accumulation of N\(_2\)O in groundwater. Such positive correlation was also observed in other aquifers located below agricultural catchments where nitrification was the main N\(_2\)O production mechanism (Gardner et al., 2016; Hisckok et al., 2003; Vilain et al., 2012). In addition, the positive correlation between Cl\(^-\) (conservative tracer) and NO\(_3^-\) (r=0.96, Fig. C2 of the supplementary material) might indicate that NO\(_3^-\) was not affected by denitrification because their concentrations remained constant during the sampling campaigns (Fig. 4a and 4c).

The values of NO\(_3^-\) stable isotopes also suggest N\(_2\)O was produced by nitrification because all groundwater samples fell in the box of soil N (Fig. 5). Values of δ\(^{15}\)NNO\(_3\) found in groundwater (δ\(^{15}\)NNO\(_3\)=+6‰) are much lower than those expected from denitrification processes which usually present δ\(^{15}\)NNO\(_3\)>+15‰ (Otero et al., 2009; McAleer et al., 2016). Experimental studies (e.g., Anderson and Hooper, 1983; Mayer et al., 2001) have pointed out that δ\(^{18}\)ONO\(_3\) generated by nitrification can be calculated as follows:

\[
δ^{18}O_{NO_3} = 2/3 \ δ^{18}O_{water} + 1/3 \ δ^{18}O_{atmos} \quad (5)
\]
Eq. (5) shows that two oxygens come from water and one from atmospheric oxygen during the conversion of NH₄⁺ to NO₃⁻. For the Triffoy River catchment, using an isotopic value for δ¹⁸Owater of −7.3‰ obtained from a previous study (Briers et al., 2016d) and an isotopic value for δ¹⁸Oatmos of +23.5‰ (Kroopnick and Craig, 1972), the evaluated δ¹⁸ONO₃ is equal to +3‰. This value is very close to the average value for δ¹⁸ONO₃ observed in the collected groundwater samples (+2.9±1.7‰). Hence, N₂O found in groundwater seems to be produced due to nitrification in the unsaturated zone.

Methane

The oxic conditions that prevailed underground in the Triffoy River basin were not favourable for the accumulation of CH₄ in groundwater. The average concentration in river water was higher than those in groundwater (6.9 µg/L vs. 0.45 µg/L, Fig. 3), suggesting that groundwater was an insignificant source of CH₄ in the river.

Carbon dioxide

CO₂ enrichment in groundwater might occur when rain water percolates through the soil, where CO₂ is produced by processes such as microbial decomposition of organic matter (heterotrophic respiration) and root respiration (autotrophic respiration) (Tan, 2010), and subsequent leaching of CO₂ to groundwater. These processes produce an enrichment of CO₂ and groundwater pCO₂ values are typically between 10 to 100 times higher than atmospheric pCO₂. When the oversaturated groundwater is discharged in the Triffoy River, CO₂ degassing into the atmosphere takes place. This situation leads to an increase of pH in the river water and the progressive precipitation of carbonate minerals. In fact, average saturation indexes (SIs, see text S1 of the supplementary material) of carbonate minerals were higher in river water than in groundwater being 0.79 vs. 0.24 for calcite and 0.43 and −0.55 for dolomite,
indicating that river water was slightly oversaturated with respect to calcite and dolomite (Table D of the supplementary material).

Other processes that might produce CO₂ in groundwater are redox processes such as aerobic respiration and denitrification. Nevertheless, these processes were not likely to occur in the aquifer because of the presence of DO and NO₃⁻ in groundwater (see previous explanation that supports the occurrence of nitrification).

3.4 Evaluation of greenhouse gas emissions from groundwater

In this section, the importance of groundwater as an indirect source of GHGs to the atmosphere was assessed at local scale (per area of the river from Jamagne to State river sampling locations, section 3.4.1). Afterwards, to place the groundwater GHG emissions in a broader context, the resulting average emissions in section 3.4.1 were upscaled by dividing them by the total agricultural area of the Triffoy River basin (section 3.4.2).

3.4.1 Local scale

The maximal contribution of GHG emissions from groundwater to the river was assessed using Eq. (1). Average GHG fluxes from groundwater resulted in 207 kg N₂O Ha⁻¹ y⁻¹, 1.6 kg CH₄ Ha⁻¹ y⁻¹ and 1.5 × 10⁵ kg CO₂ Ha⁻¹ y⁻¹. These fluxes should be similar to those from the river to the atmosphere unless that there are other processes that consumed or produced N₂O, CH₄ and CO₂ in the river-groundwater interface. Average fluxes evaluated from river surface to the atmosphere (Eq. (2)) were similar to those evaluated with Eq. (1) for N₂O and CO₂ (126.9 kg N₂O Ha⁻¹ y⁻¹ and 9.7 × 10⁴ kg CO₂ Ha⁻¹ y⁻¹, respectively) but much higher for CH₄ (105 kg CH₄ Ha⁻¹ y⁻¹).

Monthly flux estimates using Eq. (1) for N₂O (EN₂O-Gw) and CO₂ (ECO₂-Gw) were systematically higher than those computed with Eq. (2) (EN₂O-Riv and ECO₂-Riv) (except for N₂O in May) (Fig. 6). This observation indicates that groundwater contributed to the emissions of these two gases to the atmosphere but part of the N₂O and CO₂ concentrations might had been
consumed in the river-groundwater interface. If these GHGs were not consumed before reaching the river, their average concentrations should have been similar to those observed in groundwater. However, groundwater concentrations for N$_2$O and CO$_2$ were 5 times higher than those measured in the river (50.1 µg/L vs. 10 µg/L for N$_2$O and 14,569 ppm vs. 3,168 ppm for pCO$_2$). The biggest difference in N$_2$O and CO$_2$ emissions (using Eq. (1) and Eq. (2)) occurred in January 2017 when groundwater discharge into the river was maximum. It is important to mention that N$_2$O emissions from the river to the atmosphere (Eq. (2), E$_{N2O-Riv}$) were higher than those from groundwater (Eq. (1), E$_{N2O-Gw}$) in May 2017 (Fig. 6). This observation might be explained by the low groundwater discharge into the river compared to other months (3,840 m$^3$ d$^{-1}$) and the slightly higher concentration of N$_2$O found in river water in May 2017 (Table C of the supplementary material) but also it could indicate an inflow of N$_2$O produced in the river from upstream. The opposite situation was observed for CH$_4$, whose emissions from the river to the atmosphere (E$_{CH4-Riv}$) were always one to two orders of magnitude higher than the input of CH$_4$ from the groundwater (E$_{CH4-Gw}$) (Fig. 6). This implies that the emission of CH$_4$ from the river to the atmosphere was almost exclusively sustained by in-situ production most probably in river-bed sediments or riparian areas.

### 3.4.2 Catchment scale

To evaluate the GHGs emissions at catchment scale, the average E$_{GHG-Gw}$ (Eq. (1)) were divided by the agricultural area of the Triffoy basin (26.1 km$^2$) instead of the surface of the river ($5.1 \times 10^{-3}$ km$^2$). This resulted in average fluxes of 0.040 kg Ha$^{-1}$ y$^{-1}$ for N$_2$O, $3.0 \times 10^{-4}$ kg Ha$^{-1}$ y$^{-1}$ for CH$_4$ and 29.8 kg Ha$^{-1}$ y$^{-1}$ for CO$_2$. Note that these fluxes were evaluated considering a river stretch of 2 km but the total length of the Triffoy River is 12 km (Fig. 1).

Indirect groundwater N$_2$O emissions at catchment scale were also evaluated applying the IPCC method (Eq. (4)) that requires the evaluation of the emission factor for groundwater (EF$_{5g}$). The EF$_{5g}$ coefficient evaluated in this study is 3 times higher than the default value.
proposed by the IPCC (0.0069±0.0018 vs. 0.0025). Considering that N leaching to groundwater was estimated to be 5.4 kg N Ha⁻¹ y⁻¹ in the aquifers of the Condroz region (SPW, 2010), the resulting indirect N₂O emissions from groundwater were 0.037 kg N₂O-N Ha⁻¹ y⁻¹ (0.058 kg N₂O Ha⁻¹ y⁻¹). This value is similar to the one evaluated using groundwater discharge in the river (0.040 kg N₂O Ha⁻¹ y⁻¹) and other N₂O fluxes from groundwater evaluated in aquifers located below agricultural lands. For example, similar estimates of indirect N₂O fluxes from groundwater were obtained using the IPCC methodology in the Orgeval catchment in France and major UK aquifers being 0.035 kg N₂O-N Ha⁻¹ and 0.04 kg N₂O-N Ha⁻¹ y⁻¹, respectively (Vilain et al., 2012; Hisckok et al., 2003). The IPCC approach presents some limitations because N leaching to groundwater varies from one site to another. For instance, Jahangir et al. (2013) reported that N leached varied from 8% to 38% of the total N input in four different agricultural settings, resulting in indirect N₂O groundwater fluxes ranging from 0.07 kg N₂O-N Ha⁻¹ y⁻¹ to 0.24 kg N₂O-N Ha⁻¹ y⁻¹. Slightly lower fluxes (0.004 kg N₂O-N Ha⁻¹ y⁻¹) were evaluated in the Choptank Basin in the USA (Gardner et al., 2016). The authors pointed out that groundwater was a minor source of total biogenic N₂O emissions (15% on average) from strongly gaining agricultural streams but it was the primary source of N₂ (3.5 kg N₂ Ha⁻¹ y⁻¹). Similarly, von der Heide et al. (2009) evaluated that N₂O fluxes from the shallow groundwater of the Fuhrberger Feld aquifer (Germany) were 1 to 2 orders of magnitude lower than N₂O flux at soil surface (0.044 vs. 1 kg N₂O–N Ha⁻¹ y⁻¹) and thus groundwater was a negligible pathway of atmospheric emissions.

CO₂ and CH₄ indirect fluxes from groundwater in agricultural areas have been less studied than those of N₂O. For instance, Jahangir et al. (2012) evaluated the dissolved C delivery to surface water through groundwater in selected agricultural aquifers of Ireland. Groundwater CO₂ export was up to 314 kg C Ha⁻¹ y⁻¹ (1151 kg CO₂ Ha⁻¹ y⁻¹) whereas CH₄ export was low (from 0.013 kg CH₄ Ha⁻¹ y⁻¹ to 2.30 CH₄ Ha⁻¹ y⁻¹). The authors concluded that the dissolved C
loss to surface waters via groundwater was not significant compared to total carbon (TC) content of the topsoil (0.06–0.18% of TC). Similarly, Wang et al. (2015) evaluated that CO$_2$ lost via groundwater to the stream was approximately 73 kg CO$_2$ Ha$^{-1}$ y$^{-1}$ in the Hongfeng Lake catchment (China, 1,596 km$^2$), which was insignificant compared with soil CO$_2$ emission.

To sum up, groundwater is likely to be an important source of N$_2$O and CO$_2$ in gaining streams but when measures are upscaled at the catchment-scale, these fluxes are probably relatively modest. Thus, indirect GHG emissions from groundwater seem to be a minor pathway of GHG atmospheric emissions but their quantification would help to better evaluate the C and N budgets in agricultural catchments.

4. Conclusions

As GHG concentrations have significantly increased in the atmosphere, studying their dynamics from natural systems remain a major concern. This study investigated the occurrence of N$_2$O, CH$_4$ and CO$_2$ and quantified the contribution of groundwater as an indirect source of these GHGs via river water in the agricultural catchment of the Triffoy River (Belgium). Average groundwater concentrations for N$_2$O and pCO$_2$ were higher than those found in the river samples (50 vs. 10 µg/L and 14569 vs. 3168 ppm, respectively), suggesting that groundwater could be an indirect source of GHGs to the atmosphere. Nitrification was likely to be the main source of N$_2$O in groundwater. This observation is supported by the positive relationship between N$_2$O and NO$_3^-$, the presence of DO and NO$_3^-$ and the absence of NH$_4^+$ in groundwater. The oxic conditions found in groundwater were not prone for the accumulation of CH$_4$ in the aquifer and it might be generated in river-bed or riparian zone sediments.
The role of groundwater as an indirect source of GHGs in the river-groundwater interface was evaluated through the net groundwater discharge into the river (Eq. (1)) and compared to the inputs from the river to the atmosphere (Eq. (2)). Average fluxes obtained for N$_2$O and CO$_2$ using both approaches were similar (207 vs. 126.9 kg N$_2$O Ha$^{-1}$ y$^{-1}$ and $1.5 \times 10^5$ vs. $9.7 \times 10^4$ kg CO$_2$ Ha$^{-1}$ y$^{-1}$), showing that groundwater was a source of release of these GHGs into the atmosphere. The opposite situation was observed for CH$_4$, whose average emissions from groundwater were two orders of magnitude lower than those evaluated from the river to the atmosphere (1.6 vs. 105 kg CH$_4$ Ha$^{-1}$ y$^{-1}$). This observation indicates that groundwater was an insignificant source of CH$_4$ to the atmosphere. Overall, groundwater in the studied gaining stream was a source that contributed to N$_2$O and CO$_2$ atmospheric emissions but when these emissions were up-scaled (from the river surface to the catchment area) the resulting fluxes seemed to be insignificant compared to other sources (i.e., direct N$_2$O and CO$_2$ emissions from soils). Nevertheless, their quantification would better constrain N and C budgets in natural systems.

We suggest that future research efforts should be devoted to investigating the dynamics of GHGs in groundwater, soil and river water over long time periods (i.e., hydrological year) and a wide range of flow conditions (wet and dry periods) to better understand the relative importance of each compartment as a source of GHGs to the atmosphere at a stream scale. Particular efforts should be directed to improve the understanding of GHGs production and consumption in the groundwater-river transition zone (e.g., streambed hyporheic sediments). This point will allow to better constrain global N$_2$O, CH$_4$ and CO$_2$ budgets at the river-groundwater interface and thus the N and C budgets.

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Appendix A. Supplementary material. Supplementary data associated with this article can be found in the online version.
References


Minamikawa, K., Nishimura, S., Sawamoto, T., Nakajima, Y., Yagi, K., 2010. Annual emissions of dissolved CO2, CH4, and N2O in the subsurface drainage from three cropping systems. Global change biology, 16(2), 796-809.


SPW, DGARNE, 2010. État des lieux de la masse d’eau souterraine RWM021 « Calcaires et Grès du Condroz ».


Figure captions

Figure 1. Location and main aquifers of the Triffoy River catchment (Belgium). NL= The Netherlands, LU=Luxemburg, DE=Germany, FR= France.

Figure 2. (a) Daily rainfall (mm), (b) air, river water and groundwater temperature and (c) water level (m.a.s.l) of the river water in MPZ sampling location and of groundwater at observation points MP2-6, MP3-6 and MP-4. Daily rainfall (mm) was measured by the Walloon Public Service at Modave station.

Figure 3. Average concentrations for major ions, redox indicators, metals and greenhouse gases in the Triffoy River and in the aquifer.

Figure 4. Spatial and temporal distribution of some major ions, redox indicators and greenhouse gases in river water (SW) and groundwater (GW) for the samplings campaigns carried out in December 2016 (a, b) and March 2017 (c, d). Note that the name of the sampling points is on top of the x-axis.

Figure 5. δ¹⁵N versus δ¹⁸O values of nitrate for river water (grey dots) and groundwater (black dots). The isotopic composition for the nitrate sources are taken from Kendall (1998) and Mayer (2005).

Figure 6. Flux (E) of N₂O, CO₂ and CH₄ from the aquifer to the river (E₉W) and from the river to the atmosphere (Eᵣᵣ) from October 2016 to May 2017. Fluxes are expressed in kg Ha⁻¹ y⁻¹ (per surface of river). Note the logarithmic scale for CH₄ fluxes.

Table captions

Table 1. Range and mean groundwater (7 observation points including MP-4, MP3-6, MP3-3, MP2-6, MP2-3, S1 and S2) and river water (3 sampling locations named as Jamagne, MPZ and State) concentrations for some major ions (mg/L), greenhouse gases (µg/L, ppm) and in-situ parameters in the Triffoy River basin.
Figure 1.
Figure 2.
Figure 3

This graph shows the relationship between average groundwater concentrations and average river concentrations for various compounds. The x-axis represents average river concentrations, while the y-axis shows average groundwater concentrations. Different markers and symbols represent different categories of substances:

- **Major ions (mg/L)**
- **Redox indicators (mg/L)**
- **Metals (μg/L)**
- **GHGs (μg/L, ppm)**

Key compounds include:

- **N₂O**
- **Mn**
- **Fe**
- **DO**
- **DOC**
- **CH₄**
- **pCO₂**

The data suggests a strong correlation between the concentrations of these substances in the groundwater and the river, indicating potential sources or sinks of these compounds.
Figure 5

- GW
- RIV
- $\text{NO}_3^-$ $>$ 21 mg/L
- $\text{NO}_3^-$ $<$ 21 mg/L

$\delta^{18} \text{O - NO}_3$ (%)

$\delta^{15} \text{N - NO}_3$ (%)

- $\text{NO}_3^-$ fertiliser
- $\text{NH}_4^+$ fertiliser
- Soil Norg
- Manure and septic waste
Figure 6

![Graph 1: 
\( E_{\text{N}_2\text{O}-\text{GW}} \) or \( E_{\text{N}_2\text{O}-\text{RIV}} \)

![](Graph 1)

- GW
- RIV

![Graph 2: 
\( E_{\text{CO}_2-\text{GW}} \) or \( E_{\text{CO}_2-\text{RIV}} \)

![](Graph 2)

- GW
- RIV

![Graph 3: 
\( E_{\text{CH}_4-\text{GW}} \) or \( E_{\text{CH}_4-\text{RIV}} \)

![](Graph 3)

- GW
- RIV

Legend:
- GW
- RIV

X-axis:
- Oct-16
- Dec-16
- Jan-17
- Feb-17
- Mar-17
- May-17

Y-axis:
- \( E_{\text{N}_2\text{O}} \) (kg H\text{a}^{-1} y^{-1})
- \( E_{\text{CO}_2} \) (kg H\text{a}^{-1} y^{-1})
- \( E_{\text{CH}_4} \) (kg H\text{a}^{-1} y^{-1})
| Table 1. |
|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
|                    | HCO₃⁻ (mg/L)        | Ca²⁺ (mg/L)         | Mg²⁺ (mg/L)         | NO₃⁻ (mg/L)         | N₂O (µg/L)         | CH₄ (µg/L)          | pCO₂ (ppm)          | DOC (mg/L)          | DO (mg/L)          |
| MP3-6              | 338.1-343 (340±1.7) | 96.8-97.6 (97.2±0.26) | 28.1-29.5 (28.7±0.59) | 20.84-24.1 (22.3±1.2) | 71.8-87.6 (79.1±5.2) | 0.02-0.19 (0.09±0.06) | 12,004-13,437 (12,793±582) | 0.39-1.5 (0.90±0.46) | 3.9-7.2 (4.7±1.2) |
| MP3-3              | 350.2-356.3 (353.6±2.2) | 97.8-98.3 (98.1±0.26) | 29.5-31.4 (30.1±0.79) | 19.9-22.9 (21±1.1) | 55.3-71.5 (61.6±6.1) | 0.01-0.22 (0.11±0.09) | 13,137-15,066 (14,107±784) | 0.45-1.7 (0.91±0.52) | 4.5±0.19 (9.6±1.3) |
| MP2-6              | 371.1-381.9 (374.9±4.4) | 98.5-99.3 (98.7±0.28) | 29.6-31.4 (30.7±0.63) | 16.7-21.2 (19.1±1.7) | 37.7-46.7 (43.5±3.1) | 0.1-0.18 (0.15±0.03) | 15,594-18,539 (17,365±1,164) | 0.57-1.6 (1.1±0.43) | 3-7.7 (5.1±1.5) |
| MP2-3              | 385.8-393.2 (391±3) | 99.7-100.6 (100.2±0.33) | 30.6-31.6 (31.2±0.41) | 14.2-16.4 (15.6±0.89) | 26-34.1 (30.9±3.1) | 0.12-2.61 (0.98±1.1) | 19,020-21,897 (20,000±1,138) | 0.56-1.9 (1.1±0.5) | 3.3-5.5 (4.3±0.79) |
| S1                 | 336.4-331.6 (334.5±1.8) | 102.8-103.6 (103.2±0.28) | 24.3-25.2 (24.8±0.27) | 21.4-24.7 (22.9±1.3) | 34.5-44.4 (39.5±3.9) | 0.64-4.8 (1.7±1.6) | 9,353-8,285 (8,833±400) | 0.37-1.9 (0.87±0.57) | 4.7-6.2 (5.3±0.63) |
| S2                 | 334.2-337.9 (336±1.4) | 102.6-103 (102.7±0.17) | 25.1-26.1 (25.5±0.56) | 22-25.2 (23.4±1.4) | 58.1-63.9 (59.5±2.2) | 0.03-0.14 (0.10±0.04) | 11,023-11,965 (11,399±343) | 0.50-1.6 (0.80±0.45) | 3.2-5.1 (4.4±0.63) |
| JAMAGNE            | 292.9-382.2 (326.5±32.3) | 85.8-119 (100.2±11.3) | 23.2-29.2 (24.8±2.3) | 15.5-29.6 (22.3±4.8) | 0.58-19.5 (7.6±1.4) | 3-7.5 (18.9±26) | 859-2,081 (1,61±488) | 1.3-2.8 (2.1±0.7) | 8.1-11.3 (9.3±1.4) |
| MPZ                | 330.8-349.1 (337±7.5) | 97.3-105.1 (100.9±2.8) | 24.6-27.2 (25.7±1) | 18.8-25.2 (22.2±2.3) | 12.8-18 (15.1±2.1) | 0.28-0.65 (0.42±0.13) | 3,812-4,975 (4,390±459) | 0.7-2.2 (1.3±0.6) | 8-10 (9.2±0.78) |
| STATE              | 332-338.2 (334±2.3) | 100.1-102.5 (101.3±0.86) | 24.8-26.5 (25.4±0.57) | 19.8-22.9 (21.5±1.3) | 9.7-12.4 (10.9±1) | 0.86-2.1 (1.4±0.48) | 3,281-3,973 (3,502±253) | 0.6-1.5 (9.4±0.34) | 7.5-11.1 (9.1±1.3) |

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