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Budget of N₂O emissions at the watershed scale: role of land cover and topography (the Orgeval basin, France)

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Abstract. Agricultural basins are the major source of N₂O emissions, with arable land accounting for half of the biogenic emissions worldwide. Moreover, N₂O emission strongly depends on the position of agricultural land in relation with topographical gradients, as footslope soils are often more prone to denitrification. The estimation of land surface area occupied by agricultural soils depends on the available spatial input information and resolution. Surface areas of grassland, forest and arable lands were estimated for the Orgeval sub-basin using two cover representations: the pan European CORINE Land Cover 2006 database (CLC 2006) and a combination of two databases produced by the IAU IDF (Institut d'Aménagement et d'Urbanisme de la Région d'Île-de-France), the MOS (Mode d'Occupation des Sols) combined with the ECOMOS 2000 (a land-use classification). In this study, we have analyzed how different land-cover representations influence and introduce errors into the results of regional N₂O emissions inventories. A further introduction of the topography concept was used to better identify the critical zones for N₂O emissions, a crucial issue to better adapt the strategies of N₂O emissions mitigation. Overall, we observed that a refinement of the land-cover database led to a 5 % decrease in the estimation of N₂O emissions, while the integration of the topography decreased the estimation of N₂O emissions up to 25 %.

composition), substrate availability (nitrogen and carbon) as well as land management practices (Vilain et al., 2010; Skiba et al., 1998; Smith et al., 1998).

While the processes of N₂O production occur on a scale of less than one centimeter (i.e. the micro-scale or process scale), N₂O emissions are usually measured at scales of several centimeters to several hundred meters (Schimel and Potter, 1995). For example, a measurement at a single point (the point scale) could either be representative of emissions from a closed chamber with an area of typically 0.1–1 m² or a micro-meteorological measurement of typically 10⁵ m² (10 ha) area, with the aim of obtaining results at the point scale that would reflect the micro-scale process and to extrapolate these measurements at the regional (possibly global) scale (Bouwman, 1996; Bouwman et al., 2002a, 2002b).

However, the point scale can vary substantially (Folorunso and Rolston, 1984), because of the heterogeneity of denitrification activity or the presence of “hot spots” in soil (Ambus and Christensen, 1994; van den Heuvel et al., 2009). As a result, the N₂O fluxes emitted from soils at the observation scale show a high degree of spatial and temporal variability (Parton et al., 1988; Folorunso and Rolston, 1984) with coefficients of variation on the order of 500 % (Folorunso and Rolston, 1985). Therefore, the predictive relationships between N₂O fluxes and their associated control variables are very difficult to define (Corre et al., 1996).

A large number of simulation models have been developed to predict N₂O emissions, each one having its own philosophy and performance: STICS-NOE (Brisson et al., 2003; Hénault et al., 2005), DNDC (Li, 1996; Giltrap et al., 2010), CERES-EGC (Jones and Kiniry, 1986; Gabrielle et al., 2006), NGAS (Parton et al., 1996, 2001) or DAYCENT (Parton et al., 1998; Del Grosso et al., 2001), and Image

1 Introduction

Nitrous oxide (N₂O) is mainly produced by the microbial-mediated processes of nitrification and denitrification in soils. Its formation is influenced by several factors: climate (rainfall, temperature), soils (physical and chemical

(Bouwman et al., 2006). The N₂O simulation models can be classified into three main categories: laboratory, field and regional/global levels.

Extrapolated data of N₂O emissions at the local (1–100 km) or regional (100–100 000 km) scale from point-scale measurements can be achieved using an intermediate scale, such as the plot (from 100–1000 m). A first source of error can be introduced by the scale and the accuracy of different land cover maps (Ellis, 2004; Bach et al., 2006; Schmit et al., 2006; Verburg et al., 2006). The high relation between land use and N₂O emissions highlights the importance of the land cover data when carrying out N₂O emissions inventories (Plant, 1999; Matthews et al., 2000).

Evidencing the relationship with landscape makes it possible to partition the land into units defined by the relief (topographic attributes) and land use. A significant selection of sampling units (topography) may thus allow the extrapolation of flux measurements collected at points within these units (Corre et al., 1996).

This study aims to establish a nitrous oxide budget at a sub-basin scale of 100 km² (taking into account both direct and indirect emissions from groundwater and rivers). One of the objectives was to analyze how different land cover representations potentially introduce errors into the estimations of regional N₂O emissions inventories. A second major challenge was to assess the effect of topography on the estimation of the N₂O emissions at the basin scale. Accordingly, we then discussed agri-environmental measures that can decrease N₂O emissions as well as increase water quality.

2 Study site

The Orgeval basin belongs to the Seine basin (France) and is located approximately 70 km east of Paris. The whole study basin covers around 106 km². Annual rainfall is about 700 mm and the climate is semi-oceanic. The mean annual temperature is between 10 and 11 °C; the coldest month being January (mean temperature, 0.6 °C) and the warmest August (mean air temperature, 18 °C). The Orgeval watershed is particular in that it is highly homogenous in terms of pedology, climate and topography (mean altitude, 148 m, with few slopes except in the valleys).

Most of the Orgeval catchment surface is covered with a quaternary loess deposit (up to 10 m thick). The top layer comprises loess silt and the sublayer is enriched in clay, in winter producing a shallow water table and waterlogged soils due to its low permeability. Underneath the loess layer, two tertiary aquifer formations separated by discontinuous grey clay and a loamy gypsum layer interact with the streams (Mégnyen, 1977). The shallowest formation is the Brie Limestone Oligocene formation, with a relatively short water residence time. The deepest formation is the Champigny Limestone Eocene, with a longer water residence time. The river incises all layers in its lower course and when the valley

cuts through the impermeable green clay layer; springs located at the bottom of the Brie Limestone formation emerge and join the river. Most of the basin's surface area is artificially drained (about 90 % of the usable agricultural area) and dominated by agricultural land (82 %, i.e. 87 km²); the remaining surface is covered by woods (17 % of the surface, i.e. 19 km²) and urban zones or roads (1 % of the surface) (Fig. 1). Agriculture is dominated by grain crop rotation (with wheat, maize and barley) and field beans as the main rotation.

3 Material and methods

3.1 Laboratory determination of nitrification, denitrification and nitrous oxide production potentials in batch slurries

Emissions sources of nitrous oxide were assessed in laboratory experiments. Soils of the transect were placed in ideal optimal conditions for nitrification and denitrification to determine the maximum nitrification and denitrification rates as well as the nitrous oxide production by the two mechanisms and the ratio of (N₂O produced)/(nitrate reduced or produced). Briefly, five experiments were carried out to determine the mean nitrification and denitrification potentials in 2009 and 2010 at various seasons and cropping conditions. For each experiment, soil samples were collected in two different locations along the slope (i.e. slope and footslope) and incubated for 4 h to 6 h in triplicates, at laboratory temperature (20 °C), in the dark, in oxic or anoxic conditions, and N substrate addition (NO₃[−] saturation and anoxia for denitrification; NH₄⁺ saturation and oxic conditions for nitrification) (see Garnier et al., 2010 for the methodology, results in Vilain et al., 2012; Vilain et al., unpublished data).

3.2 Soil N₂O flux in situ measurement

The nitrous oxide flux measurements were conducted weekly to bimonthly using the closed-chamber technique (Hutchinson and Livingston, 1993). This method, fully described in Vilain et al. (2010), consisted in measuring the gas fluxes from series of five aluminum non-vented and hermetically closed chambers (open bases of 50 cm × 50 cm × 30 cm). Four gas samples were taken from each chamber headspace with a 30 mL Terumo syringe and transferred to a 12.5 mL pre-evacuated glass vial (Labco Exetainer) for transport to the laboratory. N₂O concentrations in gas samples were analyzed in the laboratory using a gas chromatograph (Varian 3800) coupled with an electron capture detector (ECD). The gases were separated on a pre-column and a column packed with a Hayesep Q 80/100 mesh. Concentrations were calculated by comparing peak areas integrated with those obtained with standard N₂O concentrations (0.205, 0.540 and 3.30 ppm). N₂O fluxes were determined by calculating the

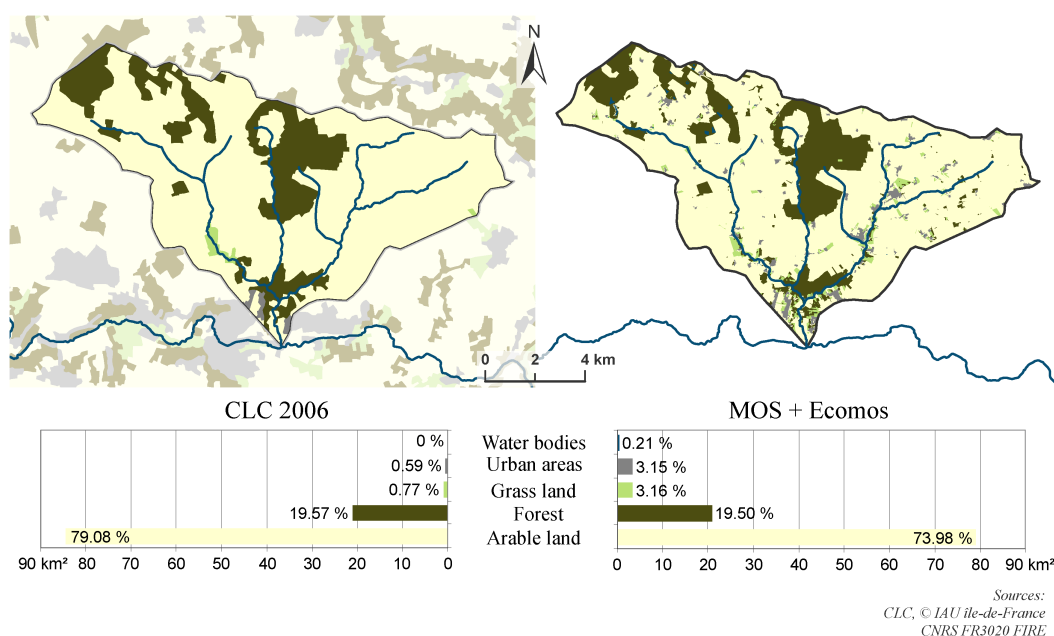


Fig. 1. Land use in the Orgeval basin in terms of forest, grassland and cropland. Urban areas are shaded grey. The drainage network is also indicated.

linear regression slope of the N₂O concentration as a function of the sampling time (Livingston and Hutchinson, 1995) and adjusted for area and chamber volume. A sample set was accepted only when it yielded a statistically significant linear regression R^2 value according to the number of values taken into account.

Measurements (21 dates from May 2008 to August 2009) were taken on two agricultural plots chosen along a north-westward falling slope reaching the Avenelles River with an average inclination of 6% in five topographical landscape positions from the shoulder to the footslope position. During this time period, plots were successively cropped to wheat/barley, an oat intercrop and corn. The sampled field can be assumed to be representative of the whole Orgeval watershed in terms of agricultural practices and especially fertilizer application.

3.3 Digital maps

3.3.1 Land use

The estimation of land-cover-based nitrous oxide emissions from the Orgeval basin is based on land use maps of the basin. Two databases with different resolutions were compared. The first one is the pan-European CORINE Land Cover 2006 database (CLC 2006) produced by the European Environmental Agency (EEA, 2007), which classifies lands into 44 classes. The minimum size of each polygon is 25 hectares. The database homogeneously covers the study area and using high-level aggregation classes (third level),

the Orgeval basin is distributed into four CLC 2006 classes: arable land (class codes 211 and 242) with 79.08%, forests (classes 311 and 324) with 19.57%, grassland (class 231) with 0.76% and urban areas (class 112) with 0.59%. Giving the relatively small scale of the study area (104 km²), the CLC 2006 database lacks precision and underestimates the area covered by grass and urban lands due to their fragmented nature (often less than 25 ha) (Fig. 1, left panel).

To correct this imprecision, a second database was used: it is a combination of two databases, both produced by the Institut d'Aménagement et d'Urbanisme de la Région d'Île-de-France (IAU IDF, Urban Planning and Development Agency for the Paris Ile de France Region). The MOS (Mode d'Occupation des Sols, Land use) is a land-use classification in 81 classes covering the Île-de-France region with a geometric precision of 1/5000 (IAU, 2005a). The 25-m resolution raster, available free of charge on their website (<http://www.iau-idf.fr/cartes/cartes-et-donnees-a-telecharger/donnees-a-telecharger.html>), was used. It corresponds to the year 2003 and the classes are aggregated into 11 items. The MOS is mainly designed for urban planning; therefore seven out of the 11 classes detail urban land types and grasslands are aggregated with arable lands. This database was thus combined with the ECOMOS 2000, a land use classification also produced by the IAU IDF and available on their website (IAU, 2005b). It details the “natural” classes from the MOS 1999 (forest and agricultural land) into 146 classes (distributed in six levels), excluding arable lands. The ECOMOS maps 2000 m² polygons. The third level was used to extract forests and grasslands that were

merged with the vectorized MOS data, thus dividing the “natural” classes into arable land, grassland and forest. For the Orgeval basin, this new combined land-use database (MOS + ECOMOS) gives: 73.98 % arable lands, 19.50 % forests, 3.16 % grasslands, 3.15 % urban areas and 0.21 % water bodies (Fig. 1, right panel).

The use of MOS + ECOMOS instead of CLC 2006 helps to accurately take grassland into account, reducing the part of cropland by almost 6 %.

3.3.2 Topographic index

To extend the analysis even further, we developed an index to differentiate topographical landscape positions on cropland, as this was shown to largely influence the N₂O emissions (Pennock et al., 1992; van Kessel et al., 1993; Izaurralde et al., 2004; Vilain et al., 2010). The topographical index was first suggested as an indicator for surface runoff contributing areas by Kirkby (1975) and was the basis for the rainfall-runoff model called TOPMODEL (Beven and Kirkby, 1979). The most commonly used form of the index is defined as $\ln(\alpha/\tan \beta)$, where α is the upslope contributing area to a given point of the catchment and β is a local surface slope angle (see Beven, 2001). This index represents the propensity of any point to become saturated. High topographic index values are good general indicators of wetlands (Curie et al., 2007; Mérot et al., 2003). In this study, the topographic index was adapted into a Concentration Flux Position index (CFP index). Indeed high values of topographic index are a good indicator of wetness, but slope and shoulder positions are not well discriminated by a low value of this topographic index. We then built this CFP index by mixing the topographic index map and the slope map, allowing a clearer distinction between the footslope, slope and shoulder positions. The topographic index map was calculated from a 25-m resolution digital elevation model produced by the Institut Géographique National (IGN) and is divided into three classes following the landscape segmentation approach proposed by Pennock et al. (1987):

1. The footslope class corresponds to areas where the topographic index is greater than the threshold value of 13 (see Curie et al., 2007). These areas with high topographic index values represent areas that are likely to be saturated. This class corresponds to the thalwegs and to areas located immediately at the foot of prominent reliefs such as buttes.
2. The slope class was determined using the slope map without any topographic index threshold. This class corresponds to the areas where the slope is greater than 2 %.
3. The shoulder class corresponds to the areas where the slope is less than 2 % and the altitude higher than 100 m without any topographic index threshold.

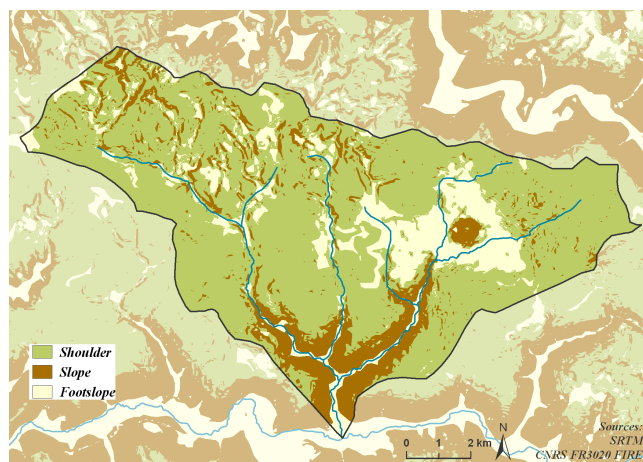


Fig. 2. Topographical map of the Orgeval basin.

3.3.3 Upscaling methods

Applying the three landscape position classes to the cropland class of the land-use databases (CLC 2006 and MOS + ECOMOS) allowed us to upscale N₂O emissions to the Orgeval basin scale with two new approaches: topography × CLC 2006 and topography × (MOS + ECOMOS).

3.4 Water sampling

3.4.1 River

Dissolved N₂O concentrations in river water were monitored monthly in the Orgeval basin from January 2008 to December 2009. First- to third-order streams (Strahler stream order are used to define stream size based on a hierarchy of tributaries, first order being the smallest permanent stream) were sampled (see Fig. 3) and considered representative of all of the watershed's streams. Water samples from the river were directly taken in the riverbed in a 2 L bottle and transported to the laboratory for further analysis after storage at 4 °C. Water samples for N₂O were directly collected in 100 mL glass flasks, without air bubbles, fixed with HgCl₂ 6 % in order to stop any biological activity, and sealed with a rubber septum excluding any headspace gas.

3.4.2 Groundwater

Three piezometers were installed along a transect over an elevation gradient (mean slope, 2.2 %) from agricultural fields toward the stream including three slope positions (see Vilain et al., 2011): (i) plateau, (ii) midslope and (iii) river bank. The two piezometers in the plateau and midslope were inserted at a 15 m depth and reached the phreatic groundwater of the Brie. The piezometer situated in the River bank was inserted at a 3 m depth and reached the green clay layer. All were slotted on the bottom 1 m and wrapped with a 250 µm

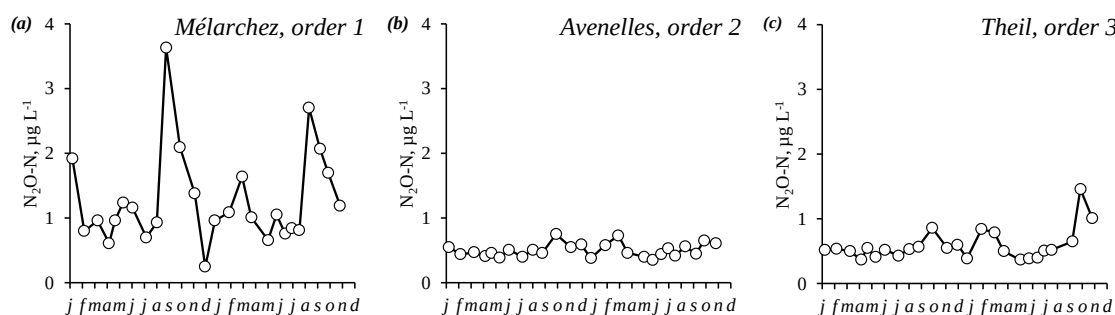


Fig. 3. Nitrous oxide concentrations between January 2007 and December 2008 in rivers at: **(a)** Mélarchez, first order; **(b)** Avenelles, second order and **(c)** Theil, third order.

seamless polyester filter sock to prevent coarse sand particles from entering the well. Groundwater was sampled using an immersed pump from April 2008 to April 2010, with the piezometer emptied by flushing out water prior to collecting the sample in order to remove the standing water. Water samples were treated the same way as river samples.

3.5 Chemical measurements

3.5.1 Dissolved inorganic nitrogen

Ammonium was measured on filtered water (GF/F 0.4 µm porosity) with an autoanalyzer (Quattro, Bran and Luebbe) using the indophenol blue method (Slawyk and MacIsaac, 1972). Nitrate was measured on filtered water, after cadmium reduction to NO₂⁻, and NO₂⁻ was also automatically measured with the sulphanilamide method according to (Jones, 1984) prior to cadmium reduction of NO₃⁻.

3.5.2 Dissolved nitrous oxide

Nitrous oxide in water samples was determined with a gas chromatograph (Perichrom PR 2100) equipped with an electron capture detector (ECD). An aliquot (20 mL) of the water sample was degassed with an argon–methane (90/10) mixture, trapped and concentrated in a molecular sieve. After desorption, N₂O concentrations were determined in triplicate.

3.6 Calculation of indirect emissions by rivers and aquifers

3.6.1 River

The N₂O flux across the water–atmosphere interface (F) can be calculated for each stream-order river of the Seine drainage network according to the relation:

$$F = K_{N_2O} N_2O - N_2O_{eq} \quad (1)$$

with:

F , (µgN m⁻² h⁻¹): flux of N₂O from the water column to the atmosphere

$[N_2O]$, (µgN L⁻¹): is the mean N₂O concentration in river water

$[N_2O]_{eq}$, (µgN L⁻¹): is the concentration at saturation for the atmospheric N₂O concentration

K_{N_2O} , (m h⁻¹): is the gas transfer velocity

The saturation concentration of N₂O in water at the present ambient atmospheric concentration (310 ppb) was determined using temperature-dependent values of N₂O solubility in water (Weiss and Price, 1980). This solubility can be expressed by the following polynomial relationship:

$$N_2O_{eq}, \mu\text{gN L}^{-1} = 0.0002T^2 - 0.0167T + 0.5038 \quad (2)$$

where T is the temperature in °C.

According to the work by Wanninkhof (1992) and Borges et al. (2004), the gas transfer velocity K_{N_2O} (m h⁻¹) in rivers, under conditions where the wind speed can be ignored, can be expressed as:

$$K_{N_2O} = 1.719 [(600/Sc_{N_2O}) \times (v/d)]^{0.5} \quad (3)$$

with:

v (m s⁻¹): is the water flow rate

d (m): is the depth of the water column

The values were validated by field experiment in the studied area (see Fig. 6, Garnier et al., 2009).

Sc_{N_2O} : is the Schmidt number, defined as the ratio between kinematic viscosity and mass diffusivity. It expresses the effect of temperature and the specificity of N₂O with respect to other gases on gas transfer properties. The Schmidt number for N₂O can be expressed as (Jähne et al., 1984):

$$Sc_{N_2O} = 2056 - 137T + 4.317T^2 - 0.05435T^3 \quad (4)$$

The corresponding surface areas and N₂O fluxes from rivers of each stream order in the Orgeval river drainage network, under typical high-flow and low-flow conditions, are gathered in Table 1.

Table 1. Nitrous oxide fluxes at the water–air interface for the summer and the winter period for different stream orders of the Orgeval basin.

Order	Surface water area (km ²)	Summer flux (mgN m ⁻² d ⁻¹)	Winter flux (mgN m ⁻² d ⁻¹)
First	0.1709	8.91 ± 7.65	4.67 ± 2.76
Second	0.0654	1.17 ± 0.47	0.84 ± 0.50
Third	0.0171	1.03 ± 0.45	1.05 ± 0.94

3.6.2 Groundwater

Indirect emissions from groundwater can be estimated using hydrogeological data. We assumed that all the N₂O in the groundwater discharge is released into the atmosphere from agricultural drains or directly by diffusion from the water table to the unsaturated zone (Garnier et al., 2009), and we used the estimated daily groundwater N₂O concentrations based on two-weeks interval measurements (considering a constant concentration rate beginning with the date of each sampling until the next sampling) and the daily water flow, for the Avenelles sub-basin (4570 ha). Then the N₂O flux emerging at springs can be estimated using the relation described by Verhoff et al. (1980):

$$\text{Flx} = \frac{\sum C_i Q_i}{n \times a} \times 365 \quad (5)$$

where Flx = N₂O flux, in kgN ha yr⁻¹,

C_i = discrete instantaneous concentration (kg N₂O-N L⁻¹),

Q_i = corresponding instantaneous discharge (L s⁻¹),

n = study duration (days)

a = sub-basin area (ha)

4 Sources, emissions and transfer of nitrous oxide at the continuum scale

4.1 Nitrous oxide production by nitrification and denitrification in soils

Although the potential rates of nitrate reduction and production by denitrification and nitrification, respectively, are on the same order of magnitude, a very significant difference occurs when regarding both the nitrous oxide production and the ratio of nitrous oxide produced by the two mechanisms (see Fig. 4). In order to determine the main mechanism responsible for the nitrous oxide concentrations in the groundwater, it is interesting to note that the ratio of N₂O produced by nitrification of 0.28 % is close to the mean ratio found in the plateau piezometer (0.26 %; see Vilain et al., 2011). On the other hand, regarding the seasonal peaks observed

either after fertilization or heavy autumn rainfalls, they can be much higher and closer to the 45 % ratio found by denitrification in laboratory. From these measurements and laboratory experiments we can assume that over a year, nitrification would be the process which occurs most often in soils across the landscape. On the contrary, the denitrification process would occur in fewer occasions and rather in some wet hotspots (such as the footslope positions) during specific conditions such as fertilizer application associated with a higher soil moisture and hypoxia (e.g. high rainfall), conditions necessary for the denitrification process to take place (Bateman and Baggs, 2005; Davidson and Schimel, 1995; Linn and Doran, 1984). However, quantitatively the denitrification contribution can produce a great part of N₂O as the amounts of N₂O produced by denitrification are much greater than by nitrification (see the N₂O/NO₃⁻ ratios).

4.2 Measured N₂O fluxes in different land-use types

Measurements of N₂O emissions from a variety of land uses in agricultural, forest and grassland systems were undertaken in 2008 and 2009. Annual emission rates were then calculated as a function of land use (simple emission factors; see Table 2) and sub-classified as a function of topography for the agricultural lands, following the landscape segmentation approach proposed by Pennock et al. (1987). The entire landscape was then divided into three segments (shoulder, slope and footslope) and the experimentally determined emission rates were assigned to each of these segments (see Table 2). This procedure highlights the importance of the difference in nitrous oxide emissions between the different topographic positions, with the highest emissions in low topographical positions (emission factor, 4.02 ± 2.20 kg N₂O-N ha⁻¹ yr⁻¹) with a decrease going up the slope (1.48 ± 0.90 kg N₂O-N ha⁻¹ yr⁻¹ in the slope position and 1.06 ± 0.50 kg N₂O-N ha⁻¹ yr⁻¹ in the shoulder position). As shown in Vilain et al. (2010), two main factors drive these highest emissions by footslope soils: (i) a much greater soil moisture which enhances denitrification and then higher N₂O fluxes, and (ii) a higher mineral N availability (NO₃⁻) resulting from runoff. For the other land uses (i.e. forest and grassland), we did not consider the influence of topography and applied the same emission rate regardless of topographic position, i.e. 0.55 ± 0.04 and 0.69 ± 0.06 kg N₂O-N ha⁻¹ yr⁻¹ for forest and grassland, respectively. When not considering the influence of topography for agricultural land, the simple mean emission rate used was 2.01 ± 0.54 kg N₂O-N ha⁻¹ yr⁻¹ (from Vilain et al., 2010).

4.3 Indirect emissions

4.3.1 By groundwater: EF5g

According to the previously described calculation (see the Materials and Methods section) and taking into account the

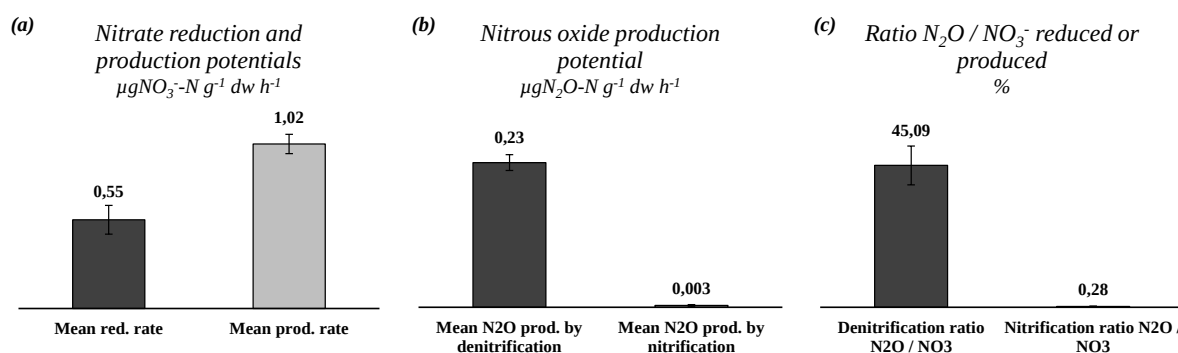


Fig. 4. Results of batch slurries: **(a)** potential rates of nitrate reduction by denitrification and production by nitrification; **(b)** potential N₂O production and **(c)** ratio of N₂O production to nitrate reduced (denitrification) or produced (nitrification).

Table 2. Nitrous oxide emission for the types of land use associated with their respective surface area in the basin and calculations from coefficients including topographic segmentation.

	Emission coefficient $\text{kgN}_2\text{O-N km}^{-2} \text{ yr}^{-1}$	Land area km^2	Calculation from emission coefficient $\text{kgN}_2\text{O-N yr}^{-1}$
Mean Cropland	200.75 ± 54	78.94	$15,847.36 \pm 4262.76$
Shoulder	105.85 ± 50	58.76	6219.76 ± 2938
Slope	147.83 ± 90	8.00	1182.63 ± 720
Footslope	401.50 ± 22	12.18	4890.57 ± 267.96
Forest	54.75 ± 40	20.81	1139.35 ± 832.4
Grassland	69.35 ± 60	3.37	233.64 ± 202.2

N₂O concentrations from April 2008 to April 2010 in the plateau piezometer, the indirect N₂O flux from groundwater was estimated at $161.5 \text{ kg N}_2\text{O-N yr}^{-1}$ for the entire Orgeval basin (Vilain et al., 2011). This calculation implies that there is no denitrification in the groundwater, assumption based on a previous work in the area which showed the limestone aquifers of the Seine basin have a very limited denitrification capacity (Sebilo 2003; Sebilo et al., 2003).

4.3.2 By Rivers: EF5r

The methodology proposed by Garnier et al. (2009) based on the determination of gas transfer velocities for all stream orders was followed. Then the observed supersaturation of dissolved N₂O concentrations in water of all stream orders were multiplied by the corresponding gas transfer rate and by the corresponding water surface area (Table 1), the result representing the indirect N₂O from drainage network emissions at the Orgeval basin scale (Fig. 2). Dissolved N₂O concentrations were higher in the first-order river (Mélarchez), ranging from 0.25 to $3.63 \mu\text{gN}_2\text{O-N L}^{-1}$ (mean, $1.27 \pm 0.36 \mu\text{gN}_2\text{O-N L}^{-1}$) than in the second-order rivers (Avenelles) and third-order rivers (Theil), with concentrations ranging from 0.35 to $0.75 \mu\text{gN}_2\text{O-N L}^{-1}$ (mean, $0.50 \pm 0.05 \mu\text{gN}_2\text{O-N L}^{-1}$) and

from 0.37 to $1.46 \mu\text{gN}_2\text{O-N L}^{-1}$ (mean, $0.59 \pm 0.12 \mu\text{gN}_2\text{O-N L}^{-1}$), respectively (Fig. 2). Temperature varied from 5 to 19°C and the mean was 10°C in winter and 15°C in summer.

The calculated summer emissions for the whole Orgeval basin were four times higher compared to winter emissions ($1.67 \pm 0.66 \text{ kgN}_2\text{O-N day}^{-1}$ vs. $0.42 \pm 0.09 \text{ kgN}_2\text{O-N day}^{-1}$, see Fig. 5). This trend confirms the findings of Garnier et al. (2009) at the larger scale of the entire Seine basin ($75\,000 \text{ km}^2$) for which summer emissions were twice as high as winter emissions. As also mentioned in Garnier et al. (2009), N₂O fluxes contribution of first orders was much higher (91 % in summer and 71 % in winter) than the second and third orders together.

Taking into account these calculated emission factors, the annual emission from the Orgeval basin drainage network can be estimated at $382 \pm 137 \text{ kgN}_2\text{O-N yr}^{-1}$.

5 Orgeval basin scale upscaling of N₂O emissions

Nitrous oxide emissions were calculated using the four different upscaling methods based on land-cover databases and topography (CLC 2006, MOS+ECOMOS, Topo $\times$ CLC

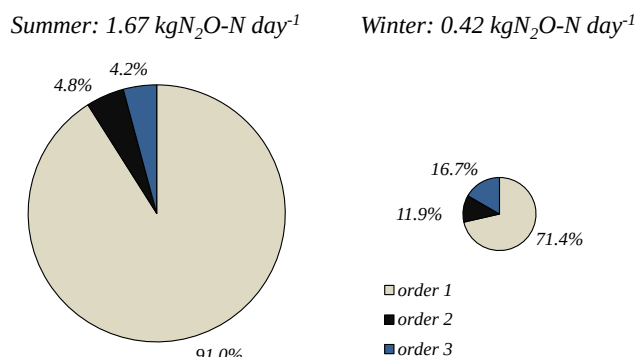


Fig. 5. Distribution of the daily N₂O emissions of the Orgeval drainage network, as a function of stream order for a winter and a summer period.

2006, Topo × (MOS+ECOMOS)). To each land use and topography class was applied the N₂O emission coefficients detailed in Table 2. Maps showing the predicted spatial distribution of nitrous oxide emissions rates in the Orgeval basin (expressed per surface area) under the four methods are presented in Fig. 6. Total annual N₂O emissions for the whole Orgeval basin are given in Table 3 by land-use class and for each upscaling method. Using the highest resolution database (MOS+ECOMOS) reduces the N₂O emissions by more than 5 % compared to CLC 2006-based methods. When considering topography-based methods, the estimations were more than 20 % lower. By combining the added values of both approaches, e.g., a more precise land-cover database and topography classes, N₂O emissions estimations were lowered by almost 25 % (from 18.1 to 13.6 tons of N₂O-N a year for the whole Orgeval basin).

Table 4 presents the contribution of each landscape position class to the total budget. Both methods show that 50 % of the N₂O emissions in the Orgeval basin come from soils in the shoulder position, around 38 % from the footslope position and 12 % from the slope.

6 Discussion

6.1 Direct vs. indirect sources of N₂O

Nitrous oxide is produced in soil (and also to a lesser extent in aquifers and river sediments) mainly by the two mechanisms of nitrification and denitrification. Once produced in soil, N₂O can be either directly emitted to the atmosphere (direct emissions, Vilain et al., 2010) or stored in the soil pores and subsequently leached into the aquifer and then transported to the stream, leading to indirect emissions (Vilain et al., 2011; Garnier et al., 2009). Moreover, besides losses to the atmosphere, further reduction of N₂O might be taken into account as soil microbes can consume N₂O molecules before reaching up the atmosphere

(Chapuis-Lardy et al., 2006). Therefore, this expressed indirect flux should be considered as an upper bound flux (see Vilain et al., 2011).

The novelty of this study is that it combines direct measurements of both direct and indirect N₂O emissions (N₂O indirect emissions being concentration-based estimates) on the same agricultural sub-basin. Regarding the results of the estimations reported herein, it is clear that the total annual budget of N₂O emissions is driven by the direct emissions by soils, which account for 96 % of the total emissions (see Fig. 7). Indirect emissions by rivers and groundwater account for 3 and 1 %, respectively of the total emissions (Fig. 7).

6.2 Catchment nitrous oxide budget

At the basin scale, N₂O emissions were the highest in the footslope position on fertilized fields. The 11.4 % of the basin area occupied by this combination of land use and topographic class contributes 35.8 % of the annual N₂O emissions. The lowest emissions were found in forest zones, accounting for 19.5 % of the Orgeval basin and contributing 8.3 % of the annual emissions. On the whole, taking into account the highest resolution direct N₂O estimations from soils (i.e. Topo × (MOS + ECOMOS)) and the indirect emissions from groundwater and rivers, the N₂O budget for the whole Orgeval sub-basin can be estimated at 14.21×10^3 kg N₂O-N yr⁻¹.

This estimation, with regard to the sub-basin area, is equivalent to 1.33 kg N₂O-N ha⁻¹ yr⁻¹ considering both direct and indirect emissions and 1.28 kg N₂O-N ha⁻¹ yr⁻¹ considering only direct emissions, giving a proportion of 4 % for the indirect emissions. This estimation is well within the range of previous regional estimations in northern France, under similar climatic and pedologic conditions, from 0.84 to 2.0 kg N₂O-N ha⁻¹ yr⁻¹, and slightly lower than our previous estimation of 2.0 kg N₂O-N ha⁻¹ yr⁻¹ for the whole Seine basin (Garnier et al., 2009). These experimental values are well within the range found with modelling approaches. The CERES-EGC biophysical soil-crop model coupled with the AROPAJ economic model gave N₂O emissions in Picardie from 1.07 to 1.97 kg N₂O-N ha⁻¹ yr⁻¹ (Durandea et al., 2010) while in the Ile-de-France region, again using the CERES-EGC model, Lehuger (2009) estimated N₂O emissions from 0.84 to 1.29 kg N₂O-N ha⁻¹ yr⁻¹. Gabrielle et al. (2006) used the same model run with geo-referenced input data on soils, weather and land use to map N₂O emissions from wheat-cropped soils and estimated N₂O emissions at 1.37 kg N₂O-N ha⁻¹ yr⁻¹.

The nitrous oxide emissions at the regional level can be considered in two ways: as a magnitude of emissions or as a response of N fertilization applied. We have here considered only emissions, based on both topography and land use, even though the information on fertilizer use at the basin scale can be found and could improve this modelling exercise.

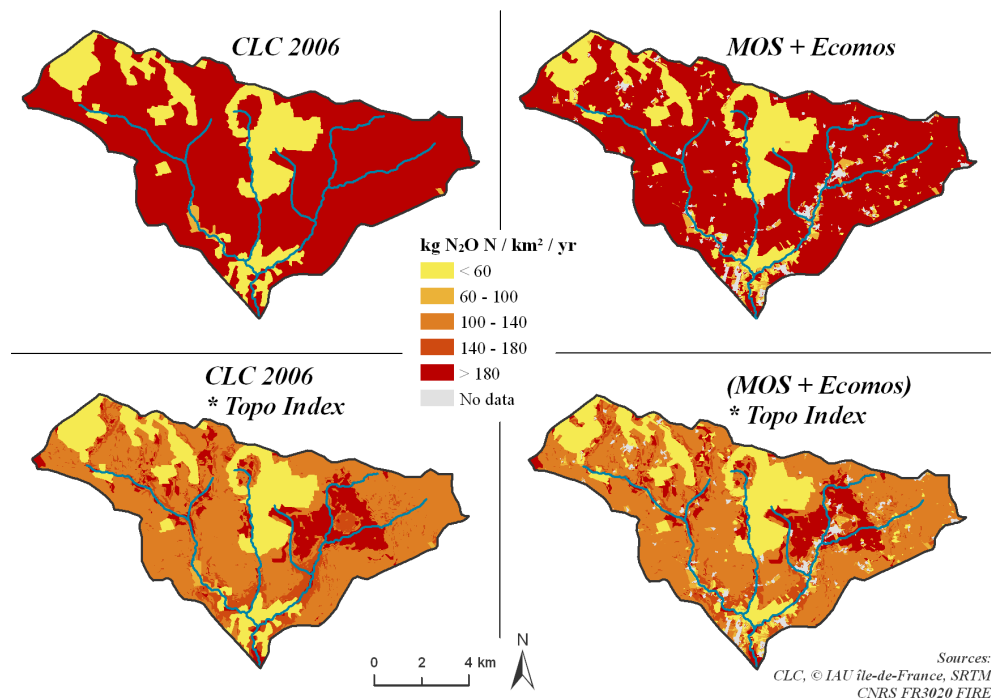


Fig. 6. Estimation of nitrous oxide emissions as a function of the land cover database and the topography.

Table 3. N₂O emission estimations for the Orgeval basin by main land use type and calculated by each upscaling method (in kgN₂O-N yr⁻¹). CLC: Corine Land Cover; MOS: Mode d’Occupation des Sols; ECOMOS: land use classification produced by the IAU IDF.

	CLC 2006	MOS + ECOMOS	Topo + CLC 2006	Topo + MOS + ECOMOS
Arable	16,959.80 ± 4562.04	15,847.36 ± 4262.80	13,201.26 ± 3447.27	12,292.95 ± 3269.18
Forest	1144.41 ± 836.10	1139.35 ± 832.40	1144.41 ± 836.10	1139.35 ± 832.40
Grass	56.73 ± 49.08	233.64 ± 202.14	56.73 ± 49.08	233.64 ± 202.14
Total	18,161 ± 4638	17,220 ± 4348	14,402 ± 3548	13,666 ± 3380

Table 4. Contribution of the three topographic classes to the total N₂O flux, given for the two upscaling methods based on topography and land use (in kgN₂O-N yr⁻¹).

	Topo × CLC 2006	Topo × (MOS + ECOMOS)
Shoulder	7259.93 ± 3333.67	7023.78 ± 3173.05
Slope	1727.33 ± 525.04	1540.48 ± 431.99
Footslope	5415.13 ± 703.32	5101.68 ± 657.76
Total	14,402 ± 3447.27	13,666 ± 3269.18

However, Freibauer (2003) modelled N₂O emissions at the European scale and showed a poor relationship between these emissions and fertilizer dose (0.4% of the variability explained by the fertilizer dose). The “fertilizer dose” factor seems to lose influence as the spatial area considered increases (Gabrielle et al., 2006), confirmed by the study

reported by Kaiser et al. (1998), who found that 0.8% of the variability was explained by the fertilizer dose. Thus, not incorporating the fertilizer dose into our extrapolation may not have produced a significant error in the nitrous oxide flux estimation in the end. Especially since the sampled field is considered as representative of the whole Orgeval basin in terms of fertilization practices, the incorporation of the fertilization rates as a spatial variable was not crucial when up-scaling from fields to landscape, as N₂O emissions are assumed to be proportional to applied fertilizer.

One of the strengths of the methodology used herein is that it integrates the concept of topography into the estimation of N₂O emissions. Although this method can be refined, especially with regard to nitrogen rates applied on the field, this concept may be further used in subsequent coupling with the process-based models mentioned above (STICS-NOE, DNDC, CERES-EGC, NGAS, DAYCENT, etc.).

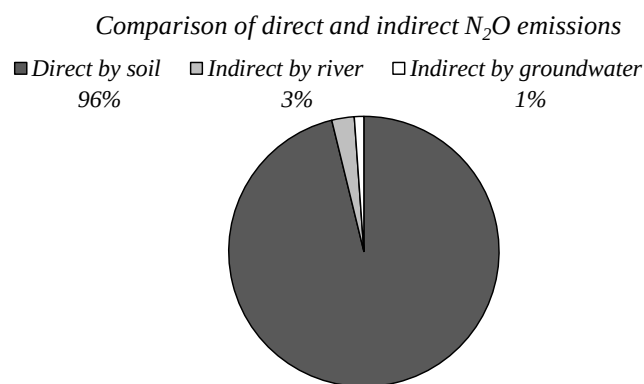


Fig. 7. Comparison of direct and indirect N₂O emissions at the Orgeval basin scale, based on the “Topo index × (MOS + ECO-MOS)” estimation.

6.3 Opportunities for nitrous oxide emissions mitigation

A promising direction for nitrous oxide emissions mitigation is the enlargement of buffer strip zones, particularly in low topographical positions. Schultz et al. (2009) reported that the riparian buffer zones have to be adjusted to fit the site. Indeed, all adjacent upland arable lands have different characteristics and then each one requires individual consideration in order to achieve the objectives in terms of nitrate reduction minimizing N₂O emissions. Landscape features can vary along the same water body such as presence or absence of wetlands, width of the floodplain, slope and soil type (Palone, 1998). In terms of ecological engineering, a conversion to agroforestry seems to be promising both in terms of nitrogen retention and removal, carbon sequestration, biodiversity conservation and soil enrichment (Jose, 2009; Montagnini and Nair, 2004). Moreover, employing agroforestry practices can provide food and fiber while maintaining habitats for threatened species and maintaining local biodiversity and associated ecosystem services such as pollination and pest control (Foley et al., 2005). Agroforestry systems such as riparian buffers have been proposed to control non-point source pollution coming from agricultural fields as they reduce the velocity of runoff by mechanisms such as infiltration, sediment deposition and nutrient retention (Jose, 2009). The effectiveness of these measures has been proved by several studies such as those reported by Udawatta et al. (2002), Anderson et al. (2009) and Lee et al. (2003), the latter showing a 20 % increase in nutrient retention in woody stem buffer compared to a switchgrass buffer. Trees with deep roots in agroforestry systems can even improve groundwater quality by taking up leached nutrient by tree roots. These nutrients are then recycled back into the system through root turnover and litterfall, increasing the nutrient use efficiency of the system (Van Noordwijk et al., 1996; Allen et al., 2004).

A further alternative is to develop buffer strip biomass by harvesting (Spinelli et al., 2006). A conversion of buffer strip to biofuel products (such as switchgrass or miscanthus) could facilitate the expansion of buffer strips suggested above, because the loss of farmer income would be reduced by promoting the products of the riparian buffer zone (Isenhardt et al., 2000; Lee et al., 2003). In a modelling exercise, Gopalakrishnan et al. (2012) investigated such an alternative cropping system where bioenergy crops are grown in buffer strips adjacent to current agricultural crops in the buffer strips. Their results indicated that growing bioenergy crops in buffer strips mitigated nutrient runoff, reduced nitrate concentrations in leachate by 60–70 % as well as resulted in a reduction of 50–90 % of nitrous oxide emissions compared with traditional cropping systems. However, water consumption by these deep root trees should be simultaneously considered in a perspective of water availability reduction due to climate change.

We tested an extreme hypothetical scenario where agriculture was excluded from the low topographical positions. For this purpose, we simply replaced the value of the emission coefficient corresponding to the agricultural foot-slope position (401.50 kgN₂O-N km⁻² yr⁻¹) with the emission coefficient corresponding to grassland, (69.35 kgN₂O-N km⁻² yr⁻¹), which can be assumed a value comparable to the ones found for bioenergy crops without fertilization. Considering this scenario, with a 15.4 % loss of arable land, N₂O emissions of the whole watershed would decreased by 29 % (i.e. 9620 vs. 13 666 kgN₂O-N yr⁻¹).

In conclusion, we have shown that the spatial resolution of the land-use data, as well as the integration of the topography are two important criteria for estimating N₂O emissions at the basin scale. A major challenge for precision conservation in greenhouse gas mitigation can be a variable rate application of N fertilizer in lower slope segments to ensure the highest possible fertilizer use efficiency and hence reduce N₂O emissions from these segments (Pennock, 2005).

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