Supporting Information

4 figures; 9 tables

Improved Environmental Life Cycle Assessment of Crop Production at the Catchment Scale via a Process-Based Nitrogen Simulation Model

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Calculation of N_2O emissions in AGRIBALYSE

Direct and indirect N_2O emissions were calculated according to emission factors used in the IPCC Tier 1 method.[1] However, the effect of land-use change was ignored. Therefore, in AGRIBALYSE, on-site N_2O emissions were calculated according to the following equation:

$$F_{N2O\text{-}N} = 0.01 \times (F_{NF} + F_{CR} + 14/17 \times F_{NH3} + 14/46 \times F_{NOX}) + 0.0075 \times 14/62 \times F_{NO3}$$

where $F_{N2O\text{-}N}$ is the amount of on-site N_2O emissions (kg N/ha); F_{NF} the amount of N-fertilizer inputs (kg N/ha); F_{CR} the amount of N released by crop resides (kg N/ha); and F_{NH3}, F_{NOX}, and F_{NO3} amounts of on-site NH_3 volatilisation (kg NH_3/ha), NO_X volatilisation (kg NO_X/ha), and NO_3^- leaching (kg NO_3^-/ha), respectively.

Parameterization and calibration of TNT2

Predicted discharge measured at the outlet of a catchment was calibrated via trial-and-error within a physically realistic range of parameters.[2] Parameters for denitrification[3] and organic matter mineralization[2,4] were used to calibrate NO_3^--N fluxes at the outlet.

Cropping-system data used by TNT2 for the calibration period (1994-2002) are based on surveys. The land use of Kervidy-Naizin, considered constant in the study, is mainly dedicated to agriculture with intensive livestock farming. Twenty-three farms have fields in this catchment. In 2010, 20% of the total surface was covered by cereals, 30% by maize, and 20% by temporary or permanent grassland; the remaining 30% was dedicated to minor agricultural crops, woods and hedges, and infrastructure (e.g. roads). Animal production includes indoor production of pigs and poultry, fed partly with grains grown in the catchment but mainly with imported grains and protein crops, and intensive production of dairy and beef cattle, fed with forage grown in the catchment supplemented with imported protein crops. A systematic on-field inventory of summer crops was performed from 1993 to 2002.[5] A complementary dataset, from a neighboring catchment with similar farming activities (the Fremeur catchment, 10 km from Kervidy-Naizin), was used to determine winter land-cover allocation rules and agricultural practices.[6] From these surveys, each farming system was described by its specific crop successions (dates of sowing and harvesting) and manure and mineral fertilizer management (type and quantity). These cropping-system data were used as input into TNT2.

The accuracy of TNT2 predictions was evaluated by comparing daily predicted discharge and NO_3^--N fluxes at the outlet against those observed during the calibration period and calculating the numeric criteria percentage bias (PBIAS[7]), Nash-Sutcliffe index (NS[8]), and coefficient of determination (R^2). The calibration period was designed to cover a wide spectrum of hydrological conditions, including high precipitation (e.g., 1994-1995 and 2000-2001; see Fig. 2a in ESM1 in Salmon-Monviola et al. (2013)[4]). For the calibration period, simulated daily water fluxes accurately reflected observed values, with a NS of 0.82, a R^2 of 0.84, and a PBIAS of -15%. The intensity and temporal dynamics of high precipitation events (1995 and 2000-2001) were well predicted, although the model tended to slightly underestimate water fluxes. The model predicted observed daily NO_3^--N fluxes for the calibration (NS = 0.82, R^2 = 0.83, PBIAS = -7%) period quite well despite of, given negative values of PBIAS, a slight tendency to underestimate NO_3^--N fluxes. Predicted mean soil denitrification (31 kg N/ha/yr) in 1994-2010 was similar to that (32 kg N/ha/yr) predicted by another modeling approach applied to the same catchment.[9] N mineralization in French soils was estimated as 90-160 kg N/ha/yr,[10,11] while the model predicted mean N mineralization of 120 kg N/ha/yr, which is within the range of observations.

Based on the performance rating[12], predicted discharge and NO_3^--N fluxes can be considered "good" (NS > 0.65 and |PBIAS| ≤ 15%) for a calibration period. Considering these results and validation of NO_3^- removal by soil denitrification and N mineralization, we consider that TNT2 assesses accurately water and N flows in the Kervidy-Naizin catchment with real cropping systems. From this step, we consider TNT2 is well calibrated and we can test with confidence virtual cropping systems with the combined model TNT-LCA..

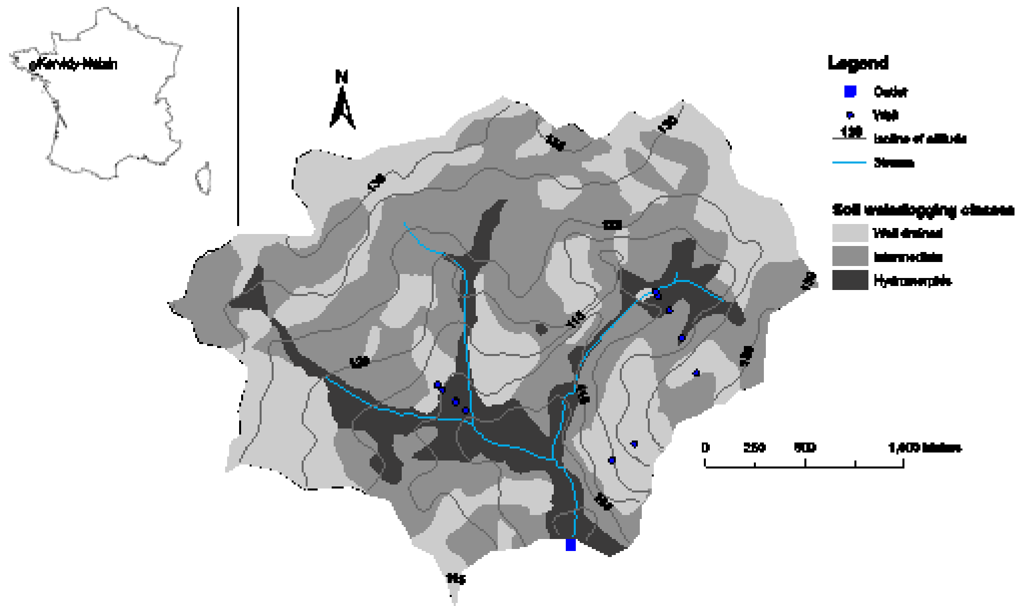

Figure S1. The catchment Kervidy-Naizin in Brittany, western France

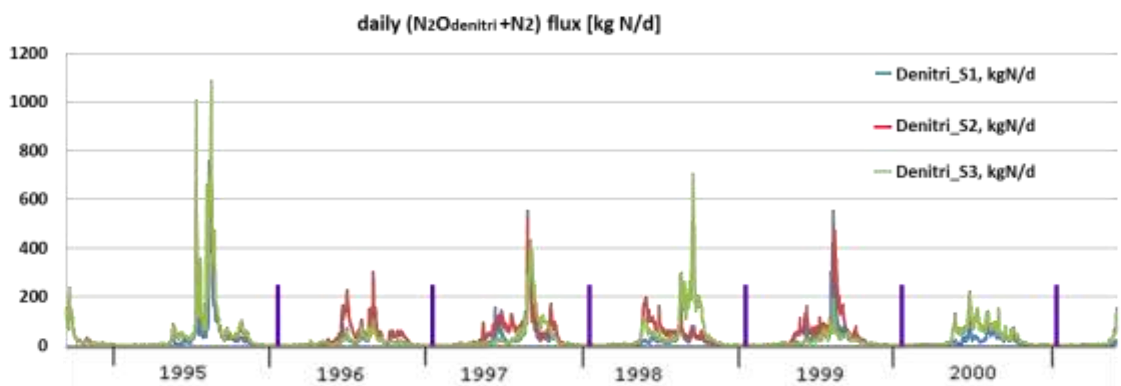

Figure S2. Time series of daily fluxes of total denitrification loss ($N_2O_{denitri}$+N_2) for the entire catchment (kg N/day). Vertical purple lines represent emission-wave-based inventory periods.

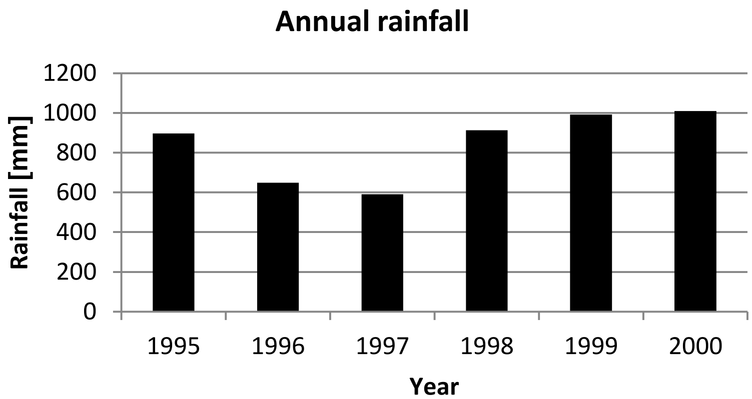

Figure S3. Annual rainfall in the Kervidy-Naizin catchment from 1995-2000

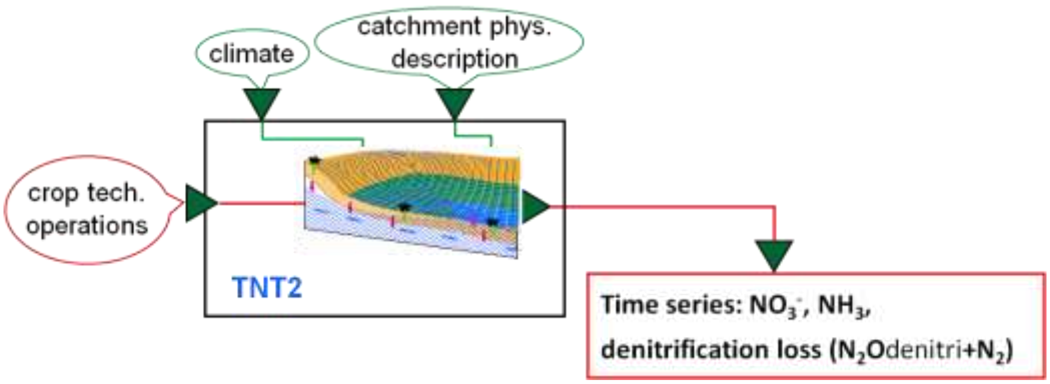

Figure S4. Parameters and input/output data of TNT2. Green lines stand for parameters and red lines for input/output data. Climate parameters: temperature, rainfall, global radiation, and potential evapotranspiration. Parameters for catchment physical description: digital elevation model (20m*20m), hydrological network, soil types and raster maps, field types and raster maps, water discharge observed at the outlet of a catchment. Crop technical operations (and crop sequences): sowing, fertilization, grazing, harvesting, etc.

Table S1. Substances, impact categories, and characterisation factors used in TNT2-LCA

Substance	Formula	Pathway	Climate Change	Eutrophication
			GWP100 (kg CO_2 eq.)[13]	EP (kg PO_4^- eq.)[14]
Ammonia	NH_3	air		0.35
Carbon dioxide	CO_2	air	1	
Dinitrogen monoxide	N_2O	air	298	
Methane	CH_4	air	25	
Nitrate	NO_3^-	water		0.10
Nitrogen oxides	NO_x	air		0.13
Phosphate	PO_4^-	water		1
Phosphorus	P	water		3.06

Table S2 Crop technical operations, based on survey data, assumed for the three cropping systems in TNT2-LCA

Crop	Date	Operation	Type	Rate, kg N/ha
Grass	August 31	sowing	grass	
	March 1	applying mineral N fertilizer		25.0
	April 4	applying mineral N fertilizer		50.0
	June 1	grazing		
	July 30	grazing		
	September 15	grazing		
Silage maize	April 25	sowing	silage maize	
	April 26	applying organic N fertilizer	pig slurry	258.5
	April 27	applying organic N fertilizer	cattle slurry	68.9
	September 24	harvesting	whole plant	
Wheat	October 25	sowing	wheat	
	October 26	applying organic N fertilizer	cattle slurry	55.0
	February 10	applying mineral N fertilizer		200.0
	July 24	harvesting	grain	
Pea	March 15	sowing	pea	
	May 30	applying mineral N fertilizer		49.9
	July 1	harvesting	grain	
Potato	April 15	sowing	potato	
	April 16	applying mineral N fertilizer		124.0
	July 14	harvesting	tuber	
Rapeseed	September 5	sowing	rapeseed	
	September 6	applying organic N fertilizer	pig slurry	159.6
	March 15	applying mineral N fertilizer		90.0
	July 4	harvesting	grain	
Mustard, early	September 2	sowing	mustard	
	February 28	harvesting	whole plant left on the field	
Mustard	October 2	sowing	mustard	
	March 1	harvesting	whole plant left on the field	

Table S3. Climate change impacts (kg CO_2 eq./ha/yr) estimated by AGRIBALYSE and TNT2-LCA for the three systems under study. Results for TNT2 are based on the percentage of total denitrification loss that is N_2O, set at 0.3% and 60%. Mean values are followed by the standard deviation in brackets.

Method	Syst.	C1	C2	C3	C4	C5	C6	Mean
AGRIBALYSE	S1	1667	1667	1667	1667	1667	1667	1667 (0)
	S2	2342	2342	2342	2342	2342	2342	2342 (0)
	S3	2342	2840	929	3503	2854	2342	2469 (792)
TNT2-LCA	S1	1653	1635	1646	1635	1644	1635	1641 (7)
(N_2O=0.3%)	S2	1109	1086	1098	1085	1095	1087	1093 (9)
	S3	1112	1644	563	2385	1582	1087	1395 (569)
TNT2-LCA	S1	7778	4207	6223	4016	5895	4192	5385 (1377)
(N_2O=60%)	S2	11157	6588	9041	6352	8341	6853	8055 (1692)
	S3	11734	3904	6367	10842	4128	6794	7295 (3026)

Table S4. Eutrophication impacts (kg PO_4^- eq./ha/yr) estimated by AGRIBALYSE and TNT2-LCA for the three systems under study. Mean values are followed by the standard deviation in brackets.

Method	Syst.	C1	C2	C3	C4	C5	C6	Mean
AGRIBALYSE	S1	13.4	13.4	13.4	13.4	13.4	13.4	13.4 (0.0)
	S2	31.3	31.3	31.3	31.3	31.3	31.3	31.3 (0.0)
	S3	31.3	24.0	18.7	23.7	24.4	36.6	26.5 (5.8)
TNT2-LCA	S1	15.7	11.8	15.9	16.7	18.8	27.8	17.8 (4.9)
	S2	34.9	29.8	42.2	44.4	48.8	68.3	44.7 (12.2)
	S3	35.8	16.3	19.4	31.3	29.8	55.8	31.4 (12.8)

Table S5. On-site N_2O emissions (kg N_2O-N/ha/yr) estimated by AGRIBALYSE and TNT2-LCA for the three systems under study. Predictions of TNT2-LCA are based on a percentage of total denitrification loss that is N_2O equal to 11%. Mean values are followed by the standard deviation in brackets. HtH: harvest to harvest

Model	Period	Syst.	C1	C2	C3	C4	C5	C6	Mean
AGRIBALYSE	Calendar year	S1	0.1	0.1	0.1	0.1	0.1	0.1	0.1 (0.0)
	HtH	S2	2.7	2.7	2.7	2.7	2.7	2.7	2.7 (0.0)
	HtH	S3	2.7	2.6	0.8	2.5	2.8	2.7	2.4 (0.7)
TNT2-LCA	Emission-wave-based period	S1	2.4	1.0	1.8	0.9	1.7	1.0	1.5 (0.5)
		S2	4.0	2.2	3.1	2.1	2.9	2.3	2.7 (0.7)
		S3	4.2	0.9	2.3	3.3	1.0	2.2	2.3 (1.2)

Table S6. On-site N_2O emissions (kg N_2O-N/ha/yr) estimated by AGRIBALYSE and TNT2-LCA for the three systems under study. Predictions of TNT2-LCA are based on a percentage of total denitrification loss that is N_2O equal to 0.8%. Mean values are followed by the standard deviation in brackets. HtH: harvest to harvest

Model	Period	Syst.	C1	C2	C3	C4	C5	C6	Mean
AGRIBALYSE	Calendar year	S1	0.1	0.1	0.1	0.1	0.1	0.1	0.1 (0.0)
	HtH	S2	2.7	2.7	2.7	2.7	2.7	2.7	2.7 (0.0)
	HtH	S3	2.7	2.6	0.8	2.5	2.8	2.7	2.4 (0.7)
TNT2	Emission-wave-based period	S1	0.2	0.1	0.1	0.1	0.1	0.1	0.1 (0.1)
		S2	0.4	0.2	0.2	0.2	0.2	0.2	0.2 (0.1)
		S3	0.4	0.1	0.2	0.2	0.1	0.2	0.2 (0.1)

Table S7. Ranges of on-site N_2O emissions (kg N_2O-N/ha) for wheat and rapeseed produced in the Brittany region, France, according to this study and AGRIBALYSE, and according to Gabrielle et al.[4] in the Ile de France region, France.

Crop	This study	AGRIBALYSE	Gabrielle et al.[15]
Wheat	0.02-4.80	2.60	0.11-2.98
Rapeseed	0.03-5.50	2.80	0.10-0.87

Table S8. Dry-matter crop yield predicted by TNT2 for six annual crops/grass (C1-C6) of three cropping systems (S1-S3) and compared to those estimated by AGRIBALYSE

Syst.	**Period** [1]	**Crop**	**Harvested**	**Yield, kg dry matter/ha**		
				TNT2	**AGRIBALYSE**	**Diff.** [3]
S1_C1	1 Jan 1995-31 Dec 1995	grass	n.a. [2]	7289	7380	-1%
S1_C2	1 Jan 1996-31 Dec 1996	grass	n.a.	7690	7380	4%
S1_C3	1 Jan 1997-31 Dec 1997	grass	n.a.	8563	7380	16%
S1_C4	1 Jan 1998-31 Dec 1998	grass	n.a.	9296	7380	26%
S1_C5	1 Jan 1999-31 Dec 1999	grass	n.a.	8442	7380	14%
S1_C6	1 Jan 2000-31 Dec 2000	grass	n.a.	9479	7380	28%
S1	Mean	grass	n.a.	8460	7380	15%
S2_C1	30 Aug 1994-24 Sep 1995	silage maize	whole plant	18446	12200	51%
S2_C2	25 Sep 1996-24 Sep 1996	silage maize	whole plant	13718	12200	12%
S2_C3	25 Sep 1997-24 Sep 1997	silage maize	whole plant	16818	12200	38%
S2_C4	25 Sep 1998-24 Sep 1998	silage maize	whole plant	17133	12200	40%
S2_C5	25 Sep 1999-24 Sep 1999	silage maize	whole plant	20401	12200	67%
S2_C6	25 Sep 2000-24 Sep 2000	silage maize	whole plant	18053	12200	48%
S2	Mean	silage maize	whole plant	17428	12200	43%
S3_C1	30 Aug 1994-24 Sep 1995	silage maize	whole plant	18501	12200	52%
S3_C2	25 Sep 1995-24 Jul 1996	wheat	grain	8178	6035	36%
S3_C3	25 Jul 1996-1 Jul 1997	pea	grain	5520	3910	41%
S3_C4	2 Jul 1997-14 Jul 1998	potato	tuber	9025	8983	0%
S3_C5	15 Jul 1998-4 Jul 1999	rapeseed	grain	5029	2951	70%
S3_C6	5 Jul 1999-24 Sep 2000	silage maize	whole plant	18064	12200	48%
S3	Mean			10720	7713	39%

[1] Period: for grazed grass, one calendar year; for an annual crop, “harvest to harvest”

[2] n.a.: not applicable, as grass was only grazed

[3] Diff.: relative difference in TNT2-predicted yield compared to that estimated by AGRIBALYSE

Table S9. Crops that are available in AGRIBALYSE (v1.1), crops that are validated in TNT2, and crops that can be studied using TNT2-LCA. Y: Yes.

Crop	**Applicability**		
	AGRIBALYSE	**TNT2**	**TNT2-LCA**
alfalfa	Y		
annual ryegrass		Y	
apple	Y		
barley	Y	Y	Y
broccoli		Y	
cabbage		Y	
carrot	Y		
cider apple	Y		
clementine	Y		
cocoa	Y		
coffee	Y		
faba bean	Y		
haricot bean		Y	
grain maize	Y	Y	Y
grass	Y	Y	Y
jasmine rice	Y		
mango	Y		
oat		Y	
oil palm fruit	Y		
ornamental shrub	Y		
pea	Y	Y	Y
peach	Y		
perennial ryegrass		Y	
potato	Y	Y	Y
rapeseed	Y	Y	Y
rose	Y		
shallot		Y	
silage maize	Y	Y	Y
spinach		Y	
sugar beet	Y	Y	Y
sunflower	Y		
tomato	Y		
triticale	Y	Y	Y
wheat	Y	Y	Y
white mustard		Y	
wine grape	Y		

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