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Improving Estimates of Nitrogen Emissions for Life Cycle Assessment of Cropping Systems at the Scale of an Agricultural Territory

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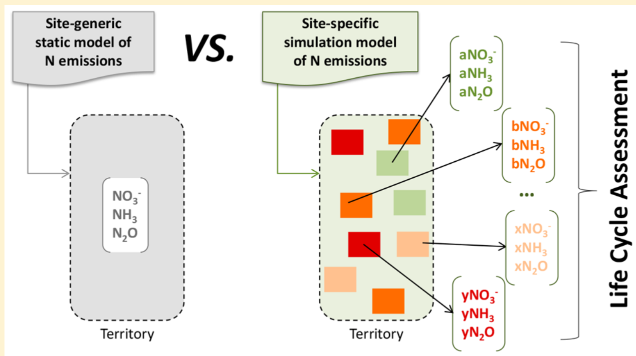
Supporting Information

ABSTRACT: In life cycle assessment (LCA), simple models are currently used to estimate cropping system nitrogen (N) emissions on farms. At large spatial scales (e.g., countries), these models are valid. At a smaller spatial scale (e.g., territories), these models may be less accurate, since they completely or partially ignore local conditions such as management practices, soil or climate. The purpose of this study was to consider the variability of those factors when estimating N emissions in LCA at the watershed scale. To this end, Syst'N, decision-support software based on a simulation model of crop and soil N dynamics at field and crop-rotation scales, was applied to predict N emissions from cropping systems in a coastal watershed (Lieue de Grève, France). Syst'N predictions were compared to N emissions estimated by AGRIBALYSE, a static site-dependent method at field and single-crop scales. Syst'N was more sensitive to site-specific soil properties than AGRIBALYSE. Estimates of N emissions that include spatial variability in soil and climate therefore become possible in LCA when a simulation model such as Syst'N is used in the inventory phase.



1. INTRODUCTION

Despite numerous regulations resulting from Nitrate and Water Framework Directives, contamination of soil, water, and air by nitrogen (N) emissions from agricultural activities remains a major concern[1,2] because the emissions generate many impacts: pollution of groundwater, eutrophication of surface and marine water, decreased biodiversity, soil acidification and global warming.[3] Techniques to mitigate these emissions are well documented and can be combined at field (i.e., cropping system), farm (i.e., production system) and territory scales. However, avoiding pollution swapping (i.e., transfer of emission from one pollutant, for example, NO_3^-, to another, for example, NH_3, CO_2) requires assessing N emissions using a multicriteria environmental approach, such as life cycle assessment (LCA). According to van der Werf et al.,[4] life cycle assessment (LCA) is a pertinent method to assess impacts of agriculture. Current LCA are mainly carried out at the farm scale.[5−7] To help local stakeholders manage N emissions and impacts from agricultural activities, environmental impacts (e.g., eutrophication, acidification) stemming from these emissions should be assessed at the regional scale. According to Nitschelm et al.,[8] spatially explicit data need to be integrated in LCA of agricultural territories (i.e., territorial LCA) because several emissions, such as N, because of agricultural activities vary as a function of farming practices (e.g., fertilization) and biophysical characteristics of the surroundings (e.g., weather, soil type).

Farm-scale LCA tools (e.g., EDEN[5]) require a large amount of data, which are often difficult to obtain. Hence, assessment at territory or watershed scales is much more time-consuming and often lacks the necessary farm data. Therefore, LCA practitioners currently estimate N emissions with simple models, often based on emissions factors (e.g., IPCC) or risk tables (e.g., as implemented for nitrate (NO_3^-) emissions in the AGRIBALYSE[9] life cycle inventory (LCI) database). These models exclude or approximate effects of (1) management practices, which can be defined as techniques (e.g., tillage, sowing and harvesting, fertilizer and pesticide application, management of crop residues) which make it possible to control the environment and to obtain a given crop or livestock production, (2) crop rotations, and (3) biophysical characteristics (e.g., soil, climate) on N emissions, although these factors are known to influence emissions from the soil-plant system.[10,11] These simple approaches can estimate N emissions relatively accurately at large spatial scales and low resolutions (e.g., country, world). However, at higher resolutions (e.g., field, farm, territory), there is a need to improve estimates of N emissions in LCA, since local conditions greatly influence N emissions and variability in these conditions influences N

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emissions in space and time. This need becomes particularly crucial when assessing effects of alternative scenarios of agricultural activities.

To this end, simulation models were integrated into LCA. For example, the CERES-ECG model,[12] which estimates daily N emissions at the field scale, was used to predict nitrous oxide (N_2O) emissions at the landscape scale.[13,14] At a larger scale, the TNT2 model,[15] which integrates the field scale (i.e., crop management, soil and climate conditions) and the watershed scale (i.e., hydrology) to predict daily NO_3^- flux at a watershed outlet, was used in LCA.[16] Liao et al.[16] showed the ability of simulation models in LCA to address the nonlinearity between N fertilizer inputs and onsite N emissions, which result from complex biogeochemical processes; simpler models may over- or underestimate NO_3^- emissions by ignoring local climate conditions and fertilization practices. Such complex simulation models, however, require expert knowledge on their use. Moreover, due to the amount of input data, TNT2 can be applied only to small watersheds (i.e., few hundreds of km^2).

The objective of this study was to consider agricultural practices and soil and climate variability when estimating N emissions in LCA at a watershed scale. One interesting approach consists of considering a territory as a mosaic of farms associated with a typology of cropping systems, whose N fluxes can be simulated at the field scale with Syst'N.[17] Syst'N is a decision-support software based on an N simulation model (i.e., STICS[18]) relatively simpler than others at the same scale. Syst'N requires few input data and has a user-friendly interface, and its predictions are sensitive to agricultural practices and soil and climate conditions.[11]

In this study, we focused on the influence of agricultural practices and soil variability on predicted NO_3^- and ammonia (NH_3) emissions and compared the predictions to emissions estimated using site-generic modeling, as used for the AGRIBALYSE LCI database. We applied the method to the case study of the Lieue de Grève (LdG) watershed, for which N fluxes have already been simulated[19] and LCAs using AGRIBALYSE LCI data have been performed.[20] This watershed has been intensively studied because, despite moderate NO_3^- fluxes with a mean concentration in water of about 30 mg·L^{-1} (below the European Union standard of 50 mg·L^{-1}), it has experienced acute eutrophication problems with recurrent green algae blooms in its bay since the 1970s. Using the LdG watershed as a case study, we investigated benefits and limitations of using the simulation model Syst'N to predict N emissions from cropping systems instead of the classic approach in LCA (i.e., simple models).

2. MATERIALS AND METHODS

2.1. Models Used to Estimate N Emissions. *2.1.1. LCI Database.* Non-spatialized N emissions were estimated using emission models implemented for the French agricultural LCI database AGRIBALYSE.[9] For grasslands, it uses the DEAC model[21,22] for NO_3^- emissions. For crops, it uses a static model developed by Tailleur et al.,[23] based on expert knowledge, that estimates NO_3^- emissions by combining a crop risk factor and a soil risk factor (see Table S1 for the list of input data used, details in "The nitrate risk factor calculation in AGRIBALYSE model" in Supporting Information). Classes of NO_3^- leaching risk are determined by combining these crop and soil factors without considering the temporal dimension (see Tailleur et al.[23] for combination results). AGRIBALYSE assumes that N-fertilizer input does not exceed crop requirements, though this assumption does not always hold true in reality.

NH_3 emissions from volatilization of organic and chemical fertilizers were determined at the field scale using the EMEP/CORINAIR[24] and EMEP/EEA[25] models. Emissions factors depend on the emission source, fertilizer type (i.e., animal species, chemical or organic) and form (solid or liquid).[9] These models of NO_3^- and NH_3 emissions were applied to each crop individually and therefore did not take crop sequence into account. Hereafter, we refer to these models as "AGRIBALYSE".

2.1.2. Syst'N. Syst'N is decision-support software developed by INRA and French technical institutes to calculate N emissions to decrease N losses from cropping systems.[26] The biophysical model simulates daily N fluxes in the soil-crop-atmosphere system. Processes simulated include soil N mineralization and denitrification, crop growth, N uptake, water balance, and N emissions to water (as NO_3) and air (as NH_3, N_2 and N_2O). Input data consist of description of a crop sequence, agricultural management practices, soil characteristics and climate (see Table S2 for the list of input data used). Syst'N includes a database of a variety of soil and climate conditions if users do not have a complete description of their system. The biophysical model is adapted to a range of crops (i.e., wheat, barley, maize, pea, rapeseed, sunflower), grasslands, and catch crops (i.e., white mustard, ryegrass).[17] It also includes postprocessing routines for simulation results to calculate N balances at various time steps, and a graphical interface to help nonspecialist users interpret simulation results. Syst'N was evaluated and used in an 86 km^2 watershed by Dupas et al.,[11] who showed that it was able to reproduce effects of soil properties and agricultural practices on NO_3^- leaching. The model can also distinguish effects of different soil depths, N contents and fertilization practices on N water quality at the catchment scale.

2.2. Case Study. *2.2.1. The Lieue de Grève Watershed.* We applied the two models to the case study of the Lieue de Grève (LdG) watershed, a 120 km^2 watershed in Brittany, France (48°N, 3°W), whose bay experiences annual algal blooms. These occur due to a combination of NO_3^- emissions from agricultural activities and characteristics of the bay (shallow water, low water renewal), which favors algal blooms. According to Perrot et al.,[27] eutrophication problems could be avoided in this area if NO_3^- concentration at the outlet were approximately 10 mg·L^{-1}, which would require extremely low emissions from agricultural land. Several research projects have been conducted on this watershed to generate solutions to reduce N emissions.[28−30] Land use is divided among agriculture (68% of the total area), woodland (24%) and urban area (8%). Agricultural Area (AA) is divided among 170 farms, 96% of them conventional and 4% organic. The main production is cow milk, using up to 85% of the AA to produce 39.7 kt dairy milk per year. Other types of production such as beef cattle and swine (the latter occupying about 3% of AA) are also present. Most AA is covered by grasslands (45%), cereals (27%), and silage maize (20%), followed by rapeseed and vegetables.[19,31,32]

2.2.2. Typology of Cropping Systems and Their Distribution in the Watershed. Sebillotte[10] defined a cropping system as the crop succession plus technical management routines used on crops in the rotation. Here, we describe how we defined a typology of cropping systems consistent with the reality of the LdG watershed. Cropping systems in the LdG watershed are typical of those of Brittany,[31,33] dominated by crop rotations,

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Table 1. Characteristics of Cropping Systems in the Lieue de Grève Watershed, Brittany, France[a]

cropping system	short name	rotation duration (years)	percentage of watershed area (%)	chemical fertilization (kg N/year)	organic fertilization (solid) (kg N/year)	organic fertilization (liquid) (kg N/year)	fertilization equivalent (kg N/year)	soil cover indicator
maize−cereal	M−C	2	11	53	66	100	116	0.30
maize−cereal−cereal	M−C−C	3	8	40−100	0−53	0−105	92−110	0.23
maize−maize−cereal	M−M−C	3	5.5	72	106	0	93	0.20
maize−cereal−maize−cereal−cauliflower	M−C−M−C−Cau	5	2.5	40	62	15	60	0.44
maize−cereal−rapeseed−cereal	M−C−R−C	4	2	50	0	91	96	0.43
maize−cereal−mixed grassland	M−C−Gm	9	6	0−33	0−50	0−31	6−33	0.84
maize−maize−maize−cereal−mixed grassland	M−M−M−C−Gm	8	7.5	15−55	46	0	24−64	0.58
mixed grassland	Gm	6	5.5	0−107	0−83	0−72	17−116	0.92
grazed grassland	Gg	6	5.5	0−107	0	0−215	76−108	0.92
nonfertilized mixed grassland-Cereal	Gm(nf)−C	7	>0.5	10	0	16	18	0.80
fertilized mixed grassland−cereal	Gm(f)−C	6	>0.5	93	0	90	138	0.77

[a]Soil cover indicator is a soil-cover factor (range = 0−1) during the drainage period (mid-October to the end of April) that averages autumn-winter soil-cover factors of each crop in the rotation.

ley-arable rotations and grasslands. To reduce the number of cropping systems analyzed, Nitschelm et al.[34] defined a typology of 13 farm types that differed in agricultural production and practices. Extensive farm surveys describing crop rotations and management practices (e.g., yields, sowing and harvesting dates, amounts of fertilizers and pesticides used) and livestock (e.g., production levels, numbers of animals, types and quantities of feed, grazing management) for each of the 13 farm types were available from Mabon[32] and from a survey by the Brittany Chamber of Agriculture. While cash-crop management practices were thoroughly documented,[31] data on grassland management came from results of the ACASSYA project.[29,35]

We identified 33 cropping systems for the 13 farm types, based on the three main parameters defined by Sebillotte:[10] (1) crop type (i.e., maize, cereals, rapeseed, vegetables, grasslands), (2) crop sequence, and (3) fertilization (i.e., types and quantities of fertilizer) (Table S3). These cropping systems can be clustered as 11 cropping systems according to rotation type, percentage of watershed area and fertilizer inputs (Table 1). Parameters describing each cropping system were as follows:

- Duration of the crop rotation (in years).
- Percentage of AA of the LdG watershed that the cropping system covers.
- Types and total amounts of fertilizer inputs (kg N/year). We calculated mean annual N fertilization equivalents by weighting the N content of each fertilizer type and summing the weighted fertilizer inputs of each crop in the rotation. On the basis of expert knowledge about the most common manure types, application methods and season of application in the LdG, weights were chosen from coefficients of chemical N fertilizer equivalents calculated by COMIFER[36] (i.e., defined as the ratio of the N in a chemical fertilizer such as ammonium nitrate to the N in an organic fertilizer that becomes available to a crop): 1 for chemical fertilizer, 0.5 for liquid manure, and 0.2 for solid manure.
- A soil-cover factor (range = 0−1) which is an expert based indicator calculated during the drainage period (mid-October to the end of April) that averages autumn-winter soil-cover factors of each crop in the rotation: 0 for bare soil, 0.1 for winter cereals, 0.5 for catch crops and newly sown grasslands[37] and 1 for rapeseed, winter vegetables (i.e., cauliflower), and grasslands.

The 33 cropping systems were classified as (1) crop-only systems, mainly maize and cereals rotations (33% of cropping systems); (2) ley-arable rotations, with 4−5 years of grasslands and 2−4 years of crops (31% of cropping systems), and (3) permanent grasslands (≥6 years) (36% of cropping systems). Fertilizer inputs were chemical, solid organic, liquid organic, or a mix of all three.

It should be noted that, because of the algal bloom problem in Brittany, agricultural fields are not allowed to remain bare during winter; thus, catch crops are used every time maize follows a cereal crop. Based on expert knowledge, we differentiated three types of grassland management: mixed (cut and grazed) and not fertilized (Gm(nf)), mixed and fertilized (Gm(f)) and intensively grazed and fertilized (Gg).

2.3. N Assessment at the Regional Scale in the LdG Watershed. Both AGRIBALYSE and Syst'N models were used to estimate NO_3^- and NH_3 emissions of the cropping systems located on the LdG watershed. Here, we describe how we modeled NO_3^- and NH_3 emissions of the cropping systems using the AGRIBALYSE and Syst'N models and then performed a sensitivity analysis of Syst'N predictions to determine effects of soil and interannual climate variability.

2.3.1. Simulating N Emissions from Cropping Systems Using Models Implemented by AGRIBALYSE. Since the models implemented by AGRIBALYSE are already validated for use in French systems,[9] we did not assess their validity. To estimate NO_3^- emissions, we first determined the crop risk factor for

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each crop of each cropping system (see Table S4 for details). Then, we determined the soil risk factor for each crop of each cropping system. We made the following assumptions:

- Rooting depth of 100 cm for cereals, maize, rapeseed and grasslands, 35 cm for cauliflower;
- Dominant soil texture, silt, the most common dominant soil texture in the LdG watershed;
- Drained water, 450 mm, the mean value in the LdG watershed;
- Soil organic matter (SOM) content, since the LdG watershed has soils with SOM both lower and higher than 3%, we modeled both.

For most crops (i.e., when the following crop was a cereal, maize, rapeseed, or grassland), we calculated a "moderate" (SOM < 3%) or "high" (SOM > 3%) soil risk factor. For crops followed by cauliflower, the soil risk factor was "high" (SOM < 3%) or "very high" (SOM > 3%). Crop and soil risk factors were then aggregated to obtain NO_3^- leaching estimates for each crop of each cropping system. NH_3 emissions were determined by multiplying quantities of organic and chemical fertilizers by emission factors that vary depending on fertilizer type (e.g., ammonium nitrate/urea, solid/liquid manure). In the LdG watershed, we assumed that only ammonium nitrate is used for chemical fertilization, since it was the only chemical fertilizer mentioned in the farm surveys.[29,32] Organic fertilizers were mainly cow manure and pig slurry, except for one farm which used broiler manure. Since the LCI of AGRIBALYSE calculates emissions per crop, we then summed NO_3^- and NH_3 emissions of all crops of each cropping system. Mean NO_3^- and NH_3 emissions were calculated by dividing these total emissions by the duration of the crop rotation to express final results per year and per hectare for each cropping system.

2.3.2. Simulating N Emissions from Cropping Systems Using Syst'N. Unlike AGRIBALYSE, Syst'N simulates NO_3^- and NH_3 emissions at the cropping system scale. The input data needed concern management practices, soil and climate (Table S3). Input data to describe management practices for each crop of each rotation were obtained from farm surveys[29,32] for crop sowing and harvesting dates, crop fertilization (e.g., quantities of organic and chemical fertilizers, time of application), presence of catch crops (e.g., type, sowing and harvesting dates), tillage (e.g., type, soil depth, date), irrigation (e.g., water quantity) and, for grassland, dates of grazing and mowing.

Daily climate data were obtained from Météo France for 1999–2014 for the Trémel weather station (48° 36′ 14″ N, 3° 36′ 37″ W), located at the edge of the LdG watershed, and assumed to be representative of it. The LdG climate is temperate, with mean annual rainfall of 973 mm, mean annual temperature of 11.6 °C and mean global solar radiation of 11.1 MJ/m^2 from 1999 to 2014 (source: Météo France). For these simulations, we focused on effects of soil variability and we therefore chose the period September 2008 to August 2009, with mean rainfall of 973 mm and mean temperature of 11.4 °C as the "average" year most similar to long-term means in the LdG watershed (Figure S1). This weather year was repeated for each year of each simulation.

Soil types and characteristics were extracted from 1:250 000 soil maps in the Sols de Bretagne database.[38] This database[39] distinguishes soils within Soil Map Units (SMUs), each containing 1–11 soil types called Soil Type Units (STUs). STUs are defined as areas with homogeneous soil-forming factors, such as morphology, geology, and climate. We used the maps, available for the entire region, to define STUs within the LdG watershed. We identified 142 STUs in 14 SMUs, whose soil properties we took from the STU with the largest surface area in each SMU. Since some SMUs had similar characteristics, we ultimately represented all soils in the LdG watershed with seven SMUs, using their areas and biophysical characteristics as soil parameters in the models (Table S5). Soil type locations are shown in Figure S2.

In the LdG watershed, soils developed on acidic rock (granite or schist) are usually high in total SOM, some of which is stable. Like other soil N models, Syst'N is sensitive to SOM content when predicting N mineralization, but the total SOM stock measured does not directly represent the active SOM pool in the model. To avoid overestimating soil N mineralization, we calibrated SOM content of the seven soils to agree with a range of N mineralization measured in this region,[40] which resulted in a range of SOM of 2.4–3.3% for the first soil horizon at 0–30 cm.

To run simulations, we considered the spatial organization of cropping systems and soil types in the watershed; thus, we simulated only existing combinations of cropping systems and soil types. Each cropping system was simulated over the rotation period with Syst'N on the corresponding soil types of the watershed, resulting in 211 simulations. For each simulation, daily NO_3 and NH_3 emissions predicted by the model were summed for each cropping system, then averaged over the rotation duration, to express final results per year and per hectare for each cropping system.

2.3.3. Simulation Analysis. Syst'N predictions for each cropping system were first analyzed statistically to assess variability in its N emissions among soil types. To do so, standard deviations (SD) were determined to quantify variability in NO_3^- and NH_3 emissions due to differences in soil type. Mean emissions of the 11 cropping systems were then compared to those of AGRIBALYSE to determine the pertinence (quality/cost) of using Syst'N for an agricultural territory. Next, we sought to identify factors explaining differences in Syst'N predictions of N emissions. Multiple factor analysis (MFA) and hierarchical clustering on principal components (HCPC) were performed to create a cropping system typology and identify the relative influence of input variables likely to influence differences in predicted NO_3^- and NH_3 emissions: fertilization equivalent, soil cover during the drainage period, soil depth and SOM. Linear regressions were then calculated to explain the influence of management practices and biophysical characteristics in the watershed on the variability in NO_3^- and NH_3 emissions.

2.3.4. Sensitivity Analysis Using Syst'N. We performed a sensitivity analysis to quantify the influence of two input parameters—soil and climate—on emissions of NO_3^- and NH_3 predicted by Syst'N. Two major soil properties influence NO_3^- emissions and possibly NH_3 emissions: depth and SOM content. We tested four combinations of them: shallow with low SOM (90 cm, 2.4%), shallow with high SOM (90 cm, 3.3%), deep with low SOM (140 cm, 2.4%) and deep with high SOM (140 cm, 3.3%). Among climate properties, temperature and rainfall influence NO_3^- and possibly NH_3 emissions. Since mean annual temperature varied little among years in our weather data set, we tested three contrasting rainfall regimes (dry, average and rainy):

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Table 2. Mean and Standard Deviation (SD, i.e., Variability Due to Soil Type) of NO_3 and NH_3 Emissions Predicted by AGRIBALYSE and Syst'N Per Cropping System[a]

	AGRIBALYSE				Syst'N			
	NO_3^- (kg N·ha^{-1}·yr^{-1})		NH_3 (kg N·ha^{-1}·yr^{-1})		NO_3^- (kg N·ha^{-1}·yr^{-1})		NH_3 (kg N·ha^{-1}·yr^{-1})	
cropping system	mean	SD	mean	SD	mean	SD	mean	SD
M−C	41	9	17	0	61	12	6	0.03
M−C−C	38	8	15	0	49	7	9	4
M−M−C	33	8	14	0	51	8	15	0.06
M−C−M−C−Cau	29	6	12	0	73	8	5	1
M−C−R−C	34	12	15	0	44	8	10	0.04
M−C−Gm	21	2	8	0	25	7	6	2
M−M−M−C−Gm	26	6	11	0	39	6	4	3
Gm	20	0	8	0	32	17	25	8
Gg	20	0	8	0	61	14	19	12
Gm(nf)−C	18	2	7	0	29	2	12	1
Gm(f)−C	18	2	7	0	46	9	24	1
mean	27	5	11	0	46	9	12	4

[a]M: Maize preceded by a catch crop. C: Winter cereal (i.e., wheat, triticale, barley). Cau: Cauliflower. R: Rapeseed. Gm: Mixed grasslands (cut and grazed). Gg: Grazed grasslands with fertilizers. nf: Non-fertilized. f: fertilized.

- 488 mm of annual rainfall (September 2010 to August 2011), which corresponds to a dry winter (September to April) (312 mm). Winter drainage was approximately 50 mm.
- 972 mm of annual rainfall (September 2008 to August 2009), which corresponds to an average winter (714 mm). Winter drainage was approximately 450 mm.
- 1363 mm of annual rainfall (September 2013 to August 2014), which corresponds to a wet winter (1052 mm). Winter drainage was approximately 800 mm.

The sensitivity analysis was applied to five cropping systems (M−C, M−C−M−C−Cau, M−C−R−C, M−C−Gm, and Gm) to encompass the diversity of crops and management practices among cropping systems.

3. RESULTS AND DISCUSSION

3.1. Predicted N Emissions from Cropping Systems Using AGRIBALYSE and Syst'N. Using AGRIBALYSE, mean (±1 SD) N emissions predicted for the 11 main cropping systems in the LdG were 27 (±8) kg N-NO_3/ha, and 11 (±4) kg N-NH_3/ha (Table 2). N emissions predicted for all 33 cropping systems were similar: 26 (±7) kg N-NO_3/ha and 10 (±3) kg N-NH_3/ha (Table S6).

Using Syst'N, mean (±1 SD) N emissions predicted for the 11 main cropping systems in the LdG were 45 (±15) kg N-NO_3/ha, and 12 (±7) kg N-NH_3/ha (Table 2). Mean (±1 SD) N emissions predicted for all 33 cropping systems were similar: 42 (±14) kg N-NO_3/ha and 12 (±8) kg N-NH_3/ha (Table S7). Thus, we can consider that the 11 cropping systems are representative of all cropping systems in the LdG watershed for NO_3 and NH_3 emissions.

3.2. Comparison of NO_3^- Emissions Predicted by AGRIBALYSE and Syst'N. For the LdG case study, AGRIBALYSE models considered soil variability only due to differences in its SOM content, resulting in two estimates of NO_3^- emissions for each cropping system (Figure 1). Differences in NO_3^- emissions between soils with low (<3%) and high (>3%) SOM content ranged from 3 to 23 kg N/ha/year. No differences between these two soil types were observed for grassland cropping systems (Gm and Gg), since AGRIBALYSE does not consider soil variability in grasslands.

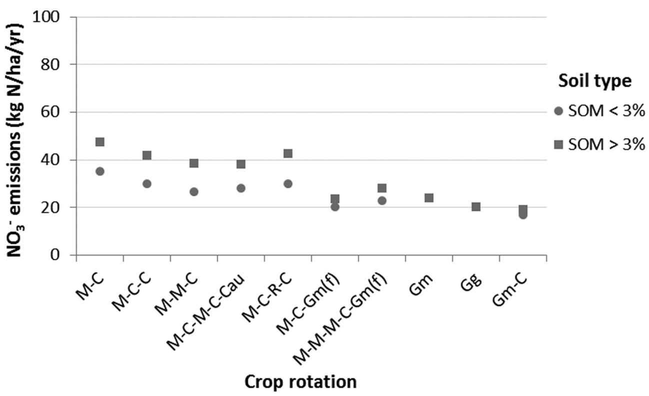

Figure 1. NO_3^- emissions (kg N/ha/yr) from cropping systems estimated by AGRIBALYSE model for soils with soil organic matter (SOM) content less than or greater than 3%. See Table 1 for definitions of the crop-rotation abbreviations.

On the other hand, NO_3^- emissions predicted by Syst'N varied for all cropping systems according to differences in soil types (Figure 2). Differences in predicted NO_3^- emissions ranged from 5 to 40 kg N/ha/year. Soils with the lowest and highest NO_3^- emissions predicted by Syst'N (numbers 402 and 1028, respectively) differed in texture (57% silt vs 51% sand, respectively) and depth (125 vs 102 cm, respectively). NO_3^- leaching of the rotation M-C-Gm was lower than that of other cropping systems because it was found in two organic farms with unusually low applications of organic fertilizer. Comparing the two models, AGRIBALYSE models estimated mean NO_3^- emissions 3−37 kg N/ha/year, i.e. 10−67% lower than those predicted by Syst'N (Figure 3). The main reason for these differences, besides AGRIBALYSE's assumption of "well managed" crops compared to Syst'N's simulation of real management practices, is the difference in modeling between AGRIBALYSE and Syst'N. Indeed, Syst'N considers a wider range of local conditions to predict NO_3^- and NH_3 emissions, and therefore its results are expected to be more realistic than those of AGRIBALYSE. Another important point is that Syst'N considers soil N dynamics at the scale of an entire rotation, which AGRIBALYSE's crop-by-crop approach does not do. These results are consistent with those of Liao et al.,[16] who

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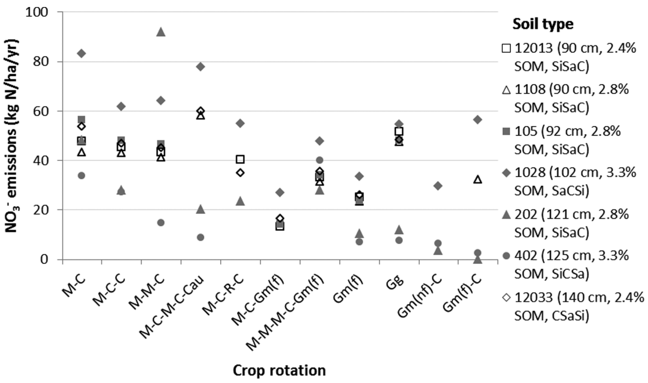

Figure 2. NO_3^- emissions (kg N/ha/yr) from cropping systems estimated by the Syst'N model for each of the seven soil types studied in the Lieue de Grève watershed. Soils in the legend are listed in order of increasing depth and characterized in term of soil type code, depth, SOM %, texture code (Si: silt; Sa: sand; C: clay), see Table S7 for the whole soil types description. See Table 1 for definitions of the crop-rotation abbreviations.

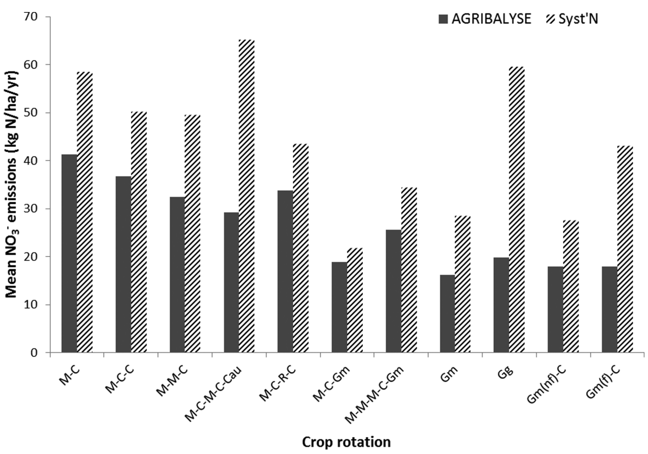

Figure 3. Comparison of mean NO_3^- emissions (kg N/ha/yr) from cropping systems estimated by AGRIBALYSE and Syst'N models. See Table 1 for definitions of the crop-rotation abbreviations.

found a difference in estimated NO_3^- emissions between AGRIBALYSE and TNT2 of 2−70 kg N/ha.

3.3. NO_3^- Emission Sensitivity to Soil and Climate.

Syst'N predictions of NO_3^- leaching increased with annual rainfall for all cropping systems, which is consistent with observations in the literature (Figure S4). Predicted NO_3^- leaching also increased for deeper soils and those with higher SOM content, because for a given SOM content, deep soils (∼140 cm) in the LdG induce more mineralization than shallow soils (∼90 cm). This is due to soil texture and its percentage of stones, which directly influence the amount of NO_3^- that can potentially mineralize. In addition, soil characteristics (including depth) also affect growing-degree days of crops, whose transpiration influences soil moisture and thus the amount of NO_3^- mineralized. Finally, Syst'N is known to somewhat overestimate the influence of the percentage of stones on predicted soil moisture. In very rainy years, both deep and shallow soils are completely leached, and in our study, deep soil contained more NO_3^- than shallow soil. In dry or medium years, soil depth had an important effect, because only some of the NO_3^- present in the soil had time to be leached during the winter, depending on soil depth.

3.4. Factors Influencing N Emissions.

The MFA and HCPC identified three clusters that explained 58% of total variance (Figure S3). The first axis opposed fertilization and high NO_3^- and NH_3 emissions vs soil-cover indicators and low NO_3^- and NH_3 emissions, while the second axis was driven by soil properties. Cluster 1 contained cropping systems with high fertilizer inputs and high NO_3^- and NH_3 emissions, mainly those dominated by annual crops. Most of them were located on deep soils with high SOM. Mean (±1 SD) emissions for cluster 1 were 92 (±15) kg N-NO_3^-/ha and 17 (±9) kg N-NH_3/ha. Clusters 2 and 3 contained cropping systems with lower fertilizer input and lower NO_3^- and NH_3 emissions, mainly those with grasslands (permanent or in rotation with crops), on shallow soils with low SOM for cluster 2 and on deep soils with high SOM for cluster 3. Mean (±1 SD) emissions were 35 (±14) kg N-NO_3^-/ha and 11 (±6) kg N-NH_3/ha for cluster 2 and 30 (±12) kg N-NO_3^-/ha and 7 (±2) kg N-NH_3/ha for cluster 3.

MFA and HCPC clustering provided an initial overview of cropping system N emissions in the LdG watershed. We observed a positive linear correlation between fertilizer inputs and NO_3^- or NH_3 emissions (Figure 4a and b). Even though

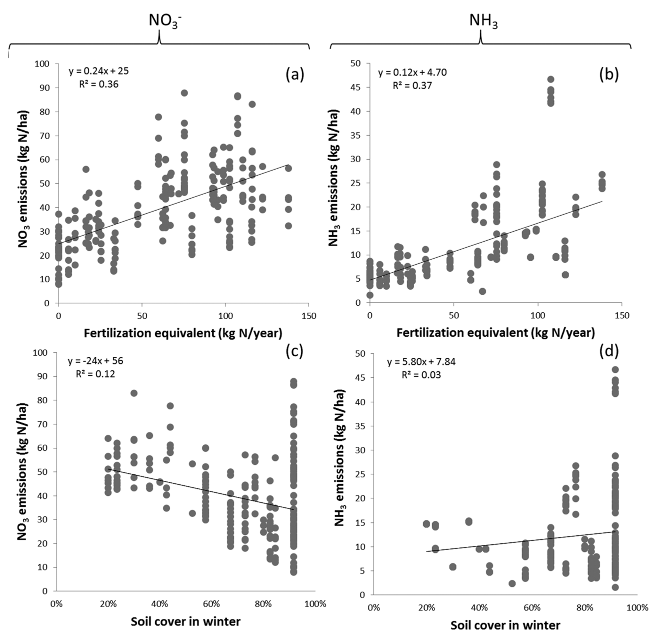

Figure 4. NO_3^- and NH_3 emissions predicted by Syst'N for combinations of soil type and cropping system in the Lieue de Grève watershed as a function of (a and b) fertilization equivalent and (c and d) soil cover indicator.

correlations were weak (R^2 = 0.36 and 0.37, SD_{slope} = 1.56 and 0.76, $SD_{intercept}$ = 0.02 and 0.01, significance of F value = 1.46 × 10^{-23} and 3.65 × 10^{-24}, respectively), trends for NO_3^- and NH_3 emissions were as expected. Cropping systems with low fertilizer inputs were more likely to produce low mean NO_3^- and NH_3 emissions, which may have been related in part to the lower variability in emissions from such cropping systems (Figures 4a and b). Cropping systems with low soil cover in winter were more likely to leach more NO_3^-, but the correlation was weak (R^2 = 0.12, SD_{slope} = 3.27, $SD_{intercept}$ = 4.42, significance of F value = 1.70 × 10^{-7}), due to high variability in emissions from and management of grasslands (from cut to intensively grazed) (Figure 4c). No trend was

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observed between soil cover in winter and NH_3 emissions (Figure 4d, R^2 = 0.03, SD_{slope} = 1.69, $SD_{intercept}$ = 2.28, significance of F value = 0.01) since crops tended to receive chemical fertilizers, while grassland-based systems again showed high variability in management practices and thus high variability in NH_3 emissions.

Variability in emissions thus results from several interacting factors. Emissions predicted by Syst'N differ because of interactions between management practices (e.g., fertilization) and biophysical characteristics of the watershed (e.g., soil type), something that simpler models or emissions factors cannot simulate.

4. METHODOLOGICAL DISCUSSION

4.1. Using Syst'N in LCA. Syst'N can represent both spatial and temporal dimensions of cropping systems, something that static models build to assess emissions of one crop cannot do. When studying impacts in a region (e.g., a watershed), as the obvious functional unit is area-based, it is an advantage to consider impacts of one hectare of land over a certain time period. In such a case, using N emissions from cropping systems as LCA input makes sense, and using a simulation model such as Syst'N to predict these emissions per ha is fairly straightforward.

Most LCA studies, however, study impacts of products, for which the obvious functional unit is mass-based, for example, 1 kg of wheat. In such a case, using Syst'N remains useful, but it becomes necessary to allocate N emissions among the crops (i.e., crops and their associated intercrops) in crop rotations. Several methods to allocate NO_3^- emissions are possible: (1) equally among all crops; (2) according to each crop's duration; (3) according to each crop's N balance or (4) based on the local drainage (i.e., natural removal of surface and subsurface water from a field) period (if present), as suggested by Liao et al.[16] Allocating NO_3^- emissions equally among crops is the simplest method, but it may not represent reality since different crops and management practices do result in different NO_3^- emissions in the real world. In contrast, allocating NO_3^- emissions according to the duration of each crop considers both crop types and practices. In this method, one sums the NO_3^- emitted from the sowing of one crop to the sowing of the following crop ("StS") and allocates it to the first crop. StS allocation may bias emission estimates, however,[16] since crops with shorter StS intervals are attributed lower NO_3^- emissions, even though they may have high NO_3^- emissions. Indeed, crops such as maize can be sown and harvested between two drainage periods, when NO_3^- accumulates in the soil. Since this NO_3^- is then leached during the next drainage period, using StS allocation for an autumn-sown following crop will therefore allocate the stored NO_3^- to the following crop rather than to the maize.

The third method attempts to avoid this bias by calculating, for each crop in the rotation, an N balance, which equals N input (from one or more sources, such as N fertilizer and N fixation) minus N output (N in aboveground crop biomass removed from the field). The N balance indicates whether any "surplus" N can be lost from each crop by any pathway (e.g., nitrate leaching, ammonia volatilization). This value, expressed as a percentage of total N surplus of all crops in the rotation, can be used to allocate total nitrate leaching among these crops.

The fourth method, allocating NO_3^- emissions based on the local drainage period, attempts to capture lag times between surplus soil N and NO_3^- emissions. In this method, one sums NO_3^- emissions from the beginning of the drainage period to beginning of the next one and allocates the sum to the crop present at the beginning of the period. This method allows more realistic allocation of NO_3^- emissions to the crops at the origin of these emissions. It still may have a bias, however, since some crops (e.g., wheat) can be fertilized during the drainage period. In this case, NO_3^- emitted due to fertilization early in the year can be allocated to the previous crop. Given differences and uncertainties in these methods, research is still needed in this area.

4.2. Limits of Using Syst'N in LCA. *4.2.1. Data Availability and Uncertainty.* Syst'N requires less input data than other mechanistic N simulation models (e.g., STICS, CERES-ECG). Nonetheless, it requires a large set of data on agricultural practices, soil and climate. One challenge was to use only available data: in our case study, most of the necessary data had already been collected or were available in local databases. To apply it to another watersheds would require access to extensive surveys of several farms (i.e., cropping system types and management), which are often difficult to obtain and time-consuming. Fortunately, soil and climate data are increasingly available from national soil and climate databases at scales more suitable for territorial LCA.

Despite access to high-quality data, uncertainties in input data remain. Data on farm practices were obtained from surveys, whose data are not always reliable for crops and difficult to obtain for grasslands. As mentioned, data gaps regarding management practices in grasslands were filled with expert knowledge, which contributed to uncertainties in Syst'N predictions of N emissions. Moreover, this study was based on data from a watershed in which long-term efforts to reduce NO_3^- emissions led to better fertilization practices (and that varied less among farms) than those in less NO_3^--sensitive areas in Brittany. Thus, for these cropping systems, we cannot conclude which parameter influences variability in NO_3^- emissions the most. To do so would require a dedicated study, which we recommend for future research.

Soil types were defined on the basis of SMUs, whose soil properties (e.g., depth, SOM) came from the STU with the largest area in each SMU. To refine these soil classes, soil types could be defined at the STU level. The Sols de Bretagne database is currently spatializing STUs in Brittany, which could be used to refine soil properties in future modeling studies.

4.2.2. Model Availability and Uncertainty. Some of the uncertainty in Syst'N predictions also comes from the model itself. As in all crop simulation models, equations in Syst'N cannot reproduce exactly the processes influencing N fluxes.[41] This is why, before application, predictions of such models should be compared to local measured data or to results of expert local models. We used Syst'N in western France, the region for which it was calibrated;[11] using it in other regions would require adaptations or at least additional calibration. In particular, its mineralization submodel is currently being improved by considering active SOM instead of total SOM when simulating mineralization. Using Syst'N in LCA is therefore recommended if the goal and scope of the study requires considering local conditions when assessing cropping systems. For example, territorial LCA using Syst'N can evaluate effects of land-planning scenarios on nitrate emissions in sensitive coastal watersheds, which tend to have extensive survey and monitoring data. Use of Syst'N (or any other field-scale simulation model), however, renders large-scale assessment more difficult.

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4.3. Recommendation. Syst'N predicts N emissions of cropping systems at the field scale by simulating daily N fluxes in the soil-crop-atmosphere system, while AGRIBALYSE estimates N emissions using emissions and risk factors. Therefore, to estimate N emissions at the regional scale, we strongly encourage the use of more refined models such as Syst'N. Syst'N has several advantages at the regional scale: it can predict the influence of management practices and biophysical conditions on N emissions more precisely. The choice of model will depend on the goal and scope of the study. For global assessment, such as environmental labeling of food products in a country, AGRIBALYSE seems most pertinent. At the regional scale, Syst'N allows more detailed assessment by taking differences in local conditions into account. Simulation modeling of N emissions is therefore recommended for regional land-planning scenarios.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b03865.

Details on calculation of the nitrate risk factor in the AGRIBALYSE model, monthly rainfall, evapotranspiration, and mean temperature for a mean year, a dry year, and a rainy year at the Trémel station, map of the seven dominant soil types studied in the Lieue de Grève watershed, clustering multifactorial analysis, followed by hierarchical clustering on principal 54 components, on dimensions 1 and 2 of the multifactorial analysis, sensitivity analysis of Syst'N predictions, input data needed by the AGRIBALYSE and Syst'N models, characteristics of cropping systems in the Lieue de Grève watershed, calculation of crop risk factors, basic data extracted from the biophysical description of the seven dominant soil types within the Lieue de Grève watershed and distribution of the 11 main cropping systems, and mean NO_3^- and NH_3 emissions estimated by the AGRIBALYSE and Syst'N models for each cropping system (PDF)

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The authors declare no competing financial interest.

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