



# Soil N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> Fluxes in Forest, Grassland, and Tillage/No-Tillage Croplands in French Guiana (Amazonia)

Caroline Petitjean <sup>1,2</sup>, Cécile Le Gall <sup>1</sup>, Célia Pontet <sup>3</sup>, Kenji Fujisaki <sup>4</sup>, Bernard Garric <sup>3</sup>, Jean-Claude Horth <sup>5,6</sup>, Catherine Hénault <sup>7</sup> and Anne-Sophie Perrin <sup>8,\*</sup>

- <sup>1</sup> Terres Inovia, 78850 Thiverval-Grignon, France; caroline.petitjean@agroparistech.fr (C.P.); c.legall@terresinovia.fr (C.L.G.)
- <sup>2</sup> Université de Lorraine, AgroParisTech, INRA, Silva, 54000 Nancy, France
- <sup>3</sup> Terres Inovia, 31326 Castanet-Tolosan, France; c.pontet@terresinovia.fr (C.P.); b.garric@terresinovia.fr (B.G.)
- <sup>4</sup> Eco&Sols, Université de Montpellier, CIRAD, INRA, IRD, Montpellier SupAgro, 34060 Montpellier, France; kenji.fujisaki2@gmail.com
- <sup>5</sup> Terres Inovia, 97355 Macouria, Guyane française; jean-claude.horth@guyane.chambagri.fr
- <sup>6</sup> Chambre d'Agriculture de Guyane, 97333 Cayenne CEDEX, Guyane française
- <sup>7</sup> Agroécologie, AgroSup Dijon, INRA, Université de Bourgogne, Université de Bourgogne Franche-Comté, 21000 Dijon, France; catherine.henault@inra.fr
- <sup>8</sup> Terres Inovia, Eco&Sols, Université de Montpellier, CIRAD, INRA, IRD, Montpellier SupAgro, Campus de La Gaillarde, 34060 Montpellier, France
- \* Correspondence: as.perrin@terresinovia.fr; Tel.: +33(0)-4-99-61-30-45

Received: 6 December 2018; Accepted: 29 March 2019; Published: 11 April 2019



**Abstract:** The agricultural landscape of French Guiana (Amazonia) is expected to undergo substantial change as a result of rapid population growth in the region. Such changes in the landscape will lead to the conversion of tropical forests into land destined for agricultural use. Little information is available on the effect of different agricultural systems on greenhouse gas (GHG) emissions in French Guiana. For our experiment, two hectares of forest were cleared, without the use of fire, at the Combi experimental site (sandy-clayey Ferralsol) at the end of 2008. After one year with legume and grass cover, the site was modified to include the following three fertilized agricultural systems: (1) Grassland (*Brachiaria ruziziensis*, mowed), (2) cropland (maize/soybean rotation) with disc tillage, and (3) cropland (maize/soybean rotation) with no-tillage in direct seeding. Soil N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> fluxes were measured with dark chambers from May 2011 to November 2014. Our results show that grassland was a significantly lower emitter of N<sub>2</sub>O but a significantly higher emitter of CH<sub>4</sub> compared to the two cropland systems for N<sub>2</sub>O and CH<sub>4</sub> fluxes. Measurements of the net ecosystem CO<sub>2</sub> exchange would be useful to better compare the role of different agricultural systems as a source of GHGs.

**Keywords:** Amazonia; soil CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O fluxes; Ferralsol; fertilized annual crops; fertilized grassland; French Guiana; land-use change; sandy-clayey soil; tropical forest

# 1. Introduction

French Guiana is an overseas region of France located in Amazonia, South America. The demographic growth in French Guiana is rapid: The population, 259,865 inhabitants in 2015 [1], is expected to reach 574,000 inhabitants by 2040 [2]. Tropical forest covers more than 90% of the land surface in French Guiana [3]. Nevertheless, the population growth has led to urban and agricultural expansion to the detriment of forests. Indeed, for the 2008–2012 period, deforestation occurred at a rate



of 3300 haper year, and the deforested land was mainly converted into cropped areas for subsistence farming or family/small-scale farming and for infrastructure development [4]. As is common in other tropical humid regions, slash-and-burn practices are widely used by French Guianese farmers [5,6]. However, deforestation by burning causes the release of much larger quantities of greenhouse gas (GHG) compared to the quantity released by natural decomposition of deforested biomass. Burning has been estimated to multiply the global warming potential of the deforestation process by a factor of 5 (over a 100-year period) compared with a fire-free alternative, and the exacerbated effects are primarily due to methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ) emitted during the burning phase [7]. Biomass burning also leads to the direct loss of organic matter and chemical elements (e.g., N, P, K, Mg, Ca) from soils by volatilization or ash-particle transfer as well as rapid drainage [8–10], particularly in hilly reliefs such as those on the Guiana shield. Finally, burning forests might have secondary negative influences on the health of local populations. Indeed, in the Brazilian Amazon, Farella et al. [11] showed that biomass burning led to a loss in soil mercury content: Mercury leached into the rivers and became a potential health threat through aquatic chain contamination. Thus, it would be preferable if, in the effort to provide more land for agricultural and therefore food production purposes, French Guiana chose to use fire-free deforestation methods rather than slash-and-burn practices and considered developing agricultural practices that would reduce the GHG budget.

The effects of land-use changes in tropical areas on GHG fluxes are still too poorly documented and constrained over the world to determine comprehensive annual estimates. In Amazonia, carbon (C) and nitrogen (N) biogeochemical cycling perturbations after the conversion of tropical forest into agricultural areas were mainly studied in Brazil using chronosequence (synchronic) approaches. Comparisons of  $N_2O$ ,  $CH_4$ , or carbon dioxide ( $CO_2$ ) fluxes between (secondary or primary) forest and pastures were investigated (often separately) in the context of degraded/active cattle pastures or the restoration process of pastures, all of which were installed after forest burning. To assess the impact of forest conversion into pasture on GHG emissions, several studies have been carried out in the Rondônia state (Southwestern Brazilian Amazonia) on Acrisol (e.g., [12–17]) and in the Pará state (Eastern Brazilian Amazonia) on Ferralsol (e.g., [18,19]), and the pastures in these studies were managed without N mineral inputs. From studying soil CH<sub>4</sub> fluxes, Steudler et al. [13] and Verchot et al. [19] highlighted that forest soils were a sink for  $CH_4$ , with maximum uptake during the dry season. Pasture soils were also found to consume CH<sub>4</sub> during the dry season but at lower rates than forest soils, and when soil moisture increased, active pasture soils became a source of CH<sub>4</sub> [13,19]. In the context of restoring pasture productivity, Passianoto et al. [20] evaluated the effects of soil tillage/no-tillage and fertilization on GHG fluxes; their study was also in the state of Rondônia (Brazil). For tillage treatment, soil CO<sub>2</sub> emissions and cumulative N<sub>2</sub>O emissions over the first two months following tillage (20 cm deep) were higher than those measured from no-tillage and control (i.e., unmanaged pasture) treatments. For both managed treatments (tillage and no-tillage), the highest soil  $N_2O$  fluxes were measured after N fertilization [20].

Data on GHG emissions from fertilized croplands in tillage or no-tillage regimes are scarce in Amazonia, although these practices are now significantly represented in this biome. In a recent review on N<sub>2</sub>O fluxes from soils for different land uses in Brazil, Meurer et al. [21] concluded that, until now, "pastures have been studied in rainforest biomes, and croplands in cerrado biomes. Therefore, no predictions can be made on the behavior of N<sub>2</sub>O fluxes from croplands in the rainforest biome". Further, CH<sub>4</sub> consumption by tropical soils and the impacts of crop and fertilizer types still need to be assessed in most agroecosystems to complete the data already acquired (e.g., [22,23]). In the Peruvian Amazon, Palm et al. [24] assessed N<sub>2</sub>O and CH<sub>4</sub> fluxes for croplands on Acrisol. In this study, average soil N<sub>2</sub>O fluxes from cropping systems were higher (2–3 times) than those from the forest (secondary forest), mainly because of N fertilization. In low-input cropping systems (30 kg N.ha<sup>-1</sup> as urea applied one time), average CH<sub>4</sub> consumption was reduced (by up to half) compared to forest soil, whereas in high-input cropping systems (100 kg N.ha<sup>-1</sup> as urea, with application split between two dates), net CH<sub>4</sub> production was measured [24]. The uncertainty of GHG assessments related to natural humid ecosystems, forests, and agricultural areas in the tropics and subtropics remains high because of the scarcity of data, with sampling periods that are often short. Further, GHG fluxes are characterized by high spatial and temporal variabilities (e.g., [25,26]) and hotspots and hot moments. McClain et al. [27] defined biogeochemical hotspots as "areas that show disproportionately high reaction rates relative to the surrounding area" and hot moments as "short periods of time that show disproportionately high reaction rates relative to longer intervening time periods". Thus, more data sets are needed to complete regional and global estimates that are already established (e.g., [28–32]). In tropical French Guianese forests, soil respiration (i.e.,  $CO_2$  fluxes) has been studied by several authors (e.g., [33–37]), but it was only recently that Courtois et al. [38] studied  $CO_2$ ,  $CH_4$ , and  $N_2O$  fluxes simultaneously in forest topographical positions. To our knowledge, these GHG fluxes from different agricultural systems in French Guiana have not been simultaneously assessed until now.

At the Combi experimental site (Ferralsol), two hectares were deforested using a fire-free method, called chop-and-mulch, and three fertilized agricultural systems were set up: (1) Grassland, (2) cropland with disc tillage, and (3) cropland with no-tillage in direct seeding. At this experimental site, Petitjean et al. [39] compared N<sub>2</sub>O fluxes from forest soils with those from the three agricultural systems between the 19th and 31st months after forest conversion. The same diachronic experiment was used by Perrin et al. [40] and Fujisaki et al. [41] to report the organic carbon changes in the soils at this site from forest to 5-year-old agricultural systems. Here, we propose to simultaneously measure the main GHG fluxes ( $CO_2$ ,  $CH_4$ ,  $N_2O$ ) from the three agricultural systems and forest. The objectives of this paper are to (1) provide a first assessment of major soil GHG fluxes for fertilized grassland and fertilized croplands in French Guiana, (2) compare GHGs from these different agricultural systems, (3) identify the best set of soil parameters that can explain the variation in GHG fluxes from these soils, and (4) improve regional (Northern Amazonia) trace gas data from agricultural soils. In light of the previous studies carried out in Amazonia, we hypothesized that grassland and croplands will be CH<sub>4</sub> emitters, at least during wet seasons [13,19,24], and that N fertilization will lead to higher soil N<sub>2</sub>O emissions [20,24,39]. We also hypothesized that the no-tillage cropland system will have lower soil  $CO_2$  emissions [20] and similar  $N_2O$  fluxes [39] relative to the disc tillage cropland system.

# 2. Materials and Methods

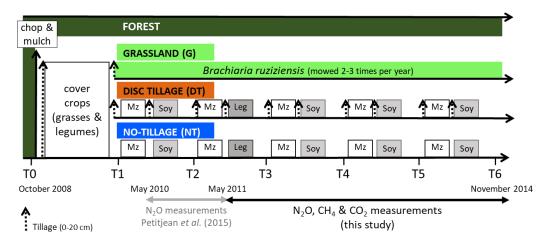
# 2.1. Study Site

The Combi experimental site (5°17′N, 52°55′W) is located 12 km south of Sinnamary, French Guiana, on the northeastern part of the Guiana Shield. The wet tropical climate (AMi type) is directly influenced by the seasonal north/south movements of the Inter-Tropical Convergence Zone, with a dry season from August to November (with monthly rainfall of less than 150 mm) and a wet season for the rest of the year. A short dry season in February/March usually interrupts the wet season. French Guiana shows a large precipitation gradient: From 1700 mm to 3500 mm from the northwestern to the southeastern part. The mean annual air temperature measured in Sinnamary is around 27 °C; evapotranspiration (Penman) is constant throughout the year, not exceeding 6 mm per day.

The sandy-clayey, nutrient-poor soil is classified as Hyperferralic Ferralsol [42]. This soil has a low water retention capacity and a porosity that favors vertical drainage. The slope of the site does not exceed 10% (for more information about forest soil parameters, see Perrin et al. [40]).

The clearing of two hectares of forest to establish pasture and croplands occurred in October 2008 (dry season) with the fire-free chop-and-mulch method. Trees and stems with small diameters were mechanically chopped, and residual trunks were piled in windrows and carefully removed from the site the following year. A grass–legume mixture was sown after the soil was limed and incorporated with discs to a 20 cm depth. In October 2009, this cover crop and the remaining large wood chips from the forest trees were chopped into smaller pieces and incorporated into the first 20 cm of soil (for more

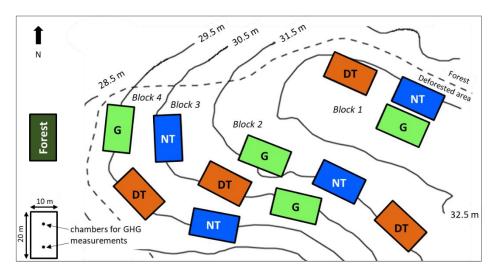
details about the chop-and-mulch method, see Perrin et al. [40]). Figure 1 shows the history of the Combi experimental site.



**Figure 1.** History of the Combi experimental site (French Guiana) from October 2008 to November 2014. After deforestation and one year with legume and grass cover, three agricultural systems were set up: Grassland (G) and croplands (maize/soybean rotation) with either disc tillage (DT) or no-tillage in direct seeding (NT). Mz = maize, Leg = legumes, Soy = soybean.

# 2.2. Experimental Design and Agricultural Systems

Over the deforested area, three agricultural systems were delimited with a randomized complete block design: Four blocks, i.e., four plots  $(10 \times 20 \text{ m})$ , per agricultural system (Figure 2). In the adjacent forest, one plot  $(10 \times 20 \text{ m})$  was also set up as a reference of the native ecosystem's soil parameters and GHG fluxes (Figure 2).



**Figure 2.** Experimental design at the Combi site (French Guiana): Randomized complete block design delimited over the deforested area. In the adjacent forest, one plot was also set up as a reference of the native ecosystem's soil parameters and GHG fluxes. Two chambers were installed for soil gas measurements within each experimental plot. G = grassland, DT = disc tillage cropland, NT = no-tillage cropland.

The three agricultural systems studied were the following:

• Grassland (G): Grassland of Brachiaria ruziziensis cv. ruzi mowed 2–3 times per year;

- Disc tillage (DT): Maize (*Zea mays* L.)/soybean (*Glycine max* L. Merr) crop rotation with disc tillage using two passes of a heavy disc harrow (0–20 cm);
- No-tillage (NT): Maize (Zea mays L.)/soybean (Glycine max L. Merr) rotation under no-tillage with direct seeding.

In 2011, because of a soybean seed supply problem, the soybean crop was replaced by a mixture of legumes (*Crotalaria juncea* and *Stylosanthes Campo Grande*) in the DT and NT systems (Figure 1).

The amounts of fertilizers and dolomite added to the three agricultural systems are shown in Table 1, as is the aboveground biomass production (yields and residues left on the field) (for more details, see Perrin et al. [40] and Fujisaki et al. [41]). The amounts of fertilizers were calculated using technical references published by Embrapa (Empresa Brasileira de Pesquisa Agropecuária = Brazilian Agricultural Research Corporation); we calculated nutrient balances on the basis of the needs of the crops and adjusted the values according to plant and soil analyses.

**Table 1.** Amounts of fertilizers (N,  $P_2O_5$ , and  $K_2O$ ) and dolomite (30% CaO, 20% MgO) added to the three agricultural systems (G: Grassland, DT: Disc tillage cropland, NT: No-tillage cropland) and aboveground biomass production (yields and residues left on the field). Means are computed for four crop cycles (2010–2014) and are followed by standard errors. Yields and residues of the mixture of legumes (in 2011) are included with soybean data. See Perrin et al. [40] for details.

System		N (kg ha <sup>-1</sup> year <sup>-1</sup> )	P <sub>2</sub> O <sub>5</sub> (kg ha <sup>-1</sup> year <sup>-1</sup> )	K <sub>2</sub> O (kg ha <sup>-1</sup> year <sup>-1</sup> )	Dolomite (t ha <sup>-1</sup> year <sup>-1</sup> )	Aboveground Biomass (t C ha <sup>-1</sup> year <sup>-1</sup> )		
G		50-60	50-60	50-60	1	Export	$4.76\pm0.68$	
9		30-00	30-00	30-00	1	Restitution	$1.85\pm0.34$	
	Maize	140–173	73-80	78-80		Yield	$2.10\pm0.08$	
DT	Walze	140-175	75-60	78-80	1	Residues	$3.43 \pm 0.10$	
	Soybean	0	72–80	78-80		Yield	$1.50 \pm 0.06$	
	ooybean			78-80		Residues	$2.29 \pm 0.21$	
	Maize	140–173	73-80	78-80		Yield	$2.10 \pm 0.12$	
NT	Widize	140-175	73-80	78-80	1	Residues	$3.37 \pm 0.17$	
	Soybean	0	72-80	78-80		Yield	$1.60 \pm 0.07$	
	eeybeun		72-00	70-00		Residues	$2.34 \pm 0.11$	

Soil carbon content was measured in the three agricultural systems each year from 2011 to 2014; the results are presented in Table 2.

**Table 2.** Soil carbon content (% dry matter) measured in three agricultural systems. Means are followed by standard error (n = 24). Letters indicate a statistical difference between systems computed with a Tukey test at p < 0.05. Italic letters refer to nonparametric analysis (Kruskal–Wallis test). See Perrin et al. [40] for details.

Date	System	0–5 cm	5–10 cm	
	Grassland	$2.00 \pm 0.08 \text{ a}$	$2.05\pm0.08~\mathrm{a}$	
T2—October 2010	Disc tillage	$2.03 \pm 0.08 \text{ a}$	$1.91\pm0.07~ab$	
-	No-tillage	$1.93\pm0.08~\mathrm{a}$	$1.72\pm0.06~b$	
	Grassland	$2.16\pm0.07~a$	$1.97\pm0.06~\mathrm{a}$	
T3—October 2011	Disc tillage	$1.84\pm0.06~b$	$1.86\pm0.05~\mathrm{a}$	
-	No-tillage	$1.84\pm0.06~b$	$1.60\pm0.04~b$	
	Grassland	$2.30 \pm 0.07 \text{ a}$	$2.07\pm0.08~a$	
T4—October 2012	Disc tillage	$1.86\pm0.06~b$	$1.75\pm0.04~b$	
-	No-tillage	$2.12 \pm 0.07 \text{ a}$	$1.68\pm0.06~b$	
	Grassland	$2.17 \pm 0.07$ a	$2.02 \pm 0.08 a$	
T5—October 2013	Disc tillage	$1.82\pm0.05b$	$1.75\pm0.05\;b$	
-	No-tillage	$1.99\pm0.07~ab$	$1.66\pm0.05b$	

#### 2.3. Measurements of Trace Gas Fluxes

Fluxes of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O were measured using dark circular chambers (fixed base + removable lid). The stainless-steel bases (diameter: 0.35 m, height: 0.16 m) were inserted 0.06 m into the soil surface, and the aluminum lids were placed onto the chambers just before GHG sampling. A securely bonded pressure-cooker seal ensured air-tightness. A reflective film insulated the bases and lids to minimize heating of the chambers. Two such gas sampling chambers were installed per plot, i.e., a total of eight chambers per agricultural system and two chambers for the forest plot (Figure 2). The two bases were placed in the middle of the plot in relation to the width of the plot (i.e., at 5 m from the edges) and at 5 and 15 m in the lengthwise direction (see Figure 2). In the cropland systems (DT and NT), chambers were set up in the inter-rows and thus did not include aboveground vegetation. Similarly, there was no aboveground vegetation included inside the chamber in the forest plot. Thus, for both cropland systems and forest, the  $CO_2$  emissions correspond to soil respiration (belowground autotrophic respiration + heterotrophic respiration). In the grassland system, because the chambers included Brachiaria ruziziensis, CO<sub>2</sub> emissions also included aboveground autotrophic respiration. Chamber bases were permanently installed. However, in the agricultural plots, for crop-related maintenance, the bases were periodically displaced during experimentation. GHG sampling was carried out at least 24 h after the chamber bases had been reinstalled [43]. As the soil surface was not completely level, the headspace volume of the chambers (around 10.5 dm<sup>3</sup>) was measured each time they were reinstalled.

Gas sampling was conducted during the morning. Gases were sampled through a rubber septum inserted into the lid. The chambers were sealed for 30 minutes, and three successive gas samples were taken (at 0, 15, and 30 minutes): 30 mL was extracted from chambers with a syringe and immediately introduced into a 12 mL vacuum glass vial (Labco<sup>®</sup>, Lampeter, UK) until completely filling it. Gas samples were then sent by air to the laboratory (UMR EcoSys, INRA, AgroParisTech, Université Paris-Saclay) in Grignon (France). Gas concentrations were analyzed using a gas chromatograph (model Clarus<sup>®</sup> 580 from PerkinElmer<sup>®</sup>, Waltham, USA) equipped with an electron capture detector (95:5 argon:methane) for N<sub>2</sub>O determinations and a flame ionization detector (helium) for CO<sub>2</sub> and CH<sub>4</sub> measurements. The integrity of the gas concentrations in the vials was tested using sets of standards, which were sent by air to French Guiana before being returned to the laboratory in Grignon (France).

Gas fluxes were calculated using a linear regression between concentration and time. Carbon dioxide fluxes that did not yield a linear regression with  $r^2 \ge 0.95$  were rejected. In such cases, we concluded that some problems had occurred (e.g., a leak in the chamber or in the glass vials); subsequently, N<sub>2</sub>O and CH<sub>4</sub> fluxes were also rejected for these samples.

Fifty GHG sampling campaigns were conducted between May 2011 and November 2014, corresponding to 400 single-chamber measurements for each agricultural system and 100 measurements for the forest. More intensive sampling was carried out during the transition period from the dry to wet season (from November to January), which also corresponded with soil tillage dates (in the DT system), crop residue mineralization periods, and around N fertilization events for maize (for both cropland systems).

## 2.4. Rainfall and Soil Parameter Measurements

Two rain gauges with a tipping bucket (model 3029, 0.5 mm/tip from Précis Mécanique, Bezons, France) were installed on site, enabling continuous rainfall measurements.

On each gas sampling date, composite samples of the 0–15 cm soil layer were collected from each plot for soil analyses. Gravimetric water content (GWC) (24 h at 105 °C) and mineral nitrogen extractions were undertaken at the laboratory (LAMA, IRD) in Cayenne (French Guiana). The extractions of mineral nitrogen were carried out in 50 mL of 1 M KCl solution for 10 g of soil. The Griess-Ilosvay and the Koroleff with indophenol blue methods were used to measure nitrate (NO<sub>3</sub><sup>-</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>) contents, respectively [44].

The temperature was measured in the top 10 cm of the soil of each plot using a Campbell Scientific 108 probe (30-min averages were registered in a data logger (Campbell Scientific CR1000)).

#### 2.5. Statistical Analyses

Statistical analyses were carried out with the software R version 3.4.3.

To test the effect of agricultural systems on soil GHG fluxes, we used linear mixed-effects models using agricultural systems as the fixed effects and block and sampling dates as the random effects (package lmerTest, [45]). Then, a Tukey post-hoc test was used to compare the agricultural systems.

To identify the soil parameters that best explain the variation in GHG fluxes, we used generalized additive models (GAMs) (package mgcv [46]), which allow nonlinear and nonmonotonic relationships. We selected the best model, i.e., the one that explained most of the variation, using the Akaike information criterion.

Analyses were carried out on mean GHG data per plot, i.e., four replications per agricultural system on each sampling date. To achieve normality and homoscedasticity, flux data were log-transformed as  $N_2O = log(N_2O + 1.1)$ ,  $CO_2 = log(CO_2)$ , and  $CH_4 = log(CH_4 + 60)$ . A probability level of 5% was used. As  $CO_2$  emissions from grassland plots included aboveground autotrophic respiration, these data were not included in statistical analyses. As the forest plot was not included in the randomized complete block design, no statistical analyses were done with forest data.

# 3. Results

#### 3.1. Rainfall

Annual rainfall at the Combi experimental site was 2899, 3260, 3139, and 2418 mm in 2011, 2012, 2013, and 2014, respectively. Monthly rainfall data collected during this study (from May 2011 to November 2014) are reported in Figure 3. In 2012, we observed a particularly long dry season (i.e., monthly rainfall of less than 150 mm) from the beginning of July 2012 to the end of January 2013. In 2011, 2013, and 2014, the dry season ranged from August to the end of November. In March 2014, the monthly rainfall was less than 150 mm; thus, data collected on 24 March 2014 were included as dry season data. Daily rainfall data are presented in Figure 4.

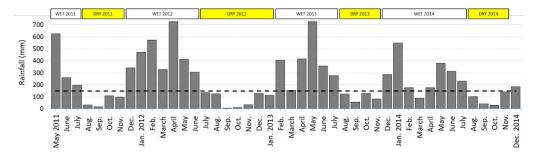
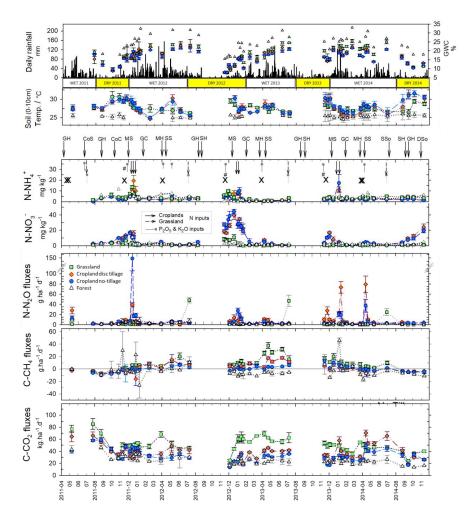


Figure 3. Monthly rainfall during the experiment (from May 2011 to November 2014) at the Combi site.



**Figure 4.** Daily rainfall, soil temperature (0–10 cm), soil gravimetric water content (0–15 cm), ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) contents (0–15 cm), fluxes of N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> for forest, grassland (G), cropland with disc tillage (DT), and cropland with no-tillage (NT) from May 2011 to November 2014 at the Combi experimental site. In grassland, CO<sub>2</sub> emissions included aboveground autotrophic respiration. GC: Regeneration cutting in G plots; GH: Grass harvest in G plots; CoS: Seeding of *Crotalaria* and *Stylosanthes* cover; CoC: Cutting of *Crotalaria* and *Stylosanthes* (residues were left on the soil surface); MS: Maize seeding; MH: Maize harvest; SS: Soybean seeding; SH: Soybean harvest; Sso: Sorghum seeding; DSo: Chemical destruction of sorghum. N inputs are 50–60 kg ha<sup>-1</sup> for each arrow except for croplands on 26 December 2012 (80 kg ha<sup>-1</sup>) and on 26 December 2013 and 06 January 2014 (75 kg ha<sup>-1</sup>). P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O inputs for each symbol are 60–80 kg ha<sup>-1</sup>, except in April and May 2012 (38 kg ha<sup>-1</sup>). Plain lines are for croplands and dashed lines are for grassland. X corresponds to disc tillage practice in the DT plots. **#** corresponds to dolomite inputs into all agricultural systems (1 t ha<sup>-1</sup>, 30% CaO and 20% MgO).

#### 3.2. Soil Parameters and GHG Fluxes

Soil parameters and GHG fluxes are presented as a time-series in Figure 4. Means and ranges for each parameter and GHG were calculated for the dry seasons and wet seasons. All data are shown in Table 3. Data are unavailable for the periods between August and November 2012 and from August to October 2013 as a result of technical issues. Thus, the fifty GHG sampling campaigns were grouped as follows: 19 dry season dates (i.e., monthly rainfall  $\leq$  150 mm) and 31 wet season dates. In the forest plot, additional technical problems prevented us from obtaining temperature data from 21 November 2011 to 29 March 2012 and from 22 January to 07 May 2013.

**Table 3.** Soil parameters and GHG fluxes measured in the three agricultural systems and in the adjacent native forest at the Combi experimental site. Values are computed for dry seasons (monthly rainfall  $\leq$ 150 mm), wet seasons, and all data (from May 2011 to November 2014). *n* = number of samples (for GHG, samples are the mean per plot). GWC = gravimetric water content, Temp. = temperature. For each GHG flux, means followed by the same letter did not differ significantly (ANOVA, *p*-value < 0.05).

		Forest		Grassland C			Crop	Cropland Disc Tillage		Cropland No-Tillage			
		Dry	Wet	All	Dry	Wet	All	Dry	Wet	All	Dry	Wet	All
Soil GWC	Mean ± SE	$21.3 \pm 1.0$	$26.9\pm0.9$	$24.8\pm0.8$	$15.2\pm0.5$	$20.8\pm0.3$	$18.7\pm0.3$	$14.2\pm0.4$	$19.2\pm0.3$	$17.3\pm0.3$	$14.0\pm0.4$	$18.3\pm0.2$	$16.7 \pm 0.2$
(%)	Range	15.0-32.0	19.0-40.0	15.0-40.0	9.0–30.0	12.0–29.0	9.0–30.0	8.0-25.0	8.0-32.0	8.0-32.0	8.0-23.3	13.0-25.0	8.0-25.0
	п	18	30	48	75	123	198	72	122	194	76	123	199
Soil Temp.	Mean $\pm$ SE	$25.4\pm0.1$	$25.2\pm0.1$	$25.3\pm0.1$	$28.2\pm0.2$	$27.2\pm0.1$	$27.6\pm0.1$	$28.8\pm0.2$	$27.3\pm0.1$	$27.9\pm0.1$	$29.0\pm0.2$	$27.5\pm0.1$	$28.1 \pm 0.1$
(°C)	Range	24.9-26.0	24.5-25.8	24.5-26.0	25.8-32.2	25.4-29.0	25.4-32.2	25.2-32.6	24.5-31.9	24.5-32.6	25.5-32.5	24.6-31.5	24.6-32.5
	п	17	17	34	75	123	198	72	122	194	72	123	195
NH4 <sup>+</sup>	Mean ± SE	$3.5 \pm 0.7$	$3.6 \pm 0.4$	$3.6 \pm 0.3$	$4.3\pm0.3$	$3.7\pm0.2$	$4.0\pm0.2$	$4.1\pm0.3$	$3.6 \pm 0.4$	$3.8 \pm 0.3$	$3.2 \pm 0.3$	$2.9\pm0.4$	$3.0 \pm 0.3$
(mg N kg <sup>-1</sup> soil)	Range	0.0–11.7	0.5–9.0	0.0–11.7	0.3–12.0	0.3–17.6	0.3–17.6	0.4–17.9	0.1-33.5	0.1-33.5	0.1–16.8	0.1–39.9	0.1–39.9
	п	17	30	47	87	123	210	84	122	206	88	123	211
NO <sub>3</sub> -	Mean $\pm$ SE	$2.4\pm0.3$	$2.3\pm0.3$	$2.4\pm0.2$	$3.1 \pm 0.4$	$0.8 \pm 0.1$	$1.8 \pm 0.2$	$16.2 \pm 1.3$	$4.0\pm0.5$	$8.9\pm0.7$	$16.5\pm1.4$	$3.8\pm0.4$	$9.1 \pm 0.8$
(mg N kg <sup>-1</sup> soil)	Range	0.4–4.7	0.7-10.9	0.4–10.9	0.1–19.8	0.1-4.9	0.1–19.8	0.6–51.9	0.2-22.5	0.2–51.9	1.1-54.7	0.3–17.8	0.3–54.7
	п	17	30	47	87	123	210	84	122	206	88	123	211
N <sub>2</sub> O Fluxes	Mean ± SE	$2.0\pm0.5$	$3.1 \pm 0.4$	$2.7 \pm 0.3$	3.5 ± 1.3	3.2 ± 0.9	3.3 ± 0.8 a	$7.4 \pm 1.0$	11.6 ± 1.9	10.0 ± 1.3 b	$6.0 \pm 0.9$	$11.5 \pm 2.7$	9.4 ± 1.7 b
(g N ha <sup>-1</sup> day <sup>-1</sup> )	Range	0.0-8.2	0.2–9.4	0.0–9.4	-0.2 to 55.0	-1.0 to 75.8	-1.0 to 75.8	0.1–56.6	0.0–139.0	0.0–139.0	1.0-47.4	0.5–231.8	0.5–231.8
	n	18	30	48	75	123	198	76	121	197	76	123	199
CH <sub>4</sub> Fluxes	Mean ± SE	$-3.1 \pm 2.6$	-2.9 ± 2.2	$-3.0 \pm 1.7$	3.3 ± 1.0	$10.0 \pm 1.0$	7.5 ± 0.8 a	$-0.8 \pm 0.6$	2.7 ± 1.0	1.4 ± 0.7 b	$-2.2 \pm 1.2$	$1.5 \pm 0.5$	0.2 ± 0.5 b
(g C ha <sup>-1</sup> day <sup>-1</sup> )	Range	-11.8 to 29.8	-26.2 to 45.9	-26.2 to 45.9	-12.5 to 24.3	-5.6 to 57.5	-12.5 to 57.5	-10.6 to 15.7	-58.6 to 44.7	-58.6 to 44.7	-58.6 to 35.2	-11.1 to 24.0	-58.6 to 35.2
	п	17	30	47	71	123	194	72	121	193	72	123	195
CO <sub>2</sub> Fluxes	Mean ± SE	23.9 ± 1.9	26.7 ± 1.2	25.6 ± 1.0	47.3 ± 1.9	52.3 ± 1.3	$50.4 \pm 1.1$	32.8 ± 1.4	$42.0\pm1.4$	38.4 ± 1.1 a	29.1 ± 1.4	34.8 ± 1.0	32.6 ± 0. b
$(\text{kg C ha}^{-1} \text{ day}^{-1})$	Range	13.6-42.8	18.2-45.2	13.6-45.2	20.4-95.9	20.9-112.1	20.4-112.1	14.3-66.9	15.0-98.0	14.3-98.0	12.2-65.6	16.6-66.3	12.2–66.
	n	18	30	48	75	123	198	76	121	197	76	123	199

As expected, the means of soil GWC measured during the wet seasons were higher than those measured during the dry seasons for each system (Table 3). For the forest, soil temperature remained relatively constant (around 25 °C) during the seasons. For deforested soils, the ranges of temperatures measured were wider, e.g., from 24.5 up to 32.6 °C in the disc tillage plots (Table 3).

For grassland, the highest  $NH_4^+$  and  $NO_3^-$  contents were measured on 15 December 2011 (mean ± SE: 13.5 ± 1.5 mg N kg<sup>-1</sup> soil) and on 20 December 2012 (10.7 ± 3.7 mg N kg<sup>-1</sup> soil), respectively. For both cropland systems, the highest  $NO_3^-$  contents were measured from November 2012 to the end of January 2013 (9 sampling dates during these 2 months), corresponding to the maize fertilization period (N inputs on 26 December 2012 and 04 January 2013). Maximum  $NO_3^-$  contents were measured on 20 December 2012 with 39.4 ± 5.1 and 44.3 ± 3.0 mg N kg<sup>-1</sup> soil (means per agricultural systems) for DT and NT, respectively. In 2011, 2013, and 2014, we observed the same pattern during the equivalent period, with increasing soil  $NO_3^-$  contents during the dry season (i.e., between September/October and December 2012 (Figure 4). The highest  $NH_4^+$  contents were measured during N inputs (maize fertilization) on 20 December 2011 for DT (19.4 ± 5.0 mg N kg<sup>-1</sup> soil) and on 07 January 2014 (17.3 ± 8.0 mg N kg<sup>-1</sup> soil) for NT.

Gas fluxes from forest soil were relatively constant throughout the duration of the experiment (Figure 4, Table 3). Three higher CH<sub>4</sub> emissions were recorded on 10 November 2011, 28 December 2011, and 07 January 2014 with 29.8, 23.0, and 45.9 g C ha<sup>-1</sup> day<sup>-1</sup> (mean per plot), respectively. Despite this, the means of the CH<sub>4</sub> fluxes from forest soil were negative for the dry and wet seasons (Table 3).

With regard to the three agricultural systems, higher  $N_2O$  emissions were measured, especially following N fertilization events (Figure 4). Some negative  $N_2O$  fluxes were measured in grassland, corresponding to approximately 4% of the measured fluxes. Grassland was a significantly lower  $N_2O$  emitter than both of the cropland systems. We did not observe a significant difference between the DT and NT cropland systems (Table 3).

Higher  $CH_4$  emissions were measured in grassland plots, especially from April to August 2013 (Figure 4); the means of  $CH_4$  emissions were positive for the dry and wet seasons (Table 3). For both croplands, the means of  $CH_4$  emissions were negative for the dry seasons and positive for the wet seasons (Table 3). Grassland showed significantly higher  $CH_4$  fluxes than both of the cropland systems; we did not observe a significant difference between the DT and NT cropland systems (Table 3).

Soil  $CO_2$  emissions were significantly higher in the DT plots than in the NT plots (Table 3).

The results from the GAMs (Table 4) showed that soil NO<sub>3</sub><sup>-</sup> content and GWC had a significant effect on all three GHG fluxes. Overall, in the agricultural systems, CH<sub>4</sub> fluxes increased as GWC increased; most of the negative fluxes (75% of the negative fluxes for the DT plots, 79% for the grassland plots, and 85% for the NT plots) were measured when GWC was  $\leq 18\%$  (Figure 5). For N<sub>2</sub>O fluxes, we observed a bell-shaped relationship; the highest emissions were measured around 20% soil GWC (Figure 5). Soil temperature had a significant effect on CO<sub>2</sub> and N<sub>2</sub>O fluxes, while NH<sub>4</sub><sup>+</sup> content had a significant effect on CH<sub>4</sub> fluxes (Table 4).

**Table 4.** Summary of the generalized additive models fitted for each GHG as a function of soil nitrate content ( $NO_3^-$ ), soil ammonium content ( $NH_4^+$ ), soil gravimetric water content (GWC), and soil temperature. For  $N_2O$  and  $CH_4$  fluxes, data of grassland and both croplands were used. For  $CO_2$  emissions, grassland data were excluded.

GHG	Models					<b>R</b> <sup>2</sup>				
N <sub>2</sub> O	$log(N_2O+1.1) \sim s(NH_4^+) + s(NO_3^-) + s(GWC) + s(temperature)$									
		Estimate	Std. Error	t value	$\Pr(> t )$					
	intercept	1.47	0.03	43.66	< 0.001					
		edf	Ref.df	F	<i>p</i> -value					
	$s(NH_4^+)$	2.48	3.09	2.54	0.06					
	s(NO <sub>3</sub> <sup>-</sup> )	7.99	8.73	25.35	< 0.001					
	s(GWC)	8.28	8.82	10.62	< 0.001					
	s(temperature)	1.00	1.00	6.75	< 0.01					
$CH_4$	$log(CH_4 + 60) \sim s(NH_4^+) + s(NO_3^-) + s(GWC)$									
		Estimate	Std. Error	t value	$\Pr(> t )$					
	intercept	4.13	0.01	457.60	< 0.001					
	-	edf	Ref.df	F	<i>p</i> -value					
	$s(NH_4^+)$	8.94	9.00	21.53	< 0.001					
	$s(NO_3^-)$	7.13	8.18	3.71	< 0.001					
	s(GWC)	1.00	1.00	7.22	< 0.01					
CO <sub>2</sub>	$log(CO_2) \sim s(NO_3^-)$	s + s(GWC) + s	(temperature)			0.29				
		Estimate	Std. Error	t value	$\Pr(> t )$					
	intercept	3.63	0.01	270.90	< 0.001					
	-	edf	Ref.df	F	<i>p</i> -value					
	$s(NO_3^-)$	5.05	6.15	15.69	< 0.001					
	s(GWC)	1.57	1.96	7.81	< 0.001					
	s(temperature)	5.39	6.56	10.35	< 0.001					
	240		•	Grasslan	d					
				Cropland	d Disc Tillage					
	190		•	Cropland	l No-Tillage					
				∆ Forest						
	1 d									
	e 140		<b>♦</b>							
	z									
	(g									
	oe xes									
	flu			i i						
	N <sub>2</sub> O fluxes (g N ha <sup>-1</sup> d <sup>-1</sup> ) 0 0 0 0			I						
	z									
	<b>8</b> 5				Δ					
	-10	ا الما الما حد حد حد جد جد ا								

CH<sub>4</sub> fluxes (g C ha<sup>-1</sup> d<sup>-1</sup>) Δ Δ -10 -30 Δ -50 -70 Soil Gravimetric Water Content (%)

**Figure 5.** Soil  $N_2O$  and  $CH_4$  fluxes from the three agricultural systems and the forest in relation to soil gravimetric water content at the Combi experimental site (GHG values are means per plot).

# 4. Discussion

#### 4.1. Soil N<sub>2</sub>O fluxes

In soils, N<sub>2</sub>O is produced by diverse abiotic and biotic (microbial) pathways [47]. The processes of aerobic nitrification (i.e., oxidation of  $NH_3$  or  $NH_4^+$  to  $NO_3^-$ ) and anaerobic denitrification (i.e., conversion of  $NO_3^-$  to  $N_2$ ) are considered to be the main contributors of  $N_2O$  emissions from natural and managed soils [48,49].

For the forest soil at the Combi experimental site, the mean N<sub>2</sub>O fluxes  $(2.7 \pm 0.3 \text{ g N ha}^{-1} \text{ day}^{-1})$  were on the same order as those previously obtained from the same experimental site in 2010–2011  $(3.8 \pm 0.5 \text{ g N ha}^{-1} \text{ day}^{-1})$  [39] and slightly lower than those measured in Brazilian forest, whose values were between 4.7 and 11.8 g N ha<sup>-1</sup> day<sup>-1</sup> [15,17,18,50]. We did not measure negative N<sub>2</sub>O fluxes in forest soil, as were reported by Courtois et al. [38].

For grassland plots, mean N<sub>2</sub>O fluxes  $(3.3 \pm 0.8 \text{ g N ha}^{-1} \text{ day}^{-1})$  were on the same order as those previously obtained from the Combi site between the 19th and 31st months after forest conversion  $(2.4 \pm 0.9 \text{ g N ha}^{-1} \text{ day}^{-1})$  [39]. Three higher fluxes were measured on 10 July 2012 (mean  $\pm$  SE:  $48.0 \pm 6.7 \text{ g N ha}^{-1} \text{ day}^{-1}$ ), 08 July 2013 ( $47.1 \pm 12.1 \text{ g N ha}^{-1} \text{ day}^{-1}$ ), and 30 June 2014 ( $24.8 \pm 24.8 \text{ g N ha}^{-1} \text{ day}^{-1}$ ) (Figure 4) and had considerable influence on the overall mean; without these higher fluxes, the mean N<sub>2</sub>O flux would be equal to  $1.0 \pm 0.1 \text{ g N ha}^{-1} \text{ day}^{-1}$ . These higher fluxes occurred after N fertilization events (Figure 4). Higher N<sub>2</sub>O fluxes were also measured for both croplands after N fertilization events (Figure 4). At the Combi experimental site, maize fertilization took place between December and January. This period also corresponds to the first rains following the dry season (Figures 3 and 4). Thus, we can assume that the rewetting of the soil and the availability of N (from N inputs) led to microbial hot moments (i.e., "short-term events or sequences of events that accelerate microbial processes as compared to the average rates", as defined by Kuzyakov and Blagodatskaya [51]) that led to N<sub>2</sub>O hot moments.

Nitrous oxide emissions generally remain low if there is low water content because of the overall low microbial activity in these conditions [52]. Maximum N<sub>2</sub>O emissions usually occurred for water-filled pore space (WFPS) ranging between 60 and 80%. In our study, we measured the highest N<sub>2</sub>O emissions at around a GWC of 20% (Figure 5), which corresponds to a WFPS of around 60% for soils with a bulk density of 1.4, which is the bulk density of agricultural soils at the Combi site (0-20 cm) [40]. In their meta-analysis, van Lent et al. [53] applied a Gaussian function to define the relationship between N<sub>2</sub>O fluxes and WFPS and confirmed that maximum N<sub>2</sub>O emissions occurred at around a WFPS of 60% for a tropical data set. We also observed a Gaussian function—or a bell-shaped relationship—between soil N<sub>2</sub>O fluxes and GWC (Figure 5). Such a distribution was previously observed by several authors during field experiments in agricultural soils (e.g., [57–59]) and laboratory experiments (e.g., [57–59]). Rabot et al. [60] also obtained the same type of relationship during a modeling approach and attributed the decrease in N<sub>2</sub>O fluxes at high water content to both the slow diffusion of gas through the soil and a high level of reduction of N<sub>2</sub>O to N<sub>2</sub>. In our study, mineral nitrogen was especially available, and the temperature was the highest when the GWC was intermediate, which could also contribute to the bell-shaped relationship.

The results of the GAM show that the best set of soil parameters explaining the variation in  $N_2O$  fluxes from agricultural soils included  $NO_3^-$  and  $NH_4^+$  contents and GWC (Table 4). Similarly, in their meta-analysis, van Lent et al. [53] highlighted that N fertilization (expressed as kg N ha<sup>-1</sup> year<sup>-1</sup>) and WFPS were the best variables for estimating  $N_2O$  fluxes from tropical agricultural soils (crops and pastures).

As observed by Petitjean et al. [39] from  $N_2O$  samples taken between the 19th and 31st months after forest conversion at the Combi site, we also found that  $N_2O$  emissions from grassland were significantly lower than emissions from croplands, yet there was no significant difference in  $N_2O$ fluxes between the two cropland systems. In the same manner, other studies conducted in Brazil (Ferralsol, clayey texture) found no significant difference between  $N_2O$  fluxes from tillage and those from no-tillage cropland systems [61,62]. Reduced or no-tillage can increase  $N_2O$  emissions when compared with tilled systems [63], especially in poorly aerated soils [64]. Indeed, no-tillage can increase soil water content and soil density (i.e., lower aeration), creating more favorable conditions for denitrification [65,66], often the main source of  $N_2O$  production in agricultural soils. However, in soils with good and medium aeration, Rochette [64] showed that no-till had no impact on  $N_2O$  emissions. The sandy-clayey soils that had low water retention capacity and low compaction at the Combi site might partly explain why the non-tillage of these soils did not lead to an increase in  $N_2O$  emissions.

#### 4.2. Soil CH<sub>4</sub> Fluxes

Soil CH<sub>4</sub> fluxes are the results of the balance between CH<sub>4</sub> production by methanogenic bacteria (during anaerobic digestion of organic matter) and its consumption by methanotrophic bacteria (i.e., oxidation of CH<sub>4</sub> to CO<sub>2</sub>): When the balance is positive, soil is a CH<sub>4</sub> emitter; when it is negative, the soil acts as a CH<sub>4</sub> sink [67].

Well-drained tropical forest soils have been reported to be a sink for CH<sub>4</sub> (e.g., [13,19,50,68,69]). In Central Rondônia (Southwestern Brazilian Amazonia), Steudler et al. [13] showed that forest soils were a sink for CH<sub>4</sub> during both the dry and wet seasons, with maximum uptake rates during the dry season. In the same way, mean CH<sub>4</sub> fluxes from forest soil at the Combi site were negative in the dry and wet seasons (Table 3). The mean CH<sub>4</sub> fluxes  $(-3.0 \pm 1.7 \text{ g C ha}^{-1} \text{ day}^{-1})$  we obtained for forest soil were on the same order as those measured by Courtois et al. [38] in other French Guianese forests. These authors observed an overall seasonal pattern of CH<sub>4</sub> fluxes from forest soils: A sink during the dry season (mean CH<sub>4</sub> fluxes equal to  $-6.6 \text{ g C ha}^{-1} \text{ day}^{-1}$ ) and a (moderate) source during the wet season (mean CH<sub>4</sub> fluxes equal to  $2.9 \text{ g C ha}^{-1} \text{ day}^{-1}$ ) [38]. We did not observe such seasonal patterns at the Combi site: The mean CH<sub>4</sub> fluxes were negative and almost similar for both the dry and wet seasons (Table 3).

Previous studies showed that the conversion of tropical forests to croplands or pastures can reduce the soil CH<sub>4</sub> sink [70,71]. Steudler et al. [13] showed that forest-to-pasture conversion led to a net source of CH<sub>4</sub> from soils (about 1 g CH<sub>4</sub> m<sup>-2</sup> year<sup>-1</sup>). Indeed, the soils of young pastures (created by the slash-and-burn technique) rapidly became CH<sub>4</sub> emitters (as early as 4 years after conversion), especially when soil moisture increased (i.e., during the wet season). The same trend was observed by Verchot et al. [19] in the state of Pará (Eastern Brazilian Amazonia): Active pastures produced CH<sub>4</sub> during the wet season, and that induced a lower annual CH<sub>4</sub> uptake compared with the primary forest. At the Combi site, the fertilized grassland *Brachiaria ruziziensis* was a net emitter of CH<sub>4</sub> (Table 3), despite some negative CH<sub>4</sub> fluxes measured. Nevertheless, we observed a seasonal trend: The mean CH<sub>4</sub> fluxes for the wet season were three times higher than those for the dry season (Table 3). We also observed a seasonal pattern for both cropland systems, with negative mean fluxes for dry seasons and positive ones for wet seasons (Table 3).

Water-filled pore space is a key factor driving CH<sub>4</sub> fluxes from tropical soils (e.g., [13,24,68]). Authors previously observed a shift from CH<sub>4</sub> consumption to CH<sub>4</sub> emission at around 40% WFPS for pasture soils (Brazilian Amazon) [13] or around 50% for six land management systems, including a high-input cropping system (Peruvian Amazon, loamy soil) [24]. At the Combi site, we found that GWC had a significant effect on CH<sub>4</sub> emissions (Table 4). Most of the negative CH<sub>4</sub> fluxes from agricultural soils were measured at a GWC  $\leq$  18% (Figure 5), i.e., WFPS of around 50%, which mainly occurred during the dry seasons.

Nitrogen fertilization at the Combi site mainly occurred during the wet seasons (Figure 4) and might partly contribute to the seasonal pattern we observed. Indeed, it has been shown (mainly under temperate climate conditions) that inorganic N inputs can act as inhibitors of methane oxidation (e.g., [72,73]), depending on the N species added [74]. However, other studies found an absence of inhibition or found stimulation of  $CH_4$  oxidation following N inputs (e.g., [75–77]).  $NO_3^-$  can also prevent methanogenesis [78]. Further research is required to better understand the interactions between ammonium, nitrate, and  $CH_4$  fluxes.

In the Peruvian Amazon, Palm et al. [24] found that annual crop systems (maize–soybean or maize–peanut) with high N inputs (100 kg N.ha<sup>-1</sup> as urea, with application split over two dates) were net CH<sub>4</sub> emitters, with annual average emissions of 1.33 kg C ha<sup>-1</sup> year<sup>-1</sup>, i.e., 3.6 g C ha<sup>-1</sup> day<sup>-1</sup> [24]. At the Combi site, the annual crop systems were also CH<sub>4</sub> emitters; however, the mean CH<sub>4</sub> fluxes were relatively low, especially for no-tillage cropland ( $0.2 \pm 0.5$  g C ha<sup>-1</sup> day<sup>-1</sup>, Table 3). We did not observe a significant difference in CH<sub>4</sub> fluxes between the two cropland systems (Table 3). These results are in agreement with the study conducted by Metay et al. [61] on Ferralsol in the Brazilian Cerrados. Indeed, these authors did not find a significant difference in CH<sub>4</sub> fluxes between the tillage treatment (offset or disc harrow, 0–15 cm) and the direct seeding mulch-based treatment with cover crops [61]. Similar to the case for N<sub>2</sub>O emissions, we can assume that the texture and the physical properties of the Combi soil might partly explain why no-tillage did not result in an increase of CH<sub>4</sub> emissions.

#### 4.3. Soil CO<sub>2</sub> Fluxes

The major components of the GHG balance are  $CO_2$  emissions [79]. Soil  $CO_2$  fluxes measured at the soil surface are the sum of belowground autotrophic respiration (roots) and heterotrophic respiration (microorganisms, invertebrates).

At the Combi site,  $CO_2$  emissions from forest soil ( $25.6 \pm 1.0 \text{ kg C ha}^{-1} \text{ day}^{-1}$ ) were on the same order as those measured by Janssens et al. [34] ( $23.8 \text{ kg C ha}^{-1} \text{ day}^{-1}$ ), yet lower than those measured by Courtois et al. [38] in other French Guianese forest soils (from 31.7 to 37.5 kg C ha<sup>-1</sup> day<sup>-1</sup> for dry and wet seasons, respectively).

Our results showed that soil CO<sub>2</sub> emissions were significantly lower in the NT system compared with the DT system. Similarly, Passianoto et al. [20] showed that, compared to the control treatment, CO<sub>2</sub> fluxes increased (37%) over the first two months following tillage (tillage plots) and decreased (7%) over the same period in the no-tillage/herbicide plots (Brazil, Rondônia state). These results are consistent with the fact that the tillage process leads to a large quantity of easily decomposable organic matter and exposes protected organic matter to decomposition by soil microorganisms.

At the Combi site, Fujisaki et al. [41] showed that soil organic carbon (SOC) stocks (0–30 cm layer) did not differ between the DT and NT systems five years after the conversion of forest to agriculture. The authors explained this result by the similarity of the C inputs in the two cropland systems [41]. Indeed, aboveground biomass left on the field (residues) was similar in the DT and NT systems (Table 1). Further, aboveground biomass production (yields) was similar in both cropland systems (Table 1). Likewise, Dimassi et al. [80] showed in a long-term (41 years) diachronic experiment (under temperate climate conditions) that tillage did not have an effect on either SOC stocks (0–28 cm and 0–58 cm layers) or crop yields and residues.

Because aboveground biomass (residues and yields) and soil organic C stocks did not differ between the two cropland systems, whereas CO<sub>2</sub> emissions were significantly higher in the DT system, we hypothesize that our results might partly overestimate the mean CO<sub>2</sub> fluxes from the DT system soil. Indeed, we used a manual measurement method, and more intensive sampling was carried out during the transition period from the dry to wet season (from November to January), which also corresponded with soil tillage dates in the DT system. Moreover, as a result of technical issues, data are unavailable for the periods between August and November 2012 and from August to October 2013, two dry periods without soil tillage. Tillage leads to modifications of soil physical parameters, such as bulk density, total porosity, and moisture content, which impact production and diffusion of CO<sub>2</sub> from soil. However, these modifications could remain only for a short period of time. Silva et al. [81] highlighted that, for a clayed textured soil, the variations in soil density and penetration resistance decreased as of the 12th day after tillage. This process of soil consolidation impacted the temporal variation in CO<sub>2</sub> emissions [81]. These authors showed that higher soil CO<sub>2</sub> emissions from an intensive tillage system are associated with a higher number of micropores and higher water retention [81]. As the CO<sub>2</sub> emissions from grassland plots included aboveground autotrophic respiration, we did not compare CO<sub>2</sub> emissions between grassland and croplands. However, we can assume that high biomass of *Brachiaria ruziziensis*, especially belowground biomass, could contribute to higher soil CO<sub>2</sub> emissions (belowground autotrophic respiration) in grassland plots compared with cropland plots.

Measurements of the net ecosystem  $CO_2$  exchange would be useful to establish a GHG balance and to better compare the role of different agricultural systems as a source of GHGs in French Guiana.

# 4.4. Suggestions for Future Research

We focused our investigation on soil GWC and N mineral content, as soil moisture (or WFPS) and N inputs have been shown to be key factors controlling N<sub>2</sub>O and CH<sub>4</sub> fluxes (e.g., [13,20,22,24,68,82]). However, we measured some GHG fluxes that were not well explained by these soil parameters. For example, negative and positive CH<sub>4</sub> fluxes were measured in the forest plot: -26.2 g C ha<sup>-1</sup> day<sup>-1</sup> at a GWC of 32% (on 10 January 2012) and 45.9 g C ha<sup>-1</sup> day<sup>-1</sup> at a GWC of 25% (on 07 January 2014), with similar NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> contents for the two dates (Figure 3). Further, we measured higher CH<sub>4</sub> emissions in grassland plots during the 2013 wet season, but we did not measure such high emissions during the 2012 and 2014 wet seasons (Figure 3). Thus, for future research on GHG fluxes from forest and agricultural soils in French Guiana, we suggest (1) using techniques allowing high-frequency measurements (e.g., [83–85]) in order to better evaluate spatial and temporal variabilities and to better 'catch' hot moments and hotspots and (2) investigating more soil and environmental parameters in order to better understand drivers of GHG fluxes from this sandy-clayey soil (Ferralsol). Further, a modeling approach could be helpful for estimating a GHG budget and/or understanding the distribution and drivers of hotspots and hot moments (e.g., [86–88]).

#### 5. Conclusions

The main objectives of this study were to measure and compare soil CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O from different fertilized agricultural systems in French Guiana. Our results show that mowed grassland (*Brachiaria ruziziensis*) was a significantly lower N<sub>2</sub>O emitter but a significantly higher CH<sub>4</sub> emitter than both of the cropland systems studied (maize/soybean rotation). We did not observe significant differences between the disc tillage and no-tillage croplands (without cover plants) for N<sub>2</sub>O and CH<sub>4</sub> fluxes. This might be partly explained by the soil texture (sandy-clayey), as well as the soil's physical properties (low water retention capacity and porosity that favor vertical drainage). Higher N<sub>2</sub>O emissions were measured during fertilization periods, but fluxes were relatively low for the rest of the time. Soil CO<sub>2</sub> fluxes were significantly lower in the no-tillage system compared with the disc tillage system. However, we hypothesize that our results might partly overestimate the mean CO<sub>2</sub> fluxes from the disc tillage system soil; therefore, the results shown here must be confirmed. As highlighted by previous studies conducted in Amazonia, we showed that soil water content and mineral N content are important drivers of GHG fluxes. Additional research needs to be conducted on GHG fluxes from French Guianese forest and agricultural soils in order to better understand the drivers of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O fluxes and to be able to estimate a more accurate annual GHG budget.

**Author Contributions:** C.H.: methodology and experimental design; C.L.G., B.G. and J.-C.H.: GHG measurements, C.P, K.F., C.P. and A.-S.P.: statistical analyses; C.P. and A.-S.P.: writing the paper with contributions of co-authors.

**Funding:** This study was partly funded by the Fonds Européens de Développement Régional (FEDER), the French Guiana Region, Terres Inovia, the Centre National d'Etudes Spatiales (CNES) and the CASDAR IP n°9049 (NO GAS -N<sub>2</sub>O: mesure et modélisation en GrAndes cultureS).

Acknowledgments: Our special thanks go to Max Sarrazin (LAMA, IRD) for the soil analytical work and to Céline Decuq, Vanessa Lecuyer (UMR EcoSys, INRA, AgroParisTech, Université Paris-Saclay) and Nicolas Smialkowsky (Terres Inovia) for GHG analyses. We are also grateful to Pierre-Richard Augustin (Terres Inovia) and Jean-Yves Goret (UMR EcoFoG) for their helpful assistance on the field. Our thanks go to three anonymous reviewers for their useful comments.

Conflicts of Interest: The authors declare no conflict of interest.

# References

- 1. INSEE (Institut National de la Statistique et des Etudes Economiques). Recensement de la population en Guyane. La démographie guyanaise toujours aussi dynamique. *INSEE Anal. Guyane* **2018**, 4.
- 2. INSEE (Institut National de la Statistique et des Etudes Economiques). Projections de population à l'horizon 2040: Plus d'un demi-million de Guyanais. *INSEE Guyane* **2011**, *71*, 4.
- 3. FAO and ITTO (Food and Agriculture Organization and International Tropical Timber Organization). *The State of Forests in the Amazon Basin, Congo Basin and Southeast Asia a Report Prepared for the Summit of the Three Rainforest Basins;* Food and Agriculture Organization: Rome, Italy, 2011; ISBN 978-92-5-106888-5.
- 4. IGN (Institut National de l'Information Géographique et Forestière). Evolution de l'occupation des sols en Guyane française entre 1990 et 2012. *L'if Feuille L'inventaire For. IGN* **2015**, *35*, 9.
- 5. Tsayem Demaze, M.; Manusset, S. L'agriculture itinérante sur brûlis en Guyane française: La fin des durabilités écologique et socioculturelle? *Les Cah. D'outre-Mer* **2008**, *61*, 31–48. [CrossRef]
- 6. Tsayem Demaze, M. Croissance démographique, pression foncière et insertion territoriale par les abattis en Guyane française. *Norois* **2008**, *206*, 111–127. [CrossRef]
- Davidson, E.A.; de Abreu Sa, T.D.; Reis Carvalho, C.J.; de Oliveira Figueiredo, R.; Kato, M.D.; Kato, O.R.; Ishida, F.Y. An integrated greenhouse gas assessment of an alternative to slash-and-burn agriculture in eastern Amazonia. *Glob. Chang. Biol.* 2008, 14, 998–1007. [CrossRef]
- 8. Mackensen, J.; Hölscher, D.; Klinge, R.; Fölster, H. Nutrient transfer to the atmosphere by burning of debris in eastern Amazonia. *For. Ecol. Manag.* **1996**, *86*, 121–128. [CrossRef]
- 9. Sommer, R.; Vlek, P.L.G.; Deane de Abreu Sá, T.; Vielhauer, K.; de Fátima Rodrigues Coelho, R.; Fölster, H. Nutrient balance of shifting cultivation by burning or mulching in the Eastern Amazon—Evidence for subsoil nutrient accumulation. *Nutr. Cycl. Agroecosyst.* **2004**, *68*, 257–271. [CrossRef]
- Soares Neto, T.G.; Carvalho, J.A.; Cortez, E.V.; Azevedo, R.G.; Oliveira, R.A.; Fidalgo, W.R.R.; Santos, J.C. Laboratory evaluation of Amazon forest biomass burning emissions. *Atmos. Environ.* 2011, 45, 7455–7461. [CrossRef]
- 11. Farella, N.; Lucotte, M.; Davidson, R.; Daigle, S. Mercury release from deforested soils triggered by base cation enrichment. *Sci. Total Environ.* **2006**, *368*, 19–29. [CrossRef]
- 12. Feigl, B.J.; Steudler, P.A.; Cerri, C.C. Effects of pasture introduction on soil CO<sub>2</sub> emissions during the dry season in the state of Rondônia, Brazil. *Biogeochemistry* **1995**, *31*, 1–14. [CrossRef]
- Steudler, P.A.; Melillo, J.M.; Feigl, B.J.; Neill, C.; Piccolo, M.C.; Cerri, C.C. Consequence of forest-to-pasture conversion on CH<sub>4</sub> fluxes in the Brazilian Amazon Basin. *J. Geophys. Res. Phys.* **1996**, *101*, 18547–18554. [CrossRef]
- 14. Garcia-Montiel, D.C.; Steudler, P.A.; Piccolo, M.C.; Melillo, J.M.; Neill, C.; Cerri, C.C. Controls on soil nitrogen oxide emissions from forest and pastures in the Brazilian Amazon. *Glob. Biogeochem. Cycles* **2001**, *15*, 1021–1030. [CrossRef]
- Melillo, J.M.; Steudler, P.A.; Feigl, B.J.; Neill, C.; Garcia, D.; Piccolo, M.C.; Cerri, C.C.; Tian, H. Nitrous oxide emissions from forests and pastures of various ages in the Brazilian Amazon. *J. Geophys. Res. Atmos.* 2001, *106*, 34179–34188. [CrossRef]
- Garcia-Montiel, D.C.; Steudler, P.A.; Piccolo, M.; Neill, C.; Melillo, J.; Cerri, C.C. Nitrogen Oxide Emissions Following Wetting of Dry Soils in Forest and Pastures in Rondônia, Brazil. *Biogeochemistry* 2003, 64, 319–336. [CrossRef]
- 17. Neill, C.; Steudler, P.A.; Garcia-Montiel, D.C.; Melillo, J.M.; Feigl, B.J.; Piccolo, M.C.; Cerri, C.C. Rates and controls of nitrous oxide and nitric oxide emissions following conversion of forest to pasture in Rondônia. *Nutr. Cycl. Agroecosyst.* **2005**, *71*, 1–15. [CrossRef]
- Verchot, L.V.; Davidson, E.A.; Cattânio, H.; Ackerman, I.L.; Erickson, H.E.; Keller, M. Land use change and biogeochemical controls of nitrogen oxide emissions from soils in eastern Amazonia. *Glob. Biogeochem. Cycles* 1999, 13, 31–46. [CrossRef]
- 19. Verchot, L.V.; Davidson, E.A.; Cattânio, J.H.; Ackerman, I.L. Land-use change and biogeochemical controls of methane fluxes in soils of Eastern Amazonia. *Ecosystems* **2000**, *3*, 41–56. [CrossRef]
- 20. Passianoto, C.C.; Ahrens, T.; Feigl, B.J.; Steudler, P.A.; do Carmo, J.B.; Melillo, J.M. Emissions of CO<sub>2</sub>, N<sub>2</sub>O, and NO in conventional and no-till management practices in Rondônia, Brazil. *Biol. Fertil. Soils* **2003**, *38*, 200–208. [CrossRef]

- Meurer, K.H.E.; Franko, U.; Stange, C.F.; Rosa, J.D.; Madari, B.E.; Jungkunst, H.F. Direct nitrous oxide (N<sub>2</sub>O) fluxes from soils under different land use in Brazil—A critical review. *Environ. Res. Lett.* 2016, *11*, 023001. [CrossRef]
- 22. Mosier, A.; Wassmann, R.; Verchot, L.; King, J.; Palm, C. Methane and Nitrogen Oxide Fluxes in Tropical Agricultural Soils: Sources, Sinks and Mechanisms. *Environ. Dev. Sustain.* **2004**, *6*, 11–49. [CrossRef]
- 23. Mohanty, S.; Kollah, B.; Chaudhary, R.S.; Singh, A.B.; Singh, M. Methane uptake in tropical soybean–wheat agroecosystem under different fertilizer regimes. *Environ. Earth Sci.* **2015**, *74*, 5049–5061. [CrossRef]
- Palm, C.A.; Alegre, J.C.; Arevalo, L.; Mutuo, P.K.; Mosier, A.R.; Coe, R. Nitrous oxide and methane fluxes in six different land use systems in the Peruvian Amazon. *Glob. Biogeochem. Cycles* 2002, *16*, 21–1–21–13. [CrossRef]
- 25. Choudhary, M.; Akramkhanov, A.; Saggar, S. Nitrous oxide emissions from a New Zealand cropped soil: Tillage effects, spatial and seasonal variability. *Agric. Ecosyst. Environ.* **2002**, *93*, 33–43. [CrossRef]
- 26. Mathieu, O.; Leveque, J.; Henault, C.; Milloux, M.; Bizouard, F.; Andreux, F. Emissions and spatial variability of N<sub>2</sub>O, N<sub>2</sub>, and nitrous oxide mole fraction at the field scale, revealed with 15N isotopic techniques. *Soil Biol. Biochem.* **2006**, *38*, 941–951. [CrossRef]
- 27. McClain, M.E.; Boyer, E.W.; Dent, C.L.; Gergel, S.E.; Grimm, N.B.; Groffman, P.M.; Hart, S.C.; Harvey, J.W.; Johnston, C.A.; Mayorga, E.; et al. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. *Ecosystems* **2003**, *6*, 301–312. [CrossRef]
- 28. Potter, C.S.; Davidson, E.A.; Verchot, L.V. Estimation of global biogeochemical controls and seasonality in soil methane consumption. *Chemosphere* **1996**, *32*, 2219–2246. [CrossRef]
- Stehfest, E.; Bouwman, L. N<sub>2</sub>O and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycl. Agroecosyst.* 2006, 74, 207–228. [CrossRef]
- 30. Werner, C.; Kiese, R.; Butterbach-Bahl, K. Soil-atmosphere exchange of N<sub>2</sub>O, CH<sub>4</sub>, and CO<sub>2</sub> and controlling environmental factors for tropical rain forest sites in western Kenya. *J. Geophys. Res.* **2007**, *112*. [CrossRef]
- Kort, E.A.; Patra, P.K.; Ishijima, K.; Daube, B.C.; Jiménez, R.; Elkins, J.; Hurst, D.; Moore, F.L.; Sweeney, C.; Wofsy, S.C. Tropospheric distribution and variability of N<sub>2</sub>O: Evidence for strong tropical emissions. *Geophys. Res. Lett.* 2011, 38, L15806. [CrossRef]
- 32. Castaldi, S.; Bertolini, T.; Valente, A.; Chiti, T.; Valentini, R. Nitrous oxide emissions from soil of an African rain forest in Ghana. *Biogeosciences* **2013**, *10*, 4179–4187. [CrossRef]
- Buchmann, N.; Guehl, J.-M.; Barigah, T.S.; Ehleringer, J.R. Interseasonal comparison of CO<sub>2</sub> concentrations, isotopic composition, and carbon dynamics in an Amazonian rainforest (French Guiana). *Oecologia* 1997, 110, 120–131. [CrossRef]
- 34. Janssens, I.A.; Têtè Barigah, S.; Ceulemans, R. Soil CO<sub>2</sub> efflux rates in different tropical vegetation types in French Guiana. *Ann. Des. Sci. For.* **1998**, *55*, 671–680. [CrossRef]
- 35. Epron, D.; Bosc, A.; Bonal, D.; Freycon, V. Spatial variation of soil respiration across a topographic gradient in a tropical rain forest in French Guiana. *J. Trop. Ecol.* **2006**, *22*, 565–574. [CrossRef]
- Bonal, D.; Bosc, A.; Ponton, S.; Goret, J.-Y.; Burban, B.; Gross, P.; Bonnefond, J.-M.; Elbers, J.; Longdoz, B.; Epron, D.; et al. Impact of severe dry season on net ecosystem exchange in the Neotropical rainforest of French Guiana. *Glob. Chang. Biol.* 2008, 14, 1917–1933. [CrossRef]
- 37. Bréchet, L.; Ponton, S.; Alméras, T.; Bonal, D.; Epron, D. Does spatial distribution of tree size account for spatial variation in soil respiration in a tropical forest? *Plant Soil* **2011**, *347*, 293–303. [CrossRef]
- 38. Courtois, E.A.; Stahl, C.; Van den Berge, J.; Bréchet, L.; Van Langenhove, L.; Richter, A.; Urbina, I.; Soong, J.L.; Peñuelas, J.; Janssens, I.A. Spatial Variation of Soil CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O Fluxes Across Topographical Positions in Tropical Forests of the Guiana Shield. *Ecosystems* **2018**, *21*, 1445–1458. [CrossRef]
- 39. Petitjean, C.; Hénault, C.; Perrin, A.-S.; Pontet, C.; Metay, A.; Bernoux, M.; Jehanno, T.; Viard, A.; Roggy, J.-C. Soil N<sub>2</sub>O emissions in French Guiana after the conversion of tropical forest to agriculture with the chop-and-mulch method. *Agric. Ecosyst. Environ.* **2015**, *208*, 64–74. [CrossRef]
- 40. Perrin, A.-S.; Fujisaki, K.; Petitjean, C.; Sarrazin, M.; Godet, M.; Garric, B.; Horth, J.-C.; Balbino, L.C.; Filho, A.S.; de Almeida Machado, P.L.O.; et al. Conversion of forest to agriculture in Amazonia with the chop-and-mulch method: Does it improve the soil carbon stock? *Agric. Ecosyst. Environ.* **2014**, *184*, 101–114. [CrossRef]

- Fujisaki, K.; Perrin, A.-S.; Garric, B.; Balesdent, J.; Brossard, M. Soil organic carbon changes after deforestation and agrosystem establishment in Amazonia: An assessment by diachronic approach. *Agric. Ecosyst. Environ.* 2017, 245, 63–73. [CrossRef]
- 42. IUSS Working Group WRB. World Reference Base for Soil Resources 2014, Update 2015 International Soil Classification System for Naming Soils and Creating Legends for Soil Maps; World Soil Resources Reports No. 106; FAO: Rome, Italy, 2015; ISBN 978-92-5-108369-7.
- 43. Parkin, T.B.; Venterea, R.T. Sampling Protocols. Chapter 3. Chamber-Based Trace Gas Flux Measurements. In *Sampling Protocols*; Follett, R.F., Ed.; USDA-ARS: Washington, DC, USA, 2010; pp. 3-1–3-29.
- 44. Aminot, A.; Kérouel, R. Dosage Automatique des Nutriments Dans les Eaux Marines: Méthodes en flux continu. In *Méthodes D'analyse en Milieu Marin*, 1st ed.; Quae, Ed.; MEDD: Paris, France, 2007; ISBN 978-2-7592-0023-8.
- 45. Kuznetsova, A.; Brockhoff, P.B.; Christensen, R.H.B. Lmertest Package: Tests in Linear Mixed Effects Models. *J. Stat. Softw.* **2017**, *82*, 82. [CrossRef]
- Wood, S.N. Fast stable restricted maximum likelihood and marginal likelihood estimation of semiparametric generalized linear models: Estimation of Semiparametric Generalized Linear Models. J. R. Stat. Soc. Ser. B 2011, 73, 3–36. [CrossRef]
- 47. Butterbach-Bahl, K.; Baggs, E.M.; Dannenmann, M.; Kiese, R.; Zechmeister-Boltenstern, S. Nitrous oxide emissions from soils: How well do we understand the processes and their controls? *Philos. Trans. R. Soc. B Biol. Sci.* **2013**, *368*, 20130122. [CrossRef]
- Braker, G.; Conrad, R. Diversity, Structure, and Size of N<sub>2</sub>O-Producing Microbial Communities in Soils—What Matters for Their Functioning? In *Advances in Applied Microbiology*; Elsevier: Amsterdam, The Netherlands, 2011; Volume 75, pp. 33–70. ISBN 978-0-12-387046-9.
- 49. Syakila, A.; Kroeze, C. The global nitrous oxide budget revisited. *Greenh. Gas Meas. Manag.* 2011, *1*, 17–26. [CrossRef]
- 50. Davidson, E.A.; Nepstad, D.C.; Ishida, F.Y.; Brando, P.M. Effects of an experimental drought and recovery on soil emissions of carbon dioxide, methane, nitrous oxide, and nitric oxide in a moist tropical forest. *Glob. Chang. Biol.* **2008**, *14*, 2582–2590. [CrossRef]
- 51. Kuzyakov, Y.; Blagodatskaya, E. Microbial hotspots and hot moments in soil: Concept & review. *Soil Biol. Biochem.* **2015**, *83*, 184–199.
- 52. Paul, E.A.; Clark, F.E. Soil Microbiology and Biochemistry, 2nd ed.; Academic Press: San Diego, CA, USA, 1996.
- Van Lent, J.; Hergoualc'h, K.; Verchot, L.V. Reviews and syntheses: Soil N<sub>2</sub>O and NO emissions from land use and land-use change in the tropics and subtropics: A meta-analysis. *Biogeosciences* 2015, 12, 7299–7313. [CrossRef]
- 54. Schmidt, U.; Thöni, H.; Kaupenjohann, M. Using a boundary line approach to analyze N<sub>2</sub>O flux data from agricultural soils. *Nutr. Cycl. Agroecosyst.* **2000**, *57*, 119–129. [CrossRef]
- Laville, P.; Lehuger, S.; Loubet, B.; Chaumartin, F.; Cellier, P. Effect of management, climate and soil conditions on N<sub>2</sub>O and NO emissions from an arable crop rotation using high temporal resolution measurements. *Agric. For. Meteorol.* 2011, 151, 228–240. [CrossRef]
- 56. Rafique, R.; Hennessy, D.; Kiely, G. Nitrous Oxide Emission from Grazed Grassland under Different Management Systems. *Ecosystems* **2011**, *14*, 563–582. [CrossRef]
- 57. Ciarlo, E.; Conti, M.; Bartoloni, N.; Rubio, G. The effect of moisture on nitrous oxide emissions from soil and the N<sub>2</sub>O/(N<sub>2</sub>O+N<sub>2</sub>) ratio under laboratory conditions. *Biol. Fertil. Soils* **2007**, *43*, 675–681. [CrossRef]
- Castellano, M.J.; Schmidt, J.P.; Kaye, J.P.; Walker, C.; Graham, C.B.; Lin, H.; Dell, C.J. Hydrological and biogeochemical controls on the timing and magnitude of nitrous oxide flux across an agricultural landscape. *Glob. Chang. Biol.* 2010, *16*, 2711–2720. [CrossRef]
- 59. Balaine, N.; Clough, T.J.; Beare, M.H.; Thomas, S.M.; Meenken, E.D.; Ross, J.G. Changes in Relative Gas Diffusivity Explain Soil Nitrous Oxide Flux Dynamics. *Soil Sci. Soc. Am. J.* **2013**, *77*, 1496. [CrossRef]
- 60. Rabot, E.; Cousin, I.; Hénault, C. A modeling approach of the relationship between nitrous oxide fluxes from soils and the water-filled pore space. *Biogeochemistry* **2015**, *122*, 395–408. [CrossRef]
- 61. Metay, A.; Oliver, R.; Scopel, E.; Douzet, J.-M.; Aloisio Alves Moreira, J.; Maraux, F.; Feigl, B.J.; Feller, C. N<sub>2</sub>O and CH<sub>4</sub> emissions from soils under conventional and no-till management practices in Goiânia (Cerrados, Brazil). *Geoderma* **2007**, *141*, 78–88. [CrossRef]

- 62. Jantalia, C.P.; dos Santos, H.P.; Urquiaga, S.; Boddey, R.M.; Alves, B.J.R. Fluxes of nitrous oxide from soil under different crop rotations and tillage systems in the South of Brazil. *Nutr. Cycl. Agroecosyste.* **2008**, *82*, 161–173. [CrossRef]
- Li, C.; Frolking, S.; Butterbach-Bahl, K. Carbon Sequestration in Arable Soils is Likely to Increase Nitrous Oxide Emissions, Offsetting Reductions in Climate Radiative Forcing. *Clim. Chang.* 2005, 72, 321–338. [CrossRef]
- 64. Rochette, P. No-till only increases N<sub>2</sub>O emissions in poorly-aerated soils. *Soil Tillage Res.* **2008**, 101, 97–100. [CrossRef]
- 65. Linn, D.M.; Doran, J.W. Effect of Water-Filled Pore Space on Carbon Dioxide and Nitrous Oxide Production in Tilled and Nontilled Soils. *Soil Sci. Soc. Am. J.* **1984**, *48*, 1267. [CrossRef]
- Palma, R.M.; Rímolo, M.; Saubidet, M.I.; Conti, M.E. Influence of tillage system on denitrification in maize-cropped soils. *Biol. Fertil. Soils* 1997, 25, 142–146. [CrossRef]
- 67. Le Mer, J.; Roger, P. Production, oxidation, emission and consumption of methane by soils: A review. *Eur. J. Soil Biol.* **2001**, *37*, 25–50. [CrossRef]
- Keller, M.; Reiners, W.A. Soil-atmosphere exchange of nitrous oxide, nitric oxide, and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica. *Glob. Biogeochem. Cycles* 1994, *8*, 399–409. [CrossRef]
- 69. Kiese, R.; Wochele, S.; Butterbach-Bahl, K. Site specific and regional estimates of methane uptake by tropical rainforest soils in north eastern Australia. *Plant Soil* **2008**, *309*, 211–226. [CrossRef]
- 70. Keller, M.; Mitre, M.E.; Stallard, R.F. Consumption of atmospheric methane in soils of central Panama: Effects of agricultural development. *Glob. Biogeochem. Cycles* **1990**, *4*, 21–27. [CrossRef]
- 71. Keller, M.; Jacob, D.J.; Wofsy, S.C.; Harriss, R.C. Effects of tropical deforestation on global and regional atmospheric chemistry. *Clim. Chang.* **1991**, *19*, 139–158. [CrossRef]
- 72. Steudler, P.A.; Bowden, R.D.; Melillo, J.M.; Aber, J.D. Influence of nitrogen fertilization on methane uptake in temperate forest soils. *Nature* **1989**, *341*, 314–316. [CrossRef]
- 73. Wang, Z.-P.; Ineson, P. Methane oxidation in a temperate coniferous forest soil: Effects of inorganic N. *Soil Biol. Biochem.* **2003**, *35*, 427–433. [CrossRef]
- Reay, D.S.; Nedwell, D.B. Methane oxidation in temperate soils: Effects of inorganic N. Soil Biol. Biochem. 2004, 36, 2059–2065. [CrossRef]
- 75. De Visscher, A.; Cleemput, O.V. Induction of enhanced CH<sub>4</sub> oxidation in soils: NH<sub>4</sub><sup>+</sup> inhibition patterns. *Soil Biol. Biochem.* **2003**, *35*, 907–913. [CrossRef]
- Inselsbacher, E.; Wanek, W.; Ripka, K.; Hackl, E.; Sessitsch, A.; Strauss, J.; Zechmeister-Boltenstern, S. Greenhouse gas fluxes respond to different N fertilizer types due to altered plant-soil-microbe interactions. *Plant Soil* 2011, 343, 17–35. [CrossRef]
- 77. Sitaula, B.K.; Hansen, S.; Bonilla, J.I.; Bakken, L.R. Methane oxidation potentials and fluxes in agricultural soil: Effects of fertilisation and soil compaction. *Biogeochemistry* **2000**, *48*, 323–339. [CrossRef]
- 78. Klüber, H.D.; Conrad, R. Effects of nitrate, nitrite, NO and N<sub>2</sub>O on methanogenesis and other redox processes in anoxic rice field soil. *Fems Microbiol. Ecol.* **1998**, *25*, 301–318. [CrossRef]
- 79. IPCC. Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change; Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., et al., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2014; ISBN 978-1-107-05821-7.
- Dimassi, B.; Mary, B.; Wylleman, R.; Labreuche, J.; Couture, D.; Piraux, F.; Cohan, J.-P. Long-term effect of contrasted tillage and crop management on soil carbon dynamics during 41 years. *Agric. Ecosyst. Environ.* 2014, 188, 134–146. [CrossRef]
- 81. De Oliveira Silva, B.; Moitinho, M.R.; de Araújo Santos, G.A.; Teixeira, D.D.; Fernandes, C.; La Scala, N., Jr. Soil CO<sub>2</sub> emission and short-term soil pore class distribution after tillage operations. *Soil Tillage Res.* **2019**, *186*, 224–232. [CrossRef]
- Hickman, J.E.; Tully, K.L.; Groffman, P.M.; Diru, W.; Palm, C.A. A potential tipping point in tropical agriculture: Avoiding rapid increases in nitrous oxide fluxes from agricultural intensification in Kenya: Non-linear N<sub>2</sub>O in tropical agriculture. *J. Geophys. Res. Biogeosci.* 2015, 120, 938–951. [CrossRef]
- Arora, B.; Wainwright, H.M.; Dwivedi, D.; Vaughn, L.J.S.; Curtis, J.B.; Torn, M.S.; Dafflon, B.; Hubbard, S.S. Evaluating temporal controls on greenhouse gas (GHG) fluxes in an Arctic tundra environment: An entropy-based approach. *Sci. Total Environ.* 2019, 649, 284–299. [CrossRef]

- 84. Courtois, E.A.; Stahl, C.; Burban, B.; Van den Berge, J.; Berveiller, D.; Bréchet, L.; Soong, J.L.; Arriga, N.; Peñuelas, J.; Janssens, I.A. Automatic high-frequency measurements of full soil greenhouse gas fluxes in a tropical forest. *Biogeosciences* **2019**, *16*, 785–796. [CrossRef]
- 85. Savage, K.; Phillips, R.; Davidson, E. High temporal frequency measurements of greenhouse gas emissions from soils. *Biogeosciences* **2014**, *11*, 2709–2720. [CrossRef]
- 86. Chen, D.; Li, Y.; Grace, P.; Mosier, A.R. N<sub>2</sub>O emissions from agricultural lands: A synthesis of simulation approaches. *Plant Soil* **2008**, *309*, 169–189. [CrossRef]
- 87. Dwivedi, D.; Arora, B.; Steefel, C.I.; Dafflon, B.; Versteeg, R. Hot Spots and Hot Moments of Nitrogen in a Riparian Corridor. *Water Resour. Res.* **2018**, *54*, 205–222. [CrossRef]
- Lugato, E.; Zuliani, M.; Alberti, G.; Vedove, G.D.; Gioli, B.; Miglietta, F.; Peressotti, A. Application of DNDC biogeochemistry model to estimate greenhouse gas emissions from Italian agricultural areas at high spatial resolution. *Agric. Ecosyst. Environ.* 2010, 139, 546–556. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).