agriculture

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Efflux of Soil Nitrous Oxide from Applied Fertilizer Containing Organic Materials in *Citrus unshiu* Field in Southwestern Japan

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Academic Editor: Ryusuke Hatano
Received: 7 December 2016; Accepted: 2 February 2017; Published: 8 February 2017

Abstract: Nitrous oxide (N_2O) emissions from agricultural fields are an important source of the increasing atmospheric N_2O concentration. We conducted a two-year investigation of soil N_2O emissions induced by the application of combined organic and synthetic fertilizer (COS) and distilled silage waste (DSW). Three experimental treatments were applied to a *Citrus unshiu* field in January 2013 in Ehime, Japan: no fertilizer (NF), COS, and DSW. The applied nitrogen (N) from DSW was 192 and 244 kg N ha^{-1} in the first and second years, respectively, although the N application in COS was 192 kg N ha^{-1} in both years. The main N forms in COS and DSW were ammonium- and nitrate-N, respectively. Soil N_2O and carbon dioxide fluxes, soil chemical properties, and mineral N leaching from topsoil were measured. The soil N_2O flux increased after fertilization in COS and DSW, and a higher N_2O efflux after supplemental fertilization was induced by warm and wet soil conditions. The emission factor of N_2O was higher in COS (2.02%) than in DSW (1.18%), while N leaching was higher in DSW than in COS. The organic materials remaining after the application possibly increased the N_2O emissions in the summer season. Therefore, to mitigate N_2O emissions in citrus orchards, fertilizer containing organic materials should be applied during a cool and dry season.

Keywords: emission factor; citrus orchard; combined organic and synthetic fertilizer; distilled silage waste

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1. Introduction

Recent global climate change is due to the increasing artificial emissions of atmospheric greenhouse gases [1]. Therefore, mitigating greenhouse gas emissions is one of the current important global issues. Nitrous oxide (N_2O), a greenhouse gas (GHG) that is 298 times stronger than carbon dioxide (CO_2), is one of the major GHGs emitted from the agriculture sector [2]. Soil N_2O emissions from applied nitrogen (N) fertilizer dominate the global anthropogenic N_2O emissions in the agricultural sector [3]. Because the processes producing N_2O in soil are mainly nitrification (by-product) and denitrification (intermediate product) by soil microbes, N_2O is produced and emitted from soil when N fertilizers, such as ammonium (NH_4^+)- and nitrate (NO_3^-)-N, are applied to agricultural fields [4,5]. Thus, it is important to mitigate N_2O emissions induced by N fertilizers for reducing GHG emissions in the agriculture sector.

Several studies have reported techniques for reducing soil N_2O emissions from agricultural fields. The utilization of nitrification inhibitors and coated fertilizers can reduce soil N_2O emissions produced by the process of nitrification or denitrification [6,7]. Sequestration of carbon (C) by applying organic materials such as feedlot manure compost can also reduce the enhanced greenhouse effect, although the application of organic material to soil increases soil N_2O emissions [8]. Because the application of organic materials to agricultural soil can supply essential elements for plant growth and improve soil physical conditions and microbial diversity, it is generally regarded as an effective practice not only for sustainable agriculture but also for climate change [9]. However, there are limited studies about the effect of organic material application on soil N_2O emissions in citrus orchard fields, an important agricultural land use.

In citrus orchard fields, (1) fruit is harvested in the winter season; (2) fertilizers are applied after the harvest until the early summer season; and (3) soil is not often tilled. Because the soil microbial activity is low under low temperatures, the application of fertilizer in the winter season may not induce higher soil N_2O emissions in citrus orchard fields. On the other hand, a higher soil bulk density due to undisturbed soil inhibiting soil gas diffusion to the atmosphere can establish a reduced soil condition and lead to the production of N_2O via denitrification. Only Okuda et al. [10] reported relatively lower soil N_2O emissions and N_2O emission factors induced by applied N fertilizer compared to those of other land uses in Japan. Further, there are no other whole-year studies investigating soil N_2O emissions induced not only by synthetic but also by organic fertilizers in citrus orchard fields.

Some of the harvested citrus fruit is processed for producing citrus juice. In the Ehime Prefecture, one of the largest agricultural areas for producing citrus fruit in Japan, bio-ethanol is produced using citrus molasses, a sugar-rich, citrus-processing waste. In the process, distilled silage waste (DSW), which has a high concentration of NO_3^-, is discharged. Although the DSW is usually treated as industrial waste, applying it to citrus orchard fields can supply N and essential nutrients removed from the fields by the harvest. This can also reduce the cost for industrial waste disposal. The objectives of this study were (1) investigating the pattern of soil N_2O emissions induced by two different types of materials applied as fertilizer, combined organic and synthetic fertilizer (COS) and DSW; and (2) evaluating the controlling factors of soil N_2O emissions in a citrus orchard field.

2. Materials and Methods

2.1. Study Site

This two-year study, starting January 2013, was conducted in a *Citrus unshiu* Marcow. “Miyagawa-wase” field (1200 m^2) at Ehime University Farm (33°57′ N, 132°47′ E, 26 m asl). The study field had a gentle slope (10.1°). Tree seedlings were planted in 1980, and plant density was 640 trees ha^{-1}. The soil type was classified as brown forest soil, and the top soil (0–7 cm) texture was sandy clay. The total C and N concentrations and C:N ratio in the surface layer were 22.2 g C kg^{-1}, 2.71 g N kg^{-1}, and 8.23, respectively. The soil bulk density and cation exchange capacity were 1.34 $g \cdot cm^{-3}$ and 11.8 $cmol_c \cdot kg^{-1}$, respectively. The fine soil (0–30 cm) contained a total mass C of 49.4 Mg C ha^{-1}. Details of the soil physical and chemical characteristics are provided in Table 1. The site has a 30-year (1981–2010) mean annual air temperature and annual precipitation of 16.5 °C and 1315 mm, respectively.

Table 1. Physical and chemical characteristics of soil in a citrus orchard field in southwestern Japan.

Depth	Bulk Density	Soil Texture			Total Carbon	Total Nitrogen	C:N Ratio	CEC §
		Sand	Silt	Clay				
(cm)	($g \cdot cm^{-3}$)	(%)			($g \cdot kg^{-1}$)			($cmol_c \cdot kg^{-1}$)
0–7	1.34	57.3	12.6	30.1	22.2	2.71	8.23	11.8
7–25	1.41	47.9	15.7	36.4	8.73	1.15	7.60	11.1
25–62	1.42	42.5	16.8	40.8	9.07	1.09	8.30	11.7
62–71	1.41	38.6	17.4	44.1	10.8	1.35	7.97	12.9
71–100	1.50	40.5	15.3	44.2	3.29	0.48	6.96	9.74

§ Cation exchange capacity.

2.2. Treatments and Management Practices

We began the treatments in January 2013. Three trees at the top, middle, and toe of the study site were selected for each treatment (no fertilizer, NF; combined organic and synthetic fertilizer, COS; distilled silage waste, DSW). Fertilization under the tree canopy in COS and DSW treatments was carried out in January as basal fertilization (28 January 2013, 20 January 2014) and in March as supplemental fertilization (22 March 2013, 29 March 2014). For COS, 96 kg N ha^{-1} of organic and synthetic fertilizer twice (total 192 kg N ha^{-1}) as basal and supplemental applications in the form of 5 mm pellets was manually broadcasted. Carbon, N, phosphorus (P), and potassium (K) concentrations in the organic and synthetic fertilizer were 22.6%, 8.0%, 2.6%, and 5.0%, respectively. Ammonium-N comprised 50% of the N in the COS fertilizer. For the DSW fertilization, 96 kg N ha^{-1} (total 192 kg N ha^{-1} in 2013) and 122 kg N ha^{-1} (total 244 kg N ha^{-1} in 2014) of DSW was applied as a basal fertilizer. Raw organic materials COS were fish meal, steamed feather meal, steamed bone meal, and rapeseed cake (Ehime-Tyuo Nigata Yuuki-Ryujyo, Daitou Hiryou, Kumamoto, Japan). Because the N content of DSW was different each year, the applied N in 2014 was 1.27 times higher than that in 2013. Chemical characteristics of DSW are provided in Table 2. Before application, the pH of the DSW was adjusted to 6.2 by using calcium hydroxide. Before application, the DSW was diluted 1:10 ration using tap water. The same amount of tap water was applied to the NF and COS treatments at fertilization.

Table 2. Chemical characteristics of distilled silage waste.

	Year	
	2013	**2014**
Water content (%)	69.4	64.4
Total carbon (g C L^{-1})	149	146
Total nitrogen (g N L^{-1})	17.3	20.2
C:N ratio	8.62	7.21
Ammonium content (g N L^{-1})	0.13	2.44
Nitrate content (g N L^{-1})	12.9	18.4
Total phosphorus (g P L^{-1})	0.81	1.40
Total potassium (g K L^{-1})	18.6	20.1
Total calcium (g Ca L^{-1})	20.4	17.8
Total sodium (g Na L^{-1})	0.52	6.9

2.3. Measurement of Soil Nitrous Oxide and Carbon Dioxide Emission and Calculation of Emission Factor

Soil N_2O and CO_2 fluxes were measured by the closed chamber technique described in Toma et al. [11]. Before the start of the experiment, stainless steel bases were installed under the tree canopy on the upper (East) side of the trees in each treatment. Stainless steel chambers were placed on the bases, and gas samples were collected at 0, 30, and 60 minutes for N_2O and 0, 6, and 12 minutes for CO_2 measurements from the time the chambers were deployed. Nitrous oxide and CO_2 concentrations were measured using a gas chromatography equipped with an electron capture detector (GC-14B, Shimadzu, Kyoto, Japan) and CO_2 controller (ZFP9GC11, Fuji Electric, Tokyo, Japan), respectively.

Each gas flux was calculated by non-linear regression, and integrated values were determined by the trapezoidal method, both based on the methods in Toma et al. [11] and Oomori et al. [12]. Cumulative emissions of soil N_2O were calculated in the period after basal fertilization (F1: from 23 January to 22 March 2013 and from 20 January to 28 March 2014), supplemental fertilization (F2: 22 March to 26 May 2013 and from 28 March to 30 May 2014), summer (S: from 26 May to 22 August 2013 and 30 May to 25 August 2014), and the other period (from 22 August 2013 to 20 January 2014 and from 25 August to 22 December 2014).

Based on the calculation method provided by Toma et al. [13], the emission factor for N_2O (EF) was calculated using annual N_2O emission (kg N ha^{-1}·$year^{-1}$) and applied N (kg N ha^{-1}·$year^{-1}$) as following equation:

$$\text{EF (\%)} = (\text{annual } N_2O \text{ emission in COS or DSW} - \text{annual } N_2O \text{ emission in NF})/\text{applied N} \times 100 \quad (1)$$

Decomposition rate of applied organic materials was defined as the differences in CO_2 flux between NF and COS or DSW treatments [14,15].

2.4. Measurements of Mineral Nitrogen Leaching from Surface Soil

In each treatment, three pan lysimeters (each 0.08 m^2) were installed at a soil depth of 30 cm to collect mineral N leaching from top soil. Percolated soil solution was received by the pan lysimeters and stored into a connected bottle below the lysimeters [16]. The water samples were collected once every two or three months. Volume of water sample and NH_4^+ and NO_3^- concentrations were measured, and the amounts of leached NH_4^+ and NO_3^- (kg N ha^{-1}·$year^{-1}$) was calculated for each year.

$$\text{N leaching rate (\%)} = (\text{leached } NH_4^+ \text{ and } NO_3^- \text{ in COS or DSW} - \text{leached } NH_4^+ \text{ and } NO_3^- \text{ in NF})/\text{applied N} \times 100 \quad (2)$$

2.5. Ancillary Measurements

Mean air temperature and daily precipitation were obtained from a weather station in Matsuyama (Matsuyama Local Meteorological Office). Soil samples were collected from 0 to 10 cm depth at the time of each gas flux measurement. Collected soil samples were used to measure water content and soil pH, which was measured by dissolving soil in demineralized water (soil:water = 1:2.5) and using a pH meter (B-212, HORIBA, Kyoto, Japan). Soil samples were extracted with 10% KCl solution (soil:water = 1:10). The extract was analyzed for NH_4^+ and NO_3^- concentrations using the colorimetry with indophenol-blue and vanadium (III) chloride-*N*-ethylenediamine dihydrochloride method provided by Doane and Horwáth [17]. Soil porosity and bulk density were determined from samples collected in April 2014 using a stainless steel core (100 cm^3). Water-filled pore space (WFPS) was determined from these soil porosities and soil water contents.

2.6. Ancillary Measurements

All statistical analyses were performed using R (version 3.1.0, R Core Team, Vienna, Austria). Differences in soil N_2O emissions and EF among NF, COS, and DSW treatments, seasons, and whole years were determined using two-way ANOVA. Correlations between soil N_2O flux and decomposition rate of applied organic materials were evaluated by correlation analysis. To evaluate the factors controlling soil N_2O flux, multiple regression analysis was performed using soil pH, WFPS, and soil NH_4^+ and NO_3^- concentrations as explanatory variables.

3. Results

The soil N_2O flux increased after the basal and supplemental fertilizations in COS and DSW treatments in both years (Figure 1b,d). The maximum values of soil N_2O flux just after the fertilizations were higher in the DSW (4005 μg N m^{-2}·h^{-1} in 2013, 1730 μg N m^{-2}·h^{-1} in 2014) treatment than the COS (1074 μg N m^{-2}·h^{-1} in 2013, 689 μg N m^{-2}·h^{-1} in 2014) treatment. For both years, periods of increasing soil N_2O flux after fertilization were about two months in the COS treatment compared to about 10 days in the DSW treatment. The soil N_2O flux increased in all treatments in S. The seasonal variation in the decomposition rates of applied organic materials is provided in Figure 2. The decomposition rates of organic materials showed a pattern of seasonal variation similar to soil N_2O fluxes, increasing after the fertilizations and in S. A negative value of the decomposition rate was observed when the CO_2 flux in NF was higher than that in COS or DSW. There were significant positive correlations between soil N_2O fluxes and the decomposition rates of applied organic materials in F1 and S, while no correlations were found in the other periods (Figure 3).

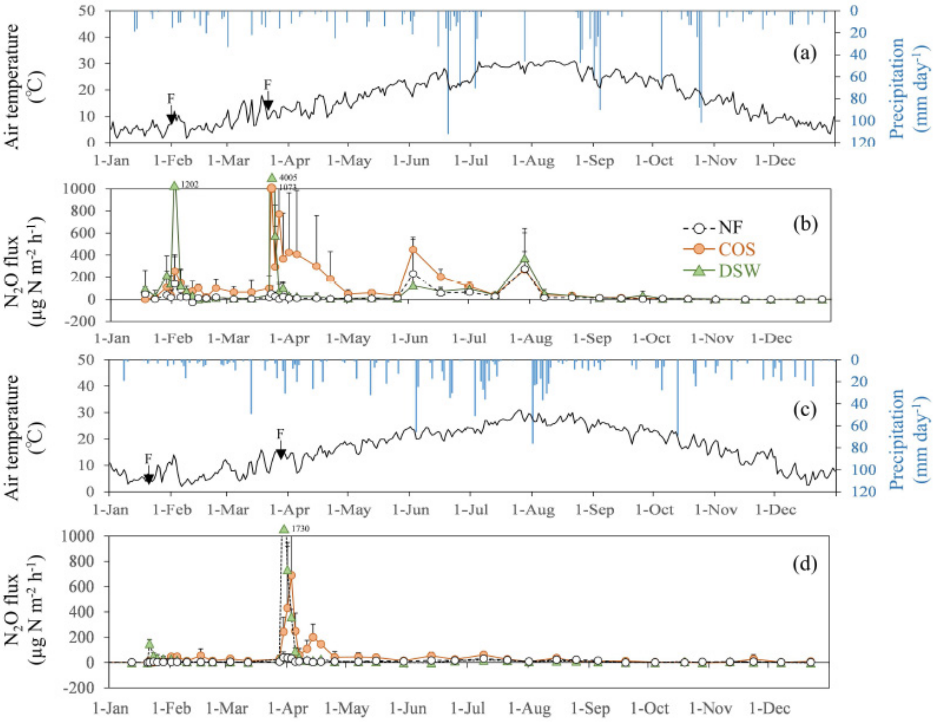

Figure 1. Seasonal variation in air temperature and precipitation in 2013 (**a**); and 2014 (**c**); soil N_2O fluxes in 2013 (**b**); and 2014 (**d**) in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan. Error bars represent standard deviations. F denotes fertilization.

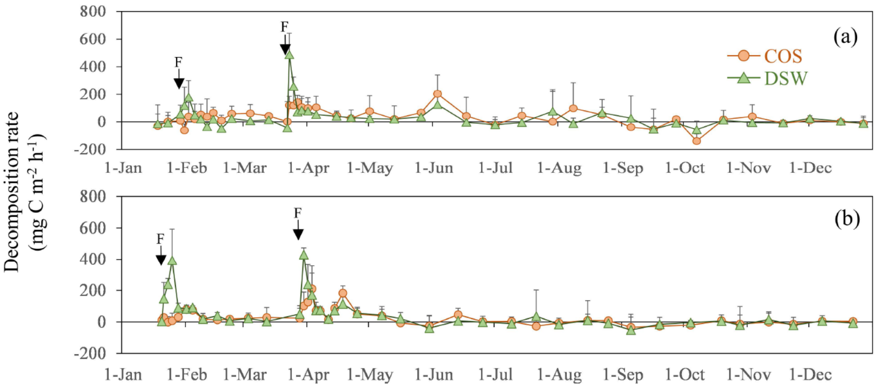

Figure 2. Decomposition rate of applied organic materials in 2013 (**a**); and 2014 (**b**) in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan. Error bars represent standard deviations. F denotes fertilization.

Periodic and annual cumulative soil N_2O emissions are shown in Table 3. In the NF treatment, the soil N_2O emission was the highest in summer (contributed 63.3% to the annual emissions) in both years. In the COS treatment, the soil N_2O emission during F1 constituted 49.1% of the annual emissions in both years. In the DSW treatment, the soil N_2O emission during F2 constituted 52.9% of the annual emissions, but the summer contribution was 39.0% in 2013. While the annual soil N_2O emissions were significantly higher in 2013 than in 2014 ($p < 0.05$), there was no significant difference in annual soil N_2O emissions among treatments. In the first year, the N application rate and the soil N_2O emissions were lower and higher than those in the second year, respectively, especially for the DSW treatment. Cumulative soil N_2O emissions in 2013 were significantly higher than those in 2014 in the F1 ($p < 0.05$) and summer ($p < 0.01$) periods. For both years, although no significant differences in EF were obtained between treatments, the EF tended to be higher in the COS treatment than in the DSW treatment (Table 3).

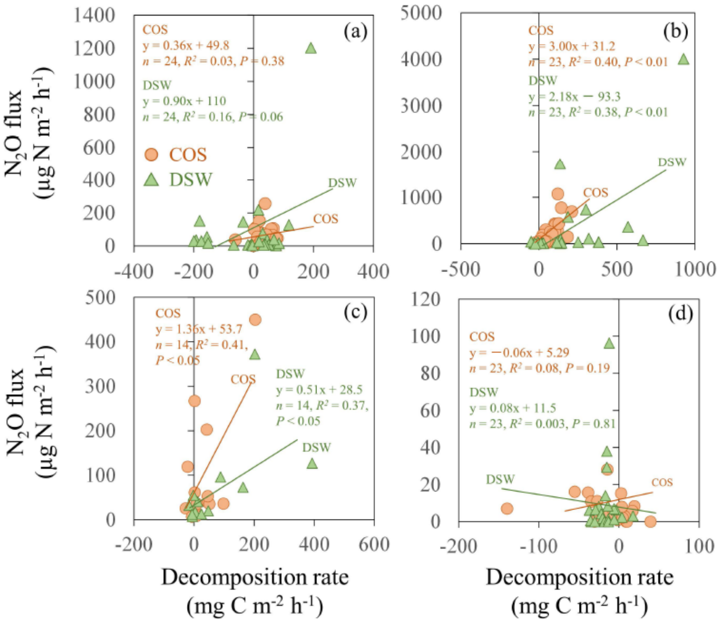

Figure 3. Relationships between soil N_2O flux and decomposition rate of applied organic materials in the season after basal fertilization (**a**); after supplemental fertilization (**b**); in summer (**c**); and in other seasons (**d**) in 2013 and 2014 in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan.

Table 3. Soil nitrous oxide (N_2O) emissions (Average ± Standard deviation) for the after basal fertilization (F1), supplemental fertilization (F2), summer (S), other seasons, and annual periods, and the emission factors (EF) of the applied organic materials in the no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard southwestern Japan.

Year	Treatment	Soil N_2O Emission (kg N ha^{-1}·period^{-1})					EF (%)
		F1	F2	S	Other	Annual	
2013	COS	1.17 ± 0.78	3.49 ± 4.49	3.39 ± 0.93	0.23 ± 0.02	8.28 ± 6.01	2.95 ± 1.62
	DSW	1.31 ± 1.15	2.04 ± 0.93	2.37 ± 1.03	0.35 ± 0.14	6.07 ± 3.09	1.80 ± 2.42
	NF	0.23 ± 0.47	0.18 ± 0.16	2.02 ± 2.22	0.18 ± 0.15	2.61 ± 2.99	nc
2014	COS	0.39 ± 0.18	1.62 ± 1.01	0.66 ± 0.19	0.21 ± 0.12	2.89 ± 1.36	1.09 ± 0.80
	DSW	0.27 ± 0.03	1.56 ± 0.27	0.23 ± 0.13	0.11 ± 0.09	2.16 ± 0.46	0.56 ± 0.22
	NF	0.07 ± 0.06	0.18 ± 0.12	0.39 ± 0.12	0.41 ± 0.47	0.78 ± 0.32	nc
Average	COS	0.78 ± 0.66	2.56 ± 3.09	2.03 ± 1.61	0.22 ± 0.08	5.58 ± 4.89	2.02 ± 1.53
	DSW	0.79 ± 0.93	1.80 ± 0.67	1.30 ± 1.34	0.23 ± 0.17	4.11 ± 2.91	1.18 ± 1.68
	NF	0.15 ± 0.31	0.18 ± 0.13	1.20 ± 1.67	0.29 ± 0.34	1.70 ± 2.15	nc
Treatment		ns	ns	ns	ns	ns	ns
Year		$p < 0.05$	ns	$p < 0.01$	ns	$p < 0.05$	ns
Treatment × Year		ns	ns	ns	ns	ns	ns

nc: not calculated, ns: not significant, F1: from 23 January to 22 March 2013 and from 20 January to 28 March 2014, F2: 22 March to 26 May 2013 and from 28 March to 30 May 2014, S: from 26 May to 22 August 2013 and 30 May to 25 August 2014, Other: from 22 August 2013 to 20 January 2014 and from 25 August to 22 December 2014.

Nitrogen leaching from the surface soil was 2.5 times higher in the DSW treatment than in the COS treatment (Table 4). The N leaching rate two-year average tended to be higher for the DSW treatment (27.0%) than for the COS treatment (10.5%).

Table 4. Mineral nitrogen (N) leaching and N leaching rate in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan. Values in parentheses represent the contributions (%) of nitrate to mineral N leaching.

Year	**Mineral N Leaching**			**N Reaching Rate**	
	(kg N ha^{-1})			**(%)**	
	NF	**COS**	**DSW**	**COS**	**DSW**
2013	7.65 (95.7)	20.7 (96.9)	47.2 (98.7)	6.87	20.6
2014	7.25 (95.6)	34.5 (90.2)	88.7 (99.0)	14.2	33.4
Average	7.45 (95.7)	27.6 (93.6)	67.9 (98.8)	10.5	27.0

WFPS mostly varied from 30% to 60% in all treatments (Figure 4). The seasonal variations in soil pH in the NF and DSW treatments were similar, while the variation was lower in the COS treatment compared to the other treatments. After fertilization, the soil NH_4^+ and NO_3^- concentrations were higher in the COS and DSW treatments than in the NF treatment. Especially in the COS treatment, the soil NH_4^+ and NO_3^- concentrations were higher and lower than those in the DSW treatment after fertilization, respectively. Based on multiple regression analysis, in the COS treatment the soil N_2O flux was positively affected by the soil NH_4^+ concentration in F2 and positively and negatively affected by the soil NO_3^- concentration and soil temperature in the summer season, respectively (Table 5). In the DSW treatment, the soil N_2O flux was positively affected by the soil NO_3^- concentration in both the F2 and summer seasons. In the NF treatment, the soil N_2O flux was positively affected by the soil NO_3^- concentration and WFPS in the summer season and by the soil NH_4^+ concentration, soil temperature, and WFPS in the other seasons.

Table 5. Multiple regression analysis of soil nitrous oxide flux and soil temperature (ST), water-filled pore space (WFPS) and soil ammonium (NH_4^+) and nitrate (NO_3^-) concentrations in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan.

Season	**Treatment**	***n***	**Factor 1**			**Factor 2**			**Factor 3**			**Constant**	***p***
				PRC	**RPRC**		**PRC**	**RPRC**		**PRC**	**RPRC**		
F1	COS	24	NS										
	DSW	24	NH_4^+	6.70	0.57							−1.06	<0.01
	NF	24	NS										
F2	COS	23	NH_4^+	4.09	0.68							78.0	<0.001
	DSW	23	NO_3^-	12.2	0.56							−516	<0.01
	NF	23	NS										
S	COS	14	NO_3^-	6.21	0.76	ST	−21.5	0.47				470	<0.001
	DSW	14	NO_3^-	4.17	0.76							−64.0	<0.01
	NF	14	NO_3^-	3.94	0.55	WFPS	2.75	0.45				−134	<0.05
Other	COS	23	NS										
	DSW	23	NS										
	NF	23	NH_4^+	0.99	0.92	ST	0.45	0.32	WFPS	0.29	0.29	−17.7	<0.001

NS: not selected, PRC: partial regression coefficient, RPRC: standardized partial regression coefficient, F1: from 23 January to 22 March 2013 and from 20 January to 28 March 2014, F2: 22 March to 26 May 2013 and from 28 March to 30 May 2014, S: from 26 May to 22 August 2013 and 30 May to 25 August 2014, Other: from 22 August 2013 to 20 January 2014 and from 25 August to 22 December 2014.

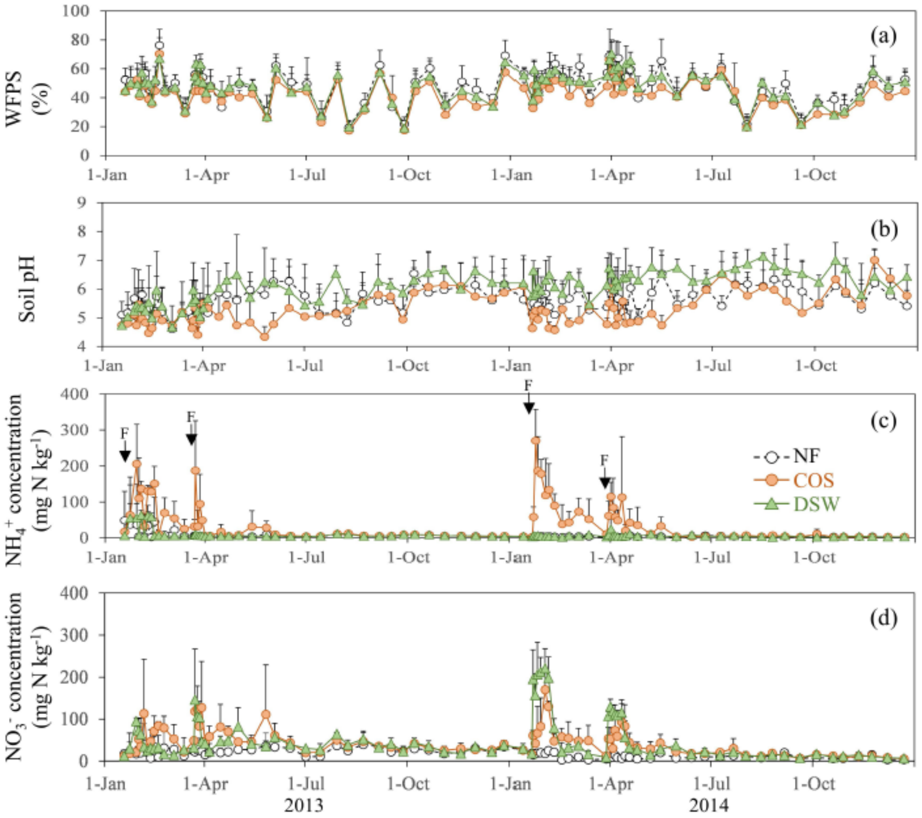

Figure 4. Seasonal variation in water-filled pore space (WFPS) (**a**); soil pH (**b**); NH_4^+ (**c**); and NO_3^- (**d**) concentrations during the study period in no fertilizer (NF), combined organic and synthetic fertilizer (COS), and distilled silage waste (DSW) treatments in a citrus orchard in southwestern Japan. Error bars represent standard deviations. F denotes fertilization.

4. Discussion

4.1. Controlling Factor of N_2O Emissions in Citrus Orchard Fields

The soil N_2O flux in summer increased with the increasing soil NO_3^- concentration and WFPS in the NF treatment. In the denitrification process, N_2O production was enhanced by increasing the soil temperature, soil moisture, and soil NO_3^- concentration under anaerobic conditions [3]. Thus, soil N_2O emissions were mainly produced by denitrification in our experimental field. The study field is located in a region with relatively little precipitation and high temperatures in summer. Therefore, the mineralization of soil organic materials and nitrification can rapidly be accelerated after rainfall in summer. Denitrification is activated in the anaerobic micro-pore space where the soil oxygen concentration is lower due to the consumption by mineralization in the presence of NO_3^- [18]. For the winter season, the positive effects of the soil temperature, soil moisture, and soil NH_4^+ concentration on the soil N_2O flux indicated that N_2O might be mainly produced through nitrification. Because of the lower WFPS and soil microbe activity in winter, winter soil conditions might not be suitable for denitrification.

In the COS treatment, the increase in the soil N_2O flux after fertilization indicated that the main source of N for N_2O production was the fertilizer. Nitrification appears to be the main process producing N_2O in soil, because both the highest peak in the soil N_2O flux and a soil N_2O flux increase were observed with the increased soil NH_4^+ concentration resulting from the basal application of the COS fertilizer. Because the main form of N in COS is NH_4^+-N and the soil temperature was lower in the F1 period, N_2O production via nitrification might be low. In the summer season, the second highest season of soil N_2O emissions in the first year in the COS treatment, the increasing soil N_2O

flux with the increasing soil NO_3^- concentration might indicate that the main process for producing N_2O was denitrification, as in the NF treatment. The close relationships between the soil N_2O flux and the decomposition rate of the applied organic materials in Figure 3c suggested that CO_2 production through mineralization and denitrification was closely linked with N_2O production. Therefore, N_2O production may be enhanced because of soil conditions suitable for both the decomposition of organic materials and denitrification when the applied organic materials remain during the summer.

The observed spike in the soil N_2O flux just after the fertilization in the DSW treatment indicated that the process of N_2O production from DSW might be different from that from the COS fertilizer. After the application of DSW, selected factors influencing the soil N_2O flux were different between F1 and F2 (Table 5), though the soil N_2O flux increased just after the fertilization in both periods. This shows that the main processes producing N_2O were nitrification and denitrification in the F1 and F2 periods, respectively. The DSW used in our study contained both NO_3^--N and organic N. The significant positive correlation between the soil N_2O flux and the decomposition rate of the applied organic materials in the DSW treatment suggested that the decomposition of organic materials contributed to the production of N_2O. After the application of DSW as a basal fertilizer, the mineralization of organic materials in the DSW supplied N for N_2O production via nitrification. Because of the lower temperatures and WFPS after the basal fertilization, N_2O production via denitrification might be lower than that via nitrification. However, after the application of DSW as a supplemental fertilizer, the decomposition of the organic material and the consumption of oxygen in the soil might be accelerated because of the higher temperatures and soil microbe activity. That can induce higher N_2O production under suitable conditions for denitrification. The significant positive correlation between the soil N_2O flux and the decomposition rate of the applied organic materials and the selected soil NO_3^- concentration influencing the soil N_2O flux in summer in the DSW treatment indicated that the decomposition of the applied and remaining organic materials in summer caused higher soil N_2O emissions as in the COS treatment. When DSW was applied in the summer to the same experimental citrus orchard, a large soil N_2O flux (maximum 1858 μg N $m^{-2} \cdot h^{-1}$) was reported [19]. Therefore, DSW should be applied in seasons with a lower temperature so as to suppress the N_2O emissions induced by the applied N.

In our experimental field, the main process for N_2O production was denitrification in the summer. However, the main process for N_2O production after fertilization in the spring season depended on the form of N in the fertilizer. When fertilizer including organic materials is applied and remains in the summer, the organic materials can enhance the N_2O efflux due to the decomposition of organic materials and denitrification under higher temperatures and rainfall. Therefore, when using an NH_4^+-N–dominated N fertilizer, applying a controlled-release fertilizer and a nitrification inhibitor is useful for suppressing soil N_2O emissions from the study field [20,21]. On the other hand, DSW being dominated by the nitrate-N form and organic materials should be applied in lower-precipitation and -temperature conditions to suppress the N_2O emissions via denitrification.

4.2. N_2O Emissions from COS and DSW

The soil N_2O emissions (1.70 kg N ha^{-1}) from the unfertilized field in our study are higher than the reported mean value (0.36 kg N ha^{-1}) in well-drained agricultural fields in Japan [22]. However, the soil N_2O emissions from citrus orchards are not included in the report by Akiyama et al. [22]. Generally, soil is not disturbed in citrus orchard fields. In upland fields, the anaerobic conditions are usually established by the no-tillage management practice because of the higher bulk density with lower aeration potential and an increase soil N_2O emissions [23]. This indicates that citrus orchard fields potentially emit higher soil N_2O than other agricultural fields in which soil is tilled under conventional management. On the other hand, a reported annual soil N_2O emission value (0.93 kg N ha^{-1}) from a fertilized citrus orchard was lower than that in our study [10]. This may mean that the soil in our study field has a higher potential for soil N_2O production. Because there are few studies of soil N_2O

emissions from citrus orchards, scientific monitoring studies should be conducted to help establish N_2O mitigation methods in citrus orchards worldwide.

In our study, the EF of DSW was approximately half that of COS, while there were no significant differences in EF among the two different fertilizers. In Japan, reported EF values were 0.32% for synthetic fertilizer in well-drained upland field and they ranged from −1.0% to 0.9% for animal manure compost in grasslands [24]. Few studies report the EF of COS; Bouwman [25] reported the EF as 1.5%. The EFs of COS and DSW in our study were higher and lower than the values reported by Bouwman [25], respectively. These results suggest that COS and DSW are fertilizers with higher and lower potentials of inducing soil N_2O efflux, respectively. This difference between the two fertilizers might be caused by differences in the forms of N that they contain. Differences in the soil N_2O flux variation between COS and DSW areas after the basal and supplemental fertilizations can support this. Because the main process of N_2O production in the DSW treatment was thought to be denitrification after fertilization, drainage and rapid consumption of organic materials may immediately change soil conditions from anaerobic to aerobic. Rapid drainage may have also contributed to the rapid decrease and lower soil NO_3^- concentration in the DSW treatment compared to that in the COS area after the basal and supplemental fertilizations (Figure 4d). Furthermore, the higher amount of N leaching in the DSW treatment than in the COS treatment conveyed that the source of N for N_2O production was leached out of the surface soil with the soil water. Thus, the lower N_2O emission potential of the DSW treatment is due to the lower retention time of N sources for N_2O production and conditions suitable for denitrification. However, the timing of the DSW application should be carefully controlled, although the leached N below the topsoil can be absorbed by citrus roots in deeper soil layers. Additional studies may be required to investigate whether the N leached from top soil will be absorbed by citrus trees or become a source of NO_3^- in ground water.

5. Conclusions

The application of fertilizer containing organic materials can increase soil N_2O emissions through nitrification and denitrification when it is applied in hot and wet seasons. Soil N_2O emissions increase if the applied organic materials remain during the summer season. COS containing mainly NH_4^+-N has a higher potential for increasing soil N_2O emissions than DSW containing mainly NO_3^--N. The lower N_2O emission potential of soil treated with DSW might be because of the shorter retention time of N and suitable conditions for denitrification in the surface soil. This, however, can potentially increase N leaching from the surface soil. Therefore, to mitigate N_2O emissions and N loss, COS should be applied in seasons with relatively cool temperatures and lower rainfall.

Acknowledgments: We would like to express appreciation for Takasi Yamauchi, Takayuki Kouno, and Naoki Ohkubo at the University Farm, Faculty of Agriculture, Ehime University.

Author Contributions: Y.T., T.H., Y.K., T.I., and H.U. conceived and designed the experiments; Y.T., T.H., and S.O. performed the experiments; Y.T., T.H., and O.N. analyzed the data; all of the authors contributed reagents/materials/analysis tools and wrote the paper.

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

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