Analysis of factors controlling soil N₂O emission by principal component and path analysis method

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Abstract: Nitrous oxide (N₂O) is a potent greenhouse gas. Mitigating N₂O emission is critical for combating global climate change and improving the ecological environment. Many studies have focused on factors affecting N₂O emission from agricultural soils, but rarely on the relationship among these factors. In the present study, continuous measurement on N₂O emission was conducted in a maize system in Griffith, Australia and the relationships between N₂O emission, soil properties and weather conditions were examined. Principal component analysis and path analysis were used to analyze these data in correlation coefficient and the direct and indirect effects to N₂O emission. Results indicated that (1) the major factors affecting N₂O emission were WFPS, mineralized nitrogen (Mineral N), daily mean temperature (Tmean) and CO₂ concentration. The factors of direct influence N₂O emission were following Mineral N, CO₂, WFPS, and Tmean. The indirect influence N₂O emission was following Tmean, WFPS, Mineral N, and CO₂ concentration. (2) The standard multiple regression describing the relationship between N₂O emission and its major factors were $Y = -37.162 + 0.5267 X_1 + 0.4331 X_2 + 0.3014 X_3 + 0.2392 X_4$ ($r = 0.924$, $p < 0.01$, $n = 151$), where Y is N₂O emission, X₁ is Mineral N, X₂ is CO₂, X₃ is WFPS and X₄ is Tmean. (3) N₂O emission from agricultural soils can be monitored and mitigated through improved management practices such as irrigation, straw retention and fertilizer application.

Key words: N₂O, Principal component analysis, path analysis, determination coefficient

Introduction

Nitrous oxide (N₂O) is a potent greenhouse gas with a higher warming potential and longer retention time compared to other major agricultural greenhouse gases like carbon dioxide and methane. The potential warming effect of N₂O is 190 - 270 times more than that of CO₂. N₂O can remain in the atmosphere for as long as 150 years (Cao *et al.* 2006). Moreover, N₂O is photochemically active and destroys ozone in the stratosphere, which increases ultraviolet radiation (Gao *et al.* 2011; Huang *et al.* 2013). Therefore, reducing N₂O emission will have significant implications for global climate change and ecology (Dambreville *et al.* 2008).

Agricultural soil is a major source of N₂O emission in the world, which has contributed to the rising atmospheric N₂O concentration in recent decades (Eichner 1990; Sozanska *et al.* 2002). The Intergovernmental Panel on Climate Change (IPCC) Second Assessment Report estimated that the total N₂O emission from farmland is $350 \times 10^4 \text{ t Ny}^{-1}$, accounting for 61.4% of anthropogenic emissions, and 23.8% of global N₂O emissions (IPCC 2007). It is important to

understand the underlying mechanism and factors affecting N₂O emission from agricultural soils

Factors affecting N₂O emission from soils have been widely studied and applied in models. For example, Nevison (1996) established the relationship between N₂O emission and mineral nitrogen (N). He also estimated the N₂O emissions amount of global farmland to be about 2.1×10^3 kt N (excluding the background value) in 1990. The regression model was used to calculate the annual N₂O emission, which was 127 kt N in the UK, 75 kt N of which was from agricultural soils (Sozanska et al. 2002). The number of published N₂O emissions measurements is increasing steadily, providing additional information about driving factors of these emissions. The factors that significantly influence agricultural N₂O emissions are N application rate, crop type, fertilizer type, soil organic C content, soil pH and texture (Stehfest and Bouwman 2006). Some of these parameters in many studies have been incorporated into models to study their effects on N₂O emission. For instance, the NGAS model was used to simulate the N₂O annual emissions amount in traditional tillage and no-tillage under different scenarios of 2639 places in the US (Mummey *et al.* 1998). The CENTURY model and IPCC method were used to calculate the farmland N₂O emission in the US (Del Grosso et al. 2005). The results showed that the N₂O emission amount of CENTURY model simulation was 25% less than that of the IPCC method. The DNDC model was used to simulate the N₂O emission amount of paddy field in India (Pathak and Wassman 2005), which estimated that the N₂O emission amount in 4.225×10^7 ha irrigated paddy field was 40-50 kt N, and the intermittent irrigation increased N₂O emissions to 50-60 kt N.

While the driving factors of N₂O emission from agricultural soils have been extensively studied, the interaction among these factors on the emission is not well understood. Path analysis, a statistical technique that differentiates between correlation and causation, has been increasingly utilized to define the best criteria for selection in biological and agronomic studies. Path analysis is a standardized partial regression analysis which appears to be helpful in partitioning the correlation coefficients into direct and indirect effects. However, no published research exists to describe the interaction of driving factors of N₂O emission by path analysis.

Therefore, the objective of the present study was to investigate the major factors controlling soil N₂O emission and their relationship, by using correlation analysis, principal component analysis and path analysis. Then, the relationship of the major factors through path analysis was analyzed, resulting in implications for mitigating agricultural N₂O emission in the study area.

Material and methods

Study area

Nitrous oxide measurements were conducted in an experimental site 5 km south of Whitton (34° 30' S, 146° 11' E), Griffith which was established in 1999 to investigate the impacts of stubble management. The experimental site was located in the heart of the Murrumbidgee Irrigation Area

(MIA) with water supply from the Murray River. The soil is a Mundiwa clay loam, Aridic natrustalf. This is a duplex soil, with a shallow a horizon (0-20 cm) of massive or weakly structured clay loam with 50-60% clay in the top and increasing down the profile. The soil organic carbon content in 0-20 cm topsoil before sowing was 0.87%. The pH was 5.5 and soil bulk density 1.37 g cm^{-3} (Jeanene et al. 1995; Table 1). Water filled pore space (WFPS) is calculated by $\text{WFPS} = (\text{soil gravimetric water content} \times \text{bulk density}) / [1 - (\text{bulk density} / \text{particle density})]$ (Linn and Doran 1984). Maize is grown at the site on beds (two rows of plants per bed) and irrigated by furrow irrigation.

Tab.1

Experimental design

The field experiment commenced on 21 April, 2010 (the first day of the experiment, defined as day 1), and finished on 30 June, 2011 (day 466). The soil preparation period was from 21 April, 2010 to 22 October, 2010. The maize growth period was from 22 October, 2010 to 10 May, 2011. The soil idle period was from 10 May, 2011 to 30 June, 2011. A randomized block design with three replicates was used in the 12 experiments. There were two maize straw treatments in the field experiment. 1) Zero fertilization, maize straw burned and left on the field (0N-burn, control experiment); 2) application of 300 kg N ha^{-1} , maize straw mulched (6750 kg ha^{-1}) and incorporated into soil soon after harvest (300N-incorporated). In the maize growth period, fertilizers were applied twice, with ten irrigation events (Table 2). The first fertilization date was 22nd October (three days before sowing) at 112 kg ha^{-1} $(\text{NH}_4)_2\text{HPO}_4$. The second fertilization was 200 kg ha^{-1} urea on 6th December, 2010.

Tab.2

The N_2O flux from the soil-plant system was measured using transparent static chambers and analyzed by gas chromatography (HP 6890 series-II) with an electron capture detector (Liu et al. 2005). This system measures fluxes daily integrated over 2 or 3 day intervals which could avoid biases and errors. The measurement is a common practice in static method of emission measurements. Three flux chamber systems were deployed, each comprising two chambers, four chamber bases, a controller/logger and two sets of four Tedlar storage bags (Wang *et al.* 2009; Phillips and Podrebarac 2009). The size of chambers was $43 \text{ cm} \times 43 \text{ cm} \times 50 \text{ cm}$, $43 \text{ cm} \times 43 \text{ cm} \times 80 \text{ cm}$, $43 \text{ cm} \times 43 \text{ cm} \times 110 \text{ cm}$; they were changed with the maize growth. Each system was powered by a 12 V 120 amp-hour battery. The battery capacity was supplemented by an 80 W solar panel that extended the period between battery changeover to between 1 and 4 weeks. Soil temperature was measured by using type K thermocouples and soil moisture was measured by using TDR (Theta Probes ML2x, Delta-T Devices Ltd, Cambridge, UK). Both sets of sensors were logged by the controller/logger unit. Gas concentrations in the Tedlar sample bags were measured off-site at Aspendale. In addition CO_2 concentration was measured directly in the field using a Gascard_II CO_2 sensor (Edinburgh Instruments, Edinburgh, UK) incorporated into each chamber controller.

Data analysis

Eight factors were considered for this study: daily maximum temperature (Tmax), daily minimum temperature (Tmin), daily mean temperature (Tmean), rainfall (Rain), daily CO₂ (CO₂), amount of irrigation, straw returned and fertilizer applied. Daily CO₂ was used to measure the microbial activities, which influenced the soil organic matter decomposition and used the available C. Irrigation, straw retention and fertilizer application were occasional and not daily operation but had residual effects on soil water and N dynamics. Therefore, water-filled pore space (WFPS) was used to reflect the water dynamics following irrigation and rainfall events, whereas soil mineral N was measured to examine the decomposition effect of straw retention and fertilizer application on N dynamics. WFPS is calculated by $WFPS = (\text{soil gravimetric water content} \times \text{bulk density}) / [1 -$

$(\text{bulk density} / \text{particle density})]$ (Linn and Doran 1984). Maize is grown at the site on beds (two rows of plants per bed) and irrigated by furrow irrigation.

As a result, seven factors which affected the N₂O emission were selected. They were maximum temperature (Tmax), daily minimum temperature (Tmin), daily mean temperature (Tmean), rainfall (Rain), daily CO₂ (CO₂), WFPS and mineralized nitrogen (Mineral N).

This study used the correlation analysis to analyze the relationship between the N₂O and the other driving factors. Then the principal component analysis method was used to choose the main driving factors. Finally, using path analysis and the determination coefficient analyzed the relationship between the N₂O and the main driving factors, interrelation of the main driving factors.

Principal component analysis is a method of multivariate statistical analysis of important variables to multiple variables through a linear transformation to choose the less (Payal *et al.* 2006). Path analysis, a development of regression analysis, can be used for the analysis of multiple variables and the linear relationship between variables. It was the development of regression analysis (Berger *et al.* 2002). The determination coefficient is the relative determination degree of the reason for the results (DYX_iX_j), Y is the dependent variable (N₂O in this research), X_i and X_j is the independent variable (the any two factors in the research). If $i=j$, it means they are the same factor. Data were analyzed by using SPSS 13.0.

Results and discussion

Correlation analysis

N₂O emission was significantly and positively correlated with Tmax, Tmin, Tmean, WFPS, CO₂ and Mineral N ($r= 0.5549, 0.5241, 0.7729, 0.8345, 0.8262, 0.8507$, respectively, $p<0.01$; Table 3). Temperature, radiation and mineral N have been shown to increase soil microbial activity and decomposition of organic matter, which influences N₂O emission (Oertel *et al.*, 2012). The arid

climate of Griffith and sandy loam texture of the soil contribute to high water loss through evaporation or infiltration. The additional soil water just met the microbial activities (Wang *et al.* 2011). The soil moisture decreased when there was no precipitation, which inhibited microbial activities and the associated N₂O emission.

N₂O emission was not correlated with rain ($r=0.0259$). Mineral N was significantly and positively correlated with Tmax, Tmin, Tmean, WFPS and CO₂ ($r = 0.7259, 0.7123, 0.7591, 0.7307, 0.5972$, respectively, $p<0.01$). Mineral N was not correlated with rain ($r=0.1398$, respectively). Both of the N₂O and MineralN was not correlated with rain. This is because of the dry climate in Griffith region. The main source of soil moisture was irrigation; 10 irrigation events were applied in one maize season (Liu and Song 2010). WFPS was significantly and positively correlated with Tmax, Tmin, Tmean and CO₂ ($r=-0.5525, 0.6952, 0.6494$ $p<0.01, 0.5031, p<0.05$, respectively,).

Tab.3

Principal component analysis

To convert observations of possibly correlated variables into values of linearly uncorrelated variables, principal component analysis method was used to determine the major driving factors of N₂O emission (Tables 4 and 5).

The combined score of the first and second principal components is larger than 1 (Table 2). The cumulative variance contribution rate of the first and second principal components was 96.83% (Table 4). Therefore, to determine the major factors influencing N₂O emissions, only the first and second components were further examined. The first principal component was analyzed as main object and the second principal component as a supplement to determining the factors influencing N₂O emissions in the present study.

The component score coefficient matrix was used to determine the main factors in each principal component (Table 5). WFPS, CO₂ and Mineral N largely accounted for the first principal component, with a characteristic vector of 2.109, 2.119 and 2.151, respectively. This implies that WFPS, CO₂ and mineral N were the main factors to drive N₂O emission. Tmean (with a characteristic vector of 1.574) contributed less to N₂O emission than WFPS. The Tmean did in the first component and it is highest in the second component (with a characteristic vector of 1.355). So the mean temperature might have played a vital function in the N₂O emission. The WFPS and CO₂ reflected the soil moisture and SOC, respectively. They mainly influenced microbial activity, which decomposed the mineral N to discharge the N₂O. They were also the main factors (Nevison *et al.* 1996). Tmean was closer than Tmax and Tmin to the optimum temperature for microbial activities. Therefore, Tmean was an important factor. Rain didn't affect N₂O emission. The climate of the Griffith region was very dry, so the main source of soil water was irrigation. Therefore Tmax, Tmin, and Rain did not play an important role in the N₂O emission.

Principal component analysis showed that WFPS, Mineral N, Tmean, Rad, Rhmean and Rhmin were more important factors affecting N₂O emission, and should be considered when designing model for more robust simulation of N₂O emission.

Tab.4

Tab.5

Path analysis

According to correlation analysis and principal component analysis, WFPS, Mineral N, CO₂ and Tmean were the main controlling factors of N₂O emission. Path analysis was used to analyze the relationship among these four factors and establish a model to determine the relative importance of direct and indirect effects on N₂O emission.

The results of stepwise multiple regression analysis is shown in Table 6. Because the table was too long, only the first and the last regression results were presented. The standard multiple regression equation of the N₂O emission was $Y = -37.162 + 0.5267 X_1 + 0.4331 X_2 + 0.3014 X_3 + 0.2392 X_4$ ($r = 0.924$, $p < 0.01$, $n = 151$), where Y is N₂O emission, X₁ is Mineral N, X₂ is CO₂, X₃ is WFPS and X₄ is Tmean. Each coefficient was the direct path coefficient of each factor in the equation. The indirect correlation coefficient between each factor was obtained by multiplying direct path coefficient by the correlation coefficient between each factor (Table 7).

WFPS, CO₂, Mineral N and Tmean showed a direct positive effect (the corresponding direct path coefficients are 0.5267, 0.4331, 0.3014 and 0.2392, respectively) and indirect positive effect (the total indirect path coefficients are 0.6604, 0.6243, 0.7580 and 0.8818, respectively) on N₂O emission (Table 7). This indicates that WFPS, CO₂, Mineral N and Tmean could directly and indirectly affect the microbial activity and decomposition of organic matter in soil and control N₂O emission. The total indirect path coefficients of WFPS, CO₂, Mineral N and Tmean were greater than direct path coefficients. This was because the WFPS, Mineral N and Tmean could influence the microbial decomposition of organic matter and the mineral N to release the N₂O (Li *et al.*, 2003). On the other hand, CO₂ was an index which can reflect the microbial activities and soil organic matter (SOM) decomposition amount. So this suggests that WFPS, CO₂, Mineral N and Tmean mostly affected N₂O emission indirectly. Because WFPS and Mineral N included the irrigation, rainfall, straw retention and fertilizer application, they may mainly indirectly affect N₂O emission. This means that the temperature, microbial activities, straw retention and amount of fertilizer and soil water could influence the N₂O emission.

The factors directly influencing N₂O emission were the following: Mineral N, CO₂, WFPS, and Tmean. Factors indirectly influencing N₂O emission were: Tmean, WFPS, Mineral N, and CO₂ concentration (Table 7). The mineral N comprised fertilizer application and straw retention. The CO₂ was used to measure microbial activity, which influenced the soil organic matter decomposition. Applied fertilizer, retained straw, and soil organic matter were the resources used

by microbes to discharge the N₂O emission. The Mineral N and CO₂ directly represented the source of the N₂O emission. The WFPS and Tmean were used to reflect the soil moisture and temperature change, which influenced the environment for microbial activity. Therefore, the resources influenced the N₂O emission more directly than the environment. Environmental factors only indirectly influenced the N₂O emission.

Tab.6
Tab.7

The determination coefficients of influencing N₂O emission factors was in the order of DyX₁X₁ (0.2774) > DyX₁X₂ (0.2725) > DyX₁X₃ (0.2320) > DyX₁X₄ (0.1913) > the others (Table 8). This confirms that Mineral N, CO₂, WFPS and Tmean and the interaction between them were the main factors driving soil N₂O emission.

Tab.8

Conclusions

This study used the correlation analysis, principal component analysis and path analysis to analyze which were the main driving factors to affect the N₂O emission and the interrelation between them. The result showed that N₂O emission was positively correlated with Tmax, Tmin, Tmean, Rad, WFPS, Mineral N and CO₂, but negatively with Rhmean, Rhmax and Rhmin. The main driving factors which influenced N₂O emission were WFPS, Mineral N, CO₂ and Tmean. Path analysis and determination coefficient analysis indicated that the standard multiple regression equation for N₂O emission and each main factor was $Y = -37.162 + 0.5267X_1 + 0.4331X_2 + 0.3014X_3 + 0.2392X_4$ ($r = 0.924$, $p < 0.01$, $n = 151$), where Y is N₂O emission, X₁ is Mineral N, X₂ is CO₂, X₃ is WFPS and X₄ is Tmean. WFPS, CO₂, Mineral N, Tmean and the interaction between them were the main factors affecting soil N₂O emission. Mineral N, CO₂ influenced the N₂O emission more directly than WFPS and Tmean. Because WFPS included the irrigation and rainfall, CO₂ reflected the microbial activities which influenced the soil organic matter decomposition. Mineral N included the decomposition of retained straw, and fertilizer application. Therefore, these results suggest that irrigation, rainfall, microbial activities, straw retention and fertilizer application likely play an important role in N₂O emission, and that management of these practices will help mitigate N₂O emission in cropping systems. The future research will focus on these soil properties to analyze the interrelation among soil properties factors, main source factors of the N₂O emission and environment factors to influence the N₂O emission.

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Table

Table 1 Selected characteristics of the soil used in the study

parameter	Soil bulk density (g/cm ³)	pH	Field capacity (%)	Wilting point (%)	Clay fraction (%)	SOC in the surface soil (%)	C/N	Initial NO ₃ ⁻ (mg N/kg)	Initial NH ₄ ⁺ (mg N/kg)
data	1.37	5.5	38.01	10.22	53.11	0.87	10.90	6.30	3.32

Table 2 Irrigation in the experiment

Data	Irrigation amount(mm)	Data	Irrigation amount (mm)
28/10/2010	197	26/11/2010	200
18/12/2010	127	27/12/2010	90
5/1/2011	82	13/1/2011	102
28/1/2011	61	15/2/2011	74
24/2/2011	76	3/3/2011	76

Table3 The correlation coefficient of N₂O emission and other factors

	Tmax	Tmin	Tmean	Rain	WFPS	CO ₂	MineralN	N ₂ O
Tmax	1.0000	0.7967**	0.9592**	0.0895	0.5525**	0.5681**	0.7259**	0.5549**
Tmin		1.0000	0.9350**	0.2351*	0.6952**	0.5114*	0.7123**	0.5241**
Tmean			1.0000	0.1627	0.6494**	0.6613**	0.7591**	0.7729**
Rain				1.0000	0.1965	0.0467	0.1398	0.0259
WFPS					1.0000	0.5031**	0.7307**	0.8345**
CO ₂						1.0000	0.5972**	0.8262**
MineralN							1.0000	0.8507**
N ₂ O								1.0000

** . Correlation is significant at the 0.01 level -2-tailed).

* . Correlation is significant at the 0.05 level -2-tailed).

Table 4 Total Variance Explained

Component	Initial Seven values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.134	85.988	85.988	8.134	85.988	85.988
2	2.168	11.451	97.439	2.168	11.451	97.439
3	1.191	1.440	98.879			
4	0.187	0.642	99.521			
5	0.086	0.232	99.753			
6	0.054	0.135	99.888			
7	0.021	0.112	100			

Table 5 Component Score Coefficient Matrix

	Component	
	1	2
Tmax	0.124	0.079
Tmin	0.039	0.116
Tmean	1.574	1.355
Rain	0.018	0.119
WFPS	2.109	0.073
CO ₂	2.119	0.313

MineralN	2.151	0.113
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Extraction Method: Principal Component Analysis.

Table 6 The standard multiple regression coefficient

		Unstandardized coefficients		Standardized coefficients		
model		B	Std. Error	Beta	t	Sig.
1	(Constant)	-3.832	2.089	-	1.835	0.069
	MineralN	0.136	0.018	0.573	7.430	0.000
...	...	...	...	...	...	...
4	(Constant)	-37.162	7.434	-	4.098	0.000
	MineralN	0.5267	0.020	0.473	3.659	0.000
	CO ₂	0.4331	0.161	0.665	2.193	0.000
	WFPS	0.3014	0.214	0.341	2.231	0.005
	Tmean	0.2392	1.698	0.451	2.452	0.004

Table 7 Path coefficient of each factor on N₂O emission

Soil factor	Direct path coefficient	Indirect path coefficient				Total	Error path coefficient
		X ₁ (MineralN)	X ₂ (CO ₂)	X ₃ (WFPS)	X ₄ (Tmean)		
X ₁ (MineralN)	0.5267	1	0.2586	0.2202	0.1815	0.6604	0.2451
X ₂ (CO ₂)	0.4331	0.3145	1	0.1516	0.1581	0.6243	
X ₃ (WFPS)	0.3014	0.3848	0.2178	1	0.1553	0.7580	
X ₄ (Tmean)	0.2392	0.3998	0.2863	0.1957	1	0.8818	

Table 8 The determination coefficient of each factor

	X ₁	X ₂	X ₃	X ₄
	(Mineral N)	(CO ₂)	(WFPS)	(Tmean)
X ₁ (MineralN)	0.2774	0.2725	0.2320	0.1913

X_2 (CO_2)	0.1876	0.1313	0.1666
X_3 (WFPS)		0.0908	0.0936
X_4 (Tmean)			0.0572

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