



UNIVERSITI PUTRA MALAYSIA

***EVALUATION OF DICYANDIAMIDE TREATED UREA AND ORGANIC
MANURE ON NITROUS OXIDE EMISSION, NITROGEN UPTAKE AND
YIELD OF RICE GROWN ON ACID SULPHATE SOIL***

S.M. SHAMSUZZAMAN

ITA 2015 17



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By

S. M. SHAMSUZZAMAN

**Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

April 2015

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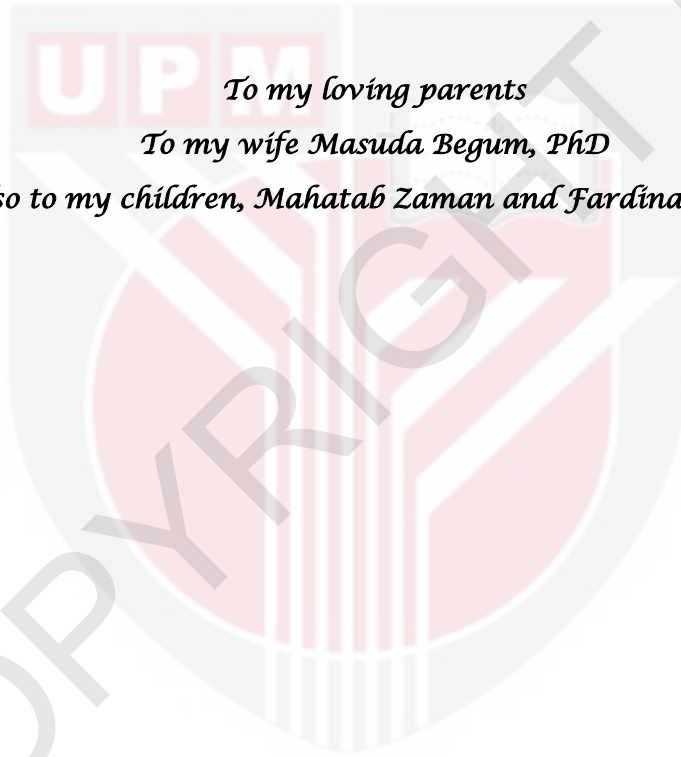


DEDICATION

To my loving parents

To my wife Masuda Begum, PhD

Also to my children, Mahatab Zaman and Fardina Zaman



Abstract of thesis presented to the Senate of University Putra Malaysia in fulfilment of the requirement for the Degree of Doctor of Philosophy

EVALUATION OF DICYANDIAMIDE TREATED UREA AND ORGANIC MANURE ON NITROUS OXIDE EMISSION, NITROGEN UPTAKE AND YIELD OF RICE GROWN ON ACID SULPHATE SOIL

By

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April 2105

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Rice soil is a major source of nitrous oxide (N_2O), and the application of N as inorganic and/or organic is an important factor affecting N_2O emissions. The nitrification inhibitor (NI), dicyandiamide (DCD) is effective in suppressing nitrification and N_2O emission. Therefore, the purpose of this study was to find out a feasible fertilization practice including DCD and organic manure (OM) for reducing N_2O emission with better yield and soil health of acid sulphate soil. An incubation study was conducted to observe the impacts of DCD with OM and urea on N dynamics and N_2O emission from acid sulphate soil. The experiment was conducted with two-level factorial: seven N sources and two NI levels. After 30 days of incubation, the mineral-N ($NH_4^+ + NO_3^-$) was highest ($255.07 \mu g g^{-1}$) for DCD with oil palm compost (OPC) + urea. The highest net N-mineralization ($213.07 \mu g g^{-1}$) was recorded for DCD with urea and net nitrification ($16.26 \mu g g^{-1}$) was recorded for urea alone, but the highest cumulative N_2O emission ($5.46 \mu g g^{-1}$) was in poultry dung (PD) + urea. In addition, DCD could effectively inhibit net N nitrification and N_2O emission (22.01-32.40%). A glasshouse experiment was conducted to investigate the effects of DCD with OM and urea on yield of MR219 rice and N_2O emission from acid sulphate soil. The experiment used a two-level factorial with four N sources and two NI levels. Nitrogen source and DCD interaction significantly increased the grain yield of rice (4.76-21.95%) compared to urea alone. The combined application of DCD with OPC + urea was most effective in a higher grain yield (22.81 g/hill), nutrient uptake; N ($631.64 g/hill$), P ($234.79 g/hill$), K ($651.01 g/hill$), and S ($87.95 g/hill$) followed by DCD with PD + urea. Seasonal peaks of N_2O flux occurred 3rd - 10th day after urea fertilization during the rice growing season with the value of $319.84-424.63 \mu m^2 h^{-1}$. Cumulative N_2O emission (CNE) during rice growth season was $3.10-3.63 kg N_2O-N ha^{-1}$ for N source and application of DCD decreased the CNE by 21.97-27.07%, respectively. A field experiment was conducted at Semerak, Kelantan, Malaysia to evaluate the influence of DCD with OM and urea on N_2O emission from MR 219 rice field and fertility of acid sulphate soil. The experimental design was similar to glasshouse experiment. The highest grain yield increase (31.62%) and total uptake of N ($164.79 kg ha^{-1}$), P ($55.42 kg ha^{-1}$), K ($153.28 kg ha^{-1}$), and S ($21.88 kg ha^{-1}$) was obtained for the application of DCD with OPC + urea followed by DCD with PD + urea. The trend of seasonal peaks of N_2O flux was similar

to glasshouse, but the values were 347.65-456.60 $\mu\text{m m}^{-2} \text{h}^{-1}$ for the N source. Cumulative N_2O emission during rice growth season was 3.27- 3.83 $\text{kg N}_2\text{O-N ha}^{-1}$ for N source. Application DCD decreased the CNE by 15.72-24.72 %. Soil pH, organic carbon, and soil primary- (N, P and K), secondary- (Ca, Mg and S) and micro-nutrient (Zn, Cu, Fe and Mn) were significantly influenced by N source only following the order of OPC + urea-N \geq PD + urea-N > rice straw + urea-N > urea-N (control). Finally, the integrated use of DCD with OPC and urea was more effective in reducing N_2O emissions with improving rice yield and soil health. Hence, combination of 13.5 kg ha^{-1} (15% of applied N) DCD with 1.8 t ha^{-1} (30% N of recommended dose) OPC and 90 kg ha^{-1} (75% N of recommended dose) urea may be the most potential combination to reduce N_2O emission, improve rice yield and health of acid sulphate soil in Malaysia.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENILAIAN UREA DAN BAJA ORGANIK DENGAN RAWATAN
DISIANDIAMID TERHADAP PEMBEBASAN GAS NITRUS OKSIDA,
PENGAMBILAN NITROGEN DAN HASIL PADI DI TANAH BERASID
SULFAT**

Oleh

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April 2015

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Sawah padi adalah sumber utama gas nitrus oksida (N_2O), dan penggunaan sumber N dari bahan bukan organik dan organik merupakan faktor penting yang mempengaruhi pelepasan gas N_2O . Perencat nitrifikasi (NI) disiandiamid (DCD) adalah berkesan dalam mengurangkan proses nitrifikasi dan pembebasan gas N_2O . Oleh itu, kajian ini dijalankan untuk mengetahui samada amalan pembajaan menggunakan DCD dan baja organik dapat mengurangkan pembebasan gas N_2O disamping meningkatkan hasil tanaman dan kesuburan tanah. Satu kajian inkubasi dijalankan untuk melihat kesan DCD bersama OM dan urea terhadap dinamik N dan pembebasan N_2O dari tanah asid sulfat. Eksperimen dijalankan secara dua peringkat faktorial: tujuh jenis sumber N dan dua jenis NI. Selepas 30 hari proses inkubasi dijalankan, mineral-N ($NH_4^+ + NO_3^-$) adalah tertinggi ($255.07 \mu g g^{-1}$) bagi DCD berserta kompos kelapa sawit + urea. Kadar bersih proses mineralisasi direkodkan bagi DCD bersama urea ($213.07 \mu g g^{-1}$) dan kadar bersih nitrifikasi ($16.26 \mu g g^{-1}$) dari rawatan urea sahaja, namun kadar kumulatif pelepasan N_2O didapati tertinggi ($5.46 \mu g g^{-1}$) dari baja tahi ayam (PD) + urea. Disiandiamid berkesan menghalang proses bersih nitrifikasi dan pelepasan N_2O (22.01-32.40%). Satu eksperimen rumah kaca dijalankan untuk menyiasat kesan DCD bersama OM dan urea terhadap hasil tanaman padi MR219 dan pembebasan N_2O dari tanah asid sulfat. Eksperimen yang dijalankan secara dua peringkat faktorial dengan empat jenis sumber N dan dua jenis sumber NI. Interaksi sumber N bersama DCD didapati meningkatkan hasil padi secara signifikan (4.76-21.95%) berbanding rawatan urea. Kombinasi rawatan DCD bersama OPC + urea adalah yang paling efektif dalam meningkatkan hasil tanaman ($22.81 g/hill$) dan pengambilan nutrien diikuti dengan rawatan DCD bersama PD dan urea. Puncak pembebasan gas N_2O berlaku pada hari ke-3 - 10 selepas pembajaan urea semasa musim pertumbuhan padi dengan anggaran $319.84-424.63 \mu m^2 h^{-1}$. Pembebasan kumulatif N_2O (CNE) semasa musim pertumbuhan padi adalah sebanyak $3.10-3.63 kg N_2O-N ha^{-1}$ bagi sumber N dan penggunaan DCD mengurangkan CNE sebanyak 21.97-27.07%. Satu kajian lapangan dijalankan di Semarak, Kelantan, Malaysia untuk mengkaji pengaruh DCD dengan OM dan urea terhadap pembebasan N_2O dari sawah padi MR 219 dan tahap kesuburan tanah asid sulfat. Rekabentuk eksperimen adalah serupa dengan eksperimen rumah kaca. Hasil tertinggi didapati meningkat (31.62%) dan jumlah pengambilan N ($164.79 kg ha^{-1}$), P

(55.42 kg ha⁻¹), K (153.28 kg ha⁻¹), dan S (21.88 kg ha⁻¹) telah diperolehi bagi aplikasi DCD bersama OPC + urea diikuti dengan DCD bersama PD + urea. Trend puncak bermusim pembebasan gas N₂O adalah serupa dengan kajian rumah kaca, namun kadar pembebasan adalah sebanyak 347.65-456.60 μg m⁻² h⁻¹ terhadap sumber N. Pembebasan N₂O kumulatif semasa musim pertumbuhan padi adalah 3.27-3.83 kg N₂O-N ha⁻¹ terhadap sumber N. Penggunaan DCD mengurangkan CNE sebanyak 15.72-24.72%. pH tanah, karbon organik dan nutrient-primer (N, P dan K), nutrient-sekunder (Ca, Mg dan S) dan nutrient-mikro (Zn, Cu, Fe dan Mn) adalah signifikan terhadap penggunaan sumber N sahaja mengikut turutan: OPC + urea-N ≥ PD + urea-N > jerami padi + urea-N > urea-N (kawalan). Kombinasi penggunaan DCD bersama OPC dan urea adalah lebih efektif dalam pengurangan pembebasan N₂O disamping meningkatkan hasil tanaman padi dan kesuburan tanah. Oleh itu, gabungan DCD bersama OPC dan urea adalah kombinasi yang paling berpotensi untuk mengurangkan pelepasan gas N₂O, meningkatkan hasil padi dan kesuburan tanah jenis asid sulfat di Malaysia.

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April 2015

I certify that a Thesis Examination Committee has met on 23 April 2015 to conduct the final examination of S. M. Shamsuzzaman on his thesis entitled "Evaluation of Dicyandiamide Treated Urea and Organic Manure on Nitrous Oxide Emission, Nitrogen Uptake and Yield of Rice Grown on Acid Sulphate Soil" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATION

AAS	- Atomic absorption spectrometry
AEN	- Apparent nitrogen efficiency
AH-N	- Alkali-hydrolyzable Nitrogen
AMO	Ammonia monooxygenase
ANOVA	- Analysis of variance
ANR	- Apparent N recovery
AOB	- Ammonia oxidizing bacteria
C/N ratio	- Carbon and nitrogen ratio
CD	- Cow dung
CEC	- Cation exchangeable capacity
CI	- Controlled irrigation
CM	- Cow manure
CNS	- Carbon nitrogen and sulphur
CP	- 2-chloro-6-(trichloromethyl)-pyridine
CRNF	- Control release nitrogen fertilizer
CV	Coefficient of variance
DAT	- Day after transplanting
DCD	- Dicyandiamide
DMPP	- 3, 4 dimethyl pyrazole phosphat
DMRT	- Duncan Multiple Range test
EC	- Electric conductivity
ECD	- Electron capture detector
EENF	- Enhanced-efficiency N fertilizers
EENF	- Enhanced-efficiency N fertilizers
EF	- Emission factor
EFB	- Palm oil empty fruit bunches
FAO	- Food and Agriculture Organization
FDE	- Fresh dairy effluent
FYM	- Farm yard manure
GHG	- Greenhouse gas
GML	- Ground magnesium limestone
GWP	- Global warming potential
HI	- Harvest index
IAEA	- International Atomic Energy Agency
ICP-MS	- Inductively coupled plasma mass spectrometer
IFA	- International Fertilizer Industry Association
INM	- Integrated nutrient management
IPCC	- Intergovernmental Panel on Climate Change
MARDI	- Malaysian Agriculture Research and Development Institute
MOP	- Muriate of potash
NBTPT	- N-(n-Butyl) Thiophosphoric Triamide

NI	- Nitrification inhibitor
NPK	- Nitrogen, Phosphorus and Potasium
NPKM	- Nitrogen, phosphorus, potasium and organic manure
NUE	- Nitrogen use efficiency
OA	- Organic amendment
OM	- Organic manure
OPC	- Oil palm compost
PCU	- Polymer-coated urea
PCUD	- Polymer-coated urea with the nitrification inhibitor dicyandiamide
PD	- Poultry dung
PFMC	- Plastic film mulching cultivation
POME	- Palm oil mill effluent
PVC	- Polyvinyl chloride (PVC) pipe
RCBD	- Randomized complete block design
RDN	- Recommended dose of nitrogen
REN	- Nitrogen recovery efficiency
RS	- Rice straw
SAS	- Statistical analysis system
SGMC	- <i>Sesbania aculeata</i> greening manuring crop
SOM	- Soil organic matter
SPAD	- Silicon Photon Activated Diode
TI	- Traditional irrigation
TN	- Total nitrogen
TSP	- Triple super phosphate
WFPS	- Water-filled pore space
WHC	- Water holding capacity

CHAPTER 1

INTRODUCTION

Nitrous oxide (N_2O) is an important trace gas that plays a significant role to global warming and the depletion of stratospheric ozone (Forster et al., 2007). The concentration of N_2O in atmosphere is lower than that of CO_2 , but its global warming potential (GWP) is 298 times higher than CO_2 (IPCC, 2007a) and it accounts for 5% of the total greenhouse effect (Houghton et al., 1996). The concentration of atmospheric N_2O has increased 16% over the last 250 years at a rate of $0.25\% \text{ year}^{-1}$ (IPCC, 2007b).

Agricultural soils have been identified as the main anthropogenic source of N_2O entering the atmosphere; globally releasing approximately $1.7\text{-}4.8 \text{ Tg } N_2O\text{-N } \text{yr}^{-1}$. It accounts for approximately 42% of anthropogenic N_2O emissions (IPCC, 2007c), and nitrogen (N) fertilization is considered as a basic source of N_2O emissions from agricultural soils (Mosier and Kroeze, 2000). Key agricultural management practices regulating N_2O formation and release from agricultural fields include use of organic manure as a fertilizer, crop cultivation and land management (Clayton et al., 1997). The type of N fertilizer and the application method also affect N_2O emissions (Ma et al., 2009). As a result, N_2O flux from soil increases with increasing N fertilization rates and intensive cropping (Mosier et al., 2004).

Rice (*Oryza sativa* L.) is the main crop of 89 countries in the world and also the staple food for half of the world population (Nachimuthu et al., 2007). Nearly 92% of the world rice is produced and consumed in Asia (Singh and Chinnusamy, 2006). In Malaysia, it is the third most important crop after oil palm and rubber with an annual production of 2154 thousand tons from 645 thousand hectares of land (USDA, 2008). Unfortunately, some of the soils in the rice farms are too acidic (acid sulfate soils) for rice cultivation, with soil pH frequently less than 3.5. When this occurs, Al and Fe contents in the solutions are usually very high. Rice yield in the area varies from year to year, but always remain within the limit of 1.29 and 3.06 tha^{-1} . According to Rutger (1981), rice plant requires pH of 5.0-7.5 to grow optimally, although it can tolerate a pH of 4.3-8.7 (Duke, 1973). Coronel (1980) also found no adverse effect of pH of 3.5-5.0 on rice root growth in a nutrient culture study in the Philippines. Ameliorative steps are needed to put acid sulfate soils into productive use.

Nitrogen (N) is the most important nutrient for rice but it is the most limiting element in almost all soils (Shukla et al., 2004). Cereals including rice accounted for approximately 50% of the worldwide N fertilizer utilized (IFA, 2009), but N recovery efficiency (REN) in rice plant is low. Based on a worldwide evaluation, REN has been observed to be around 30% in rice (Krupnik et al., 2004). This low REN is associated with large loss of N fertilizer from the soil plant system (Houshmandfar et al., 2008). Significant N losses can occur through NO_3^- leaching, NH_4^+ runoff and gaseous emissions of NH_3 and N_2O . These N losses from agricultural land pose a major threat to environmental quality worldwide as agriculture activities are reported to contributes 70% of N_2O emissions (Janzen et al., 1998).

Nitrous oxide related to rice cultivation is emitted to the atmosphere through denitrification and/or nitrification processes after chemical or organic fertilization (Tsuruta, 2002). Nitrification is the biological oxidation of NH_4^+ to NO_3^- and form NO_2^- intermediate and N_2O as by-product during this change after NH_4 fertilizer or NH_3 forming fertilizer application in aerobic soil. During denitrification process when the soil NO_3^- -N is reduced to dinitrogen (N_2), N_2O is emitted. It has been reported that N_2O is produced from paddy soil processes as a by-product of microbial nitrification and denitrification (Malla et al., 2005), which are affected by field water management and fertilizer application and so on (Xiong et al., 2007). The type of N fertilizer and the application method also affect N_2O emissions (Ma et al., 2009). Thus, controlling the mineral N supply is expected to be a useful method for reducing N_2O production (Yan et al., 2003).

The present irrigated rice system is characterized as low fertilizer N use efficiency due to over use of N fertilizers, which also poses potential adverse effects on environment and health (Jing et al., 2007). Application of urea in rice field is the potential source for N_2O . It was studied that the rice wheat system consumes very high amount of N fertilizer (about $240 \text{ kg N ha}^{-1}\text{y}^{-1}$), which has considerable impact on N_2O emissions (Pathak et al., 2002). On the other hands, the excessive application of fertilizer has made the soil environment worse year by year and has affected the growth of plants and crop yield (Bhattacharya et al., 2006).

Incorporation of organic manure (OM) with synthetic N fertilizers has been shown to support high grain yields and soil fertility in rice-wheat systems (Aulakh et al., 2001). In contrast, some studies have shown that the incorporation of crop residues generally increases the readily available C and N in soils, and therefore affects N_2O production and emissions from soils (Lemke et al., 1999). For example, Zou et al. (2005) found that the application of rape seedcake along with N fertilizer increased N_2O emissions, but combined application of wheat straw and N fertilizer decreased N_2O emissions. Therefore, it has been proved that organic fertilizer contributes to N_2O emission after soil application, but introduction of appropriate manure management techniques represents one opportunity for greenhouse gases mitigation (Cayuela et al., 2010).

Another strategy is the use of nitrification inhibitors (NIs) which has been shown to be highly effective in increasing the utilization efficiency of N by reducing leaching and nitrification/denitrification losses (Aulakh et al. 2001; Weiske et al. 2001; Hatch et al. 2005; Di and Cameron 2002, 2003). Nitrification inhibitors, such as DCD, nitrapyrin (NP) and 3,4-dimethylpyrazole phosphate (DMPP) help to slow down the conversion of NH_4^+ -N into NO_3^- -N by depressing the activities of ammonia-oxidizing microbes in soil, and thereby reducing NO_3^- -N leaching and N_2O emissions (Amberger 1989; Abbasi and Adams 2000; Di and Cameron 2002; Di et al. 2009). The DCD (containing 66.7% N) is the most widely used nitrification inhibitor because it is cheaper, nontoxic, less volatile, relatively water soluble, and relatively benign to non-target microbial communities (Zacherl and Amberger 1990; O'Callaghan et al. 2010; Di et al. 2011). Many studies have shown that DCD can significantly decrease NO_3^- leaching and N_2O emissions from cropping systems or grazed pasture systems (Di and Cameron 2002b, 2003; Di et al. 2007; Jumadi et al. 2008; Cui et al. 2011). It is well established that NIs reduce the risk for NO_3^- leaching, decrease N_2O emission, increase yield with better nutilization by plants (Zerulla et al., 2001). However, the persistence of excess NH_4^+ -N in soil for a longer time in alkaline soils may increase NH_3 volatilization (Gioacchini et

al. 2002; Banerjee et al. 2002; Asing et al. 2008) and some studies have reported that the amount of NH_3 volatilisation increased after the application of DCD (Banerjee et al. 2002; Mkhabela et al. 2006; Pi et al. 2009), while others showed DCD reducing NH_3 volatilisation (Dendooven et al. 1998; Tao et al. 2008). Dicyandiamide reduced the N_2O emission on average by 26% (Weiske et al., 2001), and reduced N_2O emission from irrigated rice by 11% (Kumar et al., 2000). Various formulations of DCD have been developed and their efficacy has been justified under a range of environmental and soil conditions (Di et al., 2007; Kelliher et al., 2008; Monaghan et al., 2009), and summarised that there was no environmental impacts from the use of these products.

To date, there are several findings of N sources (organic and inorganic) on the yield of rice and soil properties but limited study documented on the effect of DCD with organic manure and urea on N dynamics. Moreover, considerable work has been done in the past with DCD and urea for mitigating N_2O emission and enhancing N use by different crops, but very few information are available where combination of DCD, organic manure and urea are used for reducing N_2O gas emission and enhancing the use efficiency of applied urea-N by rice, and assessing their impacts on soil fertility. Rice is the third most important crops in Malaysia and urea is used to fulfil the N requirement of this crop which is consider as a main source of N_2O emission. In addition, acid sulfate soils are widespread along the coastal plains of the Malay Peninsula, with some being cultivated with rice. Following farmers' practice, rice yields are very low due to low pH and prevailing adverse conditions such as Al and/or Fe toxicity. Hence, the general objective was to find out a feasible fertilization practice including DCD and organic manure for reducing N_2O emission with better yield and soil health. The specific objectives were:

- i. to determine the effect of DCD with OM and urea on soil mineral-N content, net N-mineralization and net nitrification.
- ii. to identify the best combination of DCD with OM and urea which could minimize N_2O emission in rice growing season.
- iii. to search a feasible fertilization practice including DCD and OM for reducing chemical fertilizer for better yield and soil health.

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LIST OF PUBLICATIONS

- Shamsuzzaman, S. M.,** Hanafi, M.M., Saud, H. M., Samsuri, A.W. Begum, M. and Jantan, N. M. 2015. Impact of nitrification inhibitor with palm oil byproducts and urea on nitrogen dynamics and N₂O emission in acid sulphate soil. *Wulfenia Journal* (accepted).
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