



MONASH University

Interactions between coastal acid sulfate soils and greenhouse gas generation potential

Chang Xu

A thesis submitted for the degree of (*Doctor of Philosophy*) at
Monash University in (2021)

(*School of Earth, Atmosphere & Environment*)

Copyright notice

© The author (2021).

I certify that I have made all reasonable efforts to secure copyright permissions for third-party content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

Abstract.

Acid sulfate soils (ASS) usually contain large amounts of organic matter which can be potential sources of greenhouse gas emissions (GHGs) during decomposition in coastal wetlands and agricultural land. ASS are often found in low lying areas globally and are vulnerable to sea level rise and storm surge events. To manage ASS, liming is frequently used to reduce acidity and decrease N₂O emissions as a tool to mitigate GHG emissions by increasing soil pH. There is a knowledge gap in terms of the effects of fluctuating water tables on GHG emissions over longer periods of time. Also, the mitigation of GHG production in ASS by liming in subsoils and the mechanisms involved are still poorly known. The aim of this thesis is to determine the GHGs in ASS from coastal wetlands due to sea level rise in Australia and from agricultural land due to the post-glacial rebound by isostatic uplift in Finland and the lime treatment on ASS.

Intact soil cores from *Apium graveolens* (AG), *Leptospermum lanigerum* (LL), *Phragmites australis* (PA) and *Paspalum distichum* (PD) were collected and incubated under dry, flooded, and wet-dry cycle treatments to simulate sea level fluctuations. The results indicated that the flooded treatment decreased cumulative CO₂ emissions and cumulative N₂O emissions compared to the dry treatment. However, the flooded treatment had a higher global warming potential based on CO₂-equivalents compared to dry and wet-dry cycle treatment.

The effects of dry, flooded, and wet-dry cycle treatments on soil acidity and trace metals in ASS were also investigated at the end of the incubation experiment. The results showed that the highest net acidity occurred in the dry treatment. Brackish water inundation can provide a mechanism to prevent further oxidation of reduced inorganic sulfide (RIS) and can be an effective tool to reduce acidity by forming or reforming pyrite in temperate ASS environments.

Lime is used to manage soil pH and decrease N₂O emissions as a tool to mitigate GHG emissions. The effects of lime treatments on GHG emissions from ASS were identified in both agricultural land in Finland and coastal wetlands in Australia. Lime decreased N₂O due to the conversion from N₂O to N₂ via N₂O reductase during denitrification. Liming (CaCO₃) in ASS can generally reduce N₂O emissions, but also increase CO₂ emissions due to the dissolution of CaCO₃ and increased SOC mineralization. The total GHG emissions based on CO₂-equivalents in the lime treatments were generally higher than that in the non-limed soils due to the increased CO₂ emissions.

The overall results presented in this thesis demonstrated that CO₂ is the dominant GHG in the dry treatments while CH₄ dominates in flooded treatments. *Phragmites australis* had higher global warming potential compared with other vegetation types due to higher organic matter. Lime (CaCO₃) is important to manage

soil pH in ASS because it generally reduces N₂O emissions, but also increases CO₂ emissions due to the dissolution of CaCO₃ and increased SOC mineralization. Brackish water inundation can prevent further oxidation of RIS and reduce acidity in ASS.

Publications during enrolment

Xu, C., Wong, V.N.L., Reef, R.E., 2021. Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia. *Sci Total Environ* 763, 142949-142949.

Thesis including published works declaration

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes one original paper published in a peer reviewed journal and one submitted publication. The core theme of the thesis is to identify the relationship between acid sulfate soils and greenhouse gas emissions in coastal wetlands and agricultural land. The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the student, working within the school of Earth, Atmosphere & Environment under the supervision of Associate Professor Vanessa Wong and Associate Professor Ruth Reef.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research.

In the case of Chapters 2 to 5 my contribution to the work involved the following:

2	Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia	Published	85%. Conceptualization, Formal analysis, Investigation, original draft writing	Vanessa N.L. Wong (10%, Conceptualization, methodology, writing-Review & editing, supervision, funding acquisition) Ruth.E. Reef (5%, Writing-review & editing, supervision)	N
3	Effect of inundation on sulfide and potential acidity in coastal acid sulfate soils with different vegetation types in southern Australia	Not submitted	80%. Conceptualization, Formal analysis, Investigation, original draft writing	Vanessa N.L.Wong (15%, Conceptualization, methodology, writing-review & editing, supervision, funding acquisition) Rahul Ram (5%, Geochemical modelling, review & editing)	N
4	Effects of liming on N ₂ O and CO ₂ production in different horizons of boreal acid sulfate soil and non-acid soil	Returned for revision	75%. Conceptualization, Formal analysis, Investigation, original draft writing	Vanessa N.L.Wong (10%, Conceptualization, writing-review & editing, supervision) Anna Tuovinen (5%, Writing-review & editing)	N

				Asko Simojoki (10%, Conceptualization, methodology, writing- Review & editing, supervision, funding acquisition)	
5	Effect of lime and inundation on greenhouse gas emissions from temperate coastal wetland in southern Australia	Not submitted	90% Conceptualization, Formal analysis, Investigation, original draft writing	Vanessa N.L.Wong (10%, Conceptualization, methodology, writing- Review & editing, supervision, funding acquisition)	N

I have renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Student name: Chang Xu

Student signature:

Date:

I hereby certify that the above declaration correctly reflects the nature and extent of the student's and co-authors' contributions to this work. In instances where I am not the responsible author I have consulted with the responsible author to agree on the respective contributions of the authors.

Main Supervisor name: Vanessa Wong

Main Supervisor signature:

Date:

Acknowledgements

Throughout my PhD journey and the completion of this thesis, I am blessed with love and generosity from those around me both professionally and in my personal life. I cannot imagine finishing the degree without their input and want to thank all of them for their priceless support.

First of all, I want to express my heartfelt gratitude to my supervisors, Associate Professor Vanessa Wong, Associate Professor Ruth Reef and Dr Asko Simojoki for their devoted guidance, useful comments and dedicated support throughout the whole research work. The person I would like to thank most is my main supervisor, Associate Professor Vanessa Wong. I was lucky to be selected as a PhD student in acid sulfate soils project with my soil and water conservation research background in December 2017. In the beginning of my research work, Vanessa guided me step by step, like confirming research topics through several rounds of discussion, providing guidance for the lab work operation and assisting me with the soil sampling in the field. Vanessa also gave me offers to be demonstrators in soil science class which enriched my research experiences and gave me practical teaching experience. During the PhD journey, Vanessa not only played a role of supervisor, but also a friend caring about my career and family life. Her enthusiasm about soil science, cycling and strong leadership skills impressed me and led me all the way.

I also want to express my warmest thanks to Associate Professor Ruth Reef for her all the professional guidance, advice and encouragement. She showed me how to use R program when analysing data and helped me in identifying vegetation types for my project. Also, Ruth assisted me with the incubation experiment setup. I learnt lots of coastal ecosystem knowledge, data analysis skills, effective communication skills and women power from Ruth.

Special thanks to Dr Asko Simojoki who acted as my supervisor in the exchange project when I studied in the University of Helsinki in Finland. I highly appreciate the opportunity for lengthy discussion with him about the research plan and field sampling. Asko also showed me how to analyse acquired data effectively and assisted me with conducting experiments. I would like to express my sincere gratitude to Asko for his valuable advice for improving the manuscript through countless detailed emails and numerous zoom meetings. Asko's strict and responsible attitudes towards academics touched and inspired me.

During my research work, many people have valuable professional input in my project. Dr. Karen Little and Dr. Biplob Kumar Saha's help in my first incubation experiment and their guidance for the GHG emissions collection. Leigh Burgess prepared the PVC tubes for my incubation experiment and filed work preparation. Rachelle Pierson's assisted in performing the analysis of soluble cations analysis. Gigi Woods helped with the particle size distribution analysis. Dr. Rahul Ram assisted me with geochemical modelling in the thesis.

Special thanks to my officemate, Dr. Anindita Samsu, who supported me throughout my PhD study and encouraged me to join in the Monash Running group. I am thankful for the support from the Monash soil group and coastal group for their valuable advice and support, including Sarah, Ella, Pru, Matthew, Marycarmen and Sabrina.

I appreciate the financial support from Monash University and school of Earth, atmosphere and environment. I am grateful for the funding from the Australian Academy of Science's Thomas Davies Research Grant and Finnish National Agency of Education granting an EDUFI fellowship for my research visit to the University of Helsinki (Sep 2019 – Mar 2020). My Finnish research was carried out in the framework of FACCE ERA-GAS MAGGE-pH project.

Last but not least, I am deeply grateful for my parents' support and understanding throughout my life. Special thanks to my partner Fang Wen, who was by my side all the time. Not only did he assist me with the field sampling and lab work, he also contributed countless hours in proofreading and revision for my work during my research. Even more importantly, he encouraged me to take physical training seriously on a regular basis and was responsible for the cooking most of the time. Finally, the birth of my daughter, Aya, brought me endless happiness and taught me to become a strong, responsible and patient mom.

List of abbreviations

ASS = Acid sulfate soils

AASS = Actual acid sulfate soil

AG = Apium gravedens

AHD = Australian height datum

ANC = Acid neutralising capacity

AVS = Acid volatile sulfide

BOM = Bureau of Meteorology

CASS = Coastal acid sulfate soils

CaCO₃ = Calcium carbonate

Ca (OH)₂ = calcium hydroxide

CCMA= Corangamite Catchment Management Authority

CH₄ = Methane

CO₂-eq = CO₂-equivalents

CO₂ = Carbon dioxide

CRS = Chromium reducible sulfur

EC = Electrical conductivity

Eh = Redox potential

FF = Fineness factor

FIA = Flow Injection Analyser

FeS = Iron monosulfides

FeS₂ = Pyrite

Fe₃S₄ = Greigite

GC = Gas Chromatography

GHGs = Greenhouse gases

ICP-OES = Inductively coupled plasma - optical emission spectrometry

LL= Leptospermum lanigerum

IPCC = Intergovernmental Panel on Climate Change

N₂ = Nitrogen gas

NO = Nitric oxide

N₂O = Nitrous oxide

PA = Phragmites australis

PASS= Potential acid sulfate soils

PD = Paspalum distichum

RIS =Reduced inorganic sulfide

SO_4^{2-} = Sulfate

SOC = Soil organic carbon

SOM = Soil organic matter

SRB = Sulfate reducing bacteria

TAA = Titratable actual acidity

TN = Total nitrogen

$WFPS$ = Water filled pore space

Table of Contents

Abstract.....	II
Acknowledgements	VIII
List of abbreviations	X
List of Tables.....	XV
List of Figures	XVI
Chapter 1. Introduction	1
1.1 Acid sulfate soil theory	2
1.2 Formation of acid sulfate soils	2
1.2.1 Reduced inorganic sulfur formation	2
1.2.2 Iron sulfide oxidation and impacts	3
1.3 Distribution of acid sulfate soils	3
1.4. Acid Sulfate Soils and Greenhouse Gas Emissions	4
1.4.1 Greenhouse gas emissions.....	4
1.4.2 Drivers of GHG	5
1.5 Mitigation options to reduce environmental problems caused by ASS	8
1.6 Research Objectives	9
1.7 Thesis outline	9
1.8 References	11
Chapter 2. Effect of inundation on greenhouse gas emissions from coastal wetland soils with different vegetation types.....	18
Chapter 3. Effect of inundation on sulfide and potential acidity in coastal acid sulfate soils with different vegetation types in southern Australia.....	35
3.1 Abstract	36
3.2 Introduction.....	37
3.3. Materials and methods.....	39
3.3.1 Site description and soil collection	39
3.3.2 Experiment setup	40
3.3.3 Materials and methods	41
3.3.4 Geochemical Modelling	42
3.3.5 Statistical analysis	42

3.4. Results	43
3.4.1 Soil characterisation.....	43
3.4.2 AVS and CRS	46
3.4.3 TAA, ANC and net acidity	48
3.4.4 Trace metals and anions	50
3.4.5 Geochemical Modelling	53
3.5. Discussion	55
3.5.1 Net acidity	55
3.5.2 Dry treatment	55
3.5.3 Flooded treatment	56
3.5.4 Wet-dry cycle treatment.....	58
3.5.5 Net acidity in different vegetation types	58
3.6. Conclusion	59
3.7 References	60
<i>Chapter 4. Effects of liming on N₂O and CO₂ production in different horizons of boreal acid sulfate soil and non-acid soil</i>	<i>66</i>
<i>Chapter 5. Effect of lime and inundation on greenhouse gas emissions from temperate coastal wetlands in southern Australia</i>	<i>110</i>
5.1 Abstract	111
5.2 Introduction.....	111
5.3 Material and methods	113
5.3.1 Site description and sampling.....	113
5.3.2 Incubation Experiment.....	114
5.3.3 Soil Characterisation	116
5.4 Statistical analysis	117
5.5 Results	117
5.5.1 Soil pH, EC, redox potential, soil water content, SOC, TN and mineral N	117
5.5.2 CO ₂ emissions.....	122
5.5.3 CH ₄ emissions	124
5.5.4 N ₂ O emissions	125
5.5.5 Conversion to CO ₂ -eq.....	127
5.5.6 AVS, CRS, TAA, ANC and Net acidity	128
5.5.7 Trace metals and anions	130
5.6. Discussion	132
5.6.1 Influence of lime and inundation on AVS, CRS and acidity.....	132

5.6.2 Influence of lime and inundation on trace metals	133
5.6.3 CO ₂ emissions.....	133
5.6.4 CH ₄ emissions.....	134
5.6.5 N ₂ O emission.....	135
5.6.6 Influence of lime and inundation on GHG emissions	135
5.7 Conclusion	136
5.8 References	137
<i>Chapter 6. Discussion and concluding remarks</i>	<i>142</i>
6.1 General discussion.....	143
6.2 Future research	145
6.3 Conclusions	147
6.4 References	149

List of Tables

Table 3.1 Soluble cation and anion concentrations in Aire River water (surface water)	42
Table 3.2 Physical and chemical characteristics of the soils in the four vegetation type sites	44
Table 3.3 AVS and CRS between treatments in different soil horizons.....	47
Table 3.4 Pearson correlation analysis between RIS (AVS and CRS) and soil parameters	47
Table 5.1 Soluble cation and anion concentrations in Aire River water	115
Table 5.2 Physical and chemical characteristics of the soils	120
Table 5.3 SOC and TN after dry, flooded and wet-dry cycle treatments in both non-limed and limed soils	121
Table 5.4 Net changes of mineral N forms under different water level treatments in both non-limed and limed soils during the incubation (N mg kg ⁻¹)	122
Table 5.5 Cumulative CO ₂ , CH ₄ and N ₂ O emission in both non-limed and limed soils during incubation periods.....	124
Table 5.6 Cumulative CO ₂ , CH ₄ and N ₂ O emission after converting to CO ₂ -eq	127
Table 5.7 AVS and CRS concentrations between treatments in different soil horizons in both non-limed and limed soils	130
Table 5.8 Pearson correlation analysis between RIS (AVS and CRS) and soil parameters	130

List of Figures

Fig 3.1 Locations of sample sites AG (*Apium graveolens*), LL (*Leptospermum lanigerum*), PA (*Phragmites australis*), PD (*Paspalum distichum*) within Aire River Wildlife Reserve.40

Fig 3.2 Temporal variation in Eh and soil water content in AG (*Apium graveolens*) (a, b), LL (*Leptospermum lanigerum*) (c, d), PA (*Phragmites australis*) (e, f), PD (*Paspalum distichum*) (g, h) sites. Vertical bars denote standard error of means (n=4). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment)45

Fig 3.3 Titratable actual acidity (TAA), acid neutralisation capacity (ANC) and net acidity at the AG (*Apium graveolens*) (a, b, c), LL (*Leptospermum lanigerum*) (d, e, f), PA (*Phragmites australis*) (g, h, i), and PD (*Paspalum distichum*) sites (j, k, l). Vertical bars denote standard error of means (n=4)49

Fig 3.4 Soluble trace metals Al, Fe, Mn, Zn and Ni at the AG (*Apium graveolens*) (a, b, c, d, e), LL (*Leptospermum lanigerum*) (f, g, h, i, j), PA (*Phragmites australis*) (k, l, m, n, o), and PD (*Paspalum distichum*) sites (p, q, r, s, t). Vertical bars denote standard error of means (n=4).51

Fig 3.5 Soluble SO_4^{2-} and $\text{Cl}^-/\text{SO}_4^{2-}$ at the AG (*Apium graveolens*) (a, b, c, d), LL (*Leptospermum lanigerum*) (e, f, g, h), PA (*Phragmites australis*) (i, j, k, l), and PD (*Paspalum distichum*) sites (m, n, o, p). Vertical bars denote standard error of means (n=4).52

Fig 3.6 Chemical thermodynamic stability diagrams for Fe solubility in (A) in chloride brines (Fe^{2+} : 0.74 mg/kg; Cl^- : 61 mg/kg, 1542 mg/kg, 19400 mg/kg); and (B) sulfate waters (Fe^{2+} : 0.74 mg/kg; SO_4^{2-} : 46 mg/kg, 497 mg/kg, 2700 mg/kg); and Al solubility in (C) in chloride brines (Al^{3+} : 0.34 mg/kg; Cl^- : 61 mg/kg, 1542 mg/kg, 19400 mg/kg); and (D) sulfate waters (Al^{3+} : 0.34 mg/kg; SO_4^{2-} : 46 mg/kg, 497 mg/kg, 2700 mg/kg), as a function of pH vs. E_h (V). Solid bold lines are solubility limits and mineral stability fields, and dashed bold lines changing limits as a function of either SO_4^{2-} or Cl^- concentration. The conditions for the sulfate and chloride encountered in the present study from the Aire River water at 21°C at the beginning and end of the incubation experiments, are denoted as a function of initial, dry, flooded, and wet-dry cycles.54

Fig. 5.1 Temporal variations under dry, flooded and wet-dry cycle treatments in pH (a, b, c), Eh (d, e, f), soil water content (g, h, i). Vertical bars denote standard error of means (n=4). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS 119

Fig. 5.2 NO_3^- and NH_4^+ concentration under the dry (a, b), flooded (c, d), wet-dry cycle (e, f) in both non-limed and limed soils. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$). Vertical bars denote standard error of means ($n=4$).	120
Fig. 5.3 Temporal variations of CO_2 flux and cumulative CO_2 emissions under the dry (a, b), flooded (c, d), and wet-dry cycle (e, f) treatments. Vertical bars denote standard error of means ($n=4$). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS.	123
Fig. 5.4 Temporal variations of CH_4 flux and cumulative CH_4 emissions under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means ($n=4$). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS.....	125
Fig. 5.5 Temporal variations of N_2O flux and cumulative N_2O emissions under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means ($n=4$). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS.....	126
Fig. 5.6 TAA (Titratable actual acidity), acid neutralisation capacity (ANC) and net acidity under dry (a, b, c), flooded (d, e, f) and wet-dry cycle (g, h, i) treatments. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$). Vertical bars denote standard error of means ($n=4$).	129
Fig. 5.7 Soluble trace metals Al, Fe, Mn, and Zn under dry (a, d, g, j), flooded (b, e, h, k) and wet-dry cycle (c, f, i, l) treatments. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n=4$). Vertical bars denote standard error of means ($n=4$)......	131
Fig. 5.8 Soluble SO_4^{2-} and $\text{Cl}^-/\text{SO}_4^{2-}$ under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means ($n=4$).	132

Chapter 1. Introduction

1.1 Acid sulfate soil theory

Acid sulfate soils (ASS) are soils or sediments that contain oxidisable or partly oxidized sulfide minerals (Pons, 1973). In ASS environments, pyrite is the most prevalent sulfide mineral and usually represents the potential acidity in the system (Dent and Pons, 1995). Apart from pyrite, other oxidisable sulfides like iron monosulfides such as mackinawite, greigite and marcasite, are also present in minor amounts in ASS environment, which can be appreciable in bottom sediments of rivers, lakes and drains (Sullivan and Bush, 2000).

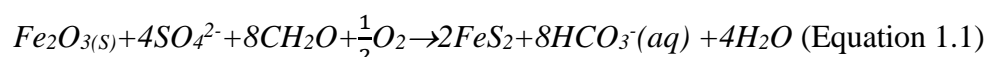
When sulfide mineral layers remain under anaerobic or waterlogged conditions, they usually have a near neutral pH and are therefore not problematic. Under these conditions, the soils are known as potential acid sulfate soils (PASS) as they have the potential to form sulfuric acid. However, sulfuric acid is generated resulting in a pH often below a value of 4 when sediments containing reduced inorganic sulfur are drained and oxidized. This results in the formation of actual acid sulfate soil (AASS) (Dent and Pons, 1995). This can be a natural process such as through coastal regression, isostatic rebound or drought caused by climate change (Boman et al., 2010a; Osterholm and Astrom, 2004), or it may be the result of anthropogenic interventions such as drainage of coastal areas for agriculture or activities during construction or mining (Astrom and Spiro, 2000; Burton et al., 2006a; Mathew et al., 2001).

1.2 Formation of acid sulfate soils

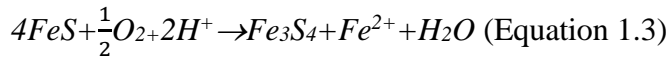
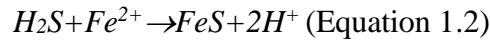
1.2.1 Reduced inorganic sulfur formation

PASS usually contains reduced inorganic sulfur (RIS) species, in the form of pyrite (FeS_2), iron monosulfides (FeS), greigite (Fe_3S_4) and elemental sulfur. RIS usually accumulates in waterlogged soils containing high amounts of organic matter, Fe (generally from Fe-containing minerals in the sediments) and dissolved sulfate, mainly derived from seawater (Dent, 1986; Fanning et al., 2002).

The formation of pyrite is catalyzed by sulfate reducing bacteria (SRB) and the reaction of pyrite formation is shown in Equation 1.

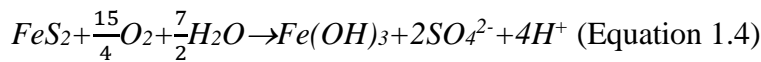


RIS species can be found in different mineral phases. Iron monosulfides (e.g. mackinawite) can form through the reaction of H_2S with free Fe^{2+} (Equation 1.2). Some intermediate species like greigite can be formed followed with the partial oxidation of mackinawite (Equation 1.3)

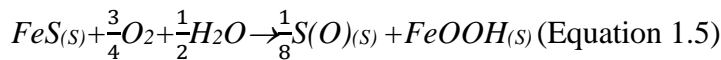


1.2.2 Iron sulfide oxidation and impacts

Pyrite is regarded as the main source of potential acidity in ASS environments. The oxidation of pyrite ultimately results in products such as Fe-hydroxides, acidity and sulfate, and involves a series of complex reactions, with several Fe and S intermediates and a highly acidic soil (Equation 1.4) (Dent, 1986; Fanning and Burch, 2000).



Iron monosulfides may also be oxidized when exposed to oxygen. Oxidation of iron monosulfides can lead to the generation of S(0) and Fe-oxyhydroxides (eg. FeOOH) (Equation 1.5) (Karimian et al., 2018)



The problems of ASS primarily arise from the large amounts of sulfuric acid that are formed when sulfide minerals are exposed to the atmosphere (Ljung et al., 2009; White et al., 2007). The acid and heavy metals can leach from the soil and enter nearby waterways and groundwater (Mosley et al., 2014c; Sohlenius and Öborn, 2004; Virtasalo et al., 2020). The acidity in drainage waters can then lead to low crop production and poor plant growth (Burton et al., 2008a; Ling et al., 2015). The disturbance of ASS in coastal areas of New South Wales and Queensland has resulted in degradation of lowland environments and estuarine water quality (Rampant and Croatto, 2003).

1.3 Distribution of acid sulfate soils

ASS have been estimated to occupy an area of over 17 Mha worldwide, including in South and Southeast Asia, West and Southern Africa, Australia, Latin America, boreal Europe, and Northern America (Andriess and Mensvoort, 2006; Ljung et al., 2009). ASS are often found in tropical coastal areas, estuarine floodplains and mangrove marshes, providing waterlogged environments for pyrite formation (Beek et al., 1980; Dent, 1986; Rabenhorst and Fanning, 2006). These coastal lands can contain high population density with high economic significance and are also desirable for agricultural and urban development (Andriess and Mensvoort, 2006; Dent and Pons, 1995).

Inland ASS can be formed under conditions where clearing of native vegetation has caused the rising of watertables, discharge of saline groundwater, and in wetlands (Fitzpatrick and Paul, 2008). Inland ASS have also been observed in rivers, streams channels, lakes, wetlands and floodplains (Creeper et al., 2013; Lamontagne et al., 2006; Wong et al., 2016a). Fitzpatrick et al. (1996) observed that ASS can form under freshwater conditions in inland areas, especially in the high rainfall (>500 mm per annum) in Australia where large changes in hydrology have occurred.

In Australia, the high probability ASS areas are estimated to be 154,269 km² and the low probability ASS areas are estimated to be 65,771 km². ASS covers an estimated 215,000 km² of which 58,000 km² is coastal ASS and 157,000 km² is inland ASS (Fitzpatrick et al., 2010). In Victoria, the area of ASS above the high water line was estimated to be about 55,000 ha (Rampant and Croatto, 2003).

In Finland, ASS represent 336,000 ha of agricultural land (Edén et al., 2012). The parent material of ASS was formed during the Litorina Sea Stage of the Baltic Sea, when the ocean water flowed into Baltic Basin. The ASS are located mainly on the coast of the Baltic Sea (Virtanen et al., 2017). The development of ASS is related to the melting of the ice and the gradual uplift of the earth's crust. The isostatic land uplift after glaciation and changes in water level of the sea promoted ASS forming processes (Mokma et al., 2000).

1.4. Acid Sulfate Soils and Greenhouse Gas Emissions

1.4.1 Greenhouse gas emissions

ASS usually contain large amounts of organic matter which can facilitate the emission of GHGs (Paasonen-Kivekäs and Yli-Halla, 2005; Šimek et al., 2011). The occurrence of large amounts of mineral nitrogen in acid sulfate soils can also lead to significant releases of nitrogen gases, including N₂O when the soil conditions and the environmental conditions promote the release (Parkin et al., 1985).

Carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) are significant greenhouse gases (GHG) that contribute to global warming (IPCC, 2007). CO₂ in soils is mainly derived from the decomposition of soil organic matter or from root respiration under aerobic condition (Amundson and Davidson, 1990).

Following the depletion of O₂, the sequence of anerobic process follows: denitrification, Mn reduction, Fe(III) reduction, SO₄²⁻ reduction and methanogenesis (Ponnamperuma, 1972). CH₄ in soils is generated by methanogenic microbes under anaerobic conditions (Dutaur and Verchot, 2007; Moore and Roulet, 1993).

N₂O emissions are usually related to soil nitrification and denitrification (Firestone et al., 1980).

Nitrification is the microbial transformation of ammonium (NH₄⁺) to nitrate (NO₃⁻) by ammonia oxidising bacteria under aerobic conditions, producing N₂O as a by-product (Kowalchuk and Stephen, 2001).

Denitrification is the microbial transformation of nitrate (NO₃⁻) to N₂ by denitrifying bacteria under anaerobic soil conditions, producing N₂O as an intermediate product (Davidson, 1992).

1.4.2 Drivers of GHG

In general, GHG emissions in wetlands are mainly influenced by soil organic matter, plant community composition, soil pH, soil water content, and water table position (Oertel et al., 2016; Whalen, 2005).

1.4.2.1 Soil organic carbon, total nitrogen, mineral nitrogen

GHG fluxes are positively correlated with soil organic carbon and total nitrogen (Chen et al., 2010; Sun et al., 2013; Tong et al., 2010; Zhang et al., 2013). When additional organic carbon is input into soils, soil respiration increases and more CO₂ can be produced (Bruce et al., 1997; Gallardo and Schlesinger, 1994). Chen et al. (2010) demonstrated that CO₂ flux was positively correlated with soil organic carbon (SOC) in mangrove soils. The increased carbon availability is conducive to methanogenesis and prone to release CH₄ (Megonigal and Schlesinger, 1997; Ziska et al., 1998). The available organic carbon is also a significant factor in providing energy to support denitrification and affect N₂O emissions (Amundson and Davidson, 1990). Previous studies showed that exogenous N had positive effects on microbial processes and the production of N₂O emissions (Lee et al., 1997; Munoz-Hincapie et al., 2002; Zhang et al., 2007). The early studies reported that N₂O emissions were positively correlated with mineral N (NH₄⁺ and NO₃⁻) as they can be metabolized by nitrifying and denitrifying microbes (Lindau and Delaune, 1991; Smith et al., 1983, Wrage et al., 2004).

1.4.2.2 Plant community composition

The dynamics of GHG emissions in coastal wetlands can be controlled by plant type due to different carbon structures in the plant parts, net primary production and aboveground biomass production (Tong et al., 2013; Xu et al., 2014). Plants provide different qualities and quantities of carbon and nitrogen into soils, which can affect the decomposition rate of organic matter (Vann and Patrick Megonigal, 2003). The potential decomposability of organic matter and N availability can be determined by the C/N ratio (Brady and Weil, 2016). Previous studies have demonstrated that herbaceous vegetation inputs tend to have a lower C/N ratio compared to woody vegetation (Bai et al., 2005). Woody roots also have more lignin and suberin than roots from herbaceous species (Armstrong and Armstrong, 2001). Soil organic matter with lower C/N ratios can

be decomposed rapidly and accelerate GHG emissions (Davidson et al., 2000). Therefore woody plants decompose more slowly than herbaceous plants.

Wetland plants can influence the rates of denitrification and methanogenesis due to the ability to change the redox potential by creating aerobic micro-sites in the rhizosphere through aerenchyma mechanisms (Philippot et al., 2009). Vegetation type can potentially affect N₂O production and transport in coastal ecosystems. Generally, plants can provide a source of root exudates and debris for nitrifiers and denitrifiers in the rhizosphere, accelerating N₂O production, however, plants can also compete for N with microorganisms in coastal wetlands and therefore inhibiting N₂O production (Yang et al., 2012).

Many studies have shown wetland plants possess aerenchyma mechanisms under inundated habitats, which can influence CH₄ production and emissions (Hirota et al., 2004; Inglett et al., 2012; Sun et al., 2013; Whalen, 2005). In coastal wetlands, Cheng et al. (2007) demonstrated that aerenchyma root systems can promote the CH₄ transport to the atmosphere under anaerobic conditions in *Phragmites australis*. The CH₄ released from wetlands through aerenchyma root tissues can account for 80-90% (Chanton et al., 2002). Thus, the plant root can affect GHG emissions in general.

1.4.2.3 Soil pH

Soil pH is a key factor that regulates chemical, biological and physical processes in soil and hence, is a significant variable to mitigate GHG emissions. The previous studies have demonstrated that soil pH had significant effects on CO₂ emissions (Andersson and Nilsson, 2001). In general, CO₂ emissions increase with rising pH values due to increased microbial activity (Hall et al., 1998; Reth et al., 2005). Management methods such as liming (CaCO₃) can affect CO₂ emissions as dissolution of the additional carbonate can release CO₂ (Grover et al., 2017).

The optimum pH of CH₄ emissions is near neutral (Dalal and Allen, 2008). Wang et al. (1993) found that the optimum pH of CH₄ production fell within the range of 6.6 to 7 and a small decrease in pH resulting from the introduction of acidic materials from neutral soils significantly decreased CH₄ production. The decreases in CH₄ production caused by low soil pH might be due to the effect of inhibiting activity of methanogens (Im et al., 2021). CH₄ emissions were enhanced by lime addition, which may be attributed to increased substrate supply for methanogenic microorganisms derived from decomposed organic matters (Murakami et al., 2005). SOC decomposition increased with lime application. Liming increased SOC solubility via either deprotonation or desorption reactions or enhanced microbial growth and (Garbuio et al., 2011; Grover et al., 2017).

Soil pH influences the denitrifiers and affects the end products of denitrification (Parkin et al., 1985; Samad et al., 2016a). During the process of denitrification, soil acidity inhibits the reduction of N_2O to N_2 , leading to N_2O becoming the more dominant end product (Parkin et al., 1985). Acidic conditions support N_2O production during denitrification by both autotrophic and heterotrophic nitrifiers (Martikainen and de Boer, 1993).

Lime addition can neutralize acidity and decreases mobility of trace metals in acidic soils due to the precipitation with increased pH (Green et al., 2007). Liming has also been widely used to decrease N_2O emissions as a tool to mitigate GHG emissions by increasing soil pH (Bakken et al., 2012; Wang et al., 2018; Zaman et al., 2007). In soils, denitrifiers reduce N_2O to N_2 by the enzyme N_2O reductase (van Spanning et al., 2007). Liming can enhance the activity of N_2O reductase and can reduce N_2O emissions via enhancing the reduction of N_2O in the soil to N_2 (Baggs et al., 2010; Stevens and Laughlin, 1998). Zaman and Nguyen (2010) showed that liming increased N_2 emissions and lowered $\text{N}_2\text{O}/\text{N}_2$ emissions ratio. However, acidic soils can stimulate N_2O production during denitrification as the low soil pH inhibits N_2O reductase to reduce the N_2O to N_2 (McMillan et al., 2016). Šimek and Cooper (2002) concluded from lab and field studies that when the soil pH decreased, the ratio of $\text{N}_2\text{O}/\text{N}_2$ increased while the relation between soil pH and potential denitrification is uncertain.

However, liming can also increase N_2O emissions in some cases (Bååth and Arnebrant, 1994; Baggs et al., 2010). Both nitrification and denitrification can be enhanced at higher soil pH and the N_2O emissions might increase (Šimek and Cooper, 2002). Qu et al. (2014) demonstrated that N_2O concentrations were much higher in the limed soils than in the non-limed soils because liming induced higher denitrification rates by promoting higher metabolic activity and enhancing the availability of soil organic matter. Similarly, Senbayram et al. (2019) observed that liming caused a significant increase in N_2O emissions due to the coupled impact of stimulated nitrification and denitrification in acidic sandy soil. Additionally, the liming effect was also moderated by soil type, soil temperature and other amendments (McMillan et al., 2016). In addition, liming (CaCO_3) is also a source of CO_2 emissions (Abalos et al., 2020), and this needs to be considered when assessing the benefit of lime as a GHG mitigation strategy.

1.4.2.4 Soil water content

Soil moisture content is an important factor affecting GHG production rates (Beringer et al., 2013). Early studies have demonstrated that the maximum respiration rate and CO_2 emissions usually occurs in soil at intermediate moisture contents (Davidson et al., 1998; Scott-Denton et al., 2003). Schaufler et al. (2010) observed that around 40% water filled pore space (WFPS) in grassland soils results in the highest CO_2 emissions. Nitrification is usually the dominant source of N_2O production under aerated conditions at WFPS

below 50-60% (Bateman and Baggs, 2005; Davidson et al., 2000). Conversely, the largest N₂O emissions are produced mainly by denitrification under more hypoxic or anaerobic conditions with an optimum often occurring near 60-70% WFPS (Davidson, 1993; Denmead et al., 2011; Dobbie and Smith, 2001; Gao et al., 2014).

1.4.2.5 Water table position

Sea level fluctuations will change the frequency and magnitude of wet and dry conditions and therefore water table levels are a key factor affecting GHGs fluxes at the water–atmosphere interface in coastal wetlands (Liu et al., 2017; Tong et al., 2013; Yang et al., 2017). In coastal wetlands, lowering the water level enhances oxygen availability in near-surface layers and accelerates decomposition rates of organic matter and aerobic respiration, leading to increased CO₂ emissions (Elberling et al., 2011; Hirota et al., 2007). CO₂ emissions from soils are elevated under aerobic conditions due to higher heterotrophic activity and respiration (Moore and Roulet, 1993).

Water table fluctuations can have a significant impact on N dynamics in terrestrial environments. Permanent flooding limits the availability of oxygen in soil and therefore reduces nitrification and lowers N₂O emissions. At very high soil water contents, N₂O is reduced to N₂ (Ruser et al., 2006). In contrast, oxic conditions and wet-dry cycles permit oxygen penetration into the soil during dry periods, thus enhancing N₂O emission by nitrification (Guo et al., 2014; Jiao et al., 2006). Rabot et al. (2016) found that N₂O produced and entrapped in the soil during the wet period can be released during dry periods in soil.

The position of the water table is a significant controlling factor on CH₄ emissions as high-water tables can cause oxygen depletion and therefore low redox potentials. With the decrease in redox potential, alternate electron acceptors are utilized in a sequence from NO₃⁻, metal oxides and SO₄²⁻ to the reduction of CO₂ to CH₄ under highly reducing conditions by methanogens (Kettunen et al., 1999; Mitsch et al., 2010).

1.5 Mitigation options to reduce environmental problems caused by ASS

Previous studies have demonstrated that remediation of ASS can include tidal-sea water inundation and freshwater inundation (Burton et al., 2011; Johnston et al., 2009a). These inundation options can promote Fe³⁺ and SO₄²⁻ reduction and lead to the reformation of reduced inorganic sulfide (RIS), like FeS₂, FeS and Fe²⁺ species in soils and decrease the acidity (Hicks et al., 2003; Keene et al., 2011; Powell and Martens, 2005). Remediation of ASS by tidal seawater inundation is effective and widely used in Australia (Burton et al., 2008a; Keene et al., 2011). The water table in coastal environments is predictable as it is affected by tides. The positive outcome from tidal inundation is that re-oxidising of RIS is less frequent due to the stable

seasonal hydrology of high water tables (Johnston et al., 2014). Conversely, remediation of ASS by freshwater inundation mainly relies on rainfall and runoff from rivers or streams. Consequently, wetland water tables in these environments have large seasonal fluctuations and large redox oscillations (Johnston et al., 2014). Therefore, where seawater is not available, surface soils have a high risk of exposure to the atmosphere during dry periods with freshwater flooding in natural environment. Exposure to the atmosphere can then lead to oxidation of RIS, acidification and increased mobile trace metals (Burton et al., 2009; Karimian et al., 2017). Also, the depletion of SO_4^{2-} relative to Fe^{3+} may constrain RIS reformation upon reflooding and lead to high concentrations of Fe^{2+} in freshwater wetlands (White et al., 1997).

1.6 Research Objectives

The primary aim of this thesis is to determine the greenhouse gas emissions in acid sulfate soils from coastal wetlands due to sea level rise in Australia and from agricultural land due to the post-glacial rebound by isostatic uplift in Finland. This research will provide improved understanding of the changes in biogeochemical cycling and greenhouse gas emissions in coastal wetlands and agricultural land. The results will assist land managers in remediating ASS using lime treatments and inundation strategies. At the same time, GHGs should be considered when lime and inundation mitigation methods are applied in coastal wetlands and agricultural lands.

The specific objectives were to:

- i. Identify the effects of inundation on GHGs under controlled conditions in coastal acid sulfate soils (CASS) with sea level rise with different vegetation types in southern Australia.
- ii. Identify the effect of inundation on soil chemistry in CASS with different vegetation types in southern Australia.
- iii. Determine the effect of lime (CaCO_3) addition on GHGs (N_2O and CO_2) and the product ratio of denitrification $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ in ASS and non-ASS under aerobic and anaerobic conditions in boreal agricultural land and coastal wetland.
- iv. Identify the effects of lime (CaCO_3) and inundation on GHGs and potential acidity in a coastal wetland soil in southern Australia.

1.7 Thesis outline

This thesis contains 6 chapters. It includes experimental Chapters 2 through to 5, which all include individual background, methods, results, discussion and result sections. Chapter 1 outlines the existing knowledge regarding ASS, GHGs and mitigation options to reduce environmental problems caused by ASS.

Chapter 2 identifies the effect of different inundation scenarios (dry, flooded, wet-dry cycle treatments) on greenhouse gas generation potential and identified that SOC, TN, mineral N, Eh, soil water content together affects GHG emissions in coastal wetlands in southern Australia. Chapter 3 demonstrates that brackish water inundation can provide a mechanism to prevent further oxidation of RIS and can be an effective tool to reduce net acidity by forming or reforming pyrite in temperate ASS environments. Chapter 4 compares different levels of lime (CaCO_3) treatments on GHGs (N_2O and CO_2) in ASS and non-ASS in boreal agricultural land and demonstrates that soil pH can change denitrification ($\text{N}_2\text{O} + \text{N}_2$) and the product ratio of denitrification $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ in ASS and non-ASS in Finland. Chapter 5 identifies the effects of lime (CaCO_3) treatment and brackish water inundation on GHGs, net acidity and trace metals in CASS in southern Australia. Chapter 6 includes a summary of all the results, followed by general discussion and possible future research directions based on the current results.

1.8 References

- Abalos, D., Liang, Z., Dörsch, P., Elsgaard, L., 2020. Trade-offs in greenhouse gas emissions across a liming-induced gradient of soil pH: Role of microbial structure and functioning. *Soil biology & biochemistry* 150, 108006.
- Amundson, R.G., Davidson, E.A., 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *Journal of Geochemical Exploration* 38, 13-41.
- Andersson, S., Nilsson, S.I., 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil biology & biochemistry* 33, 1181-1191.
- Andriesse, W., Mensvoort, M.E.F.v., 2006. Acid sulfate soils: distribution and extent, In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. CRC Press, Boca Raton, FL, pp. 14–19.
- Armstrong, J., Armstrong, W., 2001. Rice and Phragmites: effects of organic acids on growth, root permeability, and radial oxygen loss to the rhizosphere. *Am J Bot* 88, 1359-1370.
- Astrom, M., Spiro, B., 2000. Impact of isostatic uplift and ditching of sulfidic sediments on the hydrochemistry of major and trace elements and sulfur isotope ratios in streams, Western Finland. *Environmental Science & Technology* 34, 1182.
- Bååth, E., Arnebrant, K., 1994. Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. *Soil biology & biochemistry* 26, 995-1001.
- Baggs, E.M., Smales, C.L., Bateman, E.J., 2010. Changing pH shifts the microbial sources as well as the magnitude of N₂O emission from soil. *Biology and Fertility of Soils* 46, 793-805.
- Bakken, L.R., Bergaust, L., Liu, B., Frostegård, A., 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N₂O emissions from soils. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 367, 1226.
- Bateman, E.J., Baggs, E.M., 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biology and Fertility of Soils* 41, 379-388.
- Beek, K.J., Blokhuis, W.A., Driessen, P.M., Van Breemen, N., Brinkman, R., Pons, L.J., 1980. Problem soils: their reclamation and management, In: Alterra, L., Wageningen, NL (Eds.), *Land Reclamation and Water Management, Developments, Problems and Challenges*. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 43–72.
- Beringer, J., Livesley, S.J., Randle, J., Hutley, L.B., 2013. Carbon dioxide fluxes dominate the greenhouse gas exchanges of a seasonal wetland in the wet–dry tropics of northern Australia. *Agricultural and Forest Meteorology* 182-183, 239-247.
- Boman, A., Fröjdö, S., Backlund, K., Aström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.
- Brady, N.C., Weil, R.R., 2016. *The nature and properties of soils*, Fifteenth edition ed. Upper Saddle River, N.J. : Prentice Hall, Upper Saddle River, N.J.
- Bruce, A.H., Elisabeth, A.H., Robert, B.J., Chapin, F.S., Harold, A.M., Christopher, B.F., 1997. The fate of carbon in grasslands under carbon dioxide enrichment. *Nature* 388, 576.
- Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochimica et Cosmochimica Acta* 75, 3434-3451.

- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006. Elemental sulfur in drain sediments associated with acid sulfate soils. *Applied Geochemistry* 21, 1240-1247.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Hocking, R.K., Mitchell, D.R.G., Johnston, S.G., Fitzpatrick, R.W., Raven, M., McClure, S., Jang, L.Y., 2009. Iron-Monosulfide Oxidation in Natural Sediments: Resolving Microbially Mediated S Transformations Using XANES, Electron Microscopy, and Selective Extractions. *Environmental Science & Technology* 43, 3128-3134.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Johnston, S.G., Hocking, R.K., 2008. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* 253, 64-73.
- Chanton, J.P., Arkebauer, T.J., Harden, H.S., Verma, S.B., 2002. Diel variation in lacunal CH₄ and CO₂ concentration and $\delta^{13}\text{C}$ in *Phragmites australis*. *Biogeochemistry* 59, 287-301.
- Chen, G.C., Tam, N.F.Y., Ye, Y., 2010. Summer fluxes of atmospheric greenhouse gases N₂O, CH₄ and CO₂ from mangrove soil in South China. *Science of The Total Environment* 408, 2761-2767.
- Cheng, X., Peng, R., Chen, J., Luo, Y., Zhang, Q., An, S., Chen, J., Li, B., 2007. CH₄ and N₂O emissions from *Spartina alterniflora* and *Phragmites australis* in experimental mesocosms. *Chemosphere* 68, 420-427.
- Creeper, N., Fitzpatrick, R., Shand, P., 2013. The occurrence of inland acid sulphate soils in the floodplain wetlands of the Murray-Darling Basin, Australia, identified using a simplified incubation method. *Soil Use Manage* 29, 130-139.
- Dalal, R., Allen, D., 2008. TURNER REVIEW No. 18. Greenhouse gas fluxes from natural ecosystems. *Australian Journal of Botany* 56, 369-407.
- Davidson, E.A., 1992. Sources of Nitric Oxide and Nitrous Oxide following Wetting of Dry Soil. *Soil Science Society of America Journal* 56, 95-102.
- Davidson, E.A., 1993. Soil Water Content and the Ratio of Nitrous Oxide to Nitric Oxide Emitted from Soil, In: Oremland, R.S. (Ed.), *Biogeochemistry of Global Change: Radiatively Active Trace Gases Selected Papers from the Tenth International Symposium on Environmental Biogeochemistry*, San Francisco, August 19–24, 1991. Springer US, Boston, MA, pp. 369-386.
- Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. *Global Change Biology* 4, 217-227.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides. *BioScience* 50, 667-680.
- Denmead, O.T., Macdonald, B.C.T., White, I., Byrant, G., 2011. Gaseous Nitrogen Losses from Coastal Acid Sulfate Soils: A Short-Term Study. *Pedosphere* 21, 197-206.
- Dent, D., 1986. Acid sulphate soils: a baseline for research and development. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.
- Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263-276.
- Dobbie, K.E., Smith, K.A., 2001. The effects of temperature, water-filled pore space and land use on N₂O emissions from an imperfectly drained gleysol. *European Journal of Soil Science* 52, 667-673.
- Dutaur, L., Verchot, L.V., 2007. A global inventory of the soil CH₄ sink. *Global Biogeochemical Cycles* 21, n/a-n/a.
- Fanning, D.S., Burch, S.N., 2000. Coastal acid sulfate soils, In: R.I. Barnhisel (Ed.), *Reclamation of drastically disturbed lands*. ASA, CSSA, and SSSA, Madison, WI, pp. 921-937.
- Fanning, D.S., Rabenhorst, M.C., Burch, S.N., Islam, K.R., Tangren, S.A., 2002. Sulfides and sulfates, In: Dixon, J.B., Schulze, D.G., Daniels, W.L. (Eds.), *Soil mineralogy with environmental applications*. Soil Science Society of America, Madison, WI, pp. 229–260.

- Firestone, M.K., Firestone, R.B., Tiedje, J.M., 1980. Nitrous oxide from soil denitrification: factors controlling its biological production. *Science (New York, N.Y.)* 208, 749.
- Fitzpatrick, R., Marvanek, S., Powell, B., Grealish, G., 2010. Atlas of Australian Acid Sulfate Soils: recent developments and future priorities, In: Gilkes, R.J., Prakongkep, N. (Eds.), *Proceedings: 19th World Congress of Soil Science. Soil solutions for a changing world*. CSIRO, Brisbane, Australia, pp. 24-27.
- Fitzpatrick, R.W., Fritsch, E., Self, P.G., 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* 69, 1-29.
- Gallardo, A., Schlesinger, W.H., 1994. Factors limiting microbial biomass in the mineral soil and forest floor of a warm-temperate forest. *Soil Biology and Biochemistry* 26, 1409-1415.
- Gao, B., Ju, X., Su, F., Meng, Q., Oenema, O., Christie, P., Chen, X., Zhang, F., 2014. Nitrous oxide and methane emissions from optimized and alternative cereal cropping systems on the North China Plain: A two-year field study. *Sci Total Environ* 472, 112-124.
- Green, R., Waite, T.D., Melville, M.D., 2007. Treatment of Acid Sulfate Soil Drainage By Direct Application of Alkaline Reagents. *Water, air, and soil pollution* 178, 59-68.
- Grover, S.P., Butterly, C.R., Wang, X., Tang, C., 2017. The short-term effects of liming on organic carbon mineralisation in two acidic soils as affected by different rates and application depths of lime. *Biology and Fertility of Soils* 53, 431-443.
- Guo, X., Xueming, Y., Drury, C.F., Reynolds, W.D., Fan, R., 2014. The extent of soil drying and rewetting affects nitrous oxide emissions, denitrification, and nitrogen mineralization.(Report). *Soil Science Society of America Journal* 78, 194.
- Hall, J.M., Paterson, E., Killham, K., 1998. The effect of elevated CO₂ concentration and soil pH on the relationship between plant growth and rhizosphere denitrification potential. *Global Change Biology* 4, 209-216.
- Hicks, W., Fitzpatrick, R., Bowman, G., 2003. MANAGING COASTAL ACID SULFATE SOILS: THE EAST TRINITY EXAMPLE.
- Hirota, M., Tang, Y., Hu, Q., Hirata, S., Kato, T., Mo, W., Cao, G., Mariko, S., 2004. Methane emissions from different vegetation zones in a Qinghai-Tibetan Plateau wetland. *Soil Biology and Biochemistry* 36, 737-748.
- Im, S., Mostafa, A., Kim, D.-H., 2021. Use of citric acid for reducing CH₄ and H₂S emissions during storage of pig slurry and increasing biogas production: Lab- and pilot-scale test, and assessment. *The Science of the total environment* 753, 142080-142080.
- Inglett, K., Inglett, P., Reddy, K., Osborne, T., 2012. Temperature sensitivity of greenhouse gas production in wetland soils of different vegetation. *An International Journal* 108, 77-90.
- IPCC, 2007. Changes in Atmospheric Constituents and in Radioactive Forcing, *Climate Change: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Jiao, Z., Hou, A., Shi, Y., Huang, G., Wang, Y., Chen, X., 2006. Water Management Influencing Methane and Nitrous Oxide Emissions from Rice Field in Relation to Soil Redox and Microbial Community. *Communications in Soil Science and Plant Analysis* 37, 1889-1903.
- Johnston, S.G., Burton, E.D., Aaso, T., Tuckerman, G., 2014. Sulfur, iron and carbon cycling following hydrological restoration of acidic freshwater wetlands. *Chemical Geology* 371, 9-26.
- Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., Smith, D., Martens, M.A., McElnea, A.E., Ahern, C.R., Powell, B., Stephens, L.P., Wilbraham, S.T., van Heel, S., 2009. Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coastal and Shelf Science* 81, 257-266.

- Karimian, N., Johnston, S.G., Burton, E.D., 2017. Effect of cyclic redox oscillations on water quality in freshwater acid sulfate soil wetlands. *Science of The Total Environment* 581-582, 314-327.
- Keene, A.F., Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., McElnea, A.E., Ahern, C.R., Powell, B., 2011. Effects of hyper-enriched reactive Fe on sulfidisation in a tidally inundated acid sulfate soil wetland. *Biogeochemistry* 103, 263-279.
- Kowalchuk, G., Stephen, J., 2001. Ammonia-oxidizing bacteria: A model for molecular microbial ecology. *Annual Review of Microbiology* 55, 485-529.
- Lamontagne, S., Hicks, W.S., Fitzpatrick, R.W., Rogers, S., 2006. Sulfidic materials in dryland river wetlands. *Marine and Freshwater Research* 57, 775-788.
- Ling, Y.-C., Bush, R., Grice, K., Tulipani, S., Berwick, L., Moreau, J.W., 2015. Distribution of iron- and sulfate-reducing bacteria across a coastal acid sulfate soil (CASS) environment: implications for passive bioremediation by tidal inundation. *Frontiers in Microbiology* 6, 624.
- Liu, X., Ruecker, A., Song, B., Xing, J., Conner, W.H., Chow, A.T., 2017. Effects of salinity and wet-dry treatments on C and N dynamics in coastal-forested wetland soils: Implications of sea level rise. *Soil Biology and Biochemistry* 112, 56-67.
- Ljung, K., Maley, F., Cook, A., Weinstein, P., 2009. Acid sulfate soils and human health—A Millennium Ecosystem Assessment. *Environment International* 35, 1234-1242.
- Martikainen, P.J., de Boer, W., 1993. Nitrous oxide production and nitrification in acidic soil from a dutch coniferous forest. *Soil Biology and Biochemistry* 25, 343-347.
- Mathew, E.K., Panda, R.K., Nair, M., 2001. Influence of subsurface drainage on crop production and soil quality in a low-lying acid sulphate soil. *Agricultural Water Management* 47, 191-209.
- McMillan, A.M.S., Pal, P., Phillips, R.L., Palmada, T., Berben, P.H., Jha, N., Saggar, S., Luo, J., 2016. Can pH amendments in grazed pastures help reduce N₂O emissions from denitrification? – The effects of liming and urine addition on the completion of denitrification in fluvial and volcanic soils. *Soil biology & biochemistry* 93, 90-104.
- Megonigal, J.P., Schlesinger, W.H., 1997. Enhanced CH₄ Emissions from a Wetland Soil Exposed to Elevated CO₂. *Biogeochemistry* 37, 77-88.
- Mokma, D., Yli-Halla, M., Hartikainen, H., 2000. Soils in a young landscape on the coast of southern Finland.
- Moore, T.R., Roulet, N.T., 1993. Methane flux: Water table relations in northern wetlands. *Geophysical Research Letters* 20.
- Mosley, L.M., Zammit, B., Jolley, A.-M., Barnett, L., Fitzpatrick, R., 2014. Monitoring and assessment of surface water acidification following rewetting of oxidised acid sulfate soils. *Environ Monit Assess* 186, 1-18.
- Murakami, M., Furukawa, Y., Inubushi, K., 2005. Methane production after liming to tropical acid peat soil. *Soil science and plant nutrition (Tokyo)* 51, 697-699.
- Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., Erasmí, S., 2016. Greenhouse gas emissions from soils—A review. *Chemie der Erde - Geochemistry* 76, 327-352.
- Parkin, T.B., Sexstone, A.J., Tiedje, J.M., 1985. Adaptation of Denitrifying Populations to Low Soil pH. *Applied and Environmental Microbiology* 49, 1053.
- Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils, In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 29-96.

- Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, In: Dost, H. (Ed.), *Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils.* International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 13–20
- Powell, B., Martens, M., 2005. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar Pollut Bull* 51, 149-164.
- Qu, Z., Wang, J., Almøy, T., Bakken, L.R., 2014. Excessive use of nitrogen in Chinese agriculture results in high $N_2O/(N_2O+N_2)$ product ratio of denitrification, primarily due to acidification of the soils. *Global Change Biology* 20, 1685-1698.
- Rabenhorst, M.C., Fanning, D.S., 2006. Acid sulfate soils: problems, In: Lal, R. (Ed.), *Encyclopedia of Soil Science.* CRC Press, Boca Raton, FL, pp. 19–22.
- Rabot, E., Hénault, C., Cousin, I., 2016. Effect of the soil water dynamics on nitrous oxide emissions. *Geoderma* 280, 38-46.
- Rampant, P., Croatto, B.A., 2003. Acid sulfate soil hazard maps : guidelines for coastal Victoria. Department of Primary Industries.
- Reth, S., Reichstein, M., Falge, E., 2005. The effect of soil water content, soil temperature, soil pH-value and the root mass on soil CO₂ efflux – A modified model. *Plant and Soil* 268, 21-33.
- Ruser, R., Flessa, H., Russow, R., Schmidt, G., Buegger, F., Munch, J.C., 2006. Emission of N₂O, N₂ and CO₂ from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. *Soil Biology and Biochemistry* 38, 263-274.
- Samad, M.D.S., Ambarish, B., Lars, R.B., Timothy, J.C., Cecile, A.M.D.K., Karl, G.R., Gary, J.L., Sergio, E.M., 2016. Phylogenetic and functional potential links pH and N₂O emissions in pasture soils. *Scientific Reports* 6.
- Schaufler, G., Kitzler, B., Schindlbacher, A., Skiba, U., Sutton, M.A., Zechmeister - Boltenstern, S., 2010. Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. *European Journal of Soil Science* 61, 683-696.
- Scott-Denton, L.E., Sparks, K.L., Monson, R.K., 2003. Spatial and temporal controls of soil respiration rate in a high-elevation, subalpine forest. *Soil biology & biochemistry* 35, 525-534.
- Senbayram, M., Budai, A., Bol, R., Chadwick, D., Marton, L., Gündogan, R., Wu, D., 2019. Soil NO₃⁻ level and O₂ availability are key factors in controlling N₂O reduction to N₂ following long-term liming of an acidic sandy soil. *Soil biology & biochemistry* 132, 165-173.
- Šimek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science* 53, 345-354.
- Sohlenius, G., Öborn, I., 2004. Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. *Geoderma* 122, 167-175.
- Stevens, R.J., Laughlin, R.J., 1998. Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils. *Nutrient cycling in agroecosystems* 52, 131-139.
- Sullivan, L., Bush, R., 2000. The behaviour of drain sludge in acid sulfate soil areas: Some implication for acidification and waterways management, In: Slavich, P. (Ed.),
- Proceedings of a workshop on remediation and assessment of broadacre acid sulfate soils. NSW Agriculture, Wollongbar, Australia, pp. 43-48.
- Sun, Q.-Q., Shi, K., Damerell, P., Whitham, C., Yu, G.-H., Zou, C.-L., 2013. Carbon dioxide and methane fluxes: Seasonal dynamics from inland riparian ecosystems, northeast China. *Science of The Total Environment* 465, 48-55.

- Tong, C., Huang, J., Hu, Z., Jin, Y., 2013. Diurnal Variations of Carbon Dioxide, Methane, and Nitrous Oxide Vertical Fluxes in a Subtropical Estuarine Marsh on Neap and Spring Tide Days. *Journal of the Coastal and Estuarine Research Federation* 36, 633-642.
- Tong, C., Wang, W.-Q., Zeng, C.-S., Marrs, R., 2010. Methane (CH₄) emission from a tidal marsh in the Min River estuary, southeast China. *Journal of Environmental Science and Health, Part A* 45, 506-516.
- van Spanning, R.J.M., Richardson, D.J., Ferguson, S.J., 2007. Chapter 1 - Introduction to the Biochemistry and Molecular Biology of Denitrification. Elsevier B.V, pp. 3,I-20,II.
- Vann, C., Patrick Megonigal, J., 2003. Elevated CO₂ and water depth regulation of methane emissions: Comparison of woody and non-woody wetland plant species. *Biogeochemistry* 63, 117-134.
- Virtanen, S., Puustinen, M., Yli-Halla, M., 2017. Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate soil fields – based on soil redox potential and pH measurements. *Geoderma* 308, 252-259.
- Wang, Y., Guo, J., Vogt, R.D., Mulder, J., Wang, J., Zhang, X., 2018. Soil pH as the chief modifier for regional nitrous oxide emissions: New evidence and implications for global estimates and mitigation. *Glob Chang Biol* 24, e617-e626.
- Wang, Z.P., DeLaune, R.D., Patrick, W.H., Jr, Masscheleyn, P.H., 1993. Soil Redox and pH Effects on Methane Production in a Flooded Rice Soil. *Soil Science Society of America Journal*.
- Whalen, S.C., 2005. Biogeochemistry of Methane Exchange between Natural Wetlands and the Atmosphere. *Environmental Engineering Science* 22, 73-94.
- White, I., Melville, M., Macdonald, B., Quirk, R., Hawken, R., Tunks, M., Buckley, D., Beattie, R., Williams, J., Heath, L., 2007. From conflicts to wise practice agreement and national strategy: cooperative learning and coastal stewardship in estuarine floodplain management, Tweed River, eastern Australia. *Journal of Cleaner Production* 15, 1545-1558.
- White, I., Melville, M.D., Wilson, B.P., Sammut, J., 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management* 5, 55-72.
- Wong, V.N.L., Cheetham, M.D., Bush, R.T., Sullivan, L.A., Ward, N.J., 2016. Accumulation of sulfidic sediments in a channelised inland river system, southern Australia. *Marine and Freshwater Research* 67, 1655-1666.
- Xu, X., Zou, X., Cao, L., Zhamangulova, N., Zhao, Y., Tang, D., Liu, D., 2014. Seasonal and spatial dynamics of greenhouse gas emissions under various vegetation covers in a coastal saline wetland in southeast China. *Ecological Engineering* 73, 469-477.
- Yang, W.-B., Yuan, C.-S., Tong, C., Yang, P., Yang, L., Huang, B.-Q., 2017. Diurnal variation of CO₂, CH₄, and N₂O emission fluxes continuously monitored in-situ in three environmental habitats in a subtropical estuarine wetland. *Marine Pollution Bulletin* 119, 289-298.
- Yli - Halla, M., Puustinen, M., Koskiaho, J., 1999. Area of cultivated acid sulfate soils in Finland. *Soil Use and Management* 15, 62-67.
- Zaman, M., Nguyen, M., 2010. Effect of lime or zeolite on N₂O and N₂ emissions from a pastoral soil treated with urine or nitrate-N fertilizer under field conditions. *Agriculture, Ecosystems & Environment* 136, 254-261.
- Zaman, M., Nguyen, M.L., Matheson, F., Blennerhassett, J.D., Quin, B.F., 2007. Can soil amendments (zeolite or lime) shift the balance between nitrous oxide and dinitrogen emissions from pasture and wetland soils receiving urine or urea-N? *Australian Journal of Soil Research* 45, 543-553.
- Zhang, Y., Wang, L., Xie, X., Huang, L., Wu, Y., 2013. Effects of invasion of *Spartina alterniflora* and exogenous N deposition on N₂O emissions in a coastal salt marsh. *Ecological Engineering* 58, 77-83.

Ziska, L.H., Moya, T.B., Wassmann, R., Namuco, O.S., Lantin, R.S., Aduna, J.B., Abao Jr, E., Bronson, K.F., Neue, H.U., Olszyk, D., 1998. Long-term growth at elevated carbon dioxide stimulates methane emission in tropical paddy rice. *Global Change Biology* 4, 657-665.

Chapter 2. Effect of inundation on greenhouse gas emissions from coastal wetland soils with different vegetation types

This thesis chapter is based on the final manuscript published in the peer-reviewed Science of the Total Environment.



Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia

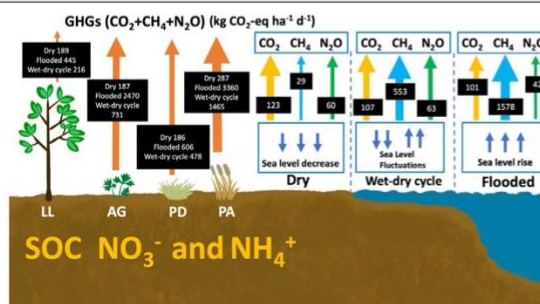
C. Xu, V.N.L. Wong*, R.E. Reef

School of Earth, Atmosphere and Environment, Monash University, Wellington Road, Clayton, VIC 3800, Australia

HIGHLIGHTS

- Coastal wetlands usually contain large amounts of organic matter which can be potential sources of greenhouse gas emissions
- We subjected soil cores to three inundation treatments; dry, flooded and wet-dry cycles from four vegetation types
- Positive correlations were found between soil organic carbon and CO₂ flux, and SOC and CH₄ flux.
- NO₂ and NO₃ concentrations were positively correlated with N₂O emissions when subjected to wet-dry cycles.
- Inundation decreased cumulative CO₂ emissions and N₂O emissions, but increased CH₄ emissions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 August 2020

Received in revised form 30 September 2020

Accepted 8 October 2020

Available online 15 October 2020

Editor: Jan Vymazal

Keywords:

Coastal wetland
Soil organic carbon
Inundation
Redox potential
Greenhouse gases
Woody vegetation
Herbaceous vegetation

ABSTRACT

Predicted sea level fluctuations and sea level rise with climate change will lead to inundation of coastal and estuarine soils. Coastal wetlands usually contain large amounts of organic matter, which can be potential sources of greenhouse gas emissions (GHGs; CO₂, CH₄, N₂O) during decomposition, but there are limited studies on the effects of sea level variation on GHGs in coastal wetlands. We measured the effect of brackish water inundation and wetting and drying cycles on GHG emissions from coastal wetland soil cores that supported four different vegetation types: *Apium graveolens* (AG), *Leptospermum lanigerum* (LL), *Phragmites australis* (PA) and *Paspalum distichum* (PD) from the estuarine floodplain of the Aire River in south-western Victoria, Australia. Intact soil cores were incubated under either dry, flooded, or a 14 day wet-dry cycle treatments for a total of 56 days at a constant temperature of 23 °C. CO₂, CH₄, and N₂O fluxes were investigated in closed chambers and measured with gas chromatography. In the dry treatment, a positive correlation was found between soil organic carbon (SOC) and CO₂ flux, and between SOC and CH₄ flux. Higher SOC is indicative of higher amounts of soil organic matter (SOM) which acts as a source of substrate for microbes to produce CO₂ or CH₄ emissions under aerobic or anaerobic conditions. The NO₂⁻ and NO₃⁻ concentrations were positively correlated with N₂O emissions in the wet-dry cycle treatment. NO₂⁻ and NO₃⁻ provide a supply of substrate for denitrification. The flooded treatment decreased cumulative CO₂ emissions by 34%, 25% and 14% at the LL, PA, PD sites, respectively, and decreased cumulative N₂O emissions by 42%, 39% and 43% at the AG, LL and PA sites, compared to the dry treatment. The wet-dry cycle treatment and dry treatment decreased cumulative CH₄ emissions for all vegetation types compared to the flooded treatment. The redox potential (Eh) was negatively correlated with CH₄ flux and positively

* Corresponding author.

E-mail address: vanessa.wong@monash.edu (V.N.L. Wong).

correlated N_2O flux at all sites. This study highlights the significance of sea level fluctuations when estimating GHG flux from coastal and estuarine floodplains which are highly vulnerable to inundation, and the role of SOC and mineral N as important drivers affecting GHG flux.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Globally, coastal wetlands occupy an estimated area of 66 Mha, which accounts for 10% of total wetland area (Lehner and Döll, 2004). Coastal wetlands can store organic carbon for long periods due to the slow decomposition rates which occur in anaerobic conditions as wetlands are permanently or temporarily flooded (Bouillon et al., 2008; Marín-Muñiz et al., 2015; Mitsch et al., 2013). Coastal wetlands occur in a zone between terrestrial and aquatic coastal ecosystems which represents a highly dynamic interface of mineral formation and sediment transport (Livesley and Andrusiak, 2012; Yang et al., 2017). The water table of coastal floodplains can be lowered by natural processes, including marine regression, isostatic uplift or drought caused by climate change (Boman et al., 2010; Mosley and Fleming, 2009), or may be the result of anthropogenic interventions such as extensive constructed drainage networks to facilitate the expansion of agricultural land and to remove surface water after flooding (Astrom and Spiro, 2000; Dent and Pons, 1995; Johnston et al., 2009; Mathew et al., 2001; Matthew and Megonigal, 2013). Lowered groundwater levels can increase decomposition of stored organic matter. At the same time, due to the low elevation and proximity to the ocean, coastal floodplains are more susceptible to inundation by seawater intrusion and sea level rise (Johnston et al., 2005; Webb et al., 2016; Wong et al., 2015) which alters carbon and nitrogen cycling and produces greenhouse gas (GHGs) emissions. Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are the main GHGs in these environments (IPCC, 2006).

Vegetation type and species composition in wetlands influences GHG emissions by controlling net primary production, organic matter input and organic matter quality (Marín-Muñiz et al., 2015; Van der Nat and Middelburg, 2000). Plants provide different quantities of C and N input into soils (Leifeld, 2018) which affects the rate at which organic matter is decomposed, and potentially, the GHGs that are produced during decomposition. The C/N ratio in soils is used to determine the potential decomposability of organic matter and the rate at which N is available to microorganisms. Soils which support herbaceous vegetation tend to have a lower C/N ratio compared to soil which supports woody vegetation as woody plants limit the supply of labile carbon for exudates and subsequent deposition belowground (Bai et al., 2005). Furthermore, these plants also have a lower N content. Organic matter with low C/N ratio generally decomposes rapidly and enhances GHG emissions as the decomposition of organic matter can be limited if there is insufficient N to support microbial growth and activity. Soil organic matter with lower C/N ratios can also indicate higher potential for nitrogen mineralization which can enhance N_2O emissions (Davidson et al., 2000; Trinsoutrot et al., 2000). N_2O emissions are generally negatively correlated with the C/N ratio, with lower N_2O emissions when the C/N ratio is above 30 (Pilegaard et al., 2006). At higher C/N ratios, especially when the C/N ratio exceeds 25, soil microbes will deplete the mineral nitrogen (NO_3^- and NH_4^+) and subsequently lower N_2O emissions (Gentile et al., 2008; Muhammad et al., 2011).

Because coastal wetlands are affected by tidal fluctuations, these wetlands experience both anaerobic and aerobic conditions, which can provide an ideal environment for higher decomposition rates of organic matter and associated production of GHGs (Altor and Mitsch, 2008; Hirota et al., 2007; Mitsch, 2015). A number of studies have quantified GHG emissions in different coastal ecosystems, typically in (1) estuarine saltmarshes (Bartlett et al., 1987; Maher et al., 2015; Poffenbarger et al., 2011; Tong et al., 2013), (2) mangrove swamps (Chen et al., 2010; Ganguly et al., 2008; Livesley and Andrusiak, 2012),

(3) coastal lagoons (Chuang et al., 2017; Gupta et al., 2008; Mendoza Mojica et al., 2013) and (4) tidal freshwater marshes (Megonigal and Schlesinger, 2002; Van der Nat and Middelburg, 2000; Weston et al., 2011).

GHG emissions are largely controlled by water level fluctuations, tidal water height and soil temperature in these environments (Hirota et al., 2007; Sun et al., 2014; Tong et al., 2013). Aboveground biomass and composition of plants are also important controlling factors (Hirota et al., 2007; Tong et al., 2013) as these can influence below-ground processes. Chen et al. (2012) found that higher SOC and mineral N contributed to higher GHG emissions in mangroves, while Gribsholt et al. (2005) concluded that a large marsh surface was crucial for N transformation and nitrifiers produced N_2O under low O_2 concentrations and high NH_4^+ availability.

Coastal wetlands have high temporal and spatial variations in GHG emissions that can be directly related to the water table depth (Chen et al., 2012; Olsson et al., 2015). The intermittent tidal (wet-dry) cycles induces alternating aerobic and anaerobic conditions and subsequent variations in redox potential (Eh) (Sun et al., 2014; Webb et al., 2016; Yang et al., 2017), affecting mineralization of soil organic matter (SOM) (Groffman and Tiedje, 1988; Harrison-Kirk et al., 2013; Rabot et al., 2016). Wet-dry cycles also occur over longer time periods due to seasonal changes from precipitation, storm surge events and seasonal flooding (Livesley and Andrusiak, 2012). Under aerobic conditions when watertables are lower, decomposition of SOM is rapid. Higher water tables due to flooding or sea level rise causes O_2 to decrease and aerobic oxidation of organic matter is also decreased as anaerobic respiration occurs. The redox reactions occur in descending order of standard reduction potential (E^0) due to decreasing energy yields (Ponnamperuma, 1972). When O_2 is depleted, NO_3^- reduces N_2 when the Eh decreases below +250 mV (Sparks, 2003). With the decrease in Eh under flooded conditions, alternate electron acceptors are utilized in a sequence from NO_3^- to N_2 or N_2O , Mn^{4+} to Mn^{2+} , Fe^{3+} to Fe^{2+} , SO_4^{2-} to H_2S and CO_2 to CH_4 (Kettunen et al., 1999; Mitsch et al., 2010). In submerged soils, the decomposition of the organic matter is dependent on facultative and obligate anaerobic microbes which operate at a much lower energy than aerobic microbes. Therefore organic matter decomposition rate is much lower in flooded soils (Degens, 1965).

Soil CO_2 exchange is a combination of decomposition of soil organic matter and plant root (autotrophic) respiration (Amundson and Davidson, 1990). When additional organic carbon is input into soils, soil respiration increases and more CO_2 can be produced (Bruce et al., 1997; Gallardo and Schlesinger, 1994). CO_2 emissions from soils are higher under aerobic conditions compared to anaerobic conditions due to higher heterotrophic activity and respiration (Moore and Roulet, 1993; Scanlon and Moore, 2000) and higher decomposition of organic matter rates (Chen et al., 2012; Hirota et al., 2007). Aerobic conditions during wet-dry cycles can further increase the activity and respiration of microbes and the decomposition rate of organic matter in soils (Denef et al., 2001; Liu et al., 2013). Higher CO_2 fluxes can occur after rewetting (Ruser et al., 2006). Reduced microbial decomposition occurs during dry periods and a flush of microbial activity occurs during the wet periods of wet-dry cycles (Lundquist et al., 1999).

N_2O is produced in soils by two main biological processes: nitrification and denitrification (Davidson et al., 2000; Wrage et al., 2001). In soils and sediments, N_2O is produced as a by-product of nitrification during the microbial transformation of NH_4^+ to NO_3^- by ammonia oxidising bacteria under aerobic conditions (Kowalchuk and Stephen,

2001). However, during denitrification, N_2O is produced as an intermediate product in the microbial transformation of NO_3^- to N_2 by denitrifying bacteria under anaerobic soil conditions (Knowles, 1982). In coastal wetlands, the inputs of N are derived from N-fixation, fertilizer, groundwater, tidal inputs and atmospheric deposition (Moseman-Valtierra et al., 2011; Zhang et al., 2013). The mineralization of organic N rate varies between coastal wetlands depending on organic matter quantity and lability. Previous studies showed that mineral N (NH_4^+ and NO_3^-) promoted N_2O emissions since it can be metabolised by both nitrifiers and denitrifiers in soils (Moseman-Valtierra et al., 2011; Seitzinger and Kroeze, 1998; Wrage et al., 2004). The dominance of nitrification or denitrification as the principle source of N_2O depends on whether the soils are aerobic or anaerobic and availability of mineral N (Davidson, 1992).

Under aerobic conditions, N_2O production is mainly due to nitrification with high NH_4^+ concentration and O_2 availability (Lindau and Delaune, 1991; Smith et al., 1983). For example, Gribsholt et al. (2005) found that 31% of added NH_4^+ was transformed to N_2O in the presence of O_2 in a tidal freshwater marsh. In coastal wetlands, denitrification depends on O_2 availability, the source of NO_3^- , and organic carbon. The NO_3^- supply for denitrification is derived from tidal water, groundwater, and precipitation or directly from nitrification.

Under flooded conditions, N_2O might further be reduced to N_2 by denitrifying bacteria so that N_2 is the dominant end product of denitrification rather than N_2O (Rusch and Rennenberg, 1998; Ruser et al., 2006). Denitrification in saturated conditions usually produces <10% N_2O as the end product (Smith et al., 1983). However, coastal wetlands can become sources of N_2O where NO_3^- concentrations are high (Moseman-Valtierra et al., 2011). For example, Allen et al. (2007) summarized that denitrification is the main contributor to N_2O emissions in subtropical mangrove sediment with high NO_3^- which was derived from groundwater where the Eh was negative. However, short-term N_2O pulses after rewetting dry soils have also been observed in some studies (Firestone and Tiedje, 1979; Smith and Parsons, 1985).

CH_4 in wetland soils is generated by methanogenesis during decomposition of organic matter under anaerobic conditions (Dutaur and Verchot, 2007; Moore and Roulet, 1993). Vegetation can promote methanogenesis directly through root exudation and indirectly by enhancing C input. In coastal wetlands, aerenchyma root systems facilitate CH_4 transport from soil to the atmosphere during anaerobic conditions. (Chanton et al., 2002; Cheng et al., 2007).

While previous studies (Van der Nat and Middelburg, 2000; Webb et al., 2016; Zhang et al., 2013) have measured one or two GHGs in wetland ecosystems and focused on the short-term tidal fluctuation effects on GHGs emissions, there is a knowledge gap in terms of the effect of fluctuating water tables on GHG emissions (CH_4 , CO_2 and N_2O) over longer periods of time in coastal wetlands, which can occur with sea level rise and storm surge events. To improve our understanding of GHG production in coastal wetlands, we studied the CH_4 , CO_2 and N_2O fluxes and their relationship with inundation treatments under controlled conditions. In our study, we selected four different vegetation types representing typical plants in coastal wetlands which are commonly found in wetland areas in southern Australia. The following hypotheses were identified (1) Different vegetation provides different qualities and quantities of SOC and N input to the soil to affect GHG flux; (2) Wet-dry cycle treatment will affect SOC and N transformation and enhance GHG flux compared to permanently flooded treatment.

2. Materials and methods

2.1. Site description and sampling

Samples were collected from the Aire River floodplain, located in the Otway Ranges to the west of Apollo Bay in south-western Victoria (38°47'43.1" S, 143°28'37" E), Australia (Fig. 1). The Aire River is one of the largest rivers in south-western Victoria and enters the sea via a

large estuarine lake complex west of Cape Otway. The total catchment of Aire River Valley is 35,310 ha with a river length of 44 km and estuary length of 7.1 km according to the Corangamite Catchment Management Authority (CCMA) (CCMA, 2015). The Aire River Valley is a floodplain of the Calder, Aire and Ford river systems and these rivers combine close to the Aire River East Campground before flowing to the sea at the Aire River Mouth. The Aire River estuary mouth is intermittently closed to the sea (CCMA, 2014) and as a result, the depth of Aire River estuary can change significantly from its upper reaches to where it connects to the sea. The Aire River floodplain hosts significant Ecological Vegetation Classes (EVCs), including brackish hermland, coastal dune scrub, coastal dune grassland in the lower estuary and estuarine wetland, and swamp scrub, tall marsh, swampy riparian woodland in the upper estuary (CCMA, 2015). Sites were located in four different vegetation types, including *Apium graveolens* (AG), *Leptospermum lanigerum* (LL), *Phragmites australis* (PA), and *Paspalum distichum* (PD). *Apium graveolens* (AG) is a herbaceous species, *Leptospermum lanigerum* (LL) is a woody species of tea tree, *Phragmites australis* (PA) is a common reed, and *Paspalum distichum* (PD) is a fast-growing grass. The PA (38°47'43.1" S, 143°28'37.1" E; -18 m Australian height datum (AHD) where 0 m AHD is approximately at sea level) and LL (38°47'42.1" S, 143°28'33.5" E; +9 m AHD) sites were located in a wildlife reserve and AG (38°46'14.11" S, 143°27'37.3" E; +8 m AHD) and PD (38°46'01.6" S, 143°28'09.9" E; +3 m AHD) sites were located in grazed areas which were drained. The climate at Aire River is a cool maritime climate, the region has an average annual rainfall of 894.8 mm, ranging from 41.6 mm (February) to 106.4 mm (July). The mean annual temperature is 17.3 °C varying from 13 °C (July) to 21.5 °C (January) (Bureau of Meteorology (BOM), 2019).

A total of 48 intact soil cores were collected from the top 20 cm of soil by pushing down a PVC tube (h = 40 cm, d = 10 cm) sharpened at the bottom. All the plant material was removed from the soil surface by scalping prior to core collection. The cores were excavated and capped at the bottom, sealed with parafilm and plastic wrap for transport. The cores were kept cool at 4 °C until analysis. Additional bulk soil from 0–5 cm, 5–10 cm, 10–20 cm soil layer from each site was sampled for characterisation, with one subsample placed in to a freezer at -80 °C, and one sub sample air-dried and sieved at 2 mm until further analysis (Rayment and Lyons, 2011). According to the Australian Soil Classification (Isbell, 2016), the soil profiles were classified as a Hydrosol at the PA site, a Dermosol at the AG and PD sites, and a Tenosol at the LL site (Isbell, 2016). The soil profiles were analogous to a Histosol, Mollisol and Entisol (USDA Soil Taxonomy) (Soil Survey Staff, 2014) at the PA, AG and PD, and LL sites.

2.2. Incubation experiment

Soils were incubated in PVC tubes (d = 10 cm, h = 40 cm) under dry conditions, flooded conditions, and alternate wet-dry cycles of 14-d each for a total of 56 days. The dry treatment did not have water added and soil moisture content decreased during the incubation period. In the flooded treatment, the soils were flooded with Aire River water (Table 1) which was maintained at 5 cm above the soil surface and the volume of the overlying Aire River water was 392.5 cm³ for the duration of the experiment. In the wet-dry cycle treatment, soils were initially flooded with 5 cm of overlying Aire River water in the first 7 days and drained for the following 7 days during 1 cycle. The alternating wet-dry cycles were chosen to simulate episodic events such as storm surges in coastal wetlands and repeated four times. All cores were incubated at a constant room temperature of 23 °C. There were four replicates for each treatment.

GHG (CH_4 , CO_2 and N_2O) emissions of each soil core were collected at Day 1, 3, 6, 10, 14, 17, 21, 24, 28, 31, 35, 38, 42, 45, 49, 52 and 56. We sampled the gas emissions at 0 and 10 min in duplicate after closing the chamber. Gas emissions were collected using a 25-ml gas-tight syringe (SGE, 25MDR-LL-GT) within 10 s and transferred into pre-evacuated 12-ml Exetainer® vials with silicon septa (Labco, UK). The

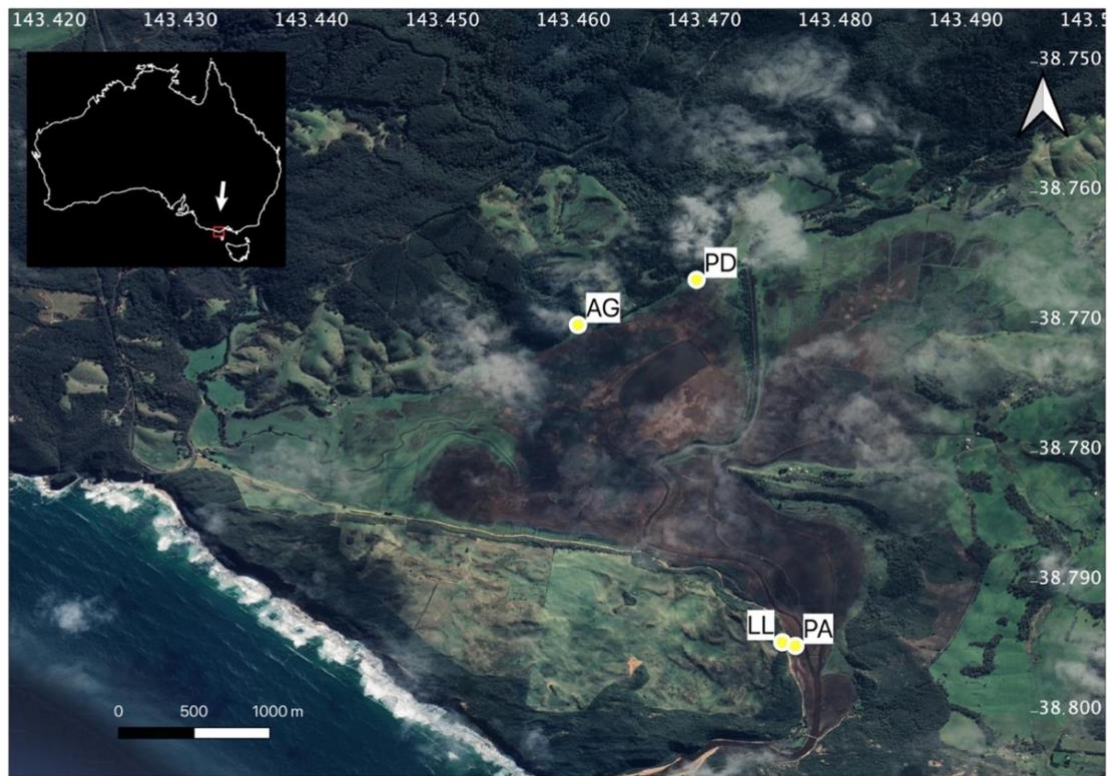


Fig. 1. Locations of sample sites AG (*Apium graveolens*), LL (*Leptospermum lanigerum*), PA (*Phragmites australis*), PD (*Paspalum distichum*) within the Aire River Wildlife Reserve.

Table 1
Soluble cation and anion concentrations in Aire River water (surface water).

Site	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
Aire River water	55.33	141.65	1227.45	1993.39	0.4	106.51

GHG concentrations were measured using an Agilent 7890 gas chromatograph (GC). The flux rates, F_{CH_4} , F_{CO_2} , F_{N_2O} , were calculated using Eqs. (1) and (2). All CH_4 , CO_2 , N_2O flux rates were corrected for air temperature during the measurement and presented as [$\mu\text{g m}^{-2} \text{h}^{-1}$]

$$F_{CH_4 \text{ or } CO_2 \text{ or } N_2O} = \frac{b \times V_{CH} \times MW \times 60 \times 10^6}{A_{CH} \times MV_{corr} \times 10^9} \quad (1)$$

where A_{CH} is the basal area of the measuring chamber [m^2]; b is increase in concentration [ppb/min]; MW_{CH_4-C} is the molecular weight of CH_4-C [12 g/mol]; MW_{CO_2-C} is the molecular weight of CO_2-C [44 g/mol]; MW_{N_2O-N} is the molecular weight of N_2O-N [44 g/mol]; MV_{corr} is the temperature-corrected molecular volume [m^3/mol]; V_{CH} is the volume of the measuring chamber [m^3].

$$MV_{corr} = 0.02241 \times \left(\frac{273.15 + T}{273.15} \right) \quad (2)$$

where MV_{corr} is as defined above; T is air temperature during the measurement [$^{\circ}\text{C}$]; 0.02241 m^3 is the molar volume of an ideal gas at 1 atm, 273.15.

The cumulative CH_4 , CO_2 and N_2O emissions ($\text{g m}^{-2} \text{d}^{-1}$) were calculated by the flux rate value ($\text{mg m}^{-2} \text{h}^{-1}$) of all sampling data during the incubation periods (56 days).

In the end, GHGs were converted to CO_2 -equivalents ($CO_2\text{-eq}$) based on global warming potential of 25 for CH_4 and 298 for N_2O to compare the greenhouse gas impacts between the different inundation treatments.

2.3. Soil characterisation

Frozen soil samples were thawed under N_2 before analysis. Soils were oven-dried at 85°C and lightly crushed and sieved to 2 mm. Soil pH, electrical conductivity (EC) were measured in 1:5 soil:water extracts (Rayment and Lyons, 2011). Soil pH and EC were measured using a Conductivity-TDS-Salinity pH-ORP-Temperature meter. Soluble cations (Ca, Cu, Fe, K, Na, Mg, Mn, Zn, Si, Al and Pb) in 1:5 soil:water extracts were measured by inductively coupled plasma - optical emission spectrometry (ICP-OES) (iCAP,7000 series). Dissolved nutrients (NO_3^- , NO_2^- and NH_4^+) were analysed on a Lachat QC 8500 Flow Injection Analyser (FIA). The starting soil moisture content and bulk density were determined by weight after drying at 105°C for 24 h. Soil organic carbon (SOC) and total nitrogen (TN) content were measured on dried (85°C) soil samples by high temperature combustion using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Soil particle size distribution was analysed by Beckman Coulter 13320 laser diffraction analysis after pretreatment with 10% H_2O_2 to remove organic matter. The Eh and soil water content in the treated cores were measured by platinum electrodes and HS2 Hydrosense II system (model CS 659), respectively, when the GHG samples were taken during the incubation period.

2.4. Statistical analysis

The means of emission flux of the four vegetation sites and three inundation treatments were obtained from the four replicates for each treatment. The area under the curve was applied to calculate the cumulative CO₂, N₂O and CH₄ emissions (g m⁻² d⁻¹). One-way analysis of variance (ANOVA) in combination with a post-hoc Tukey test was conducted to detect significant changes ($p < 0.05$) in cumulative emissions (CO₂, CH₄ and N₂O) and main soil characteristics between dry, flooded and wet-dry cycle treatments and between different vegetation types. All the analyses were performed using Prism 8 and R studio.

3. Results

3.1. Soil organic carbon, total nitrogen, mineral nitrogen

SOC was significantly different between all the vegetation types ($p < 0.05$). The SOC concentration decreased with depth from a mean (\pm s.e.m.) of $6.02 \pm 0.12\%$ in the 0–5 cm layer to $4.24 \pm 0.01\%$ in the 10–20 cm layer in the AG site, and from $5.48 \pm 0.4\%$ in the 0–5 cm layer to $4.44 \pm 0.27\%$ in the 10–20 cm layer in the LL site, and from $20.42 \pm 0.33\%$ in the 0–5 cm layer to $16.87 \pm 1.07\%$ in the 10–20 cm layer in the PA site, and from $7.6 \pm 0.54\%$ in the 0–5 cm layer to $5.38 \pm 0.08\%$ in the 10–20 cm layer in the PD site. The PA site had highest SOC concentration compared with the other three vegetation types, followed by the PD, AG and LL sites (Table 2).

The TN concentration differed significantly between the AG, LL and PA sites ($p < 0.05$) and between the LL, PA and PD sites ($p < 0.05$). The TN concentration decreased with depth from a mean (\pm s.e.m.) of $0.72 \pm 0.01\%$ in the 0–5 cm layer to $0.54 \pm 0.01\%$ in the 10–20 cm layer in the AG site, and from $0.47 \pm 0.04\%$ in the 0–5 cm layer to $0.43 \pm 0.025\%$ in the 10–20 cm layer in the LL site, and from $1.77 \pm 0.05\%$ in the 0–5 cm layer to $1.51 \pm 0.08\%$ in the 10–20 cm layer in the PA site, and from $0.88 \pm 0.14\%$ in the 0–5 cm layer to $0.57 \pm 0.01\%$ in the 10–20 cm layer in the PD site. The NH₄⁺ concentration was the highest in the 0–5 cm layer in all sites. The PA site had the highest TN concentration and NH₄⁺ concentration compared with the other three sites (Table 2).

The C/N ratios of the AG and PD sites were lower than those in the PA and LL sites. The C/N ratio ranged from 7.66 ± 0.28 in the 5–10 cm layer to 8.36 ± 0.17 in the 0–5 cm layer in the AG site, and from 8.79 ± 0.75 in the 0–5 cm layer to 9.44 ± 0.03 in the 10–20 cm layer in the PD site (Table 2).

The NO₃⁻ concentrations were significantly different between the LL site and the AG, PA, PD sites ($p < 0.05$). The NH₄⁺ concentrations were also significantly different between the PA site and the AG, LL, PD sites ($p < 0.05$) (Table 2). Fig. 2 shows the NO₃⁻ and NH₄⁺ concentration at the end of inundation treatments. In the dry treatment, the NO₃⁻ and NO₂⁻ concentrations significantly increased in all sites compared to the initial soils. The average NO₃⁻ concentrations in the soil profile were 30.12 mg kg^{-1} in the AG site (Fig. 2a), 3.21 mg kg^{-1} in the LL site (Fig. 2d), 20.95 mg kg^{-1} in the PA site (Fig. 2g) and 5.98 mg kg^{-1} in the PD site (Fig. 2j) in the dry treatment. The PA site had the highest NO₃⁻ concentration in the 0–5 cm layer (47.10 mg kg^{-1}) and decreased with depth to the 10–20 cm layer (0.70 mg kg^{-1}) (Fig. 2g). In the flooded treatment, NO₃⁻ and NO₂⁻ concentrations decreased compared to initial soils in all sites (Fig. 2).

A significant decrease in NO₃⁻ concentration was observed under the flooded treatment in the AG, LL, PD sites compared to the initial soils (Fig. 2a, d, g, j). The NO₃⁻ concentration decreased from $0.51 \pm 0.29 \text{ mg kg}^{-1}$ to $0.33 \pm 0.1 \text{ mg kg}^{-1}$ in the AG site (Fig. 2a), from $1.69 \pm 0.75 \text{ mg kg}^{-1}$ to $0.07 \pm 0.05 \text{ mg kg}^{-1}$ in the LL site (Fig. 2d), and from $0.2 \pm 0.12 \text{ mg kg}^{-1}$ to $0.12 \pm 0.1 \text{ mg kg}^{-1}$ in the PD site (Fig. 2j). The NH₄⁺ concentrations significantly increased in all sites in the flooded treatment, followed by the wet-dry cycle treatment and the dry treatment. The average NH₄⁺ concentration in the soil profile was 80.43 mg kg^{-1} in the AG site (Fig. 2c), 13.41 mg kg^{-1} in the LL site (Fig. 2f), $159.33 \text{ mg kg}^{-1}$ in the PA site (Fig. 2i) and 49.75 mg kg^{-1} in the PD site (Fig. 2l) in the flooded treatment.

The PA and LL sites had a sandier texture compared with the AG and PD sites. The soil texture in the PA site was a silty fine sand and at the LL site was a silty medium sand. The soil textures in the AG and PD sites were both fine silt. All the sites were slightly acidic to acidic. In all sites, the 0–5 cm soil horizon had the highest EC. The PA site had the highest EC and soil water content through the soil profile compared with the other three vegetation types. Bulk density increased with soil depth in all sites. The soil water content decreased with depth in all sites (Table 2).

Table 2
Physical and chemical characteristics of the soils in the four vegetation type sites.

Sites	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	EC (mS cm ⁻¹)	Bulk density (g cm ⁻³)	Soil water content (%)	SOC (%)	Total N (%)	C/N	NO ₃ ⁻ (mg kg ⁻¹)	NO ₂ ⁻ (mg kg ⁻¹)	NH ₄ ⁺ (mg kg ⁻¹)
AG	0–5	0	73	27.1	5.8	0.18	0.75 ± 0.02	29.81 ± 2.28	6.02	0.72	8.36	0.51	0.17	4.1 ± 0.6
	5–10	0	81	19.4	5.4	0.14	0.88 ± 0.01	26.23 ± 1.08	± 0.12	± 0.01	± 0.17	± 0.29	± 0.12	2.7 ± 0.1
	10–20	0	75	25.2	5.23	0.13	0.87 ± 0.04	24.02 ± 0.14	5.285	0.69	7.66	1.58	0.02	
LL	0–5	84.8	12	3.3	6.63	0.52	0.95 ± 0.01	25.30 ± 4.03	± 0.02	± 0.01	± 0.28	± 0.21	± 0.001	1.9 ± 0.1
	5–10	79.6	15	5.5	6.26	0.26	0.97 ± 0.03	16.23 ± 0.35	4.24	0.54	7.85	1.20	0.46	
	10–20	68.9	23	8.6	6.33	0.30	1.02 ± 0.02	18.36 ± 1.37	± 0.01	± 0.01	± 0.13	± 0.43	± 0.45	
PA	0–5	58.6	37	4.2	5.39	2.18	0.33 ± 0.01	83.34 ± 1.3	± 0.04	0.47	11.79	1.69	1.36	5.15
	5–10	62.9	33	4.1	4.95	1.91	0.37 ± 0.02	80.25 ± 1.65	± 0.4	± 0.04	± 0.03	± 0.75	± 0.3	± 0.35
	10–20	34.2	57	9.2	5.32	2.14	0.38 ± 0.01	70.64 ± 0.96	± 0.02	± 0.025	± 0.02	± 0.28	± 0.06	
PD	0–5	0	83	17.5	5.24	0.34	0.78 ± 0.02	34.32 ± 0.93	20.42	1.77	11.54	<0.005	0.05	28 ± 2.2
	5–10	0	78	22.5	5.19	0.23	0.87 ± 0.02	28.29 ± 0.42	± 0.33	± 0.05	± 0.14	± 0.019	± 0.019	
	10–20	0	79	21.3	5.27	0.27	0.92 ± 0.01	30.60 ± 0.64	22.82	1.91	11.98	<0.005	0.03	25.2
					± 0.01	± 0.02			± 0.34	± 0.03	± 0.34	± 0.003	± 0.003	± 0.29
					± 0.02	± 0.06			16.87	1.51	11.2	<0.005	0.01	19.4
					± 0.005	± 0.003			± 1.07	± 0.08	± 0.15	± 0.001	± 0.001	± 0.3
					± 0.01	± 0.001			7.60	0.88	8.79	0.2	0.08	2.45
					± 0.03	± 0.001			± 0.54	± 0.14	± 0.75	± 0.012	± 0.006	± 0.25
									4.99	0.54	9.24	0.27	0.03	1.15
									± 0.07	± 0.02	± 0.22	± 0.25	± 0.004	± 0.05
									5.38	0.57	9.44	0.13	0.06	2.2
									± 0.08	± 0.01	± 0.03	± 0.12	± 0.01	± 0.13

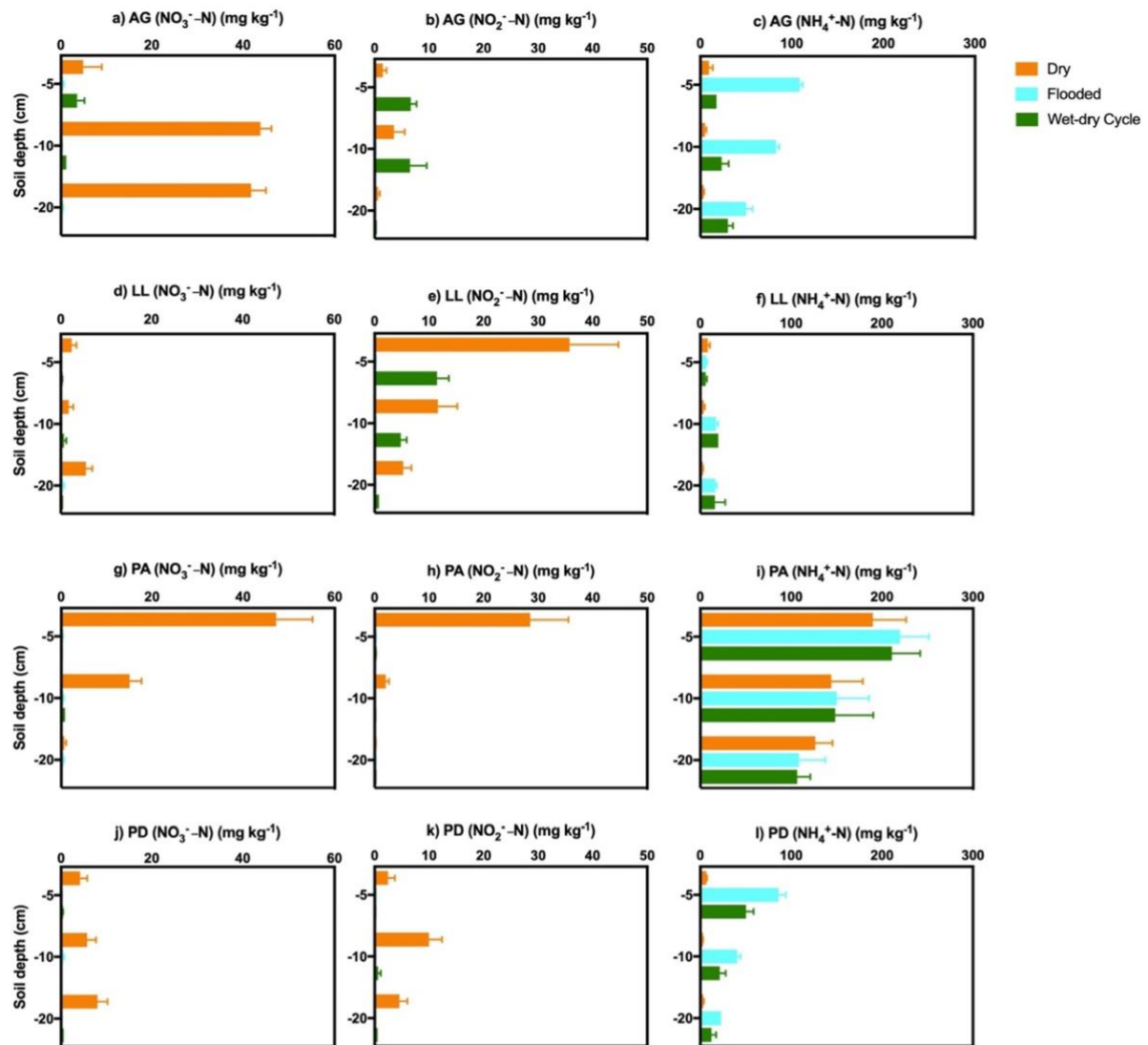


Fig. 2. NO_3^- , NO_2^- and NH_4^+ concentrations at the AG (*Apium graveolens*) (a, b, c), LL (*Leptospermum lanigerum*) (d, e, f), PA (*Phragmites australis*) (g, h, i), and PD (*Paspalum distichum*) sites (j, k, l). Vertical bars denote standard error of means ($n = 4$).

3.2. Soil water content

Fig. 3 shows soil water content declined with time in the dry treatment. In the dry treatment, soil water content decreased by 59.60%, 35.07%, 12.97% and 59.75% in the AG, LL, PA and PD sites, respectively, by the end of the treatment. All vegetation types remained saturated in the flooded treatment and the soil water content was 100% in all sites. The wet-dry cycle treatment led to the soil water content fluctuating according to the cycles. In each wet-dry cycle treatment soil water content decreased by 65.8%, 71.5%, 19.1% and 56.4% on average in the AG, LL, PA and PD sites, respectively, from flooded periods to dry periods (Fig. 3).

3.3. Redox potential

The Eh of the soil rapidly changed following changes in water level. The highest Eh in the dry treatment was +286.75 mV in the PD site,

with a mean Eh of +163.58, +204.65, +149.52 and +207.73 mV in the AG, LL, PA and PD sites, respectively. The minimum Eh under the flooded treatment was -385.11 mV in the AG with a mean Eh of 260.78, -213.55, -173.2, and -215.23 mV in the AG, LL, PA and PD sites, respectively (Fig. 4). When soils were subjected to the wet-dry cycle treatment, Eh oscillated between -201.25 and +133.25 mV in the AG site (Fig. 4a), between -201.14 and +89.45 mV in the LL site (Fig. 4b), between -281.75 and +136.75 mV in the PA site (Fig. 4c), between -220.75 and +44.5 mV in the PD site (Fig. 4d).

3.4. CO₂ emissions

The highest CO₂ flux in the dry treatment occurred on Day 14 with 727.81 (± 113.94) mg m⁻² h⁻¹ in the AG site (Fig. 5a), on Day 35 with 830.04 (± 86.48) mg m⁻² h⁻¹ in the LL site (Fig. 5c), on Day 35 with 740.45 (± 50) mg m⁻² h⁻¹ in the PA site (Fig. 5e). In the flooded treatments, the highest CO₂ flux occurred on Day 38 with 982.31 (\pm

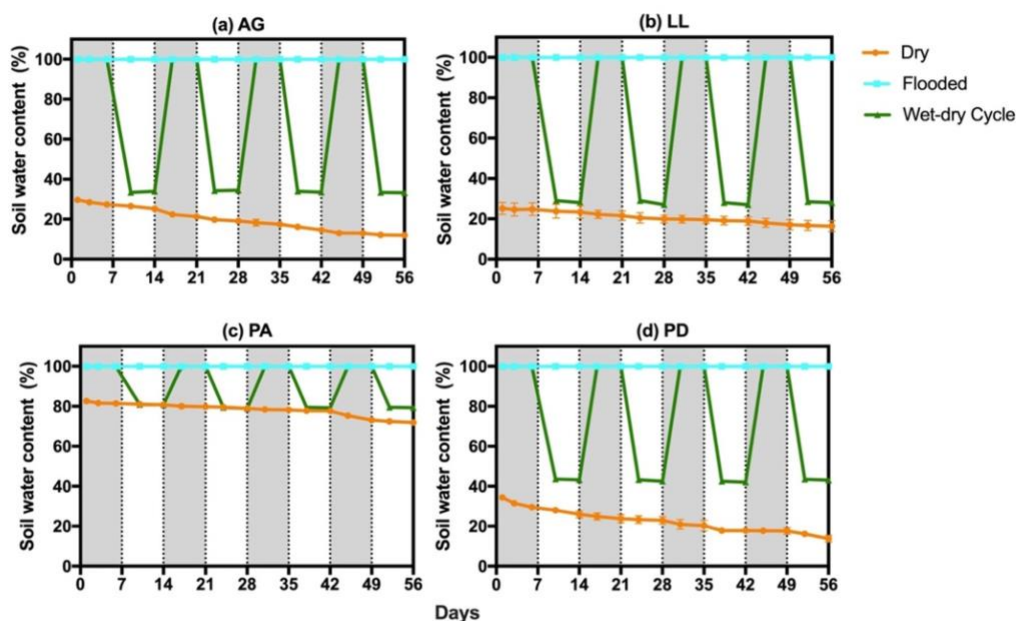


Fig. 3. Temporal variation in soil water content in (a) AG (*Apium graveolens*), (b) LL (*Leptospermum lanigerum*), (c) PA (*Phragmites australis*), (d) PD (*Paspalum distichum*) sites. Vertical bars denote standard error of means ($n = 4$). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment).

174.41 $\text{mg m}^{-2} \text{h}^{-1}$ in the AG site (Fig. 5a), on Day 35 with 576.39 (± 70.77) $\text{mg m}^{-2} \text{h}^{-1}$ in the LL site (Fig. 5c), on Day 31 with 828.72 (± 183.94) $\text{mg m}^{-2} \text{h}^{-1}$ in the PA site (Fig. 5e) and on Day 35 with 710.84 (± 87.11) $\text{mg m}^{-2} \text{h}^{-1}$ in the PD site (Fig. 5g). The CO_2 flux was lower when the soils were flooded compared to the dry periods in each wet-dry cycle. The re-wetting in each cycle decreased soil CO_2 flux by 60–71% in the AG site (Fig. 5a), 18–66% in the LL site (Fig. 5c),

28–47% in the PA site (Fig. 5e), 34–72% in the PD site compared to the dry periods (Fig. 5g).

Generally, the cumulative CO_2 emissions differed significantly between the dry, flooded and wet-dry cycle treatments in the AG, LL and PD sites ($p < 0.05$) and between the PA site and the AG, LL and PD sites under the dry treatment ($p < 0.05$). In the dry treatment, the highest cumulative CO_2 emissions occurred in the PA site with 804.41

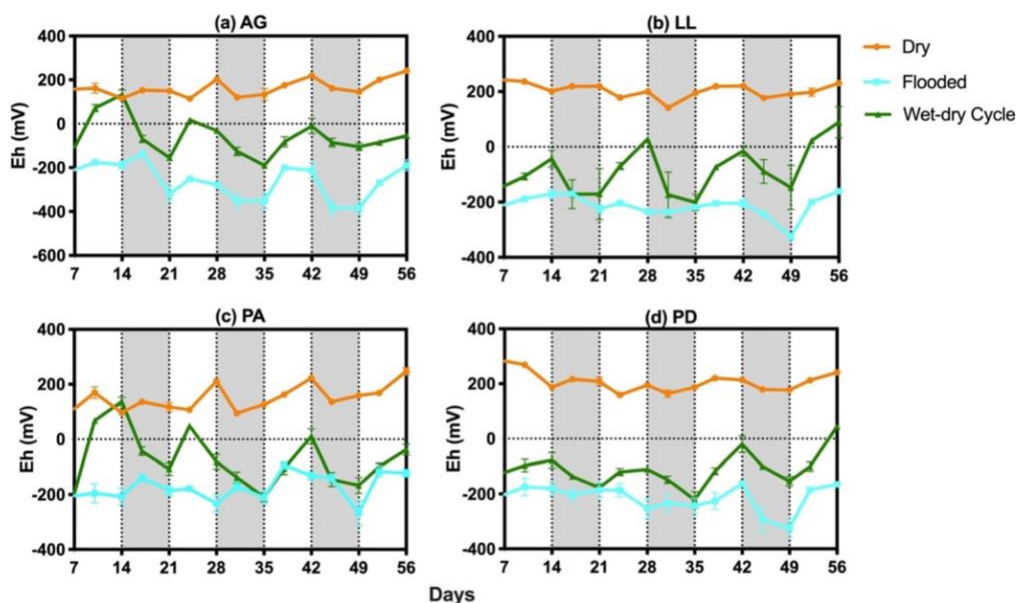


Fig. 4. Temporal variation in Eh of the soil profiles in (a) AG (*Apium graveolens*), (b) LL (*Leptospermum lanigerum*), (c) PA (*Phragmites australis*), (d) PD (*Paspalum distichum*) sites. Vertical bars denote standard error of means ($n = 4$). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment).

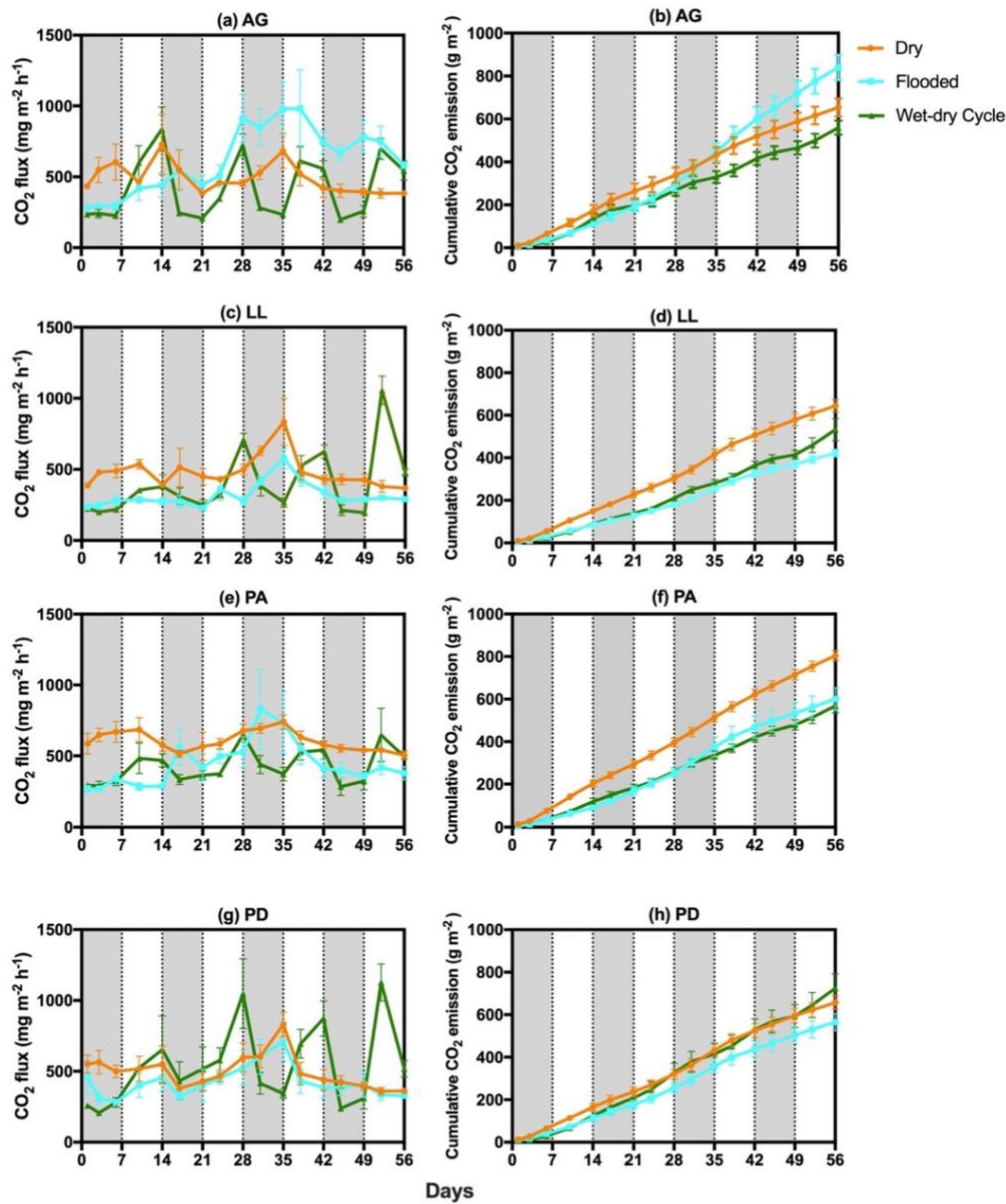


Fig. 5. Temporal variations of CO₂ flux and cumulative CO₂ emissions at the AG (*Apium graveolens*) (a, b), LL (*Leptospermum lanigerum*) (c, d), PA (*Phragmites australis*) (e, f) and PD (*Paspalum distichum*) sites (g, h). Vertical bars denote standard error of means ($n = 4$). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment).

(± 24.33) g m⁻² (Fig. 5f), followed by the PD site with 656.95 (± 33.67) g m⁻² (Fig. 5h), the LL site with 644.34 (± 30.56) g m⁻² (Fig. 5d) and the AG site with 653.41 (± 41.61) g m⁻² (Fig. 5b). The AG site had the highest cumulative emissions under the flooded treatment, with 840 (± 59.13) g m⁻². The PD site had the highest cumulative emissions under the wet-dry cycle treatment with 724.72 (± 57.68) g m⁻² (Fig. 5h). The wet-dry cycle treatment had significantly lowered cumulative CO₂ emissions to 559.2 (± 33.15), 533.2 (± 42.27) and 568.6 (± 33.59) g m⁻² in the AG, LL and PA sites (Fig. 5b, d, f). The LL site had relatively lower cumulative CO₂ emissions compared to other sites in all treatments (Fig. 5d).

3.5. CH₄ emissions

The highest CH₄ flux in the dry treatment occurred on Day 28 with 2.35 (± 0.24) mg m⁻² h⁻¹ in the AG site (Fig. 6a), on Day 31 with 2.68 (± 0.25) mg m⁻² h⁻¹ in the LL site (Fig. 6c), on Day 6 with 55.38 (± 6.32) mg m⁻² h⁻¹ in the PA site (Fig. 6e), and on Day 17 with 2.25 (± 0.05) mg m⁻² h⁻¹ in the PD site (Fig. 6g). CH₄ emission was only detected after Day 10 in both wet-dry cycle and flooded treatments in the PA site (Fig. 6e) and was detected after 14 days in the AG, LL and PD sites (Fig. 6a, c, g). Peak values for the AG, LL, PA and PD sites occurred on Day 38, 38, 31 and 35, with 638.91 (± 63.25), 240.82 (± 38.98), 1139.93 (\pm

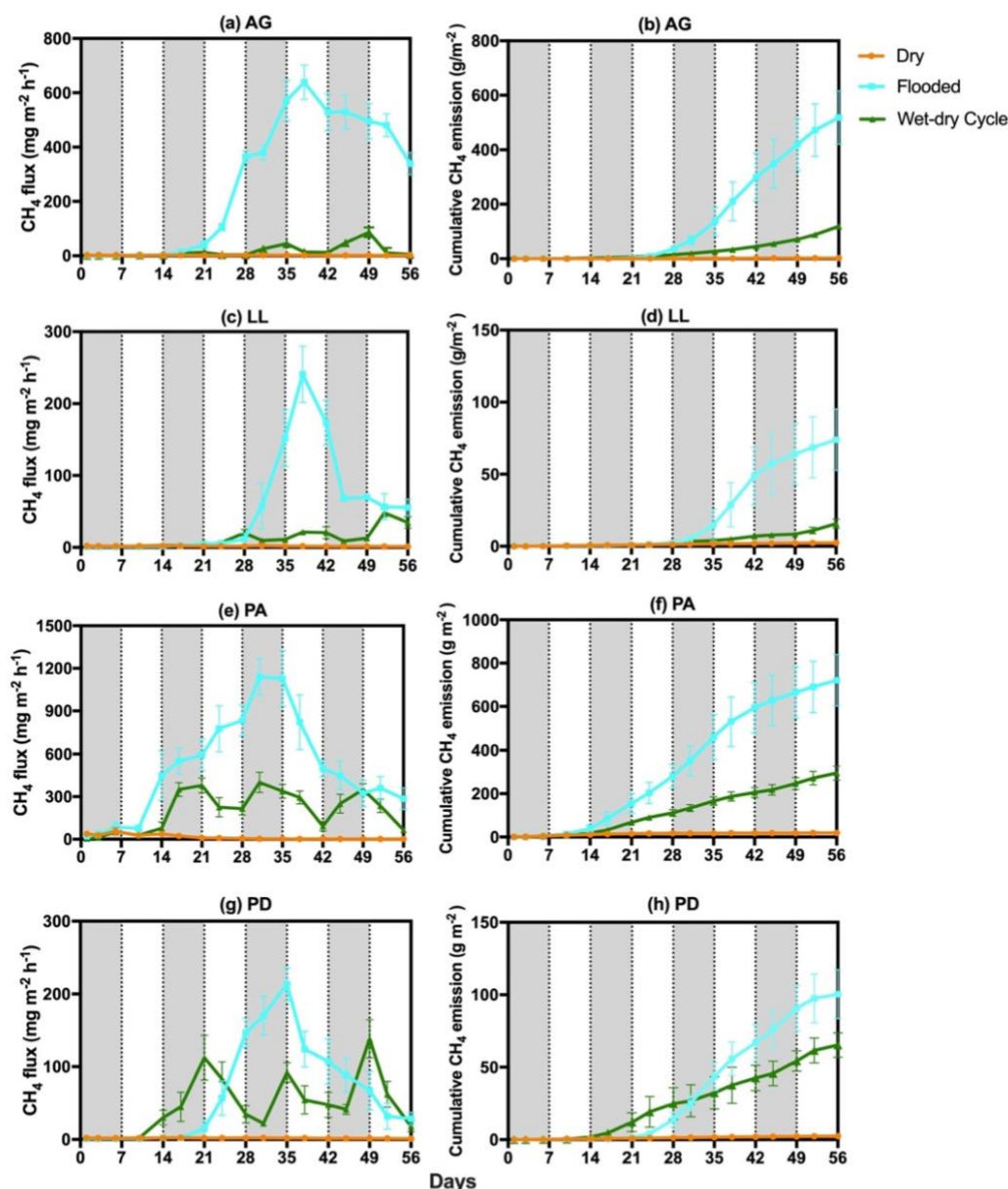


Fig. 6. Temporal variations of CH₄ flux and cumulative CH₄ emissions at the AG (*Apium graveolens*) (a, b), LL (*Leptospermum lanigerum*) (c, d), PA (*Phragmites australis*) (e, f) and PD (*Paspalum distichum*) sites (g, h). Vertical bars denote standard error of means ($n = 4$). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment).

127.93) and 213.48 (± 22.84) mg m⁻² h⁻¹, respectively, in the flooded treatments (Fig. 6a, c, e, g). CH₄ flux decreased gradually with time after the peak. In the wet-dry cycle treatment, the CH₄ flux varied according to the water level, with greater variations occurring in the PA and PD sites (Fig. 6e, g). The average CH₄ flux in the flooded periods was 2.8 times higher in the AG site (Fig. 6a), 0.5 times higher in the PA site (Fig. 6e), 0.2 times higher in the PD site (Fig. 6g) than the dry periods in wet-dry cycle treatment.

Generally, the cumulative CH₄ emissions differed significantly between the dry, flooded and wet-dry cycle treatments ($p < 0.05$), and between the four vegetation types under the wet-dry cycle treatment ($p < 0.05$). The dry treatments had significantly lower

cumulative CH₄ emissions compared to the flooded treatment. The cumulative CH₄ emission at the PA site was 16.94 (± 2.21) g m⁻² (Fig. 6f), which was more than 6 times higher than the other vegetation types in the dry treatment. The highest cumulative CH₄ emissions under the flooded treatment were 721.11 (± 59.15) g m⁻² in the PA site (Fig. 6f), which was 0.4 times higher than the AG site (Fig. 6b), 8.7 times higher than the LL site (Fig. 6d), 6.2 times higher than the PD site (Fig. 6h). The highest cumulative CH₄ emissions under the wet-dry cycle treatment occurred in the PA site (Fig. 6f), which was 1.5 times higher than the AG site (Fig. 6b), 17.9 times higher than the LL site (Fig. 6d) and 3.5 times higher than the PD site (Fig. 6h).

3.6. N₂O emissions

Fig. 7 shows that N₂O flux was higher in the dry treatments compared to the flooded treatments. In the dry treatment, the N₂O flux increased and reached its peak on Day 17 in the AG, LL, PA and PD sites with 1.04 (± 0.005), 1.14 (± 0.10), 1.04 (± 0.006) and 1.03 mg m⁻² h⁻¹ (± 0.01) respectively (Fig. 7a, c, e, g). In the flooded treatments, the peak value of N₂O flux was 0.58 (± 0.0039), 0.93 (± 0.009), 0.57 (± 0.005) and 0.89 (± 0.25) mg m⁻² h⁻¹ in the AG, LL, PA and PD sites, respectively

(Fig. 7a, c, e, g). In the AG site, higher N₂O flux occurred in dry periods, ranging from 1.45 (± 0.3) to 2.19 (± 0.47) mg m⁻² h⁻¹, from 2.02 (± 0.62) to 2.39 (± 0.53) mg m⁻² h⁻¹, from 1.92 (± 0.38) to 2.07 (± 0.52) mg m⁻² h⁻¹ in the second, third and fourth cycle, respectively (Fig. 7a). The highest N₂O flux was generated during the dry periods in the wet-dry cycle treatment for all the vegetation types. The flooded periods decreased the N₂O flux by 14–70% in the AG site (Fig. 7a), 26–48% in the LL site (Fig. 7c), 35–50% in the PA site (Fig. 7e), and 27–41% in the PD site (Fig. 7g) compared to dry periods in the wet-dry cycle treatment.

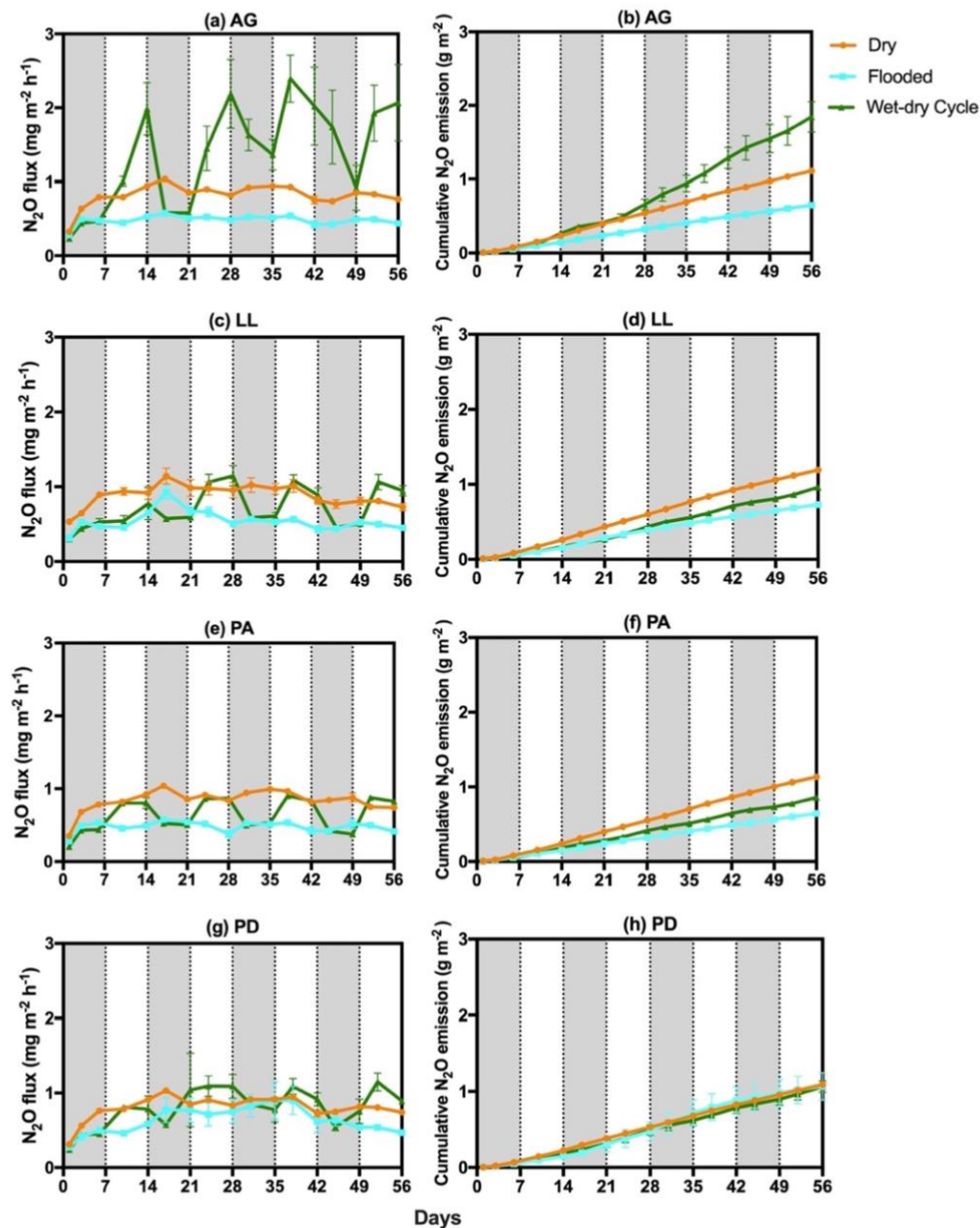


Fig. 7. Temporal variations of N₂O flux and cumulative N₂O emissions at the AG (*Apium graveolens*) (a, b), LL (*Leptospermum lanigerum*) (c, d), PA (*Phragmites australis*) (e, f) and PD (*Paspalum distichum*) site (g, h). Vertical bars denote standard error of means (n = 4). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment).

Table 3
Pearson correlation analysis between CO₂, CH₄ and N₂O emissions and soil parameters.

Parameters	CO ₂			CH ₄			N ₂ O		
	Dry	Flooded	Wet-dry cycle	Dry	Flooded	Wet-dry cycle	Dry	Flooded	Wet-dry cycle
SOC	0.64*	0.09	0.01	0.96*	0.69*	0.92*	0.04	-0.30	-0.30
TN	0.66*	0.12	0.04	0.93*	0.69*	0.92*	0.24	0.01	0.29
C/N	0.58*	-0.18	-0.08	0.79*	0.42	0.63*	0.0006	-0.45	-0.56*
NO ₃ ⁻	0.61*	0.71*	0.004	0.97*	0.57*	-0.27	0.10	-0.06	0.92*
NO ₂ ⁻	0.24	0.25	-0.20	0.51*	0.39	-0.56	0.43	0.25	0.60*
NH ₄ ⁺	0.62*	0.46	0.11	0.98*	0.84*	0.94*	0.07	-0.23	-0.33
pH	-0.23	-0.25	-0.45	-0.26	-0.24	-0.45	0.40	-0.47	0.03
EC	0.61*	-0.09	-0.12	0.84*	0.58*	0.87*	0.04	-0.37	-0.43

Pair sample size, n = 16 for SOC, TN, C/N, NO₃⁻, NO₂⁻, NH₄⁺, pH, EC in the soil top layer (0–5 cm) after the dry, flooded and wet-dry cycle treatments in all sites.

* p = 0.05 correlations are significant.

Generally, the cumulative N₂O emissions were significantly different between the dry, flooded and wet-dry cycle treatments at the AG, LL and PA sites ($p < 0.05$), and between the AG, LL and PD sites in the flooded and wet-dry treatments ($p < 0.05$). The highest cumulative N₂O emissions under the dry treatment occurred in the LL site with 1.19 (± 0.03) g m⁻² (Fig. 7d), followed by the PA site with 1.13 (± 0.01) g m⁻² (Fig. 7f), the AG site with 1.11 (± 0.008) g m⁻² (Fig. 7b) and the PD site with 1.09 (± 0.008) g m⁻² (Fig. 7h). The flooded treatment reduced the N₂O emissions to 0.65 (± 0.007), 0.73 (± 0.02), 0.64 (± 0.01) and 1.06 (± 0.18) g m⁻², in the AG, LL, PA and PD sites respectively (Fig. 7b, d, f, h). In the wet-dry cycle treatment, the AG site had the highest cumulative N₂O emissions with 1.84 (± 0.20) g m⁻² (Fig. 7b).

3.7. Correlation between GHG emissions and environmental parameters

Table 3 summarises the Pearson correlation between the GHG emissions and environmental parameters after the dry, flooded and wet-dry cycle treatments. CO₂ emissions were positively correlated with SOC, TN content, C/N, NO₃⁻ and NH₄⁺ concentrations, and EC in the dry treatment ($p < 0.05$). CH₄ emissions were positively correlated with SOC, TN content, NH₄⁺ concentration, and EC in all treatments ($p < 0.05$). CH₄ emissions were positively correlated with C/N, NO₃⁻ and NO₂⁻ concentrations in the dry treatment ($p < 0.05$). N₂O emissions were positively correlated with NO₃⁻ and NO₂⁻ concentrations in the wet-dry cycle treatment ($p < 0.05$). N₂O emissions were negatively correlated with C/N in the wet-dry cycle treatment ($p < 0.05$) (Table 3).

Table 4 shows the Pearson correlation between GHG fluxes and soil water content and Eh in each treatment. CO₂ flux and N₂O flux were negatively correlated with soil water content in the wet-dry cycle treatment in all sites ($p < 0.05$). CH₄ flux was positively correlated with soil water content in the dry treatment in all sites ($p < 0.05$) and negatively correlated with Eh at all the sites separately ($p < 0.05$) and N₂O flux was positively correlated with Eh at all sites ($p < 0.05$).

4. Discussion

4.1. The role of vegetation type on SOC, TN and mineral N

The quantity and quality of soil organic matter, measured by SOC, are influenced by vegetation types (Dalal and Allen, 2008; Dorodnikov et al.,

2009). The PA site had the highest SOC concentration (20.42%; Table 2) compared to other sites, suggesting that these reeds had higher detritus inputs and provided a larger amount organic matter to decompose which could potentially lead to higher CO₂ and CH₄ emissions. Previous studies found that SOC from a *Phragmites australis* coastal wetland ranged between 3.48 and 21.6% (Cheng et al., 2007; Marín-Muñiz et al., 2015; Zhang et al., 2013), which was similar to our results. The lower range of SOC might due to the lower above-and below-ground biomass and stem density of *Phragmites australis*. SOC from similar grass and herbaceous species in coastal marshes ranged between 1.22 and 18.34% (Livesley and Andrusiak, 2012; Sun et al., 2013), which was consistent with our results. The SOC from the woody plants in coastal marshes ranged 2.4–16.74% (Allen et al., 2007; Livesley and Andrusiak, 2012), which was also similar to our results.

The PA site had the highest TN concentration (1.77%), followed by the PD site (0.88%), AG site (0.72%) and the LL site (0.47%) (Table 2). Previous studies have found that TN concentration in coastal wetlands ranged from 0.03–1.11% (Allen et al., 2007; Cheng et al., 2007; Morse et al., 2012), which was lower than the PA site, but similar compared with the AG, PD and LL sites. The PA site also had the highest NH₄⁺ concentration but NO₃⁻ was not detected (Table 2). This may have been due to the site being flooded at the time of sampling, and the low Eh prevented the formation of NO₃⁻ under anaerobic conditions. After the incubation treatments, the NH₄⁺ concentration increased in all sites under all treatments (Fig. 2c, f, i, l) as the mineralization of organic N leads to the formation of NH₄⁺ under both aerobic and anaerobic conditions (Tobias and Neubauer, 2019). Ponnamperna (1972) found that all the mineralizable N in flooded soils is converted to NH₄⁺ within 14 days if the temperature is favourable, which was the case in our study under controlled temperature conditions. The dry treatment significantly increased NO₃⁻ and NO₂⁻ concentrations in all sites due to nitrification as NH₄⁺ produced by mineralization is oxidized to NO₂⁻ and NO₃⁻ under aerobic conditions (Fig. 2). The flooded treatment decreased NO₃⁻ concentration at the AG, LL, PD sites due to denitrification as NO₃⁻ is reduced to N₂O or N₂ under anoxic conditions (Fig. 2a, d, g, j). The depth distribution of TN concentration in the soil profile in all sites roughly followed the similar pattern of SOC concentration. In general, TN, NH₄⁺, NO₃⁻, NO₂⁻ concentrations were the highest in the 0–5 cm layer at all sites and decreased with soil depth in the study (Table 2).

Table 4
Pearson correlation analysis between CH₄, CO₂, N₂O fluxes and soil parameters.

Parameters	Treatment	CO ₂				CH ₄				N ₂ O			
		AG	LL	PA	PD	AG	LL	PA	PD	AG	LL	PA	PD
Soil water content	Dry	0.45	-0.02	0.5*	0.32	0.58*	0.57*	0.75*	0.71*	-0.36	-0.06	-0.18	-0.48
	Flooded	0.28	-0.04	-0.1	0.08	0.24	-0.006	-0.12	0.008	-0.04	0.32	-0.15	-0.1
	Wet-dry cycle	-0.86*	-0.71*	-0.77*	-0.78*	-0.34	-0.57*	0.16	-0.36	-0.73*	-0.85*	-0.85*	-0.71*
Eh		-0.54*	0.6*	0.48*	0.21	-0.69*	-0.51*	-0.74*	-0.68*	0.89*	0.84*	0.87*	0.55*

Pair sample size, n = 17 for soil water content during dry, flooded, wet-dry cycle treatments respectively. n = 30 for Eh during dry and flooded treatments.

* p = 0.05 correlations are significant.

The C/N ratio can indicate the availability of organic matter that can be mineralized (Weil, 2016). Microbes need adequate N for microbial growth and activity so low C/N ratios can indicate low concentrations of lignin and polyphenols and higher availability of substrate, which can accelerate the speed of organic matter decomposition (Neubauer et al., 2005). The C/N ratio of the LL site (tea tree) ranged between 10.45 and 11.79. The AG and PD sites had lower C/N ratio compared to the PA and LL sites, which ranged 7.66–8.36 in the AG site (herbaceous species) and ranged 8.79–9.44 in the PD site (grass). The LL site supported woody species which contains higher lignin compared with the herbaceous species. The herbaceous plants produce more fine roots than woody species and the woody plants limit the supply of labile carbon (Desai et al., 2007; Vann and Patrick Megonigal, 2003). Yau et al. (2016) found that the C/N ratio of tea tree was 22.02 and C/N ratio of grass was 11.71 in temperate estuarine floodplain in southern Australia, which indicated herbaceous plants had lower C/N ratio in soils compared with woody plants. Soil organic matter in the AG (herbaceous species) and PD (grass) sites can be easily be decomposed compared to the LL sites (woody plant) because they have a lower C/N ratio and lower lignin (Vann and Patrick Megonigal, 2003).

4.2. Effect of inundation on soil water content and Eh

Soil water content decreased with time in the dry treatment in all sites. In the dry treatment, the Eh was between +90.75 and +247.25 mV in the AG site (Fig. 4a), was between +141.75 and +243.5 mV in the LL site (Fig. 4b), was between +90.75 and +247.25 mV in the PA site (Fig. 4c), and was between +158.75 and +286.75 mV in the PD site (Fig. 4d). Denitrification occurs when Eh is below +250 mV (Sparks, 2003) while nitrification normally occurs at Eh values greater than +200 mV (Bauza et al., 2002).

In the flooded treatment, the soil water content was 100% in all sites (Fig. 3), which is the most important factor affecting the diffusion of gases. The average Eh in the flooded treatment was −260.78, −213.55, −173.2 and −215.23 mV in the AG, LL, PA and PD sites (Fig. 4), indicating reduced conditions. Therefore, we can assume methanogenesis is the dominant gas pathway in the flooded treatment because CH₄ is produced when Eh < −200 mV (Sparks, 2003).

In the wet-dry cycle treatment, Eh ranged from +136.75 mV in the dry periods to −281.75 mV in the flooded periods (Fig. 4). In these conditions, a sequential series of anaerobic processes occurs, with decreasing Eh from denitrification, to Mn reduction, Fe³⁺ reduction and SO₄^{2−} reduction and then methanogenesis (Ponnamperuma, 1972). Decomposition of organic matter and nitrification occurs in the dry periods, and is reflected in the CO₂ and N₂O emissions, described below. These systems then switch over to methanogenesis in the flooded periods of wet-dry cycle treatment in all sites as the Eh was less than −200 mV.

4.3. Greenhouse gas emissions

4.3.1. CO₂ emissions

Soils with higher organic carbon tend to have higher mineralization rates as it reflects the larger availability of organic carbon that can be mineralized (Sutton-Grier et al., 2011). In this study, CO₂ emissions were positively correlated to SOC and C/N in the dry treatments in all sites (Table 3). The PA site had the highest SOC concentration, highest C/N (Table 2) and the highest cumulative CO₂ emission (Fig. 5f) in the dry treatment. These results supported our hypothesis that soils with higher SOC can promote higher soil respiration rates and produce CO₂ emissions in aerobic conditions (Chen et al., 2012).

CO₂ flux was higher in the dry treatment in the LL and PD sites (Fig. 5c, g) and soil water content was negatively correlated with CO₂ flux in all sites (Table 4). In dry conditions, O₂ is rapidly utilized as for microbial respiration during decomposition of organic matter to produce CO₂. Similarly, the dry periods in the wet-dry cycle treatment also led to oxic conditions and promoted soil respiration and therefore

enhanced CO₂ flux compared with flooded periods in all sites. Liu et al. (2013) also found that increased CO₂ emissions from the soil surface under dry conditions from the removal of diffusion barrier between the soil and atmosphere in rice paddy soils. The inundation treatment decreased cumulative CO₂ emissions by 34%, 25% and 14% at the LL, PA and PD sites, respectively compared to the dry treatment (Fig. 5d, f, h) because CH₄ emissions dominated. Riet et al. (2013) also found that in both peat and clay soils, rewetting of both also reduced CO₂ emissions, which was consistent with our results.

4.3.2. CH₄ emissions

In this study, CH₄ emissions were positively correlated to SOC concentration in all treatments and positively correlated with C/N in the dry treatments and wet-dry treatments in all sites (Table 3). The PA site had the highest SOC concentration, C/N and the cumulative CH₄ emission was the highest in the dry treatment among all the sites (Fig. 6f). Previous studies have also shown that CH₄ emissions can be positively correlated with the C/N ratio (Shi et al., 2014; Šimek et al., 2011; Weslien et al., 2009).

Deeper roots (>20 cm) were observed in the PA sample cores at the time of sampling, and earlier studies have indicated that PA roots can transport gases between soil and the atmosphere through the plant tissue (Van der Nat and Middelburg, 2000). Plant-mediated transport from the soil to atmosphere has been reported as the main method of CH₄ transport from deeper parts of the soil profile to the atmosphere (Chanton et al., 1992; Liu et al., 2015). While there was no vegetation in the cores, the plant roots that remained can provide a conduit to transport gases from deeper in the core to the surface.

The position of the water table in wetlands is a significant controlling factor on CH₄ emissions as higher water tables can lead to O₂ depletion and lower Eh, which was negatively correlated with CH₄ flux in all sites (Table 4). The average Eh in the flooded treatment was −260.78, −213.55, −173.2, and −215.23 mV in the AG, LL, PA and PD sites (Fig. 4), which were highly reduced. CH₄ production occurs under strict anaerobic conditions (Dutaur and Verchot, 2007). CH₄ emissions were much higher in the flooded treatment in all sites than in the dry and wet-dry cycle treatments. The soils emitted 204 times the cumulative CH₄ emissions in the AG site (Fig. 6b), 30 times in the LL site (Fig. 6d), 37 times in the PA site (Fig. 6f), 41 times in the PD site in the flooded treatment (Fig. 6h) compared with dry treatment and 1.2 times cumulative CH₄ emissions in the AG site (Fig. 6b), 5 times in the LL site (Fig. 6d), 1.4 times in the PA site (Fig. 6f), 60 times in the PD site compared to the wet-dry cycle treatment (Fig. 6h). Similarly, in peat soils, rewetting of soils increased CH₄ emissions (Minke et al., 2016; Riet et al., 2013).

4.3.3. N₂O emissions

In the dry treatment, higher NO₃[−] concentrations were observed in all sites compared to flooded and wet-dry cycle treatments (Fig. 2a, d, g, j). High NO₃[−] concentrations suggested some nitrifying activity. Under the dry treatment, it is likely that nitrifying microbes consumed most of the NH₄⁺ produced during the mineralization of organic matter and led to large accumulations of NO₂[−] and NO₃[−] (Fig. 2). The N₂O emissions were negatively correlated with C/N ratio in the wet-dry cycle treatment (Table 3). A low C/N ratio in soil profile also suggests a high potential for N mineralization (Pilegaard et al., 2006). Conversely, the high C/N ratio favours N immobilization (Aber et al., 2003).

N₂O flux was positively correlated with Eh in all sites (Table 4). More positive Eh values were correlated with higher mineralization of organic matter rate and higher nitrification rate. In the dry treatment, the Eh ranged between +90.75 and +286.75 mV (Fig. 4). Bauza et al. (2002) found nitrification usually occurs at an Eh greater than +200 mV. The high concentration of NO₃[−] and higher positive Eh in the dry treatment indicated nitrification was the predominant pathway for N₂O emissions in aerobic conditions.

A significant decrease in NO_3^- concentrations was observed under the flooded treatment in the AG, LL, PD sites compared to the initial soils (Fig. 2a, d, g, j). Flooded conditions promote denitrification when Eh values decrease below +250 mV (Sparks, 2003). The NO_3^- reduction represents the occurrence of denitrification as this is the only pathway to accumulate N_2O in the flooded treatment.

The flooded treatment decreased cumulative N_2O emissions by 42%, 39% and 43% at the AG, LL and PA sites, compared to the dry treatment (Fig. 7). Low N_2O emissions in inundated soils can be explained by four reasons i) the low release of N_2O emissions in AG, PA and PD sites in the flooded treatment may be caused by reduction of NO_3^- to N_2 by denitrifiers (Ruser et al., 2006), ii) the layer of surface water acted as a diffusion barrier and prevented emissions from diffusing from the soil to the atmosphere; iii) the low NO_3^- concentration limited the denitrification process or iv) flooding the soils could result in an increase in pH, which might affect certain enzyme activities and lower N_2O emission (Haddad et al., 2017; Haddad et al., 2013; Tabatabai et al., 2010). Seo and Delaune (2010) found the end product of a complete denitrification was N_2 when the Eh value decreased from -100 mV to -200 mV. Denitrification is the significant process for N_2O production when the soils had high NO_3^- level and Eh was negative (Allen et al., 2007; Bakken et al., 2012; Sun et al., 2014). At higher soil pH, N_2O will be reduced to N_2 by nitrous oxide reductase (Šimek and Cooper, 2002).

NH_4^+ concentrations increased under the wet-dry cycle treatments in all sites compared to the starting conditions (Fig. 2c, f, i, l) and had higher cumulative N_2O emissions compared to the flooded treatments (Fig. 7). NO_2^- and NO_3^- concentrations were positively correlated with N_2O emissions in the wet-dry cycle treatments (Table 3). In the wet-dry cycle treatment, NO_3^- produced by nitrification during the dry periods can be subject to subsequent denitrification when the soils are flooded during the flooded periods. The N_2O flux in the dry periods are much higher than that under flooded periods in all sites (Fig. 7a, c, e, g). In the dry periods of the wet-dry cycle, NH_4^+ is converted to NO_3^- and N_2O emissions were produced by nitrification as the Eh was positive. Earlier studies demonstrated that higher N_2O flux was observed in dry periods in wet-dry cycle treatments, allowing the N_2O trapped in the soil in the flooding phase to be emitted (Balaine et al., 2013; Rabot et al., 2014). In the field, Jiao et al. (2006) and Kirk (2004) also demonstrated that fluctuating water levels were favourable for N_2O emissions in intermittently drained rice fields.

4.4. Conversion to CO_2 -equivalents and the implications of inundation at a landscape scale

The Aire River floodplain is highly susceptible to sea level rise and seawater intrusion which can affect C and N cycling and GHG emissions. Based on the cumulative emissions calculation from the incubation experiment, the average CO_2 emissions in all sites was $12.32 \text{ g m}^{-2} \text{ d}^{-1}$ in the dry treatment, $10.12 \text{ g m}^{-2} \text{ d}^{-1}$ in the flooded treatment, and $10.65 \text{ g m}^{-2} \text{ d}^{-1}$ in the wet-dry cycle treatment (Fig. 5b, d, f, h). The average CH_4 emissions in all sites was $0.12 \text{ g m}^{-2} \text{ d}^{-1}$ in the dry treatment, $6.31 \text{ g m}^{-2} \text{ d}^{-1}$ in the flooded treatment, and $2.21 \text{ g m}^{-2} \text{ d}^{-1}$ in the wet-dry cycle treatment (Fig. 6b, d, f, h), and average N_2O emissions in all sites was $0.02 \text{ g m}^{-2} \text{ d}^{-1}$ in the dry treatment, $0.01 \text{ g m}^{-2} \text{ d}^{-1}$ in the flooded treatment, and $0.021 \text{ g m}^{-2} \text{ d}^{-1}$ in the wet-dry cycle treatment (Fig. 7b, d, f, h). If the Aire River floodplain is permanently dry, such as during a drought situation, the average CO_2 , CH_4 and N_2O emissions across all sites was 123.17, 1.16 and $0.20 \text{ kg ha}^{-1} \text{ d}^{-1}$. If the Aire River floodplain is permanently flooded, such as with higher sea levels, the average CO_2 , CH_4 and N_2O emissions among all sites was 101.23, 63.11 and $0.14 \text{ kg ha}^{-1} \text{ d}^{-1}$. If the Aire River floodplain is periodically with the wet-dry cycles, such as during episodic inundation events like storm surges, the average CO_2 , CH_4 and N_2O emissions among all sites was 106.50, 22.12 and $0.21 \text{ kg ha}^{-1} \text{ d}^{-1}$.

The Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2006) summarized that the median CO_2 diffusive emissions were 5.2 kg ha^{-1}

d^{-1} in warm temperate, dry conditions (Galy-Lacaux et al., 1997; Soumis et al., 2004) and $8.1 \text{ kg ha}^{-1} \text{ d}^{-1}$ in warm temperate, moist conditions (Chen et al., 2012; Marín-Muñiz et al., 2015), which is lower than our results. The IPCC (2006) found that the median CH_4 diffusive emissions were $0.044 \text{ kg ha}^{-1} \text{ d}^{-1}$ in warm temperate, dry conditions (Rosa et al., 1996; Soumis et al., 2004) and $0.15 \text{ kg ha}^{-1} \text{ d}^{-1}$ in warm temperate, moist conditions (Smith and Lewis, 1992; Tremblay et al., 2005), which are also lower than our estimations. Average N_2O emissions in the dry and flooded temperate conditions in the study were 0.20 and $0.14 \text{ kg ha}^{-1} \text{ d}^{-1}$. Previous studies have found that the N_2O emissions ranged between 0.02 and $0.28 \text{ kg ha}^{-1} \text{ d}^{-1}$ in temperate coastal wetlands (Marín-Muñiz et al., 2015; Sun et al., 2014; Yang et al., 2017), which was consistent with our results.

Furthermore, based on global warming potential of 298 for N_2O and 25 for CH_4 , GHGs were converted to CO_2 -equivalents ($\text{CO}_2\text{-eq}$). After conversion, the CO_2 , CH_4 and N_2O emissions were 123.17, 29.0, and $59.6 \text{ kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in the dry treatment, and the CO_2 , CH_4 and N_2O emissions were 101.23, 1577.75, and $41.72 \text{ kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in the flooded treatment, and the CO_2 , CH_4 and N_2O emissions were 106.50, 553.0, and $62.58 \text{ kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in the wet-dry cycle treatment. The GHG emissions in the PA site was 287.06, 3360.17, 1465.06 $\text{kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in dry, flooded and wet-dry cycle treatments. The GHG emissions in the AG site was 187.10, 2469.82, 730.57 $\text{kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in dry, flooded and wet-dry cycle treatments. The GHG emissions in the PD site was 186.06, 606.08, 477.91 $\text{kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in dry, flooded and wet-dry cycle treatments. The GHG emissions in the LL site was 189.60, 444.53, 216.14 $\text{kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$ in dry, flooded and wet-dry cycle treatments. The magnitude of the GHG emissions in the different vegetation types followed the sequence $\text{PA} > \text{AG} > \text{PD} > \text{LL}$. The average GHG emissions in the dry treatment, flooded treatment and wet-dry cycle treatment were 212.46, 1720.15 and $722.42 \text{ kg CO}_2\text{-eq ha}^{-1} \text{ d}^{-1}$, respectively, indicating that the flooded treatment had a higher global warming potential compared with dry and wet-dry cycle treatments. This study indicates that the Aire River floodplain has a higher potential for GHG emissions compared to average temperate flooded land. The dominant GHG varies according to soil moisture conditions. CO_2 comprised the principle part of total $\text{CO}_2\text{-eq}$ emissions in dry conditions while CH_4 dominates in flooded conditions. Under the wet-dry cycle treatment, CH_4 was the main gas contributing to global warming (76.6%), followed by CO_2 (14.7%) and N_2O (8.7%). Similarly, Vanselow-Algan et al. (2015) also found that GHG emissions of rewetted sites was dominated by CH_4 emissions, accounting for 88–98% of the total GHG $\text{CO}_2\text{-eq}$ emissions in peatlands.

In summary, the mineralization rates in coastal wetlands are mainly affected by the supply of SOC, quality of organic matter and the Eh (Sutton-Grier et al., 2011). With sea level rise, coastal wetlands are highly susceptible to inundation by seawater or brackish water. Under flooded conditions, the activity of aerobic bacteria are constrained by O_2 availability (Alm et al., 1999). Due to the lower energy yield, the anaerobic decomposition rate is decreased in the submerged soils. The production of CH_4 is affected by labile organic matter availability, oxidation and reduction state. Nitrification and denitrification are the primary pathways for N_2O emissions and are mainly influenced by mineral N (NO_3^- and NH_4^+), organic matter and Eh. The NH_4^+ produced by the mineralization of organic N is also affected by the quantity and lability of organic matter (Tobias et al., 2001). With lower water tables, NH_4^+ can diffuse to the oxidized surface layer and nitrification occurs. Nitrification is the dominant pathway for N_2O formation when coastal wetlands experience lower water tables with adequate supply of O_2 and NH_4^+ . The mineralization of organic N produces NH_4^+ which then can produce NO_3^- by nitrification. For example, such mineralization of organic N is significantly correlated with enzymes like arylamidase and L-aspartase (Tabatabai et al., 2010).

Higher NO_3^- concentrations can lead to higher N_2O emissions by denitrification under anaerobic conditions when organic matter is not limited. In this reaction, NO_3^- is reduced to NO_2^- and then to N_2O as an

intermediate product (Davidson, 1992). Denitrification is slow in soils with low organic matter and is enhanced by addition of organic matter. The wet-dry cycles enhance the N_2O emissions from the coastal wetland. Permanent inundation can minimize N_2O loss and lead to higher N accumulation in these wetland systems.

5. Conclusion

This study identified that SOC, TN, mineral N, water levels, Eh, soil water content together affect GHG emissions in temperate coastal wetlands. Coastal wetlands represent a large reservoir for C which directly influences CH_4 and CO_2 emissions under different inundation scenarios. Mineral N (NO_3^- and NH_4^+) affects the formation of N_2O by nitrification in aerobic conditions and denitrification under anaerobic conditions. Our study confirmed that water level fluctuations affected CH_4 , CO_2 and N_2O emissions. The flooded treatment decreased the cumulative CO_2 emissions in the PA, PD and LL sites and decreased N_2O emissions at all sites. At the same time, the flooded treatment enhanced the CH_4 emissions in all sites. The dry periods in each wet-dry cycle increased the CO_2 and N_2O flux in all sites. The wet-dry cycle treatment enhanced the N_2O emissions compared to the flooded treatment in all sites. Based on the global warming potential, CO_2 was the main gas contributing to global warming (57.9%) in the dry treatment. CH_4 was predominant contributing to global warming in the flooded treatment (91.9%) and in the wet-dry cycle treatment (76.6%). The flooded treatment had higher global warming potential compared with dry and wet-dry cycle treatments within Aire River floodplain. Further field-based studies should consider the different environmental factors affecting GHG emissions with water level fluctuation over longer periods of time.

CRedit authorship contribution statement

C. Xu: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing - original draft. **V.N.L. Wong:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Funding acquisition. **R.E. Reef:** Writing - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The work described in this paper was supported by the Australian Academy of Science's Thomas Davies Research Grant. We are grateful to Fang Wen who kindly assisted with field sampling. We thank the analysis of anions samples provided by Environmental Analysis Laboratory at Southern Cross University. We thank Leigh Burgess for helping preparing the PVC tubes. We appreciate Rachelle Pierson's assistance to perform the analysis of soluble cations analysis. We thank Gigi Woods for assistance with the particle size distribution analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.142949>.

References

Aber, J.D., Goodale, C.L., Ollinger, S.V., Smith, M.-L., Magill, A.H., Martin, M.E., Hallett, R.A., Stoddard, J.L., 2003. Is nitrogen deposition altering the nitrogen status of northeastern forests? *BioScience* 53, 375–389.

- Allen, D.E., Dalal, R.C., Rennenberg, H., Meyer, R.L., Reeves, S., Schmidt, S., 2007. Spatial and temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments and the atmosphere. *Soil Biol. Biochem.* 39, 622–631.
- Alm, J., Saarnio, S., Nykänen, H., Silvola, J., Martikainen, P., 1999. Winter CO_2 , CH_4 and N_2O fluxes on some natural and drained boreal peatlands. *Biogeochemistry* 44, 163–186.
- Altor, A., Mitsch, W., 2008. Pulsing hydrology, methane emissions and carbon dioxide fluxes in created marshes: a 2-year ecosystem study. *Wetlands* 28, 423–438.
- Amundson, R.G., Davidson, E.A., 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *J. Geochem. Explor.* 38, 13–41.
- Astrom, M., Spiro, B., 2000. Impact of isostatic uplift and ditching of sulfidic sediments on the hydrochemistry of major and trace elements and sulfur isotope ratios in streams, Western Finland. *Environ. Sci. Technol.* 34, 1182.
- Bai, J., Ouyang, H., Deng, W., Zhu, Y., Zhang, X., Wang, Q., 2005. Spatial distribution characteristics of organic matter and total nitrogen of marsh soils in river marginal wetlands. *Geoderma* 124, 181–192.
- Bakken, L.R., Bergaust, L., Liu, B., Frostegård, A., 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N_2O emissions from soils. *Philos. Trans. R. Soc. Lond. Ser. B Biol. Sci.* 367, 1226.
- Balaine, N., Clough, T., Beare, M., Thomas, S., Meenken, E., Ross, J., 2013. Changes in relative gas diffusivity explain soil nitrous oxide flux dynamics. *Soil Sci. Soc. Am. J.* 77, 1496–1505.
- Bartlett, K., Bartlett, D., Harriss, R., Sebach, D., 1987. Methane emissions along a salt marsh salinity gradient. *Biogeochemistry* 4, 183–202.
- Bauza, J.F., Morell, J.M., Corredor, J.E., 2002. Biogeochemistry of nitrous oxide production in the red mangrove (*Rhizophora mangle*) forest sediments. *Estuar. Coast. Shelf Sci.* 55, 697–704.
- Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochim. Cosmochim. Acta* 74, 1268–1281.
- Bouillon, S., Borges, A.V., Castañeda-Moya, E., Diele, K., Dittmar, T., Duke, N.C., Kristensen, E., Lee, S.Y., Marchand, C., Middelburg, J.J., Rivera-Monroy, V.H., Smith, T.J., Twilley, R.R., 2008. Mangrove production and carbon sinks: a revision of global budget estimates. *Glob. Biogeochem. Cycles* 22 (n/a–n/a).
- Bruce, A.H., Elisabeth, A.H., Robert, B.J., Chapin, F.S., Harold, A.M., Christopher, B.F., 1997. The fate of carbon in grasslands under carbon dioxide enrichment. *Nature* 388, 576.
- Bureau of Meteorology (BOM), 2019. Australian bureau of meteorology. <http://www.bom.gov.au/climate/data/index.shtml>.
- CCMA, 2014. Corangamite waterway strategy 2014–2022. https://issuu.com/gsdm/docs/waterway_strategy_2014-22.
- CCMA, 2015. Aire river estuary management plan 2015–2023. http://www.ccmaknowledgebase.vic.gov.au/soilhealth/soils_resource_details.php?resource_id=4345.
- Chanton, J., Whiting, G., Showers, W., Crill, P., 1992. Methane flux from Peltandra virginica: stable isotope tracing and chamber effects. *Glob. Biogeochem. Cycles* 6, 15–31.
- Chanton, J., Arkebauer, T., Harden, H., Verma, S., 2002. Diel variation in lacunal CH_4 and CO_2 concentration and $[delta]^{13}C$ in *Phragmites australis*. *Biogeochemistry* 59, 287–301.
- Chen, G.C., Tam, N.F.Y., Ye, Y., 2010. Summer fluxes of atmospheric greenhouse gases N_2O , CH_4 and CO_2 from mangrove soil in South China. *Sci. Total Environ.* 408, 2761–2767.
- Chen, G.C., Tam, N.F.Y., Ye, Y., 2012. Spatial and seasonal variations of atmospheric N_2O and CO_2 fluxes from a subtropical mangrove swamp and their relationships with soil characteristics. *Soil Biol. Biochem.* 48, 175–181.
- Cheng, X., Peng, R., Chen, J., Luo, Y., Zhang, Q., An, S., Chen, J., Li, B., 2007. CH_4 and N_2O emissions from *Spartina alterniflora* and *Phragmites australis* in experimental mesocosms. *Chemosphere* 68, 420–427.
- Chuang, P.C., Young, M.B., Dale, A.W., Miller, L.G., Herrera-Silveira, J.A., Paytan, A., 2017. Methane fluxes from tropical coastal lagoons surrounded by mangroves, Yucatán, Mexico. *J. Geophys. Res. Biogeosci.* 122, 1156–1174.
- Dalal, R., Allen, D., 2008. TURNER REVIEW No. 18. Greenhouse gas fluxes from natural ecosystems. *Aust. J. Bot.* 56, 369–407.
- Davidson, E.A., 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Sci. Soc. Am. J.* 56, 95–102.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a conceptual model of soil emissions of nitrous and nitric oxides. *BioScience* 50, 667–680.
- Degens, E.T., 1965. Geochemistry of sediments. *Soil Sci.* 100, 225.
- Denef, K., Six, J., Bossuyt, H., Frey, S.D., Elliott, E.T., Merckx, R., Paustian, K., 2001. Influence of dry-wet cycles on the interrelationship between aggregate, particulate organic matter, and microbial community dynamics. *Soil Biol. Biochem.* 33, 1599–1611.
- Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263–276.
- Desai, A.R., Moorcroft, P.R., Bolstad, P.V., Davis, K.J., 2007. Regional carbon fluxes from an observationally constrained dynamic ecosystem model: impacts of disturbance, CO_2 fertilization, and heterogeneous land cover. *J. Geophys. Res. Biogeosci.* 112 (n/a–n/a).
- Dorodnikov, M., Blagodatskaya, E., Blagodatsky, S., Marhan, S., Fangmeier, A., Kuzyakov, Y., 2009. Stimulation of microbial extracellular enzyme activities by elevated CO_2 depends on soil aggregate size. *Glob. Chang. Biol.* 15, 1603–1614.
- Dutaur, L., Verchot, L.V., 2007. A global inventory of the soil CH_4 sink. *Glob. Biogeochem. Cycles* 21 (n/a–n/a).
- Firestone, M.K., Tiedje, J.M., 1979. Temporal change in nitrous oxide and dinitrogen from denitrification following onset of anaerobiosis. *Appl. Environ. Microbiol.* 38, 673.
- Gallardo, A., Schlesinger, W.H., 1994. Factors limiting microbial biomass in the mineral soil and forest floor of a warm-temperate forest. *Soil Biol. Biochem.* 26, 1409–1415.
- Galy-Lacaux, C., Delmas, R., Lambert, C., Dumestre, J.-F., Labrousse, L., Richard, S., Gosse, P., 1997. Gaseous emissions and oxygen consumption in hydroelectric dams: a case study in French Guyana. *Glob. Biogeochem. Cycles* 11, 471–483.

- Ganguly, D., Dey, M., Mandal, S., De, T., Jana, T., 2008. Energy dynamics and its implication to biosphere-atmosphere exchange of CO₂ and CH₄ in a tropical mangrove forest canopy. *Atmos. Environ.* 42, 4172–4184.
- Gentile, R., Vanlauwe, B., Chivege, P., Six, J., 2008. Interactive effects from combining fertilizer and organic residue inputs on nitrogen transformations. *Soil Biol. Biochem.* 40, 2375–2384.
- Gribskov, B., T. H., Boschker, S., Struyf, E., Andersson, M., Trammer, A., De Brabandere, L., Van Damme, S., Brion, N., Meire, P., Dehairs, F., Middelburg, J.J., Heip, C.H.R., 2005. Nitrogen processing in a tidal freshwater marsh: a whole-ecosystem ¹⁵N labeling study. *Limnol. Oceanogr.* 50, 1945–1959.
- Groffman, P.M., Tiedje, J.M., 1988. Denitrification hysteresis during wetting and drying cycles in soil. *Soil Sci. Soc. Am. J.* 52, 1626.
- Gupta, G., Sarma, V., Robin, R., Raman, A., Jai Kumar, M., Rakesh, M., Subramanian, B., 2008. Influence of net ecosystem metabolism in transferring riverine organic carbon to atmospheric CO₂ in a tropical coastal lagoon (Chilka Lake, India). *Biogeochemistry* 87, 265–285.
- Haddad, S.A., Tabatabai, M.A., Loynachan, T.E., 2013. Biochemical processes controlling soil nitrogen mineralization under waterlogged conditions. *Soil Sci. Soc. Am. J.* 77, 809–816.
- Haddad, S., Tabatabai, M., Loynachan, T., 2017. Effects of liming and selected heavy metals on ammonium release in waterlogged agricultural soils. *Cooperating J. Int. Soc. Soil Sci.* 53, 153–158.
- Harrison-Kirk, T., Beare, M.H., Meenken, E.D., Condron, L.M., 2013. Soil organic matter and texture affect responses to dry/wet cycles: effects on carbon dioxide and nitrous oxide emissions. *Soil Biol. Biochem.* 57, 43–55.
- Hirota, M., Senga, Y., Seike, Y., Nohara, S., Kunii, H., 2007. Fluxes of carbon dioxide, methane and nitrous oxide in two contrasting fringing zones of coastal lagoon, Lake Nakami, Japan. *Chemosphere* 68, 597–603.
- IPCC, 2006. IPCC Guidelines for National Greenhouse Gas Inventories. Prepared by the National Greenhouse Gas Inventories Program. IGES, Japan.
- Isbell, R.F., 2016. The Australian Soil Classification. Second edition. CSIRO Publishing, Clayton, Vic.
- Jiao, Z., Hou, A., Shi, Y., Huang, G., Wang, Y., Chen, X., 2006. Water management influencing methane and nitrous oxide emissions from rice field in relation to soil redox and microbial community. *Commun. Soil Sci. Plant Anal.* 37, 1889–1903.
- Johnston, S.G., Slavich, P.G., Hirst, P., 2005. The impact of controlled tidal exchange on drainage water quality in acid sulphate soil backswamps. *Agric. Water Manag.* 73, 87–111.
- Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., Smith, D., Martens, M.A., McInnea, A.E., Ahern, C.R., Powell, B., Stephens, L.P., Wilbraham, S.T., van Heel, S., 2009. Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuar. Coast. Shelf Sci.* 81, 257–266.
- Kettunen, A., Kaitala, V., Lehtinen, A., Lohila, A., Alm, J., Silvola, J., Martikainen, P.J., 1999. Methane production and oxidation potentials in relation to water table fluctuations in two boreal mires. *Soil Biol. Biochem.* 31, 1741–1749.
- Kirk, G.J.D., 2004. *The Biogeochemistry of Submerged Soils*. 1st ed. John Wiley Sons Ltd, Chichester, Chichester.
- Knowles, R., 1982. Denitrification. *Microbiol. Rev.* 46, 43–70.
- Kowalkuk, G., Stephen, J., 2001. Ammonia-oxidizing bacteria: a model for molecular microbial ecology. *Annu. Rev. Microbiol.* 55, 485–529.
- Lehner, B., Döll, P., 2004. Development and validation of a global database of lakes, reservoirs and wetlands. *J. Hydrol.* 296, 1–22.
- Leifeld, J., 2018. Distribution of nitrous oxide emissions from managed organic soils under different land uses estimated by the peat C/N ratio to improve national GHG inventories. *Sci. Total Environ.* 631–632, 23–26.
- Lindau, C., Delaune, R., 1991. Dinitrogen and nitrous oxide emission and entrapment in *Spartina alterniflora* saltmarsh soils following addition of N-15 labelled ammonium and nitrate. *Estuar. Coast. Shelf Sci.* 32, 161–172.
- Liu, Y., Wan, K.-Y., Tao, Y., Li, Z.-G., Zhang, G.-S., Li, S.-L., Chen, F., 2013. Carbon dioxide flux from rice paddy soils in Central China: effects of intermittent flooding and draining cycles. *PLoS One* 8, e56562.
- Liu, X., Guo, Y., Hu, H., Sun, C., Zhao, X., Wei, C., 2015. Dynamics and controls of CO₂ and CH₄ emissions in the wetland of a montane permafrost region, Northeast China. *Atmos. Environ.* 122, 454–462.
- Livesley, S.J., Andrusiak, S.M., 2012. Temperate mangrove and salt marsh sediments are a small methane and nitrous oxide source but important carbon store. *Estuar. Coast. Shelf Sci.* 97, 19–27.
- Lundquist, E.J., Jackson, L.E., Scow, K.M., 1999. Wet-dry cycles affect dissolved organic carbon in two California agricultural soils. *Soil Biol. Biochem.* 31, 1031–1038.
- Maher, D.T., Cowley, K., Santos, I.R., Macklin, P., Eyre, B.D., 2015. Methane and carbon dioxide dynamics in a subtropical estuary over a diel cycle: insights from automated in situ radioactive and stable isotope measurements. *Mar. Chem.* 168, 69–79.
- Marin-Muniz, J.L., Hernández, M.E., Moreno-Casasola, P., 2015. Greenhouse gas emissions from coastal freshwater wetlands in Veracruz Mexico: effect of plant community and seasonal dynamics. *Atmos. Environ.* 107, 107–117.
- Mathew, E.K., Panda, R.K., Nair, M., 2001. Influence of subsurface drainage on crop production and soil quality in a low-lying acid sulphate soil. *Agric. Water Manag.* 47, 191–209.
- Matthew, L.K., Megonigal, J.P., 2013. Tidal wetland stability in the face of human impacts and sea-level rise. *Nature* 504, 53.
- Megonigal, J.P., Schlesinger, W.H., 2002. Methane-limited methanotrophy in tidal freshwater swamps. *Glob. Biogeochem. Cycles* 16, 35–31–35–10.
- Mendoza Mojica, M., Martínez Arroyo, A., Peralta Rosales, O., Castro Romero, T., 2013. Characterization of two Mexican tropical Pacific coastal lagoons in relation to carbon contents and emission-sequestration of CH₄ and CO₂. *Revista Internacional de Contaminación Ambiental* 29, 145–154.
- Minke, M., Augustin, J., xF., rgen, Burlo, A., Yarmashuk, T., Chuvashova, H., Thiele, A., Freibauer, A., Tikhonov, V., Hoffmann, M., 2016. Water level, vegetation composition, and plant productivity explain greenhouse gas fluxes in temperate cutover fens after inundation. *Biogeosciences* 13, 3945.
- Mitsch, W.J., 2015. *Wetlands*. 5th ed. Wiley, Hoboken, New Jersey.
- Mitsch, W., Nahlik, A., Wolski, P., Bernal, B., Zhang, L., Ramberg, L., 2010. Tropical wetlands: seasonal hydrologic pulsing, carbon sequestration, and methane emissions. *Wetl. Ecol. Manag.* 18, 573–586.
- Mitsch, W., Bernal, B., Nahlik, A., Mander, Ü., Zhang, L., Anderson, C., Jørgensen, S., Brix, H., 2013. Wetlands, carbon, and climate change. *Landsch. Ecol.* 28, 583–597.
- Moore, T.R., Roulet, N.T., 1993. Methane flux: water table relations in northern wetlands. *Geophys. Res. Lett.* 20.
- Morse, J.L., Ardón, M., Bernhardt, E.S., 2012. Greenhouse gas fluxes in southeastern U.S. coastal plain wetlands under contrasting land uses. *Ecol. Appl.* 22, 264–280.
- Moseman-Valtierra, S., Gonzalez, R., Kroeger, K.D., Tang, J., Chao, W.C., Crusius, J., Bratton, J., Green, A., Shelton, J., 2011. Short-term nitrogen additions can shift a coastal wetland from a sink to a source of N₂O. *Atmos. Environ.* 45, 4390–4397.
- Mosley, L.M., Fleming, N., 2009. Reductions in water use following rehabilitation of a flood-irrigated area on the Murray River in South Australia. *Agric. Water Manag.* 96, 1679–1682.
- Muhammad, W., Vaughan, S., Dalal, R., Menzies, N., 2011. Crop residues and fertilizer nitrogen influence residue decomposition and nitrous oxide emission from a vertisol. *Cooperating J. Int. Soc. Soil Sci.* 47, 15–23.
- Neubauer, S., Anderson, L., Neikirk, B., 2005. Nitrogen cycling and ecosystem exchanges in a Virginia tidal freshwater marsh. *Estuaries* 28, 909–922.
- Olsson, L., Ye, S., Yu, X., Wei, M., Krauss, K.W., Brix, H., 2015. Factors influencing CO₂ and CH₄ emissions from coastal wetlands in the Liaohe Delta, Northeast China. *Biogeochemistry* 12, 4965.
- Pilegaard, K., Skiba, U., Ambus, P., Beier, C., Brüggemann, N., Butterbach-Bahl, K., Dick, J., Dorsey, J., Duyzer, J., Gallagher, M., Gasche, R., Horvath, L., Kitzler, B., Leip, A., Pihlatie, M., Rosenkranz, P., Seufert, G., Vesala, T., Westrate, H., Zechmeister-Boltenstern, S., 2006. Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N₂O). *Biogeosciences* 3, 651–661.
- Poffenberger, H.J., Needelman, B.A., Megonigal, J.P., 2011. Salinity influence on methane emissions from tidal marshes. *Wetlands* 31, 831–842.
- Ponnamperuma, F.N., 1972. The chemistry of submerged soils. In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 29–96.
- Rabot, E., Hénault, C., Cousin, I., 2014. Temporal variability of nitrous oxide emissions by soils as affected by hydric history. *Soil Sci. Soc. Am. J.* 78, 434–444.
- Rabot, E., Hénault, C., Cousin, I., 2016. Effect of the soil water dynamics on nitrous oxide emissions. *Geoderma* 280, 38–46.
- Rayment, G.E., Lyons, D.J., 2011. *Soil Chemical Methods*. CSIRO, Melbourne, Australia.
- Riet, B., Hefling, M., Verhoeven, J., 2013. Rewetting drained peat meadows: risks and benefits in terms of nutrient release and greenhouse gas exchange. *Int. J. Environ. Pollut.* 224, 1–12.
- Rosa, L.P., Schaeffer, R., Santos, M.A., 1996. Are hydroelectric dams in the Brazilian Amazon significant sources of 'greenhouse' gases? *Environ. Conserv.* 23, 2–6.
- Rusch, H., Rennenberg, H., 1998. Black alder (*Alnus glutinosa* (L.) Gaertn.) trees mediate methane and nitrous oxide emission from the soil to the atmosphere. *Int. J. Plant-Soil Relatsh.* 201, 1–7.
- Ruser, R., Flessa, H., Russow, R., Schmidt, G., Buegger, F., Munch, J.C., 2006. Emission of N₂O, N₂ and CO₂ from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. *Soil Biol. Biochem.* 38, 263–274.
- Scanlon, D., Moore, T., 2000. Carbon dioxide production from peatland soil profiles: the influence of temperature, OXIC/anoxic conditions and substrate. *Soil Sci.* 165, 153–160.
- Seitzinger, S.P., Kroeze, C., 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. *Glob. Biogeochem. Cycles* 12, 93–113.
- Seo, D.C., Delaune, R.D., 2010. Fungal and bacterial mediated denitrification in wetlands: influence of sediment redox condition. *Water Res.* 44, 2441–2450.
- Shi, W.-Y., Yan, M.-J., Zhang, J.-G., Guan, J.-H., Du, S., 2014. Soil CO₂ emissions from five different types of land use on the semiarid Loess Plateau of China, with emphasis on the contribution of winter soil respiration. *Atmos. Environ.* 88, 74–82.
- Šimek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *Eur. J. Soil Sci.* 53, 345–354.
- Šimek, M., Virtanen, S., Křístůfek, V., Simojoki, A., Yli-Halla, M., 2011. Evidence of rich microbial communities in the subsoil of a boreal acid sulphate soil conducive to greenhouse gas emissions. *Agric. Ecosyst. Environ.* 140, 113–122.
- Smith, L., Lewis, W., 1992. Seasonality of methane emissions from five lakes and associated wetlands of the Colorado Rockies. *Glob. Biogeochem. Cycles* 6, 323–338.
- Smith, M.S., Parsons, L.L., 1985. Persistence of denitrifying enzyme activity in dried soils. *Appl. Environ. Microbiol.* 49, 316.
- Smith, C.J., Delaune, R.D., Patrick, W.H., 1983. Nitrous oxide emission from Gulf Coast wetlands. *Geochim. Cosmochim. Acta* 47, 1805–1814.
- Soil Survey Staff, 2014. *Keys to Soil Taxonomy*. 12th ed. USDA-Natural Resources Conservation Service, Washington, DC.
- Soumis, N., Duchemin, É., Canuel, R., Lucotte, M., 2004. Greenhouse gas emissions from reservoirs of the western United States. *Glob. Biogeochem. Cycles* 18 (n/a–n/a).
- Sparks, D.L., 2003. 8 - redox chemistry of soils. In: Sparks, D.L. (Ed.), *Environmental Soil Chemistry*. Second edition Academic Press, Burlington, pp. 245–265.
- Sun, Z., Wang, L., Tian, H., Jiang, H., Mou, X., Sun, W., 2013. Fluxes of nitrous oxide and methane in different coastal Suaeda salsa marshes of the Yellow River estuary, China. *Chemosphere* 90, 856–865.

- Sun, Z., Wang, L., Mou, X., Jiang, H., Sun, W., 2014. Spatial and temporal variations of nitrous oxide flux between coastal marsh and the atmosphere in the Yellow River estuary of China. *Environ. Sci. Pollut. Res. Int.* 21, 419–433.
- Sutton-Grier, A.E., Keller, J.K., Koch, R., Gilmour, C., Megonigal, J.P., 2011. Electron donors and acceptors influence anaerobic soil organic matter mineralization in tidal marshes. *Soil Biol. Biochem.* 43, 1576–1583.
- Tabatabai, M.A., Ekenler, M., Senwo, Z.N., 2010. Significance of enzyme activities in soil nitrogen mineralization. *Commun. Soil Sci. Plant Anal.* 41, 595–605.
- Tobias, C., Neubauer, S.C., 2019. Chapter 16 - salt marsh biogeochemistry—an overview. In: Perillo, G.M.E., Wolanski, E., Cahoon, D.R., Hopkinson, C.S. (Eds.), *Coastal Wetlands*. Elsevier, pp. 539–596.
- Tobias, C.R., Macko, S.A., Anderson, I.C., Canuel, E.A., Harvey, J.W., 2001. Tracking the fate of a high concentration groundwater nitrate plume through a fringing marsh: a combined groundwater tracer and in situ isotope enrichment study. (Statistical Data Included). *Limnol. Oceanogr.* 46, 1977.
- Tong, C., Huang, J., Hu, Z., Jin, Y., 2013. Diurnal variations of carbon dioxide, methane, and nitrous oxide vertical fluxes in a subtropical estuarine marsh on neap and spring tide days. *J. Coast. Estuar. Res. Fed.* 36, 633–642.
- Tremblay, A., Varfalvy, L., Roehm, C., Garneau, M., 2005. *GHG Emissions From Boreal Reservoirs and Natural Aquatic Ecosystems*. Springer Berlin Heidelberg, Berlin, Heidelberg, Berlin, Heidelberg.
- Trinsoutrot, I., Recous, S., Bentz, B., Linères, M., Chêneby, D., Nicolardot, B., 2000. Biochemical quality of crop residues and carbon and nitrogen mineralization kinetics under nonlimiting nitrogen conditions. *Soil Sci. Soc. Am. J.* 64, 918–926.
- Van der Nat, F.-J., Middelburg, J., 2000. Methane emission from tidal freshwater marshes. *Biogeochemistry* 49, 103–121.
- Vann, C., Patrick Megonigal, J., 2003. Elevated CO₂ and water depth regulation of methane emissions: comparison of woody and non-woody wetland plant species. *Biogeochemistry* 63, 117–134.
- Vanselow-Algan, M., Schmidt, S.R., Greven, M., Fiencke, C., Kutzbach, L., Pfeiffer, E.M., 2015. High methane emissions dominated annual greenhouse gas balances 30 years after bog rewetting. *Biogeosciences* 12, 4361.
- Webb, J.R., Santos, I.R., Tait, D.R., Sippon, J.Z., Macdonald, B.C.T., Robson, B., Maher, D.T., 2016. Divergent drivers of carbon dioxide and methane dynamics in an agricultural coastal floodplain: post-flood hydrological and biological drivers. *Chem. Geol.* 440, 313–325.
- Weil, R.R., 2016. *The Nature and Properties of Soils*. Fifteenth edition. Pearson, Columbus, Ohio.
- Weslien, P., Kasimir Klemetsson, A., Boerjesson, G., Klemetsson, L., 2009. Strong pH influence on N₂O and CH₄ fluxes from forested organic soils. *Eur. J. Soil Sci.* 60, 311–320.
- Weston, N., Vile, M., Neubauer, S., Velinsky, D., 2011. Accelerated microbial organic matter mineralization following salt-water intrusion into tidal freshwater marsh soils. *Int. J.* 102, 135–151.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Hirst, P., Sullivan, L.A., Bush, R.T., Blackford, M., 2015. Seawater inundation of coastal floodplain sediments: short-term changes in surface water and sediment geochemistry. *Chem. Geol.* 398, 32–45.
- Wrage, N., Velthof, G., van Beusichem, M., Oenema, O., 2001. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.* 33, 1723–1732.
- Wrage, N., Velthof, G., Laanbroek, H., Oenema, O., 2004. Nitrous oxide production in grassland soils: assessing the contribution of nitrifier denitrification. *Soil Biol. Biochem.* 36, 229–236.
- Yang, W.-B., Yuan, C.-S., Tong, C., Yang, P., Yang, L., Huang, B.-Q., 2017. Diurnal variation of CO₂, CH₄, and N₂O emission fluxes continuously monitored in-situ in three environmental habitats in a subtropical estuarine wetland. *Mar. Pollut. Bull.* 119, 289–298.
- Yau, C.C., Wong, V.N.L., Kennedy, D.M., 2016. Soil chemistry and acidification risk of acid sulfate soils on a temperate estuarine floodplain in southern Australia. *Soil Res.* 54.
- Zhang, Y., Wang, L., Xie, X., Huang, L., Wu, Y., 2013. Effects of invasion of *Spartina alterniflora* and exogenous N deposition on N₂O emissions in a coastal salt marsh. *Ecol. Eng.* 58, 77–83.

**Chapter 3. Effect of inundation on sulfide and potential acidity
in coastal acid sulfate soils with different vegetation types in
southern Australia**

Effect of inundation on sulfide and potential acidity in coastal acid sulfate soils with different vegetation types in southern Australia

Chang. Xu ^{1,2}, Vanessa N.L. Wong ¹ Rahul Ram¹

¹School of Earth, Atmosphere and Environment, Monash University, Wellington Road, Clayton, VIC 3800, Australia.

²Corresponding author: chang.xu@monash.edu

3.1 Abstract

Coastal wetland soils frequently have sulfidic soils at depth. Sea level fluctuations can lead to the oxidation of sulfidic sediments in acid sulfate soils (ASS) and increased potential acidity in mobilising trace metals when water levels are low. Sea level rise can cause the inundation of coastal wetland soils and reformation of reduced inorganic sulfide (RIS). We measured the effect of water level fluctuations on in soils from coastal wetland sites with four different vegetation types: *Apium graveolens* (AG), *Leptospermum lanigerum* (LL), *Phragmites australis* (PA) and *Paspalum distichum* (PD) in the estuarine floodplain of the Aire River in south-western Victoria, Australia. We assessed the effects fluctuating water levels on reduced inorganic sulfide (RIS) in terms of acid volatile sulfide (AVS) and chromium reducible sulfur (CRS), potential acidity and trace metals (Fe, Al, Mn, Zn, Ni) from. Intact soil cores were incubated under dry, flooded, and wet-dry cycle treatments of 14-d for a total of 56 days at a constant temperature of 21°C. The flooded treatment significantly increased AVS and CRS in most soil depths ($p < 0.05$). Under the dry treatment, significantly lower CRS were observed in all sites due to the CRS being oxidised when the surface layer was exposed to with lower water levels ($p < 0.05$). CRS was positively correlated with SOC in all treatments ($p < 0.05$). The highest net acidity (measure of acidity hazard of ASS) occurred in the dry treatment and lowest net acidity was observed following the flooded treatment in the AG, LL and PD sites in most soil depths. Seawater inundation was conducive to SO_4^{2-} reduction process and caused the decrease of soluble Fe and Al in the PA and PD sites. The SO_4^{2-} concentration decreased in the LL, PA, and PD sites following flooded treatment due to the reformation of CRS. Brackish water inundation provides a mechanism to prevent further oxidation of RIS and can be an effective tool to reduce acidity by forming or reforming pyrite in temperate ASS environments. These results highlight that inundation could be considered when planning remediation approaches for ASS.

Key words: Acid sulfate soils, reduced inorganic sulfide, trace metals, acidity, inundation

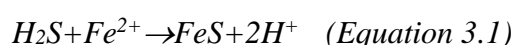
3.2 Introduction

Acid sulfate soils (ASS) are soils or sediments that contain oxidizable or partly oxidized sulfide minerals (Pons, 1973). In ASS environments, pyrite (FeS_2) is the most prevalent sulfide mineral and usually represents the potential acidity in the system (Dent and Pons, 1995). Apart from FeS_2 , other oxidizable sulfides like iron monosulfides (FeS), such as mackinawite or greigite (Fe_3S_4) can also be found in coastal marine and estuarine sediments (Morse and Rickard, 2004), but can occur in high concentrations in organic, sulfide-rich materials from ASS environments (Boman et al., 2010a; Bush et al., 2004; Macdonald et al., 2004a; Ram et al., 2021a; Ram et al., 2021b; Sullivan and Bush, 2000).

ASS have been estimated to occupy an area between 17 Mha and 25 Mha worldwide, including South and Southeast Asia, West and Southern Africa, Australia, Latin America, boreal Europe, and Northern America (Andriessse and Mensvoort, 2006; Ljung et al., 2009). Coastal ASS (CASS) are often found in tropical coastal areas, estuarine floodplains and mangrove marshes, where waterlogged environments promote FeS_2 formation (Beek et al., 1980; Dent, 1986; Rabenhorst and Fanning, 2006). In coastal regions, almost all subaqueous soils have been found to be affected by sulfidization and commonly give rise to actual acid sulfate soils when they are oxidized (Fitzpatrick et al., 2002).

Sulfidic sediments, measured by reduced inorganic sulfur (RIS), usually accumulate in waterlogged soils in inland freshwater wetlands and marine, coastal or estuarine environments. Environmental conditions that promote the formation of RIS include (1) sufficient supply of organic matter from either rooted plants or detrital additions; (2) source of Fe which is generally provided by Fe-containing minerals in the sediments; (3) supply of dissolved SO_4^{2-} . In coastal environments, the SO_4^{2-} is mainly derived from sea water (Dent, 1986; Fanning et al., 2002). Availability of organic matter predominantly controls the formation of pyrite as SO_4^{2-} and Fe minerals are abundant (Berner, 1984). RIS have been found in different mineral phases, including Fe monosulfides, pyrite and greigite. In particular, Fe monosulfides and pyrite have been widely studied (Karimian et al., 2017).

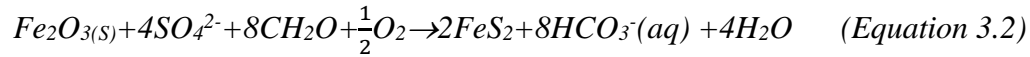
Fe monosulfides can form relatively rapidly following initial inundation or onset of waterlogged conditions (Burton et al., 2011; Karimian et al., 2018). Fe monosulfides can form through the reaction of H_2S with the free Fe^{2+} (Equation 3.1).



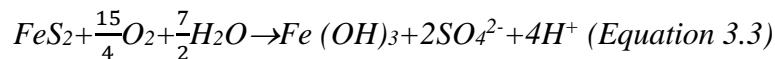
Fe monosulfide minerals can transform to pyrite under anoxic conditions and in the presence of soil organic matter and dissolved sulfide over longer time periods (Berner, 1984; Rickard and Morse, 2005). The

concentration of pyrite may be influenced by organic matter as higher pyrite concentrations have been found in flooded soils with abundant organic matter (Dent and Pons, 1995; Holmer and Nielsen, 1997)

The key components of pyrite formation reaction require organic matter, SO_4^{2-} and Fe(III) oxides and the overall reaction of pyrite formation is shown in equation 3.2 (Dent and Pons, 1995).



When mineral sulfidic layers remain under anaerobic or waterlogged conditions, they usually have a near neutral pH and are therefore not problematic. Under these conditions, the soils are known as potential acid sulfate soils (PASS) (Ljung et al., 2009; Ritsema and Groenenberg, 1993; Sullivan. et al., 2018) as they have the potential to form sulfuric acid and reduced inorganic sulfur species. Sulfuric acid is generated when sediments containing RIS are oxidized, causing the pH to decrease below 4 (Dent and Pons, 1995). Fe-S minerals (FeS_2) oxidation are regarded as the main source of potential acidity in ASS environments (Ljung et al., 2009; White et al., 2007). The oxidation of Fe-S minerals ultimately results in products such as Fe minerals such as $Fe(OH)_3$, acidity and SO_4^{2-} , and involves a series of complex reactions, with several Fe and S intermediate products and highly acidic soil (Dent, 1986; Fanning and Burch, 2000) This is shown the overall reaction in Equation 3.3 below:



TAA is used to estimate the pool of exchangeable H^+ in ASS (McElnea et al., 2002). Net Acidity is a measure of the acidity hazard of ASS. Oxidation of Fe-S minerals can be caused by natural processes such as coastal regression, isostatic uplift or drought caused by climate change (Boman et al., 2010a; Grealish et al., 2014), or it may be the result of anthropogenic interventions such as drainage of coastal areas for agriculture or activities during construction or mining (Astrom and Spiro, 2000; Burton et al., 2006a; Mathew et al., 2001). Van den Berg et al. (1998) observed pH declines and metal precipitation (Fe and Mn oxides) when water levels decreased as a result of pyrite oxidation soil during summer and sulfate reduction when the soils were inundated during winter. Boman et al. (2010a) showed that land uplift and natural drainage have caused the pyrite oxidation causing Ni and Zn to be released. Karimian et al.(2017) demonstrated that when the wetland water levels undergo large seasonal fluctuations, RIS species were easily oxidized and generate substantial acidity during dry periods followed by Fe(III) and SO_4^{2-} reducing conditions which generated alkalinity and lowered acidity, and sequestered Fe, S, Zn, Mn and As during re-flooding periods.

Tidal inundation of CASS is a potentially cost effective and landscape-scale remediation method (Burton et al., 2011; Burton et al., 2008a; Johnston et al., 2009a; Johnston et al., 2009b). Inundation can reverse the

oxidation process in ASS coastal wetlands. Re-flooding can stimulate the reduction of Fe (III) and SO_4^{2-} . Fe(III) are reduced to Fe(II) and SO_4^{2-} are reduced to H_2S (Karimian et al., 2018). Such reductive processes can decrease acidity, produce alkalinity and promote the reformation of RIS like FeS_2 and FeS (Hicks et al., 2003; Keene et al., 2011; Powell and Martens, 2005).

Labile organic carbon can provide a primary source of electron donors in soils thus is a significant factor which can affect the rate of reduction of Fe(III) and SO_4^{2-} reduction in inundated ASS soils (Blodau and Peiffer, 2003). Johnston et al. (2003) suggested that reduction processes from Fe (III) to Fe(II) and from SO_4^{2-} to H_2S were strongly influenced by the surface vegetation. Different vegetation types can exhibit large differences in the quality and lability of carbon, which can affect the decay process of organic matter (Leifeld, 2018), and influence greenhouse gas production (Marín-Muñiz et al., 2015; Xu et al., 2021). Carbon from herbaceous plants is typically more labile than carbon from woody plants (Desai et al., 2007). Organic matter decay rates can be restricted by high contents of lignin in woody species (McClaugherty and Berg, 1987; Webster and Benfield, 1986) and therefore affects sulfide mineral reformation by decreasing the rate of decomposition of organic matter.

Previous studies have measured water quality after inundation or drainage in coastal wetlands (Johnston et al., 2005; Sohlenius and Öborn, 2004; White et al., 1997; Wong et al., 2010, 2013; Wong et al., 2015). However, studies which identify the impact of sea level rise and storm surge events on Fe sulfide minerals and acidity in CASS environments are limited. These events can be simulated by subjecting soils to inundation treatments which include extended dry periods, flooded periods and wet-dry cycles. The aims of our research are to 1) identify and compare the effects of dry, flooded and wet-dry cycle treatments in a CASS environment on soil acidity, RIS and trace metals, and 2) assess the effects of different vegetation types on RIS formation.

3.3. Materials and methods

3.3.1 Site description and soil collection

Soil samples (0-20 cm) were taken from the Aire River floodplain, which is located in the Otway Ranges to the west of Apollo Bay in south-western Victoria ($38^\circ 47' 43.1''$ S, $143^\circ 28' 37''$ E), Australia (Fig. 3.1). The study area is adjacent to the sea and water table varies substantially because the estuary mouth closes intermittently (CCMA, 2014). The four vegetation types include: (1) *Apium graveolens* (AG), a herbaceous species, at located $38^\circ 46' 14.11''$ S, $143^\circ 27' 37.3''$ E; +8 m Australian height datum (AHD), where 0 m AHD is approximately at sea level; (2) *Leptospermum lanigerum* (LL), a woolly tea tree, located at $38^\circ 47' 42.1''$ S, $143^\circ 28' 33.5''$ E; +9 m AHD) sites which were located in a wildlife reserve; (3) *Phragmites australis* (PA),

a broadly distributed wetland grass, located at 38°47'43.1" S, 143°28'37.1" E; 0 m AHD; and (4) *Paspalum distichum* (PD) is a species of grass, located at 38°46'01.6" S, 143°28'09.9" E; +3 m AHD) sites which were located in grazed areas which were drained. Soil cores were taken by inserting PVC tubes (h= 40 cm, d=10 cm) to 20 cm depth. Collection sites were selected to be areas that had the least plant materials, and, if needed, scraped before extraction. The cores were then manually excavated and sealed with parafilm and plastic wrap for transport. The cores were stored in a fridge at 4°C until analysis. Subsample of each horizon (0-5 cm, 5-10 cm and 10-20cm) was placed in to a freezer at -80 °C for future analysis. Based on the Australian Soil Classification, the PA site was identified as Hydrosol, AG and PD sites were Dermosols, and the LL site was a Tenosol (Isbell, 2016). These soil profiles were analogous to a Histosol, Mollisol and Entisol (USDA Soil Taxonomy) (Soil Survey Staff, 2014) at the PA, AG and PD, and LL sites, respectively.

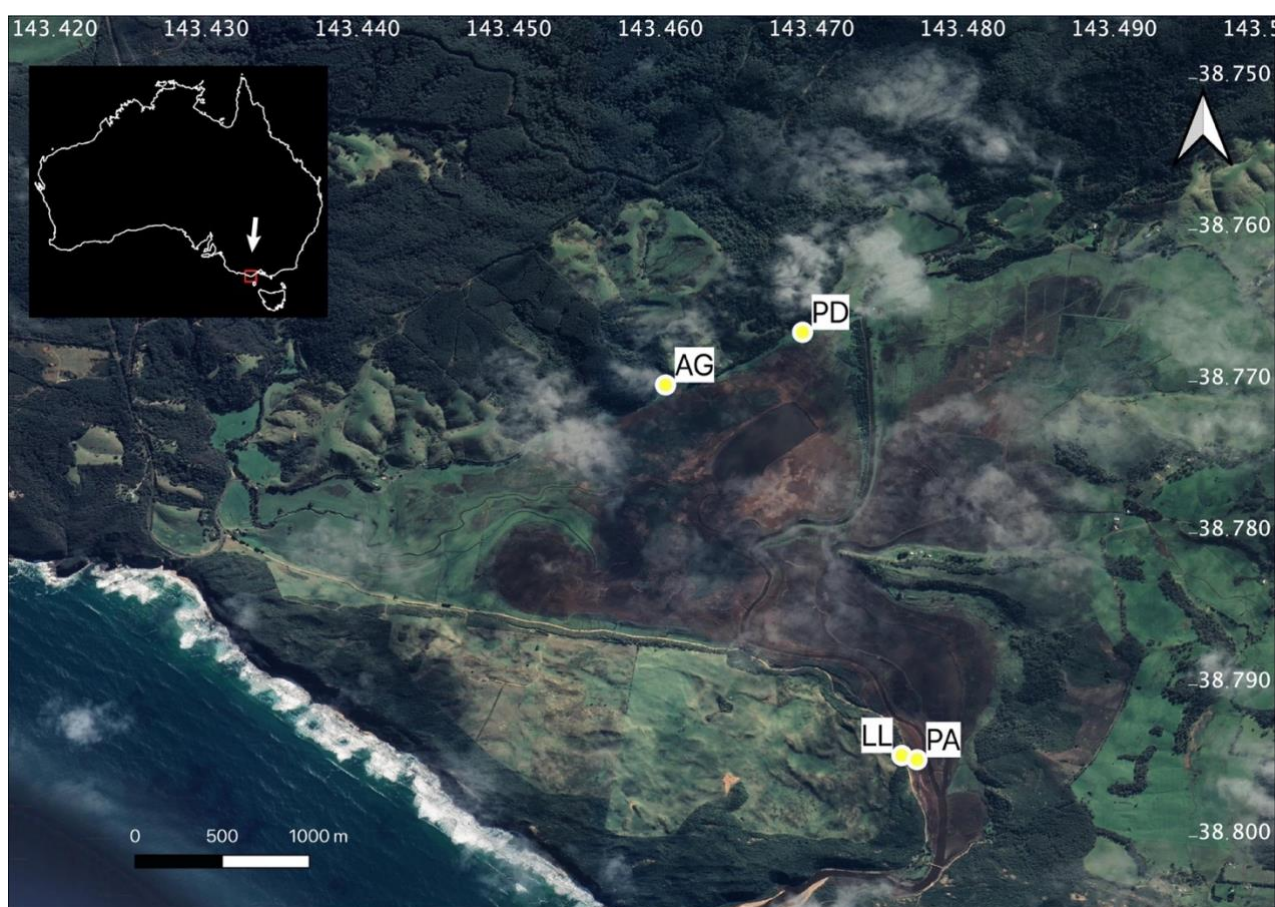


Fig 3.1 Locations of sample sites AG (*Apium graveolens*), LL (*Leptospermum lanigerum*), PA (*Phragmites australis*), PD (*Paspalum distichum*) within Aire River Wildlife Reserve.

3.3.2 Experiment setup

In this study, soil core incubation experiments were incubated at constant room temperature at 23 °C at three different water table treatments: dry, flooded and wet-dry cycles of 14 days each for a total of 56 days. The dry treatment did not involve added moisture. The flooded treatment was flooded with Aire River water (Table 3.1) at 5 cm above the soil surface with weekly addition to count for evaporative loss to the

atmosphere. In the wet-dry treatment, soil cores were initially flooded at 5 cm above soil surface for the first one week, and drained for the next week to finish one cycle. Each cycle was repeated for four times. Four replicates were included in each treatment.

3.3.3 Materials and methods

The starting soil moisture content and bulk density were measured by weighing after drying at 105°C for 24 h. The Eh and soil water content during the incubation were analysed by platinum electrodes and HS₂ Hydrosense II system (model CS 659), respectively. Soil samples were oven-dried at 85°C for 24 hours, and then crushed and sieved to 2 mm. Soil pH, electrical conductivity (EC) were measured in 1:5 v/v soil:water extracts (Rayment and Lyons, 2011). Soil pH and EC were measured using a Conductivity-TDS-Salinity pH-ORP-Temperature meter. Soluble cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) and trace metals (Al, Fe, Mn, Zn, Ni) in liquid extracts were measured by inductively coupled plasma - optical emission spectrometry (ICP-OES) (iCAP, 7000 series). Dissolved anions (SO₄²⁻, Cl⁻) were analysed on a Lachat QC 8500 Flow Injection Analyser (FIA). Perkin Elmer 2400 Series II CHNS/ O Analyzer was used to analyse soil organic carbon (SOC) and total nitrogen (TN) content through high temperature combustion. Beckham Coulter 13320 laser diffraction analysis was applied to measure soil particle size distribution after pretreatment with 10% H₂O₂ to remove organic matter.

Titrateable actual acidity (TAA) was measured based on the method described in Rayment and Lyons (2011). TAA was extracted by shaking 1 g of finely ground soil with 40 mL of 1M KCl for 4 h. The 1M KCl extract was subsequently titrated against 0.05 M NaOH using an auto-titrator. Acid neutralising capacity (ANC) analysis followed the method from Rayment and Lyons (2011). The suspension was prepared by mixing 1 g of finely ground soil with 25 mL of deionised water and 25 mL of 0.1 M HCl and was placed on a hot plate and boiled for 2 min. The suspension was titrated with 0.25 M NaOH to 7 with an auto-titrator to determine the ANC.

Reduced inorganic sulfur (RIS) was measured based on a three-step sequential extraction process (Burton et al., 2008b). Reduced inorganic sulfides mainly include acid volatile sulfide (AVS) and chromium reducible sulfur (CRS). The AVS fraction mainly consists of Fe monosulfides (FeS) and the CRS fraction measures pyrite (FeS₂) (Lasorsa and Casas, 1996). Acid volatile sulfide was extracted by shaking 2 g of soil with 10 mL of 6 M HCl/0.1M ascorbic acid in gas tight 50 mL centrifuge tubes for 18 h. The evolved H₂S (g) was trapped in 3% Zn acetate in 2 M NaOH, and then quantified through iodometric titration with 0.025 M sodium thiosulfate. CRS was extracted by shaking with acidified CrCl₂ solution for 48 h (Burton et al., 2008b). The evolved H₂S (g) was trapped in 3% Zn acetate in 2M NaOH. CRS was subsequently measured by iodometric titration with 0.025 M sodium thiosulfate. Samples were analyzed with four replicates.

Net acidity was calculated based on acid-base accounting and the equation was calculated via Equation 3.4 and expressed in mol H⁺ kg⁻¹.

$$\text{Net acidity} = (\text{AVS} + \text{CRS}) + \text{TAA} - (\text{ANC}/\text{FF}) \text{ (Equation 3.4)}$$

Where a minimum fineness factor (FF) of 1.5 was applied.

Table 3.1 Soluble cation and anion concentrations in Aire River water (surface water)

Site	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)
Aire River water	55.3	141.7	1227.5	1993.4	0.4	106.5

3.3.4 Geochemical Modelling

Geochemical modelling was done using Geochemist's Workbench (Bethke, 2007), using thermodynamic properties from a modified version of the Lawrence Livermore National Laboratory database (version 9). Updated properties for Fe and Al were taken from Ram et al. (2021b). The Cl⁻ concentrations for modelling were set to the lowest and mean Cl⁻ concentration that were extracted (61 mg/kg and 1542 mg/kg) in this study, and the maximum concentration was set to 19400 mg/kg because it is the concentration of Cl⁻ in seawater (Levinson, 1968). The mean Fe²⁺ concentration that was extracted for modelling was set to 0.74 mg/kg. The SO₄²⁻ concentration for modelling were set to the lowest and mean SO₄²⁻ concentration that were extracted (46 mg/kg and 497 mg/kg) in this study, and the maximum concentration was set to 2700 mg/kg because it is the concentration of SO₄²⁻ in seawater (Levinson, 1968). The mean Al³⁺ concentrations that was extracted for modelling was set to 0.34 mg/kg.

3.3.5 Statistical analysis

One-way analysis of variance (ANOVA) in combination with a post-hoc Tukey test was conducted to detect significant difference in AVS and CRS between the dry, flooded and wet-dry cycle treatments ($p < 0.05$). One-way ANOVA was used to determine the significant differences of main soil characteristics (SOC, TN) between the sites ($p < 0.05$). Pearson correlation analysis was applied between RIS (AVS and CRS) and other soil parameters respectively. All the analyses were performed using GraphPad Prism 8.

3.4. Results

3.4.1 Soil characterisation

The initial soil properties were shown in Table 3.2. The PA and LL sites had a sandier texture compared with the AG and PD sites. The soil pH indicated that all the sites were slightly acidic to acidic. The EC and soil water content decreased with soil depth at all site, with the highest values both occurring in the PA site. Bulk density increased with soil depth in all sites (Table 3.2). The initial SOC and TN were significantly different between the sites respectively ($p < 0.05$). The highest SOC and TN concentration occurred in the 0-5 cm soil layer in all sites, with the highest SOC and TN concentration occurring in the PA site (Table 3.2). The C/N ratios of the AG and PD sites were lower than those in the PA and LL sites (Table 3.2). In the dry treatment, soil pH generally decreased at all sites, with the greatest decrease occurring in the LL site. The soil pH increased following flooded treatment in the AG, PA and PD sites. The soil pH decreased in the AG and LL site while did not have much change in the PA and PD site following wet-dry cycle treatment (Table S3.1). The soil EC increased after all water table treatments, with the greatest EC occurring in the PA site (Table S3.1). The soil water content declined with time in the dry treatment in all sites (Fig. 3.2a, c, e, g). In the flooded treatment, the soil water content was 100% in all sites as the soils were inundated. In wet-dry cycle treatment, soil water content decreased from flooded condition to dry condition (Fig. 3.2a, c, e, g). The Eh of the soil changed rapidly with the fluctuation of water level. The Eh was between +100 and +210 mV at all sites under dry treatment. The Eh were generally below -170 mV at all sites under flooded treatment (Fig. 3.2b, d, f, h). Under wet-dry cycle treatment, Eh oscillated from ~ -200 mV to ~ +100 mV at all sites.

Table 3.2 Physical and chemical characteristics of the soils in the four vegetation type sites

Sites	Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	EC (mS cm ⁻¹)	Bulk Density (g cm ⁻³)	Soil water content (%)	SOC (%)	Total N (%)	C/N
AG	0-5	0	73	27	5.8 ± 0.02	0.18 ± 0.01	0.75 ± 0.02	29.8 ± 2.3	6.0 ± 0.1	0.7 ± 0.01	8.4 ± 0.2
	5-10	0	81	19	5.4 ± 0.02	0.14 ± 0.01	0.88 ± 0.01	26.2 ± 1.1	5.3 ± 0.1	0.7 ± 0.01	7.7 ± 0.3
	10-20	0	75	25	5.2 ± 0.05	0.13 ± 0.01	0.87 ± 0.04	24.0 ± 0.1	4.2 ± 0.1	0.5 ± 0.01	7.9 ± 0.1
LL	0-5	85	12	3	6.6 ± 0.09	0.52 ± 0.02	0.95 ± 0.01	25.3 ± 4.1	5.5 ± 0.4	0.5 ± 0.04	11.8 ± 0.3
	5-10	80	15	5	6.3 ± 0.06	0.26 ± 0.01	0.97 ± 0.03	16.2 ± 0.3	5.5 ± 0.4	0.5 ± 0.04	10.4 ± 0.1
	10-20	69	23	8	6.3 ± 0.01	0.30 ± 0.02	1.02 ± 0.02	18.4 ± 1.4	4.4 ± 0.3	0.4 ± 0.03	10.5 ± 0.1
PA	0-5	59	37	4	5.4 ± 0.01	2.18 ± 0.05	0.33 ± 0.01	83.3 ± 1.3	20.4 ± 0.3	1.8 ± 0.05	11.5 ± 0.1
	5-10	63	33	4	4.9 ± 0.09	1.91 ± 0.1	0.37 ± 0.02	80.2 ± 1.7	22.8 ± 0.3	1.9 ± 0.03	11.9 ± 0.3
	10-20	34	57	9	5.3 ± 0.02	2.14 ± 0.06	0.38 ± 0.01	70.6 ± 0.9	16.8 ± 1.1	1.5 ± 0.08	11.2 ± 0.2
PD	0-5	0	83	17	5.2 ± 0.01	0.34 ± 0.01	0.78 ± 0.02	34.3 ± 0.9	7.6 ± 0.5	0.9 ± 0.01	8.8 ± 0.8
	5-10	0	78	22	5.2 ± 0.01	0.23 ± 0.01	0.87 ± 0.02	28.3 ± 0.4	4.9 ± 0.1	0.5 ± 0.02	9.2 ± 0.2
	10-20	0	79	21	5.3 ± 0.03	0.27 ± 0.01	0.92 ± 0.01	30.6 ± 0.6	5.4 ± 0.1	0.6 ± 0.01	9.4 ± 0.3

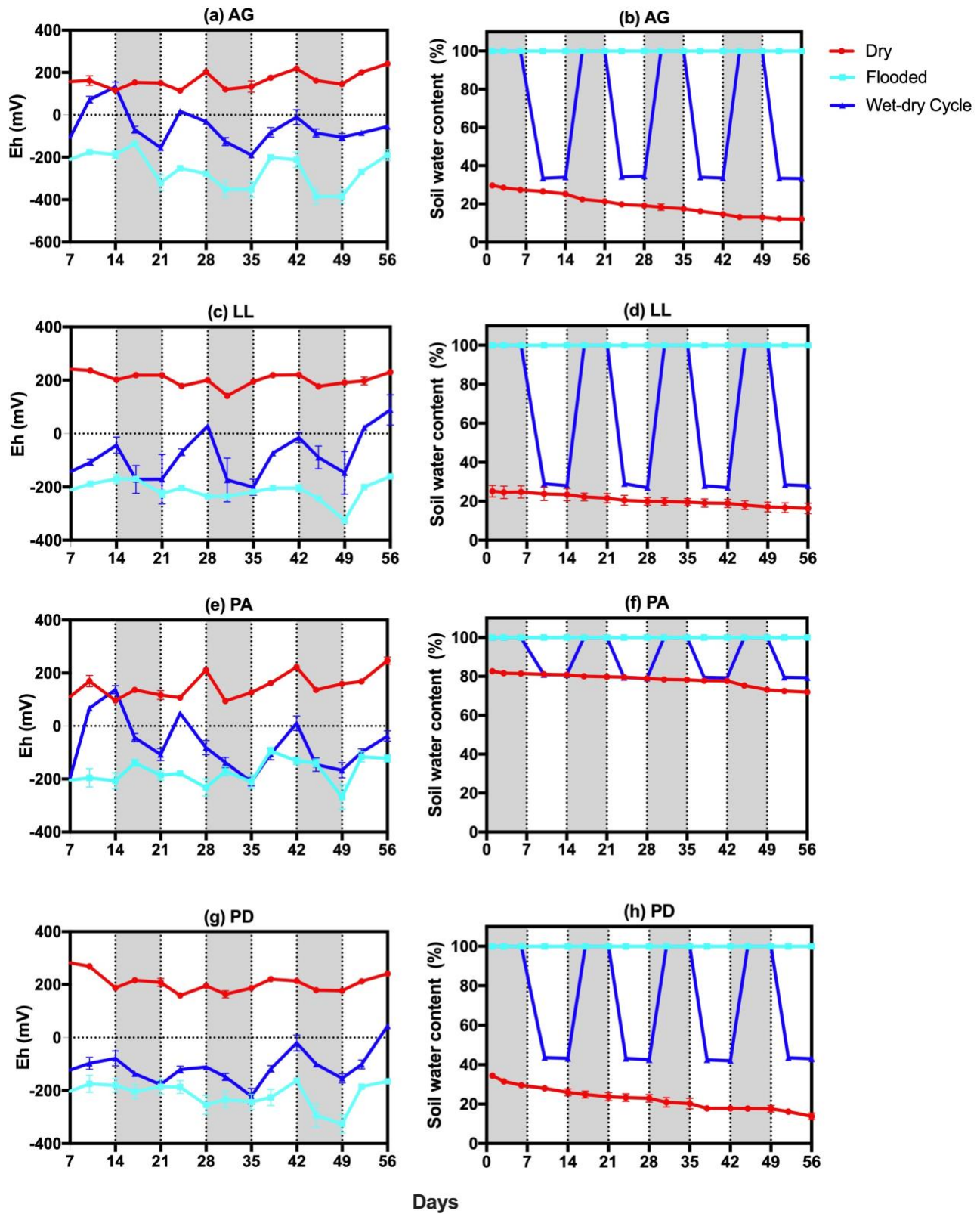


Fig 3.2 Temporal variation in Eh and soil water content in AG (*Apium graveolens*) (a, b), LL (*Leptospermum lanigerum*) (c, d), PA (*Phragmites australis*) (e, f), PD (*Paspalum distichum*) (g, h) sites. Vertical bars denote standard error of means (n=4). (Grey shaded areas represent flooded periods; white areas represent dry periods in wet-dry cycle treatment)

3.4.2 AVS and CRS

Acid volatile sulfide (AVS) and chromium reducible sulfur (CRS) were detected at the surface and at depth in all sites. The highest AVS concentrations were found in the 0-5 cm in the AG and LL sites and highest CRS concentrations were detected in the 0-5cm in the PD site in all water table treatments (Table 3.4).

Under the flooded treatment, significantly higher concentrations of AVS and CRS were found in all sites compared with other treatments in most soil depths ($p<0.05$) (Table 3.3).

Under dry conditions, the CRS concentration decreased significantly in most soil depth in all sites ($p<0.05$) (Table 3.3). Under the flooded treatment, the AVS and CRS concentrations increased significantly in most soil depths in the AG, PA and PD sites ($p<0.05$). In the wet-dry cycle treatment, the AVS and CRS concentrations decreased significantly in the LL site and the CRS concentration decreased significantly in the PA site ($p<0.05$). The CRS concentration increased significantly in the AG and PD sites under the wet-dry cycle treatment ($p<0.05$).

The AVS concentration ranged from 15 to 31 $\mu\text{g/g}$ in the AG sites, from 14 to 28 $\mu\text{g/g}$ in the LL sites, from 21 to 241 $\mu\text{g/g}$ in the PA sites, from 19 to 53 $\mu\text{g/g}$ in the PD sites in all treatments. The CRS concentration ranged from 20 to 108 $\mu\text{g/g}$ in the AG site, from 17 to 90 $\mu\text{g/g}$ in the LL site, from 171 to 3701 $\mu\text{g/g}$ in the PA site and from 16 to 189 $\mu\text{g/g}$ in the PD site in all treatments (Table 3.3). The highest AVS (241 $\mu\text{g/g}$) and CRS concentration (3701 $\mu\text{g/g}$) both occurred in the PA site under flooded treatment (Table 3). The LL site had the lowest AVS and CRS concentration under flooded treatment compared with the other vegetation types (Table 3.3).

Table 3.4 summarised the Pearson correlations between RIS and soil parameters after all treatments. AVS was positively correlated with SOC in the flooded and wet-dry cycle treatments ($p<0.05$). AVS was positively correlated with C/N following flooded treatment ($p<0.05$). AVS and CRS were negatively correlated with loss of SOC in the flooded treatment. CRS was positively correlated with SOC in all treatments ($p<0.05$). CRS was positively correlated with C/N under dry and flooded treatments ($p<0.05$).

Table 3.3 AVS and CRS between treatments in different soil horizons

Sites	Horizons (cm)	RIS	Initial ($\mu\text{g/g}$)	Dry ($\mu\text{g/g}$)	Flooded ($\mu\text{g/g}$)	Wet-dry Cycle ($\mu\text{g/g}$)
AG	0-5	AVS	19.7 ± 1.4^b	21.8 ± 3.7^b	30.5 ± 5.2^a	23.0 ± 3.2^b
		CRS	26.8 ± 2.9^c	22.5 ± 5.0^c	107.9 ± 40.3^a	48.6 ± 7.2^b
	5-10	AVS	17.4 ± 1.2^a	15.2 ± 0.8^a	20.9 ± 2.9^a	19.9 ± 3.9^a
		CRS	28.2 ± 3.1^c	20.1 ± 3.6^c	72.1 ± 8.7^a	44.9 ± 5.2^b
	10-20	AVS	36.6 ± 3.9^a	18.3 ± 1.2^b	19.3 ± 5.3^b	18.7 ± 11.2^b
		CRS	30.0 ± 3.7^a	25.7 ± 2.6^b	35.0 ± 7.9^a	32.5 ± 4.7^a
LL	0-5	AVS	35.2 ± 6.65^a	32.6 ± 2.1^a	28.4 ± 4.1^a	10.1 ± 2.5^b
		CRS	80.1 ± 7.75^a	18.6 ± 3.6^c	89.9 ± 9.2^a	39.1 ± 3.7^b
	5-10	AVS	31.9 ± 7.2^a	27.9 ± 3.1^a	19.3 ± 6.1^b	8.0 ± 1.1^b
		CRS	46.4 ± 7.2^a	16.8 ± 5.7^b	48.6 ± 2.1^a	24.7 ± 3.9^b
	10-20	AVS	27.9 ± 2.1^a	13.6 ± 3.5^a	13.8 ± 5.5^a	5.0 ± 1.1^b
		CRS	61.0 ± 1.2^a	30.3 ± 3.9^c	52.6 ± 2.4^a	43.1 ± 5.6^b
PA	0-5	AVS	22.8 ± 4.0^b	27.9 ± 5.6^b	240.6 ± 36.7^a	76.9 ± 17.9^b
		CRS	1785.9 ± 116.0^a	209.3 ± 31.1^c	1528.1 ± 192.6^a	588.5 ± 62.4^b
	5-10	AVS	44.6 ± 10.5^b	20.8 ± 5.8^b	181.5 ± 21.9^a	34.2 ± 10.4^b
		CRS	1974.7 ± 146.3^a	171.3 ± 37.2^c	1303.3 ± 134.5^b	1226.2 ± 335.1^b
	10-20	AVS	94.7 ± 13.9^b	24.5 ± 5.3^c	231.8 ± 36.2^a	84.2 ± 13.6^b
		CRS	4578.8 ± 124.9^a	501.5 ± 55.2^d	3700.8 ± 818.9^b	2299.8 ± 456.6^c
PD	0-5	AVS	27.1 ± 1.5^b	23.3 ± 4.4^b	52.5 ± 5.4^a	52.3 ± 9.7^a
		CRS	51.5 ± 10.8^c	31.9 ± 2.8^c	168.7 ± 27.4^a	136.0 ± 18.6^b
	5-10	AVS	24.8 ± 4.2^b	19.4 ± 1.8^b	45.9 ± 6.4^a	40.2 ± 4.9^a
		CRS	16.5 ± 1.40^c	29.2 ± 4.7^b	88.3 ± 3.4^a	82.2 ± 9.9^a
	10-20	AVS	34.3 ± 1.4^a	30.3 ± 4.1^a	35.7 ± 2.2^a	36.7 ± 6.5^a
		CRS	60.2 ± 7.2^a	28.6 ± 5.1^b	61.4 ± 5.9^a	53.7 ± 5.6^a

Values represent means of four replicates. Different small letter within each row represent significant difference in mean value between the treatments (one-way ANOVA, Tukey test, $p < 0.05$)

Table 3.4 Pearson correlation analysis between RIS (AVS and CRS) and soil parameters

Parameters	AVS			CRS		
	Dry	Flooded	Wet-dry cycle	Dry	Flooded	Wet-dry cycle
SOC	-0.11	0.91*	0.70*	0.87*	0.90*	0.78*
Loss of SOC	0.09	-0.68*	-0.18	0.85*	-0.69*	0.23
C/N	0.29	0.59*	0.32	0.76*	0.62*	0.46

Pair sample size, $n=16$ for SOC, loss of SOC (initial-after treatment) and C/N in the soil top layer (0-5cm) after the dry, flooded and wet-dry cycle treatments in all sites.

* $p=0.05$ correlations are significant

Table S1. soil pH and EC after the dry, flooded and wet-dry cycle treatments

Sites	Depth (cm)	pH Initial	pH Dry	pH Flooded	pH Wet-dry Cycle	EC (mS cm ⁻¹) Initial	EC (mS cm ⁻¹) Dry	EC (mS cm ⁻¹) Flooded	EC (mS cm ⁻¹) Wet-dry Cycle
AG	0-5	5.8 ± 0.02	5.6 ± 0.03	5.8 ± 0.02	4.8 ± 0.01	0.18 ± 0.001	0.25 ± 0.001	2.06 ± 0.02	1.55 ± 0.04
	5-10	5.4 ± 0.02	5.2 ± 0.02	6.0 ± 0.02	4.9 ± 0.01	0.14 ± 0.006	0.21 ± 0.001	1.14 ± 0.02	0.88 ± 0.05
	10-20	5.2 ± 0.05	4.9 ± 0.01	5.8 ± 0.04	5.0 ± 0.02	0.13 ± 0.01	0.17 ± 0.002	0.65 ± 0.04	0.56 ± 0.02
LL	0-5	6.6 ± 0.09	5.8 ± 0.08	6.2 ± 0.01	5.4 ± 0.02	0.52 ± 0.02	1.11 ± 0.05	1.64 ± 0.02	1.36 ± 0.05
	5-10	6.3 ± 0.06	5.6 ± 0.04	6.4 ± 0.02	5.8 ± 0.02	0.26 ± 0.001	0.35 ± 0.03	0.69 ± 0.03	0.76 ± 0.04
	10-20	6.3 ± 0.01	5.3 ± 0.02	5.8 ± 0.03	5.5 ± 0.01	0.30 ± 0.02	0.33 ± 0.04	0.61 ± 0.03	0.52 ± 0.06
PA	0-5	5.4 ± 0.01	4.8 ± 0.01	5.9 ± 0.02	5.4 ± 0.02	2.18 ± 0.05	3.61 ± 0.04	3.39 ± 0.02	5.41 ± 0.08
	5-10	4.9 ± 0.09	4.9 ± 0.05	5.8 ± 0.02	5.5 ± 0.01	1.91 ± 0.1	2.62 ± 0.03	2.02 ± 0.05	2.80 ± 0.03
	10-20	5.3 ± 0.02	5.2 ± 0.03	6.1 ± 0.02	5.5 ± 0.02	2.14 ± 0.06	1.73 ± 0.02	1.73 ± 0.04	2.41 ± 0.05
PD	0-5	5.2 ± 0.005	5.2 ± 0.01	5.8 ± 0.01	5.5 ± 0.01	0.34 ± 0.003	0.35 ± 0.03	2.33 ± 0.02	2.32 ± 0.02
	5-10	5.2 ± 0.01	5.1 ± 0.02	5.6 ± 0.02	5.4 ± 0.02	0.23 ± 0.001	0.28 ± 0.02	1.06 ± 0.02	1.22 ± 0.03
	10-20	5.3 ± 0.03	5.2 ± 0.03	5.5 ± 0.01	5.4 ± 0.01	0.27 ± 0.001	0.18 ± 0.01	0.63 ± 0.06	0.78 ± 0.02

3.4.3 TAA, ANC and net acidity

In the dry treatment, TAA was increased by 74-88%, 13-78%, 3-65% in the AG, PA, PD sites respectively (Fig. 3.3a, g, j), with the highest TAA occurred in the AG site (96.6 mol H⁺ t⁻¹). The net acidity was increased by 63-83%, 3-192% in the AG and PD sites (Fig. 3.3c, l).

In the flooded treatment, TAA was decreased by 90-100%, 6-100%, 25-42% in the AG, PA, PD sites, respectively. ANC was increased by 100%, 7-300%, 100% following the flooded treatment in the AG, LL and PA sites, respectively (Fig. 3.3b, e, h). The net acidity was decreased by 84-794%, 7-863%, 14-130% 3-24% in the AG, LL, PA and PD sites in all soil depth, respectively (Fig. 3.3c, f, i, l).

In the wet-dry cycle treatment, TAA was increased by 34-129%, 7-117% in the AG and PD site (Fig. 3.3a, j), and decreased by 22-37% in the PA site (Fig. 3.3g). Net acidity was increased by 37-66% and 33-220% in the AG and PD sites in the 0-10 cm layer respectively (Fig. 3.3c, l) while decreased by 7-772% and 37-55% in the LL and PA sites respectively (Fig. 3.3f, i).

The PA site had higher net acidity compared with other sites before and after all the water table treatments, with the highest net acidity of 196 mol H⁺ t⁻¹ occurred in the 10-20 cm after the wet-dry cycle treatment (Fig. 3.3i). The AG site had negative net acidity under the flooded treatment (Fig. 3.3c). The highest ANC occurred in the LL site (Fig. 3.3e) and the TAA was not detected in the LL site in all treatments (Fig. 3.3d). Net acidity was negative only in the LL site throughout the soil layers in all treatments (Fig. 3.3f).

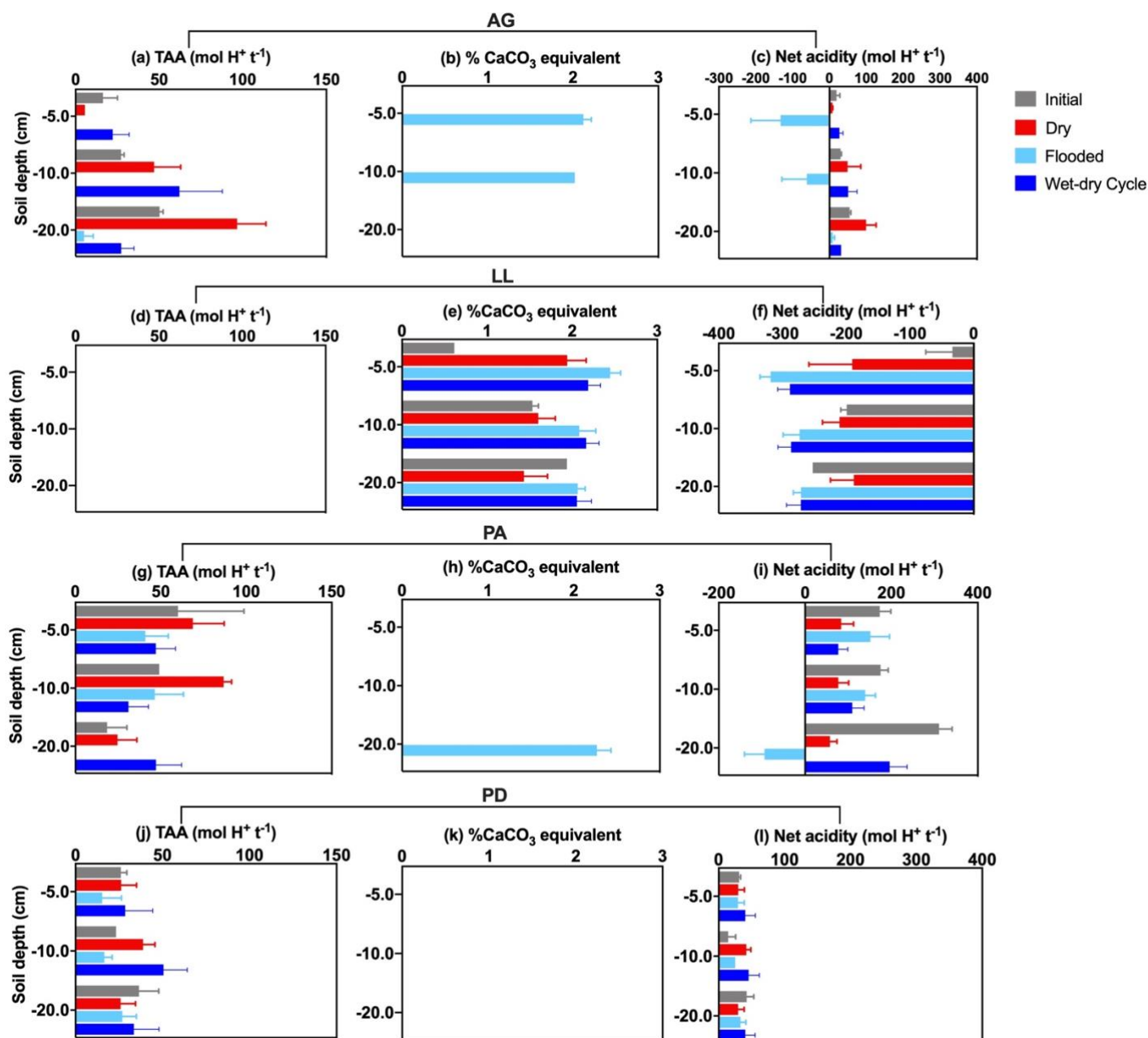


Fig 3.3 Titratable actual acidity (TAA), acid neutralisation capacity (ANC) and net acidity at the AG (*Apium graveolens*) (a, b, c), LL (*Leptospermum lanigerum*) (d, e, f), PA (*Phragmites australis*) (g, h, i), and PD (*Paspalum distichum*) sites (j, k, l). Vertical bars denote standard error of means (n=4)

3.4.4 Trace metals and anions

The highest initial Al, Mn, Zn concentration occurred in the AG site in the 10-20 cm layer. The initial Fe, Ni, SO_4^{2-} concentration remained the highest in the PA site. The initial Al, Fe, Mn, Zn, Ni, SO_4^{2-} concentration remained the lowest in the LL site. The initial Al, Fe, Mn, Zn, Ni concentration generally increased with soil depth in the AG, LL and PD sites and decreased with soils depth in the PA site.

In the dry treatment, Al concentration was significantly higher compared with other treatments in the PA and PD sites ($p < 0.05$) (Fig. 3.4k, p). Fe concentration decreased under dry treatment in the AG, PA and PD sites (Fig. 3.4b, l, q), with the minimum concentration of 0.12 mg kg^{-1} occurring in the 10-20 cm layer in the PA site. Mn concentration decreased under the dry treatment in the PD site, with the greatest decrease to a concentration of 0.09 mg kg^{-1} in the 10-20 cm layer. The SO_4^{2-} concentration increased after the dry treatment in the PA site at all depths (Fig. 3.5e). The $\text{Cl}^-/\text{SO}_4^{2-}$ ratios decrease after the dry treatment in the PA and PD sites, with the lowest $\text{Cl}^-/\text{SO}_4^{2-}$ ratio of 0.34 occurred in the 10-20 cm layer in the PA site under dry treatment. Lower $\text{Cl}^-/\text{SO}_4^{2-}$ ratios were observed in the dry treatment in all sites compared with flooded and wet-dry cycle treatments (Fig. 3.5b, d, f, h).

In the flooded treatment, Al concentration decreased in the PA and PD sites, with the minimum concentration of 0.02 mg kg^{-1} in the 0-5 cm layer in the PD site (Fig. 3.4k, p). Fe concentration increased following the flooded in the AG and LL sites (Fig. 3.4b, g), with the maximum concentration of 2.55 mg kg^{-1} occurring in the 5-10 cm layer in the AG site under the flooded treatment. Mn concentrations increased under the flooded treatment in the AG and LL sites (Fig. 3.4c, h), with the greatest increase occurring in the flooded treatment to a concentration of 6.93 mg kg^{-1} in the 0-5 cm layer in the AG site. Zn concentration decreased under flooded treatment in the PA and PD sites (Fig. 3.4 j, n, o, s, t), with the greatest decrease to 0 mg kg^{-1} in the PA and PD site. Ni concentration decreased under flooded treatment in the LL, PA and PD sites (Fig. 3.4i, j, n, o, s, t), with the greatest decrease to 0 mg kg^{-1} in the PA and PD sites. Under the flooded treatment, the SO_4^{2-} concentration decreased in the LL, PA and PD sites compared to the initial concentrations (Fig. 3.5c, e, g). The $\text{Cl}^-/\text{SO}_4^{2-}$ ratios increased following the flooded treatment in all sites (Fig. 3.5b, d, f, h), with the highest ratio of 10.6 occurring in the 0-5 cm layer in the PD site under the flooded treatment.

In the wet-dry cycle treatment, Fe, Mn concentration increased in the AG and LL sites (Fig. 3.4b, g). The SO_4^{2-} concentration increased in the wet-dry cycle treatment in the AG, LL and PD sites (Fig. 3.5a, c, g).

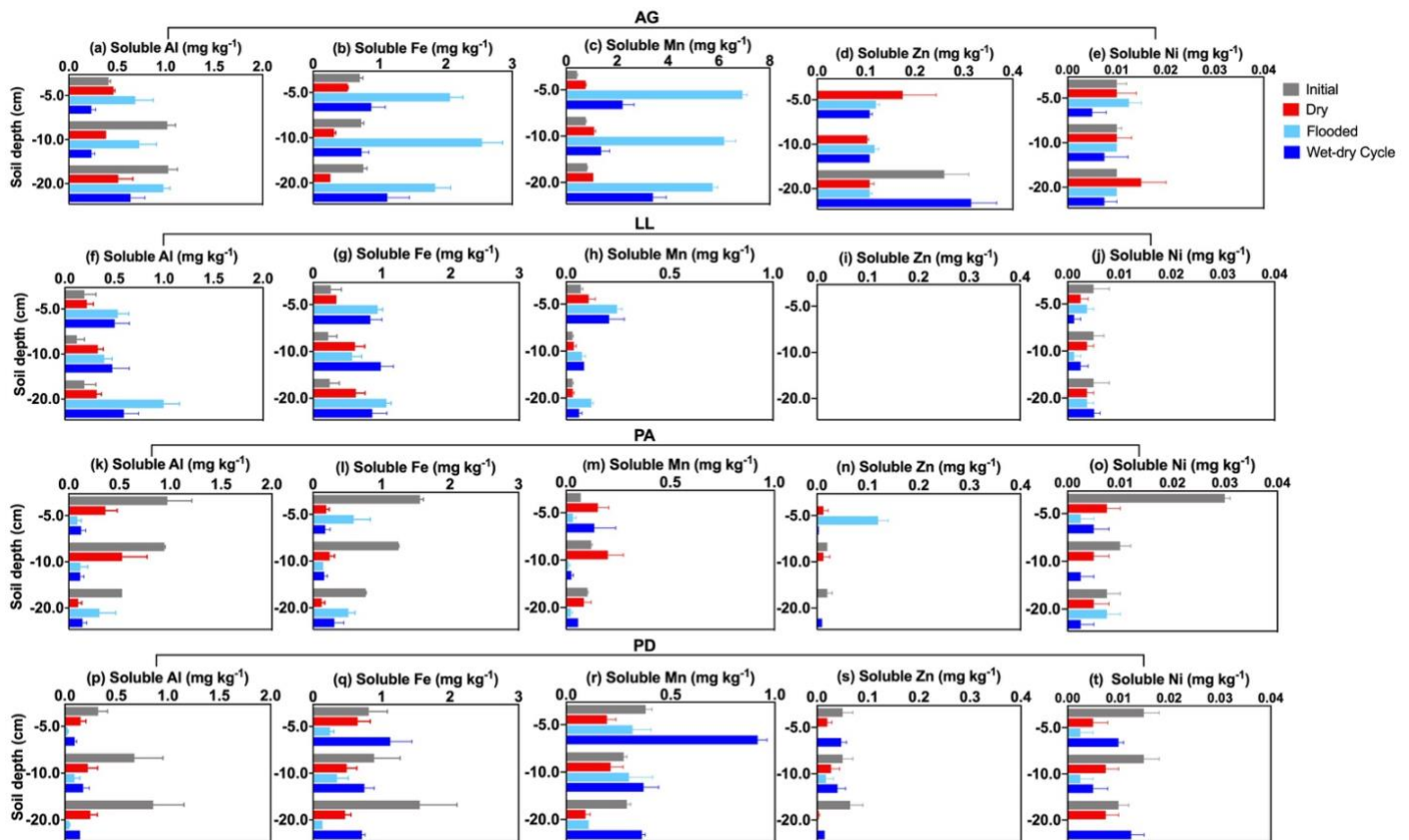


Fig 3.4 Soluble trace metals Al, Fe, Mn, Zn and Ni at the AG (*Apium graveolens*) (a, b, c, d, e), LL (*Leptospermum lanigerum*) (f, g, h, i, j), PA (*Phragmites australis*) (k, l, m, n, o), and PD (*Paspalum distichum*) sites (p, q, r, s, t). Vertical bars denote standard error of means (n=4).

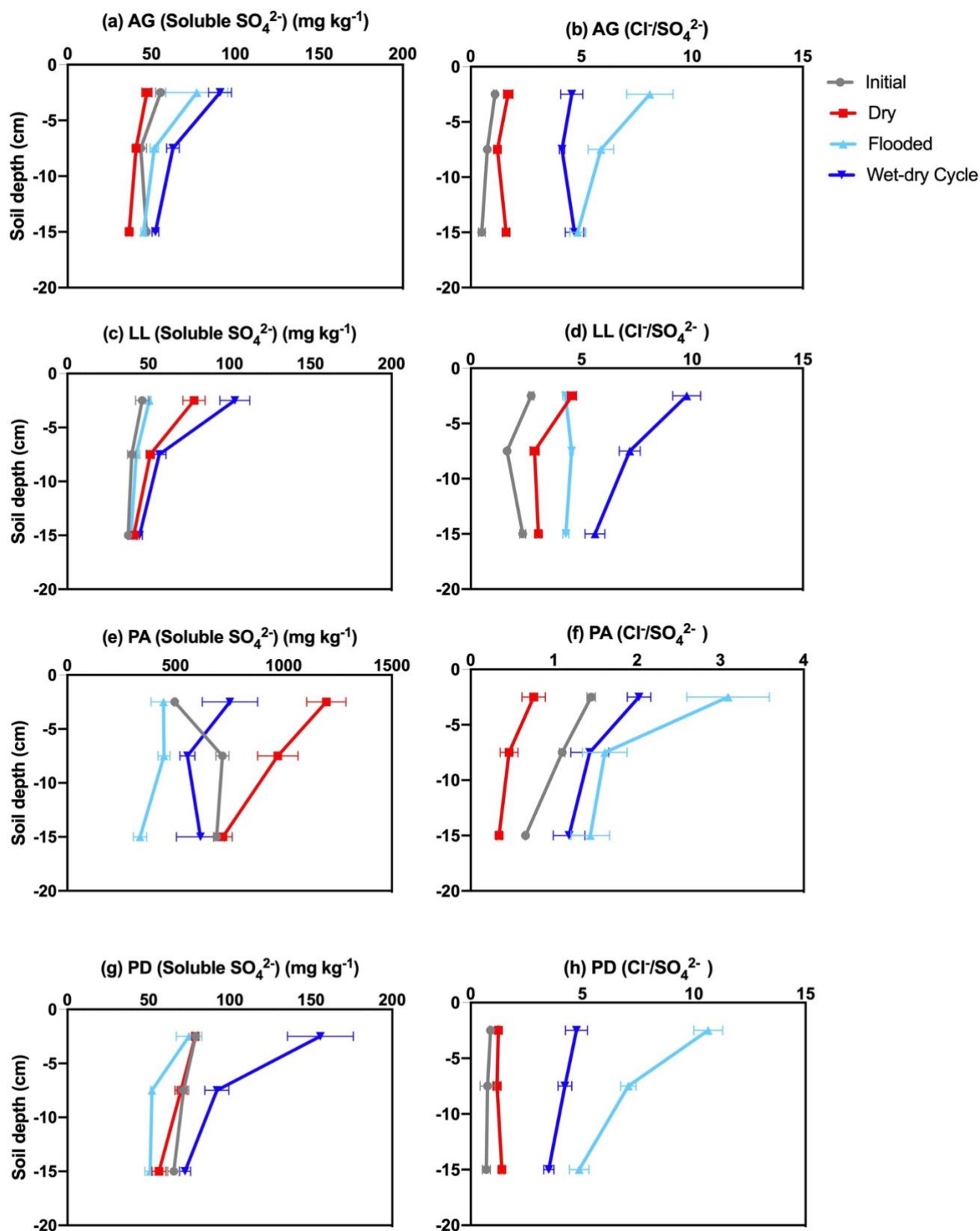


Fig 3.5 Soluble SO_4^{2-} and $\text{Cl}^-/\text{SO}_4^{2-}$ at the AG (*Apium graveolens*) (a, b, c, d), LL (*Leptospermum lanigerum*) (e, f, g, h), PA (*Phragmites australis*) (i, j, k, l), and PD (*Paspalum distichum*) sites (m, n, o, p). Vertical bars denote standard error of means (n=4).

3.4.5 Geochemical Modelling

Geochemical modelling showed that the form of Fe was dominated by FeCl_2^+ where Cl^- concentrations were high, and dominated by pyrite where SO_4^{2-} concentrations were high (Fig. 3.6A, B). Fe at lower Cl^- and SO_4^{2-} concentrations led to the formation of Fe^{2+} with lower pH and FeO(OH) with higher pH (Fig. 3.6A, B). The predominance of Fe^{2+} , FeO(OH) and magnetite at the representative activities of Fe^{2+} , Cl^- is shown in Fig. 3.6A. The Eh and pH values generally fell into the predominance region of FeO(OH) in the AG, LL and PD sites (Fig. 3.6A). Under the dry treatment, the Fe species was in the form of FeO(OH) in all vegetation types. Under the flooded and wet-dry cycle treatment, Fe was in the form of Fe^{2+} .

The dominant Fe species were Fe^{2+} , FeO(OH) and pyrite at the representative activities of Fe^{2+} and SO_4^{2-} and is shown in Fig. 3.6B. At the beginning of the experiment, Fe and SO_4^{2-} were likely to be in the form of FeO(OH) (Fig. 3.6B). Under the dry treatment, Fe species were likely to be in the form of FeO(OH) in all vegetation types (Fig. 3.6B). Under the flooded treatment, the main Fe species was likely to be in the form of pyrite (FeS_2) in all vegetation types (Fig. 3.6B). Under the wet-dry cycle treatment, the Eh and pH values suggested that Fe was in the form of soluble Fe^{2+} .

The geochemical modelling showed that the form of Al remained the same with the change of Cl^- and SO_4^{2-} concentrations (Fig. 3.6C, D). The representative activities of Al^{3+} , Cl^- is shown in Fig. 3.6C and representative activities of Al^{3+} , SO_4^{2-} is shown in Fig. 3.6D. The Eh and pH values fell into the region of Al(OH)_3 in the beginning and end of the incubation treatments (Fig. 3.6C, D). There were no changes in Al species with the increasing of Cl^- concentration and SO_4^{2-} (Fig. 3.6C, D).

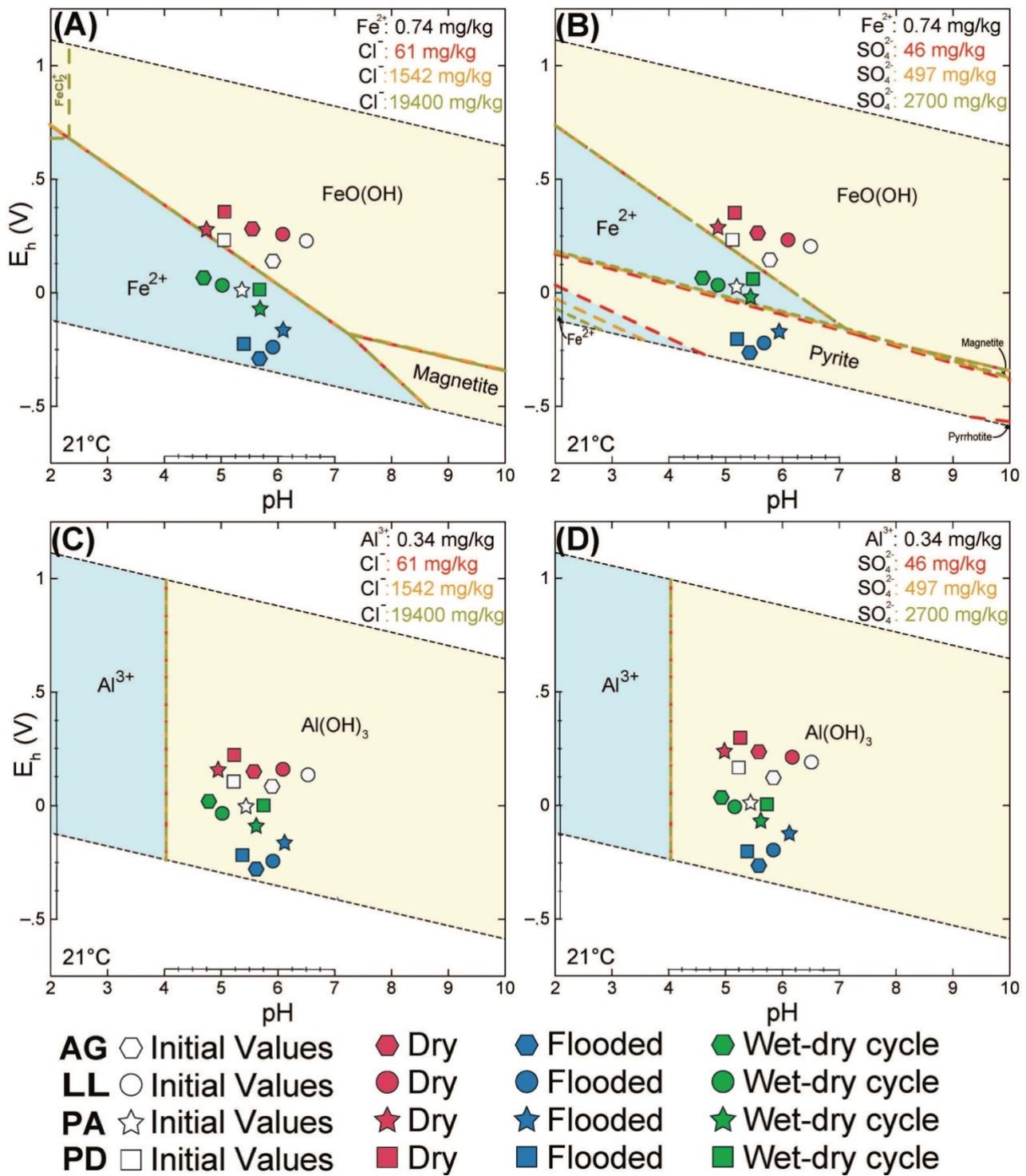


Fig 3.6 Chemical thermodynamic stability diagrams for Fe solubility in (A) in chloride brines (Fe^{2+} : 0.74 mg/kg; Cl^- : 61 mg/kg, 1542 mg/kg, 19400 mg/kg); and (B) sulfate waters (Fe^{2+} : 0.74 mg/kg; SO_4^{2-} : 46 mg/kg, 497 mg/kg, 2700 mg/kg); and Al solubility in (C) in chloride brines (Al^{3+} : 0.34 mg/kg; Cl^- : 61 mg/kg, 1542 mg/kg, 19400 mg/kg); and (D) sulfate waters (Al^{3+} : 0.34 mg/kg; SO_4^{2-} : 46 mg/kg, 497 mg/kg, 2700 mg/kg), as a function of pH vs. E_h (V). Solid bold lines are solubility limits and mineral stability fields, and dashed bold lines changing limits as a function of either SO_4^{2-} or Cl^- concentration. The conditions for the sulfate and chloride encountered in the present study from the Aire River water at 21°C at the beginning and end of the incubation experiments, are denoted as a function of initial, dry, flooded, and wet-dry cycles.

3.5. Discussion

3.5.1 Net acidity

In ASS, the oxidation of AVS and CRS can result in formation of products such as Fe minerals including $\text{Fe}(\text{OH})_3$, SO_4^{2-} and H^+ acidity while the hydrolysis of Al^{3+} and Fe^{3+} can release acidity (H^+). The brackish Aire River water can contribute to high ANC in this soil and neutralized the acidity. In coastal wetlands, the water table usually fluctuates seasonally due to precipitation, storm surge events and flooding (Livesley and Andrusiak, 2012). Cook et al. (2000) observed that considerable acidity was released from CASS following drought or low rainfall due to the oxidation of RIS and hydrolysis of Al^{3+} and Fe^{3+} .

3.5.2 Dry treatment

Net acidity generally increased after the dry treatment in the AG and PD sites, which was mainly due to the oxidation of AVS, CRS and the hydrolysis of trace metals. TAA generally increased after the dry treatment in the AG, PA and PD sites (Fig. 3.3a, g, j). Under dry conditions, the significant decreases in AVS and CRS in most soil depth in all sites ($p < 0.05$) (Table 3.3) and increase in SO_4^{2-} concentration compared with the initial concentration (Fig. 3.5) showed that AVS and CRS oxidized when the surface layer was exposed to an oxidising environment and therefore induced acidity in soils. AVS was highly reactive and oxidation of AVS can happen within hours while oxidation of CRS can occur over time periods of days (Burton et al., 2009). The incubation time in our study was 8 weeks, which provided time for the oxidation reaction. Similarly, Burton et al. (2006c) and Joukainen & Yli-Halla (2003) observed that iron sulfides decreased and SO_4^{2-} increased due to the lowering of the groundwater table.

CASS environments experience large periodic redox oscillations when water levels fluctuate. These redox oscillations can lead to accumulation of various forms of species of trace metal minerals (Al, Fe, Mn, Zn, Ni) in soil sediments (Johnston et al., 2014; Sohlenius and Öborn, 2004). Fe concentrations decreased in the dry treatments in the AG, PA and PD sites (Fig. 3.4b, i, q). Soluble Fe is mainly in the form of Fe^{2+} . The decrease in soluble Fe concentration is probably due to the further oxidation of Fe^{2+} to Fe^{3+} . Fe^{3+} can be subsequently hydrolysed and precipitated to a more stable solid (e.g. $\text{FeO}(\text{OH})$) (Fig. 3.6 A, B) which can release a large amount of acidity over time. Previous studies have also shown Fe^{3+} to decrease due to the hydrolysis and precipitation of ferric hydroxide ($\text{Fe}(\text{OH})_3$) (Boman et al., 2008; Evangelou and Zhang, 1995; Nordstrom, 1982).

In the dry treatment, Al concentration increased in the 0-5 cm layer in the AG and LL sites compared to the initial concentration (Fig. 3.4a, f). Al is highly soluble and mobile under acidic oxidizing conditions, usually in the form of Al^{3+} and Al^{3+} can produce 3 mol of H^+ via hydrolysis under low soil pH conditions (Hicks et

al., 2009). A previous study found the increase in Al accumulated in the surface horizon due to the evaporation from the soil surface in the ASS during the dry season and maintaining a shallow water table can help prevent the further formation of acidity in Vietnam (Minh et al., 1998). This result was in accordance with our finding that Al accumulated in the top horizon under dry conditions.

3.5.3 Flooded treatment

Net acidity decreased in all sites following the flooded treatment and this was mainly because of reduction of SO_4^{2-} (Fig. 3.3). Under the flooded treatment, the increase in AVS and CRS in most soil depths in all sites and the decrease in SO_4^{2-} concentration indicated the reformation of RIS species (Table 3.3). The reformation of AVS and CRS can occur by consuming SO_4^{2-} when Fe-containing minerals and soil organic matter are abundant. The initial SO_4^{2-} concentration in the Aire River water was 106.5 mg/L (Table 3.3.1) and the initial Fe^{2+} concentrations in the 0-5 cm soil layer were 0.71, 0.26, 1.56 and 0.81 mg kg^{-1} in the AG, LL, PA and PD sites respectively. SOC in the 0-5 cm soil layer was 6%, 5.5%, 20.4%, 7.6% in the AG, LL, PA and PD sites respectively (Table 3.3.2). Yuan et al. (2015) showed that the organic matter addition should be above 2% as a threshold to stimulate SO_4^{2-} reduction and form AVS in ASS.

Significantly higher concentrations of CRS were detected under flooded conditions compared to the dry treatment and wet-dry cycle treatments in all sites in most cases ($p < 0.05$). This was because the flooded treatment stimulated SO_4^{2-} reduction and resulted in the formation of AVS and CRS with the supply of organic matter and Fe containing minerals (Hicks et al., 2003). The previous studies (Burton et al., 2011; Peiffer et al., 2015) also observed high concentrations of CRS in the environment with abundant Fe containing minerals and SO_4^{2-} through microbial sulfate reduction. Secondly, the waterlogged conditions allowed the transformation of metastable AVS minerals to more stable CRS minerals within several days (Berner, 1984; Rickard, 1997). The incubation period was 56 days in our study, which provided enough time for the conversion from AVS to CRS. In this study, CRS was the dominant fraction of RIS and was 3-15 times higher than AVS at all sites. AVS ranged from 14-241 $\mu\text{g/g}$ while CRS ranged from 16-3701 $\mu\text{g/g}$ among all sites in all treatments (Table 3.4). Payne and Stolt (2017) showed similar results in that AVS ranged from 0 to 27 $\mu\text{g/g}$ and CRS ranged from 33 to 11,591 $\mu\text{g/g}$ in shallow embayments.

SO_4^{2-} concentration decreased in all sites. The reduction of SO_4^{2-} and Fe(III) oxides with the organic carbon can generate bicarbonate alkalinity (Johnston et al., 2009b) and increased in soil pH (2-3 units). High ANC was observed in the AG, LL and PA sites in some soil depths under the flooded treatment (Fig. 3.3b, e, h). This suggested that the alkalinity from the Aire River brackish water can potentially neutralize the acidity caused by the sulfide mineral oxidation in the AG, LL and PA sites. In addition, reduction of SO_4^{2-} and Fe(III) produced alkalinity, this reaction may generate mobile ions that may reduce acidity. The long-term

mitigation of acidity is to transfer these ions into solid phase, like FeS_2 (Rickard and Luther, 2007).

Karimian et al. (2017) demonstrated that Fe^{3+} and SO_4^{2-} reduction in ASS wetlands needed 8 weeks of freshwater reflooding. The brackish Aire River inundation of 8 weeks in this study can have similar effects. Burton et al. (2011) demonstrated that tidal re-flooding has neutralized the previous acidity and the SO_4^{2-} reduction rate ($300 \text{ nmol cm}^{-3} \text{ day}^{-1}$) occurred in the inter-tidal zone in the surface layer (0-60 cm). White et al. (1997) also showed that tidal flooding with brackish water can neutralize the acidity caused by the oxidized sulfidic minerals from coastal wetlands in eastern Australia.

Inundation with Aire River water caused significant changes in the concentration of trace metals. Fe^{2+} is more stable under low redox levels and where the pH is not acidic. Fe^{3+} is more stable under high redox levels and pH is low (less than 3) (Karimian et al., 2018; Lin and Herbert Jr, 1997). The Fe concentration increased in the AG and LL sites under the flooded treatment (Fig. 3.4b, g). Ponnampertuma (1972) showed that Fe reduction may include increased dissolved Fe^{2+} concentration, pH and exchangeable cations. The decrease in Fe concentration following the flooded treatment in the PA and PD sites indicated that reformation of RIS may have occurred. Flooded conditions can immobilize Fe^{2+} because FeS and FeS_2 can be formed through the reaction of H_2S with Fe^{2+} . This is in accordance with our results where FeS_2 was formed under flooded conditions, which was determined with higher CRS concentration (Table 3.3). The previous study mentioned that Fe^{2+} had negative relationships with water levels and highest Fe^{2+} values were observed at the surface sampling sites (Johnston et al., 2011).

Al^{3+} concentrations decreased following the flooded treatment in the PA and PD sites (Fig. 3.4k, p), but increased in the AG and LL sites (Fig. 3.4a, f). The soil pH increased compared with the initial state following flooded conditions at the PA and PD sites (Table S1). Inundation conditions were conducive to Fe^{3+} and SO_4^{2-} reduction and caused a slight increase in pH (Virtanen et al., 2014). Al solubility was strongly affected by soil pH and increased with lower soil pH (Astrom and Bjorklund, 1995; Fältmarsch et al., 2008). Mn can react with sulfide to form MnS . However, MnS is much more soluble than FeS (Arakaki and Morse, 1993). MnS cannot be formed when Fe concentrations are high in the sediment and therefore Mn concentrations generally increased in the flooded and wet-dry cycle treatments compared with the initial concentration (Fig. 3.4). Zn and Ni concentrations decreased following the flooded treatment and AVS was detected in the LL, PA and PD sites, suggesting that Ni and Zn can react with AVS (FeS) and decrease in solubility. AVS decreased in the LL site under the flooded treatment (Table 3.3). The increase in AVS in the PA and PD sites under the flooded treatment might be caused by AVS reacting with Ni, Zn and then reforming due to SO_4^{2-} reduction. AVS can form via the reaction of H_2S with Fe^{2+} in the flooded treatment (Karimian et al., 2018). Zn and Ni can adsorb to or precipitate with FeS (Morse and Luther, 1999), however,

ZnS and NiS are less soluble than FeS. Therefore, Zn and Ni can precipitate with sulfide preferentially over Fe.

3.5.4 Wet-dry cycle treatment

Net acidity increased in the AG and PD sites after the wet-dry cycle treatment. The frequent wet and dry cycles could result in the formation of AVS and CRS in the AG and PD sites indicated by the increase of AVS and CRS compared with the initial state (Table 3.3) during flooded periods. The soils were subsequently drained under dry periods of each wet-dry cycles, which then created an environment for the oxidation of AVS and CRS in soils and stimulated acidity release. Similarly, Sammut et al. (1996) showed that drainage in coastal estuarine floodplains can promote sulfidic mineral oxidation, the production of sulfuric acid and increase in dissolved Al^{3+} and Fe^{2+} into streams in eastern Australia. Large areas (more than 0.5×10^6 ha) of sulfidic floodplains have been drained for agriculture in eastern Australia (Sammut et al., 1994). Reflooding because of sea level rise or storm surge events will initiate a new cycle of reducing conditions and promote reformation of RIS and alkalinity production.

3.5.5 Net acidity in different vegetation types

Net acidity in the PA site was generally higher than other sites before and after the water table treatments, which was due to the highest SOC content (20.4% at the 0-5 cm layer). Root respiration and decomposition of organic matter can increase the partial pressure of CO_2 and lead to the slight decrease in pH in soil pore water. Besides, the organic acids generated from plant roots can result in decrease in pH and carboxyl groups on soil organic matter can produce acidity (Yau et al., 2016). The high SOC contents can potentially contribute to high acidity compared with other vegetation types.

Net acidity was the lowest and negative only in the LL site under all water table treatments, which was due to the lowest SOC contents and the low decomposability of organic matter. In the LL site, the lower concentrations of AVS and CRS were observed compared with other sites under the flooded treatment (Table 3.3). The LL site had the lowest SOC (5.5%) in the 0-5 cm soil layer compared with other sites. In reducing conditions, SO_4^{2-} and Fe containing minerals required decomposable organic matter as electron donors and energy sources by SO_4^{2-} reducing bacteria (Jayalath et al., 2021; Wong et al., 2016b). Also, LL was a woody species, which contains high decay-resistant compounds and therefore the organic matter was more difficult to decompose (Fioretto et al., 2005; Vann and Patrick Megonigal, 2003). Vegetation at the AG, PA and PD was dominated species which resulted in organic matter which was more labile. Previous studies showed that the decomposability of the soil organic matter was an important factor affecting the activity of SO_4^{2-} reducers in ASS (Yuan et al., 2015). Low biodegradability of SOC can limit sulfate

reduction in re-flooding sulfuric materials (Kolbl et al., 2017). Therefore, more labile and easier to decompose SOC can lead to more AVS and CRS being accumulated during the Fe and SO_4^{2-} reduction process under submerged conditions. This outcome demonstrates the effects of vegetation types and different forms of soil organic carbon in sulfate reduction processes via sulfate reducing bacteria (Jayalath et al., 2016).

3.6. Conclusion

This study demonstrated that brackish water inundation prevented further oxidation of RIS and was an effective mitigation method to reduce net acidity in the coastal ASS environment. Fe and SO_4^{2-} reduction were important geochemical process in the inundated soils in coastal wetlands. The dry treatment led to the oxidation of the Fe sulfide minerals, severe acidification and increased dissolved trace metals in the AG and LL sites in most soil depths. The highest net acidity occurred in the PA site under all treatments, due to the highest SOC content. Net acidity was negative only in the LL site under all inundation treatments, which was due to the lowest SOC contents and the low decomposability of organic matter. CRS dominated over AVS in the Aire River floodplain. CRS was positively correlated with SOC in all treatments ($p < 0.05$). Herbaceous species (AG, PA, PD sites) were conducive to reforming AVS and CRS compared to the woody species (LL site) under the flooded treatment due to the higher labile carbon composition. Further research on ASS is needed to assess the interactions of AVS and CRS with trace metals under reducing and oxidizing conditions and the trace metal mobility in long term.

3.7 References

- Andriesse, W., Mensvoort, M.E.F.v., 2006. Acid sulfate soils: distribution and extent, In: Lal, R. (Ed.), Encyclopedia of Soil Science. CRC Press, Boca Raton, FL, pp. 14–19.
- Arakaki, T., Morse, J.W., 1993. Coprecipitation and adsorption of Mn(II) with mackinawite (FeS) under conditions similar to those found in anoxic sediments. *Geochimica et Cosmochimica Acta* 57, 9-14.
- Astrom, M., Bjorklund, A., 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. *Journal of Geochemical Exploration* 55, 163-170.
- Astrom, M., Spiro, B., 2000. Impact of isostatic uplift and ditching of sulfidic sediments on the hydrochemistry of major and trace elements and sulfur isotope ratios in streams, Western Finland. *Environmental Science & Technology* 34, 1182.
- Beek, K.J., Blokhuis, W.A., Driessen, P.M., Van Breemen, N., Brinkman, R., Pons, L.J., 1980. Problem soils: their reclamation and management, In: AlterraI, L., Wageningen, NL (Eds.), Land Reclamation and Water Management, Developments, Problems and Challenges. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 43–72.
- Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochimica et Cosmochimica Acta* 48, 605-615.
- Bethke, C.M., 2007. *Geochemical and Biogeochemical Reaction Modeling*. Cambridge: Cambridge University Press, Cambridge.
- Blodau, C., Peiffer, S., 2003. Thermodynamics and organic matter: constraints on neutralization processes in sediments of highly acidic waters. *Applied Geochemistry* 18, 25-36.
- Boman, A., Åström, M., Fröjdö, S., 2008. Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide—The role of artificial drainage. *Chemical Geology* 255, 68-77.
- Boman, A., Fröjdö, S., Backlund, K., Aström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.
- Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochimica et Cosmochimica Acta* 75, 3434-3451.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006a. Elemental sulfur in drain sediments associated with acid sulfate soils. *Applied Geochemistry* 21, 1240-1247.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006b. Reduced Inorganic Sulfur Speciation in Drain Sediments from Acid Sulfate Soil Landscapes. *Environmental Science & Technology* 40, 888-893.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Hocking, R.K., Mitchell, D.R.G., Johnston, S.G., Fitzpatrick, R.W., Raven, M., McClure, S., Jang, L.Y., 2009. Iron-Monosulfide Oxidation in Natural Sediments: Resolving Microbially Mediated S Transformations Using XANES, Electron Microscopy, and Selective Extractions. *Environmental Science & Technology* 43, 3128-3134.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Johnston, S.G., Hocking, R.K., 2008a. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* 253, 64-73.
- Burton, E.D., Sullivan, L.A., Bush, R.T., Johnston, S.G., Keene, A.F., 2008b. A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* 23, 2759-2766.
- Bush, R.T., Fyfe, D., Sullivan, L.A., 2004. Occurrence and abundance of monosulfidic black ooze in coastal acid sulfate soil landscapes. *Australian Journal of Soil Research* 42, 609.

- CCMA, 2014. Corangamite Waterway Strategy 2014- 2022, https://issuu.com/gsdm/docs/waterway_strategy_2014-22.
- Cook, F.J., Hicks, W., Gardner, E.A., Carlin, G.D., Froggatt, D.W., 2000. Export of Acidity in Drainage Water from Acid Sulphate Soils. *Marine Pollution Bulletin* 41, 319-326.
- Dent, D., 1986. Acid sulphate soils: a baseline for research and development. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.
- Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263-276.
- Desai, A.R., Moorcroft, P.R., Bolstad, P.V., Davis, K.J., 2007. Regional carbon fluxes from an observationally constrained dynamic ecosystem model: Impacts of disturbance, CO₂ fertilization, and heterogeneous land cover. *Journal of Geophysical Research: Biogeosciences* 112, n/a-n/a.
- Evangelou, V.P., Zhang, Y.L., 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Critical reviews in environmental science and technology* 25, 141-199.
- Fältmarsch, R., Astrom, M., Vuori, K.-M., 2008. Environmental risks of metals mobilised from acid sulphate soils in Finland: A literature review. *Boreal Environment Research* 13, 444-456.
- Fanning, D.S., Burch, S.N., 2000. Coastal acid sulfate soils, In: R.I.Barnhisel (Ed.), *Reclamation of drastically disturbed lands*. ASA,CSSA, and SSSA, Madison,WI, pp. 921-937.
- Fanning, D.S., Rabenhorst, M.C., Burch, S.N., Islam, K.R., Tangren, S.A., 2002. Sulfides and sulfates, In: Dixon, J.B., Schulze, D.G., Daniels, W.L. (Eds.), *Soil mineralogy with environmental applications*. Soil Science Society of America, Madison, WI, pp. 229–260.
- Fioretto, A., Di Nardo, C., Papa, S., Fuggi, A., 2005. Lignin and cellulose degradation and nitrogen dynamics during decomposition of three leaf litter species in a Mediterranean ecosystem. *Soil biology & biochemistry* 37, 1083-1091.
- Fitzpatrick, R., J. Davies, P., P. Thomas, B., Merry, R., Fotheringham, D., Hicks, W., L. Barnett, E., 2002. Properties, distribution and environmental hazards of South Australian coastal acid sulfate soils.
- Grealish, G.J., Fitzpatrick, R.W., Shand, P., 2014. Regional distribution trends and properties of acid sulfate soils during severe drought in wetlands along the lower River Murray, South Australia: Supporting hazard assessment. *Geoderma Regional* 2-3, 60-71.
- Hicks, W., Fitzpatrick, R., Bowman, G., 2003. *MANAGING COASTAL ACID SULFATE SOILS: THE EAST TRINITY EXAMPLE*.
- Hicks, W.S., Bowman, G.M., Fitzpatrick, R.W., 2009. Effect of season and landscape position on the aluminium geochemistry of tropical acid sulfate soil leachate. *Australian Journal of Soil Research* 47, 137-153.
- Holmer, M., Nielsen, S.L., Nielsen, 1997. Sediment sulfur dynamics related to biomass-density patterns in *Zostera marina* (eelgrass) beds. *Marine ecology. Progress series (Halstenbek)* 146, 163-171.
- Isbell, R.F.a., 2016. *The Australian soil classification*, Second edition. ed. Clayton, Vic. CSIRO Publishing.
- Jayalath, N., Fitzpatrick, R., Mosley, L.M., Marschner, P., 2021. Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive submerged-moist cycles. *Geoderma* 385, 114892.
- Jayalath, N., Fitzpatrick, R.W., Mosley, L., Marschner, P., 2016. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. *Journal of soils and sediments* 16, 518-526.
- Johnston, S.G., Burton, E.D., Aaso, T., Tuckerman, G., 2014. Sulfur, iron and carbon cycling following hydrological restoration of acidic freshwater wetlands. *Chemical Geology* 371, 9-26.

- Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., Smith, D., Martens, M.A., McElnea, A.E., Ahern, C.R., Powell, B., Stephens, L.P., Wilbraham, S.T., van Heel, S., 2009a. Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coastal and Shelf Science* 81, 257-266.
- Johnston, S.G., Keene, A.F., Bush, R.T., Burton, E.D., Sullivan, L.A., Smith, D., McElnea, A.E., Martens, M.A., Wilbraham, S., 2009b. Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* 149, 335-346.
- Johnston, S.G., Keene, A.F., Bush, R.T., Sullivan, L.A., Wong, V.N.L., 2011. Tidally driven water column hydro-geochemistry in a remediating acidic wetland. *Journal of Hydrology* 409, 128-139.
- Johnston, S.G., Slavich, P.G., Hirst, P., 2005. Changes in surface water quality after inundation of acid sulfate soils of different vegetation cover. *Australian Journal of Soil Research* 43, 1-12.
- Johnston, S.G., Slavich, P.G., Sullivan, L.A., Hirst, P., 2003. Artificial drainage of floodwaters from sulfidic backswamps: effects on deoxygenation in an Australian estuary. *Marine and Freshwater Research* 54, 781-795.
- Joukainen, S., Yli-Halla, M., 2003. Environmental impacts and acid loads from deep sulfidic layers of two well-drained acid sulfate soils in western Finland. *Agriculture, Ecosystems & Environment* 95, 297-309.
- Karimian, N., Johnston, S.G., Burton, E.D., 2017. Effect of cyclic redox oscillations on water quality in freshwater acid sulfate soil wetlands. *Science of The Total Environment* 581-582, 314-327.
- Karimian, N., Johnston, S.G., Burton, E.D., 2018. Iron and sulfur cycling in acid sulfate soil wetlands under dynamic redox conditions: A review. *Chemosphere* 197, 803-816.
- Keene, A.F., Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., McElnea, A.E., Ahern, C.R., Powell, B., 2011. Effects of hyper-enriched reactive Fe on sulfidisation in a tidally inundated acid sulfate soil wetland. *Biogeochemistry* 103, 263-279.
- Kolbl, A., Marschner, P., Fitzpatrick, R., Mosley, L., Kogel-Knabner, I., 2017. Linking organic matter composition in acid sulfate soils to pH recovery after re-submerging. *Geoderma* 308, 350-362.
- Lasorsa, B., Casas, A., 1996. A comparison of sample handling and analytical methods for determination of acid volatile sulfides in sediment. *Marine Chemistry* 52, 211-220.
- Leifeld, J., 2018. Distribution of nitrous oxide emissions from managed organic soils under different land uses estimated by the peat C/N ratio to improve national GHG inventories. *Science of The Total Environment* 631-632, 23-26.
- Levinson, A.A., 1968. *Oceans (Foundations of Earth Science Series)* : Karl K. Turekian: Prentice-Hall, New York, 1968. Elsevier Ltd, pp. 1367-1368.
- Lin, Z., Herbert Jr, R.B., 1997. Heavy metal retention in secondary precipitates from a mine rock dump and underlying soil, Dalarna, Sweden. *Environmental geology (Berlin)* 33, 1-12.
- Livesley, S.J., Andrusiak, S.M., 2012. Temperate mangrove and salt marsh sediments are a small methane and nitrous oxide source but important carbon store. *Estuarine, Coastal and Shelf Science* 97, 19-27.
- Ljung, K., Maley, F., Cook, A., Weinstein, P., 2009. Acid sulfate soils and human health—A Millennium Ecosystem Assessment. *Environment International* 35, 1234-1242.
- Macdonald, B.C.T., Denmead, O.T., White, I., Melville, M.D., 2004. Natural sulfur dioxide emissions from sulfuric soils. *Atmospheric Environment* 38, 1473-1480.
- Marín-Muñiz, J.L., Hernández, M.E., Moreno-Casasola, P., 2015. Greenhouse gas emissions from coastal freshwater wetlands in Veracruz Mexico: Effect of plant community and seasonal dynamics. *Atmospheric Environment* 107, 107-117.

- Mathew, E.K., Panda, R.K., Nair, M., 2001. Influence of subsurface drainage on crop production and soil quality in a low-lying acid sulphate soil. *Agricultural Water Management* 47, 191-209.
- McClaugherty, C., Berg, B., 1987. Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition *Pedobiologia* 30, 101-112.
- McElnea, A.E., Ahern, C.R., Menzies, N.W., 2002. The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* 40, 1133-1157.
- Minh, L.Q., Tuong, T.P., van Mensvoort, M.E.F., Bouma, J., 1998. Soil and water table management effects on aluminum dynamics in an acid sulphate soil in Vietnam. *Agriculture, Ecosystems & Environment* 68, 255-262.
- Morse, J.W., Luther, G.W., 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta* 63, 3373-3378.
- Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. *Environ Sci Technol* 38, 131A-136A.
- Nordstrom, D.K., 1982. Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals, In: Kittrick, D.F.a.L.H. (Ed.), *Acid Sulfate Weathering*. Soil Science Society of America, pp. 37-56.
- Payne, M.K., Stolt, M.H., 2017. Understanding sulfide distribution in subaqueous soil systems in southern New England, USA. *Geoderma* 308, 207-214.
- Peiffer, S., Behrends, T., Hellige, K., Larese-Casanova, P., Wan, M., Pollok, K., 2015. Pyrite formation and mineral transformation pathways upon sulfidation of ferric hydroxides depend on mineral type and sulfide concentration. *Chemical Geology* 400, 44-55.
- Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils, In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 29-96.
- Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, In: Dost, H. (Ed.), *Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils*. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 13-20.
- Powell, B., Martens, M., 2005. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar Pollut Bull* 51, 149-164.
- Rabenhorst, M.C., Fanning, D.S., 2006. Acid sulfate soils: problems, In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. CRC Press, Boca Raton, FL, pp. 19-22.
- Ram, R., Kalnins, C., Pownceby, M.I., Ehrig, K., Etschmann, B., Spooner, N., Brugger, J., 2021a. Selective radionuclide co-sorption onto natural minerals in environmental and anthropogenic conditions. *J Hazard Mater* 409, 124989-124989.
- Ram, R., Morrisroe, L., Etschmann, B., Vaughan, J., Brugger, J., 2021b. Lead (Pb) sorption and co-precipitation on natural sulfide, sulfate and oxide minerals under environmental conditions. *Minerals engineering* 163, 106801.
- Rayment, G.E., Lyons, D.J., 2011. *Soil chemical methods*. CSIRO, Melbourne, Australia.
- Rickard, D., 1997. Kinetics of pyrite formation by the H₂S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: The rate equation. *Geochimica et Cosmochimica Acta* 61, 115-134.
- Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS). *Marine Chemistry* 97, 141-197.
- Ritsema, C., Groenenberg, J., 1993. Pyrite Oxidation, Carbonate Weathering, and Gypsum Formation in a Drained Potential Acid Sulfate Soil.

- Sammut, J., White, I., Melville, M., 1994. Stratification in acidified coastal floodplain drains. *Wetlands (Australia)*, 49-64.
- Sammut, J., White, I., Melville, M.D., 1996. Acidification of an estuarine tributary in eastern Australia due to drainage of acid sulfate soils. *Marine and Freshwater Research* 47, 669-684.
- Sohlenius, G., Öborn, I., 2004. Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. *Geoderma* 122, 167-175.
- Sullivan, L., Bush, R., 2000. The behaviour of drain sludge in acid sulfate soil areas: Some implication for acidification and waterways management, In: Slavich, P. (Ed.), *Proceedings of a workshop on remediation and assessment of broadacre acid sulfate soils*. NSW Agriculture, Wollongbar, Australia, pp. 43-48.
- Sullivan, L.A., Clay, C., Ward, N.J., Baker, A.K.M., Shand, P., 2018. National Acid Sulfate Soils Guidance - A synthesis, In: Resources, t.D.o.A.a.W. (Ed.), Australia.
- Van den Berg, G.A., Loch, J.P.G., Winkels, H.J., 1998. Effect of Fluctuating Hydrological Conditions on the Mobility of Heavy Metals in Soils of a Freshwater Estuary in the Netherlands. *Water, air, and soil pollution* 102, 377-388.
- Vann, C., Patrick Megonigal, J., 2003. Elevated CO₂ and water depth regulation of methane emissions: Comparison of woody and non-woody wetland plant species. *Biogeochemistry* 63, 117-134.
- Virtanen, S., Simojoki, A., Hartikainen, H., Yli-Halla, M., 2014. Response of pore water Al, Fe and S concentrations to waterlogging in a boreal acid sulphate soil. *Sci Total Environ* 485-486, 130-142.
- Webster, J.R., Benfield, E.F., 1986. Vascular Plant Breakdown in Freshwater Ecosystems. *Annual Review of Ecology and Systematics* 17, 567-594.
- Westrich, J.T., Berner, R.A., 1984. The Role of Sedimentary Organic Matter in Bacterial Sulfate Reduction: The G Model Tested. *Limnology and Oceanography* 29, 236-249.
- White, I., Melville, M., Macdonald, B., Quirk, R., Hawken, R., Tunks, M., Buckley, D., Beattie, R., Williams, J., Heath, L., 2007. From conflicts to wise practice agreement and national strategy: cooperative learning and coastal stewardship in estuarine floodplain management, Tweed River, eastern Australia. *Journal of Cleaner Production* 15, 1545-1558.
- White, I., Melville, M.D., Wilson, B.P., Sammut, J., 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management* 5, 55-72.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Bush, R.T., Sullivan, L.A., Slavich, P.G., 2010. Seawater causes rapid trace metal mobilisation in coastal lowland acid sulfate soils: Implications of sea level rise for water quality. *Geoderma* 160, 252-263.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Bush, R.T., Sullivan, L.A., Slavich, P.G., 2013. Seawater-induced mobilization of trace metals from mackinawite-rich estuarine sediments. *Water Res* 47, 821-832.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Hirst, P., Sullivan, L.A., Bush, R.T., Blackford, M., 2015. Seawater inundation of coastal floodplain sediments: Short-term changes in surface water and sediment geochemistry. *Chemical Geology* 398, 32-45.
- Wong, V.N.L., McNaughton, C., Pearson, A., 2016. Changes in soil organic carbon fractions after remediation of a coastal floodplain soil. *Journal of Environmental Management* 168, 280-287.
- Xu, C., Wong, V.N.L., Reef, R.E., 2021. Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia. *Sci Total Environ* 763, 142949-142949.

Yuan, C., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2015. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. *J Environ Manage* 151, 437-442.

Chapter 4. Effects of liming on N₂O and CO₂ production in different horizons of boreal acid sulfate soil and non-acid soil

This thesis chapter is based predominantly on the final manuscript **returned for revision** in the peer-reviewed Science of the Total Environment.

Effects of liming on N₂O and CO₂ production in different horizons of boreal acid sulfate soil and non-acid soil

Chang Xu¹, Vanessa N.L. Wong¹, Anna Tuovinen², Asko Simojoki^{2,3}

¹School of Earth, Atmosphere and Environment, Monash University, Wellington Road, Clayton, VIC 3800, Australia.

²Department of Agricultural Sciences, University of Helsinki, P. O. Box 56 (Biocenter 1, Viikinkaari 9), FI-00014, Finland

³Corresponding author: asko.simojoki@helsinki.fi

Abstract

In acid sulfate (AS) soils, organic rich topsoil and subsoil horizons with highly variable acidity and moisture conditions and interconnected reactions of sulfur and nitrogen make them potential sources of greenhouse gases (GHGs). Recent subsoil liming methods can reduce the acidification of sulfidic subsoils in the field. However, the mitigation of GHG production in AS subsoils by liming and the mechanisms involved, are still poorly known. We added lime to samples from different horizons of AS and non-AS soils, respectively, to study the lime effects on N₂O and CO₂ production during a 56-day oxic incubation and subsequent 72-hr anoxic incubation. Liming to pH ≥ 7 decreased oxic N₂O production in Ap1, Bg1, BC horizons of AS soil, but not in C horizon. Liming decreased N₂O production by 97-98% in Ap1 horizon, 38-50% in Bg1 horizon, and 34-36% in BC horizon, but increased it by 136- 208% in C horizon, respectively. Liming lowered anoxic N₂O production in Ap1 and Bg1 horizons and the N₂O/(N₂O+N₂) ratio in all horizons compared with unlimed AS soil. Liming decreased anoxic N₂O production by 86-94% and 78-91% in Ap1 and Bg1 horizons, but increased it by 100-500% and 50-162% in BC and C horizons, respectively. Higher carbon and nitrogen contents in AS soil as compared to non-AS soil agreed with the respectively higher cumulative oxic N₂O production in all horizons, and higher CO₂ production in Bg1, BC and C horizons, in all treatments. Overall, liming reduced the proportion of N₂O of all GHGs in most soil horizons under oxic and anoxic conditions but reduced the total GHG production as CO₂ equivalents only in the Ap1 horizon of both soils. The results suggest that liming of subsoil would not effectively mitigate GHG emissions in the field due to concurrently increased CO₂ production and denitrification.

Keywords:

Soil pH, subsoil lime treatment, denitrification, greenhouse gas production, N₂O/(N₂O+N₂)

1. Introduction

Acid sulfate soils (AS soils) are soils or sediments that contain oxidizable or partly oxidized sulfide minerals (Pons, 1973). They have been estimated to occupy an area of over 17 Mha worldwide, including South and Southeast Asia, West and Southern Africa, Australia, Latin America, Northern America and boreal Europe, especially Finland (Andriessse and Mensvoort, 2006; Ljung et al., 2009).

Sulfide-containing soil horizons that remain under anaerobic or waterlogged conditions usually have a near neutral pH and do not cause environmental problems. However, aerobic conditions promote the oxidation of sulfides and the production of sulfuric acid (Backlund et al., 2005; Boman et al., 2008). Aerobic conditions can be caused by natural processes such as coastal regression, isostatic uplift or increased droughts caused by climate change (Boman et al., 2010b), or by anthropogenic interventions such as draining for agriculture, construction or mining (Astrom and Spiro, 2000). The acidity of drainage water can lead to mobilization of aluminium and heavy metals, low crop production and poor plant growth (Burton et al., 2008a). Another potential problem caused by drainage of AS soils is the enhanced microbial activity and decomposition of soil organic matter which can result in the rapid production of N_2O due to the inherently high organic matter content and large stocks of mineral N in hypoxic AS subsoils (Paasonen-Kivekäs and Yli-Halla, 2005). Microbial decomposition of organic matter in the hypoxic subsoil of AS soils can also lead to large emissions of CO_2 (Gatland et al., 2014).

N_2O is produced in soils by two main biological processes: nitrification and denitrification (Davidson et al., 2000; Saggar et al., 2013). During nitrification, N_2O is produced as a by-product during the oxidation of NH_4^+ to NO_3^- by ammonia oxidising bacteria under mostly aerobic but slightly O_2 deficient (hypoxic) conditions (Inubushi et al., 1996; Kowalchuk and Stephen, 2001). In denitrification, NO_3^- and NO_2^- are reduced to nitric oxide (NO), nitrous oxide (N_2O) and molecular dinitrogen (N_2) gases when O_2 levels are very low (Cavigelli and Robertson, 2001), i.e. under more severe hypoxia or anoxia.

Soil CO_2 production is a combination of microbial decomposition of soil organic matter (heterotrophic) and plant root (autotrophic) respiration (Amundson and Davidson, 1990). In unvegetated soil, it is an indicator of microbial activity and decomposition (mineralization) of soil organic matter. When organic carbon is added into soils, soil respiration increases to produce more CO_2 (Bruce et al., 1997). CO_2 emissions from oxic (aerobic) soils are much larger than those from anoxic (anaerobic) soil because oxic respiration by microbes and roots is more efficient compared with anoxic respiration (Poungparn et al., 2009; Xu et al., 2021). Early studies have also demonstrated that the maximum respiration rate usually occurs in soil at intermediate moisture contents (Davidson et al., 1998; Scott-Denton et al., 2003). Schaufler et al. (2010)

observed that around 40% water filled pore space (WFPS) in grassland soils results in highest CO₂ emissions.

Soil pH is a key factor that regulates microbiological processes and affects the end products of denitrification (Parkin et al., 1985; Samad et al., 2016b). Denitrification involves the stepwise reduction of NO₃⁻ to N₂O followed by the reduction of N₂O to N₂ by N₂O reductase (Stevens and Laughlin, 1998). In a review including 50 years of research on soil pH influence on denitrification, Šimek & Cooper (2002) demonstrated a variable relationship between soil pH and denitrification but a consistent negative correlation between soil pH and N₂O/N₂ ratio. Acidic conditions support N₂O production during denitrification by both autotrophic and heterotrophic nitrifiers (Martikainen and de Boer, 1993). In acidic soils, N₂O dominates as a denitrification product over N₂ (Qu et al., 2014; Thomsen et al., 1994). Moreover, in AS soils, the interconnected reactions of nitrogen, iron and sulfur favoured by acidic conditions can also contribute to denitrification and N₂O production (MacDonald et al. 2010).

Lime treatments have been widely applied to solve the acidity issues of AS soils, typically utilizing calcium carbonate (CaCO₃) and calcium hydroxide (Ca(OH)₂) to neutralise the acidity (Dalhem et al., 2019; Johnston et al., 2012). Wu et al. (2015) found that treating the soil from an oxidized but still pyrite-containing AS subsoil horizon at 70–85 cm depth with solutions of ultrafine-grained CaCO₃ and Ca(OH)₂ increased soil pH and eventually reduced acidic discharges. Högfors-Rönnholm et al. (2018) discovered that the treatment of AS subsoil from 75-90 cm depth with CaCO₃ under both aerobic and anaerobic conditions will likely be sufficient to mitigate the acid release from AS soil. Moreover, as liming enhances the activity of N₂O reductase, it can act as a greenhouse gas mitigation strategy by enhancing the reduction of N₂O to N₂ (Liu, 2010; Samad et al., 2016b).

Many other soil and environmental factors also influence N₂O emissions and control the N₂O/ (N₂O+N₂) ratio other than pH, including soil type, organic carbon, soil NO₃⁻ availability, gaseous diffusivity and soil water content. Soil NO₃⁻-N content is an important factor affecting N₂O emissions through denitrification. Soil water content is a key factor affecting the emissions of N₂O. Nitrification is usually the dominant source of NO and N₂O production under relatively well aerated conditions at WFPS below 50-60% (Bateman and Baggs, 2005; Davidson et al., 2000). Conversely, the largest N₂O emissions are produced mainly by denitrification under more hypoxic or anaerobic conditions with a maximum often occurring near 70% WFPS (Denmead et al., 2011; Dobbie and Smith, 2001). The N₂O/N₂ ratio has often been found to decrease at a moisture conditions close to saturation, especially when the soil water content exceeds 80% (Colbourn and Dowdell, 1984; Rudaz et al., 1999). For example, Guo et al. (2014) observed that the N₂O/(N₂O+N₂) ratios were much higher in a clay loam soil rewetted to 75% WFPS than to 90% WFPS.

However, our knowledge on the magnitude and factors contributing to the N₂O production in AS soils are currently still limited. In particular, studies on the effects of liming on the rates of N₂O and CO₂ production, total denitrification (N₂O+N₂) and the product ratio of denitrification N₂O/ (N₂O+N₂) in the different horizons of AS soils are lacking. The aim of this study is to determine and compare (1) the effects of lime (CaCO₃) treatments on the production of N₂O and CO₂ in the different horizons of boreal AS and non-AS soils under oxic and anoxic conditions, and (2) the effects of lime on the total denitrification (N₂O +N₂) and the product ratio of denitrification N₂O/(N₂O+N₂) in AS and non-AS soils under anoxic conditions.

2. Materials and methods

2.1 Field site and soil characterisation

The study site was located on the Viikki research farm of the University of Helsinki. The research farm is located on the coast of the Gulf of Finland, which is part of the Baltic Sea. The sites were previously studied by Mokma et al. (2000), Šimek et al. (2011), and Šimek et al (2014). The mean annual air temperature in this area is 5.9 °C and the annual precipitation is 655 mm (a 30-year average in 1981-2010, Finnish Meteorological Institute). At 50 cm soil depth, the mean annual soil temperature is about 6 °C and the mean soil temperature in summer is about 14°C (Mokma et al., 2000; Šimek et al., 2011). The acid sulfate soil (Patoniitty: 60°13'N, 25°0'E, elevation at sea level) is representative of AS soils along the coast of Finland. The non-AS soil (Alaniitty: 60°13'N, 25°1'E with elevation about 1.5 m above average sea level) is poorly drained and formed on fine-grained sediments (Mokma et al., 2000).

Soils were sampled on 27th September 2019 by excavating large pits and characterizing the soil horizons at both sites, and then taking representative samples from each of the four selected horizons of AS and non-acid soils. At the AS soil site, the Ap1, Bg1, BC and C horizons were identified at the depths of 0-22, 31-47, 66-115 and 115-135 cm, respectively. The groundwater table was at 1.1 m depth. At the non-AS soil site, the Ap1, Bg1, BC and C horizons were identified at the depths of 0-20, 31-68, 78-115 and 133-153 cm. The groundwater table was at 1.3 m depth. Soils were sampled with spades from the unsaturated soil horizons and the saturated horizons below the groundwater level and placed into 40-L plastic boxes. According to Soil Taxonomy (Staff., 2014), the AS soil of Patoniitty is a Sulfic Cryaquept and the non-AS soil of Alaniitty is an Aquic Haplocryoll.

A representative sample of the field moist soil taken from a given horizon was mixed and subsequently divided into several sets of subsamples. The subsamples for initial mineral nitrogen analysis were immediately frozen at -20°C, whereas the subsamples for the chemical analyses were air-dried in a ventilated

oven at 35°C and sieved through 2-mm mesh, and a third set of subsamples was used for the determination of initial soil water content.

The main properties of AS soil and the non-AS are compiled in Table 1. In the AS soil, changes in pH with depth was typical for AS soils, with a slightly acidic pH in Ap1 (topsoil) and close to neutral pH in C (massive, reduced subsoil) horizons but with a pH dropping below pH 4 in the BC horizon. In contrast, the pH of the non-AS soil was close to 6 in the topsoil and at, or above 7 in all subsoil horizons.

The AS soil is an organic rich soil with high SOC contents in the Ap1 (4.6%) and C (2.7%) horizons, and even the minimum SOC content was also high, with content just below 2% in the Bg1 horizon. The non-AS soil had a high SOC content in the Ap1 horizon (2.7%) but very was very low in all subsoil horizons (Table 1). The distribution of total nitrogen content (TN) followed a similar pattern to SOC . Both AS and non-AS soils showed broadly similar patterns of decreasing NO₃⁻-N and NH₄⁺-N with depth, except for the NH₄⁺-N rich in the BC and C horizons of AS soil, and modest accumulation of NH₄⁺-N in the BC horizon of non-AS soil. The SOC, TN and mineral N (sum of NO₃⁻-N and NH₄⁺-N) content in all horizons of AS soil were higher compared with the non-AS soil (Table 1).

2.2 Setup of the incubation experiment

The oxic (day 0-56) and anoxic (day 56-59) soil incubations were carried out at room temperature (approx. 20 °C) with a time sequence as shown in Fig. 1. Soil samples were prepared as follows: 10 g of soil (dry weight basis) was packed into a 3.5-cm diameter, 12.5-cm high 120 mL glass bottles.

WFPS in the cores was calculated according to equations 1 and 2:

$$\text{WFPS} = (\theta/n) \quad (\text{Equation 1})$$

where θ (m³ m⁻³) is volumetric soil water content and n (m³ m⁻³) is soil porosity.

$$n = 1 - (\rho_b/\rho_s) \quad (\text{Equation 2})$$

Dry bulk density ρ_b was estimated by the ratio of dry mass and volume of soil in a bottle, and an average soil particle density of $\rho_s = 2.65 \text{ Mg m}^{-3}$ was assumed.

Soil WFPS was maintained constant by weighing the incubation bottles twice per week and adding MQ water as needed during Phase Oxic I.

The soil samples from each site and horizon were subjected to three experimental treatments to adjust the pH. At the beginning of Phase Oxic I, soil pH was increased by applying pure calcite (CaCO₃, EMSURE® Reag. Ph Eur) as low lime (12.5 mg g⁻¹) and high lime (25 mg g⁻¹) treatments to soil (Högfors-Rönholm et

al., 2018), and a control treatment was established with no added lime. The amounts of calcite added were based on the pre-tests of lime requirement in all studied horizons of AS soil (see Supplementary materials). The target soil pH by the high lime addition was pH 7. Based on the pre-test, we added 10 mL of 0.125 M CaCO_3 as the low lime treatment, and 10 mL of 0.25 M CaCO_3 as the high lime treatment, into homogenized soils. A volume of 10 mL MQ water was added in the control soil samples.

A total of 96 soil samples (set 1) were used for the weekly measurement of oxic N_2O and CO_2 production during Phase Oxic I at days 0, 7, 14, 21, 28, 35, 42, 49 and 56 followed by the measurement of anoxic N_2O and CO_2 production during the 72-h Phase Anoxic II (Fig. 1). Another 96 soil samples (set 2) were similarly incubated during Phase Oxic I without gas production measurement for the anoxic incubation in the presence of C_2H_2 when applying the acetylene inhibition method for the determination of total denitrification (see section 2.3). In addition, during Phase Oxic I, a separate set of 96 soils samples (set 3) (Fig. 1) was incubated separately to monitor soil pH with time at 7-day intervals.

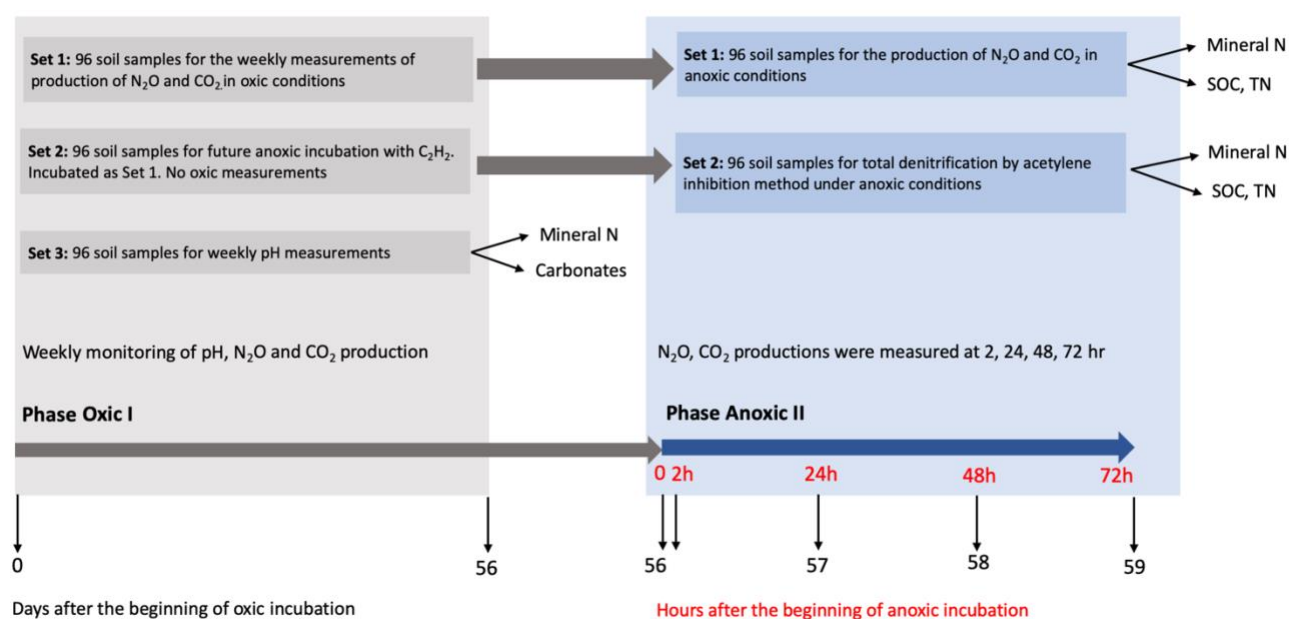


Fig. 1. Time sequence of the oxic incubation (day 0 – 56) and anoxic incubation (day 56 – 59). A total of 288 soil samples were adjusted to 70% WFPS at the beginning of incubation (2 sites x 4 horizons x 3 lime treatments x 4 replicates x 3 sets). The three lime treatments (CaCO_3) including unlimed control, low lime (12.5 mg g^{-1}) and high lime (25.0 mg g^{-1}) were applied at the beginning of Phase Oxic I.

Horizon	Depth (cm)	Bulk density (g cm ⁻³)	pH (Fresh) ^b	pH (Incubated) ^c	SOC (Soil organic carbon) (%)	TN (Total nitrogen) (%)	C/N	NO ₃ ⁻ -N (N mg kg ⁻¹)	NH ₄ ⁺ -N (N mg kg ⁻¹)
AS soil									
Ap1	0-22	0.85 ± 0.01	5.64 ± 0.005	5.57 ± 0.05	4.60 ± 0.01	0.38 ± 0.002	12.25 ± 0.11	27.76 ± 1.73	2.18 ± 0.57
Bg1	31-47	1.00 ± 0.01	4.15 ± 0.03	3.98 ± 0.005	1.89 ± 0.06	0.17 ± 0.007	10.87 ± 0.81	7.7 ± 0.21	3.82 ± 1.56
BC	66-115	0.64 ± 0.005	3.38 ± 0.04	3.08 ± 0.03	2.13 ± 0.01	0.21 ± 0.002	10.12 ± 0.03	0.11 ± 0.11	10.77 ± 2.08
C	115-135	0.54 ± 0.01	6.51 ± 0.10	4.28 ± 0.06	2.67 ± 0.01	0.29 ± 0.004	9.24 ± 0.09	0.005 ± 0.001	13.28 ± 1.97
Non-AS soil									
Ap1	0-20	1.03 ± 0.02	6.30 ± 0.03	6.46 ± 0.05	2.69 ± 0.04	0.23 ± 0.003	11.83 ± 0.04	20.79 ± 1.39	1.79 ± 0.58
Bg1	31-68	0.97 ± 0.01	7.46 ± 0.02	7.45 ± 0.02	0.33 ± 0.001	0.02 ± 0.002	15.85 ± 1.26	5.67 ± 0.34	0.42 ± 0.20
BC	78-115	1.01 ± 0.02	7.68 ± 0.05	7.76 ± 0.03	0.23 ± 0.001	0.014 ± 0.0002	16.43 ± 0.28	2.08 ± 0.26	3.64 ± 1.72
C	133-153	0.81 ± 0.005	7.22 ± 0.02	7.30 ± 0.02	0.52 ± 0.004	0.03 ± 0.0001	16.61 ± 0.30	0.1 ± 0.07	0.22 ± 0.10

Table 1. Selected physical and chemical properties^a of AS soil at Patoniitty and the non-AS soil at Alaniitty in Helsinki

^a Means ± standard errors (n = 4)

^b Fresh pH refers to the pH of soils without aerobic incubation

^c Incubated pH refers to the pH of soils after Phase Oxid I (56 days).

2.3 N₂O and CO₂ production determination

To determine the gas production rates, the headspace of the bottle was first flushed with compressed air, then the bottle was capped gastight with a butyl rubber septum until the gas samples were collected from the headspace after 24 h. A 9-ml gas sample was drawn within 10 seconds from the headspace of the incubation bottle using a gas-tight syringe and transferred into a He-flushed and pre-evacuated 3-ml Exetainer[®] vial capped with a double-wadded (PTFE/silicon-butyl) septum (VC329, Labco, UK). The gaseous composition of samples was determined by a gas chromatograph (Agilent Technologies 7890B GC custom, Santa Clara, CA, United States) connected to an autosampler and equipped with gas sampling valves and TCD, FID and ECD detectors. The air pressure in the headspace was monitored with a pressure meter (Tensimeter, Soil Measurement Systems, CA, United States) at each sampling to calculate the true gas concentration in the headspace, $c = c_s \times p_{hs}/p_0$, where, p_{hs} is the pressure in the headspace, p_0 is the normal atmospheric pressure, and c_s is the gas concentration of sample at p_0 .

The gas production rates F_{N_2O} and F_{CO_2} were calculated from the change of gas concentration in the headspace with time by using Equations 3 and 4. The N₂O and CO₂ production rates were corrected for air temperature during the measurement and presented as [$\mu\text{g kg}^{-1} \text{h}^{-1}$]

$$F_{N_2O \text{ or } CO_2} = \frac{\Delta c / \Delta t \times (V + V_w \alpha_B) \times MW \times 10^6}{\Delta t \times m_d \times MV_{corr}} \text{ (Equation 3)}$$

where $\Delta c / \Delta t$ is the temporal rate of concentration change in the headspace [$\mu\text{L L}^{-1} \text{h}^{-1}$]; V is the volume of the headspace [L]; V_w is the volume of water in the soil sample [L]; α_B is the Bunsen's gas solubility coefficient ($\alpha_B = 0.629$ for N₂O and $\alpha_B = 0.942$ for CO₂ at 20 °C); m_d is the dry mass of soil; MW is the molecular weight of gas (12 g/mol for CO₂-C and 28 g/mol N₂O-N). MV_{corr} is the temperature-corrected molar volume of ideal gas [m^3 / mol]

$$MV_{corr} = 0.02241 \times \left(\frac{273.15 + T}{273.15} \right) \text{ (Equation 4)}$$

where T is air temperature during the measurement [°C] and 0.02241 m^3 is the molar volume of an ideal gas at standard conditions of 1 atm (1013.25 hPa) and 273.15 K.

Cumulative N₂O ($\mu\text{g N}_2\text{O-N kg}^{-1}$) and CO₂ ($\text{mg CO}_2\text{-C kg}^{-1}$) production were calculated with the trapezoidal rule for the production rates ($\mu\text{g kg}^{-1} \text{h}^{-1}$) of all individual sampling data during the incubation period (56 days). The cumulative GHG production rate as CO₂-equivalents (CO₂-eq) was calculated as the sum of CO₂ and N₂O with a global warming potential of 298 used for converting N₂O to CO₂-eq. CH₄ production was

not included in our study as it was always zero or very low. For this reason, the sum of N_2O and CO_2 refers essentially to the sum of all GHGs in our study.

After Phase Oxidic I, soil samples from set 1 and set 2 were incubated for further 72 hours under anoxic conditions at 70% WFPS to support denitrification (Phase Anoxic II in Fig. 1). The C_2H_2 inhibition method, where C_2H_2 blocks the N_2O reduction to N_2 , was used to determine the rate of total denitrification ($\text{N}_2\text{O} + \text{N}_2$) (Nadeem et al., 2013; Yoshinari et al., 1977). The soil sample sets of 1 and 2 were capped with butyl rubber septum and evacuated, and the air in the headspace was replaced with N_2 to achieve strictly anaerobic conditions (Högfors-Rönholm et al., 2018). Soil samples of set 1 and 2 were incubated simultaneously. Gas production was measured by sampling the headspace at 2, 24, 48 and 72 hours after closing the bottle, applying the equations 3 and 4 for each time interval (0-2, 2-24, 24-48 and 48-72 h) separately and summing up the contributions of time intervals.

2.4 Soil physical and chemical analyses

Soil analyses were performed with four replicates. The initial soil pH and electrical conductivity (EC) were measured in a 1:2 soil:water suspension (w/v) (Rayment and Lyons, 2011) using a combination electrode and a pH meter (SCHOTT GLAS Mainz CG-843) and an EC meter (Radiometer Copenhagen, Meterlab CDM210, France).

Soil organic carbon (SOC) and total nitrogen (TN) contents were analysed from initial soil samples, and soil sample sets 1 and 2 after Phase Anoxic II incubation. Analyses were done on oven-dried (105°C) samples by Dumas combustion with a TCN-analyzer (Leco, CN828). Soil carbonate contents were determined by removing SOC by muffle furnace and determining the remaining C by Dumas combustion to allow calculation of the fractional conversion of carbonates (as detailed in Supplementary materials).

Mineral N (NO_3^- -N and NH_4^+ -N) contents were determined from initial soil samples, Phase Oxidic I soil samples (set 3) and Phase Anoxic II soils samples (set 1, 2 and 3) (Fig. 1). Samples used for mineral N determination were frozen immediately after sampling and stored at -20°C before analysis. Soil mineral N extraction was carried out by shaking a soil sample (10 g dry mass of soil) and 40 ml of 2 M KCl solution in a 100-ml bottle with an orbital shaker (180 rpm) for 2 hours (Esala, 1995). NO_3^- -N and NH_4^+ -N were analysed colorimetrically with a Gallery Plus discrete analyser (Thermo Scientific).

2.5 Statistical analysis

The mean gas production rates in each horizon under lime treatments in the AS soil and non-AS soils were based on four replicates. The cumulative N₂O production ($\mu\text{g N}_2\text{O-N kg}^{-1}$) and the cumulative CO₂ production ($\text{mg CO}_2\text{-C kg}^{-1}$) under Phase Oxid I were calculated by “area under the curve” analysis (trapezoidal method) with GraphPad Prism 8.0. One-way analysis of variance (ANOVA) and a post-hoc Tukey’s test were conducted to detect significant differences ($p < 0.05$) in the fractional conversion of carbonates and the cumulative gas production rates (N₂O and CO₂) and the GHG production rate (as CO₂-eq). All the analyses were performed using GraphPad Prism 8.0.

3. Results

3.1 Soil pH, oxic N₂O production and mineral N during Phase Oxid I

In the AS soil, the target pH of 7 was achieved within 2-3 weeks by all low lime and high lime treatments, except for the low lime treatment of BC horizon in which pH peaked at 6.5 after 1 week and steadily decreased thereafter (Fig. 2a, c, e, g). In all horizons of the non-AS soil, the pH exceeded 7 immediately after application of the lime treatments (Fig. 2b, d, f, h).

In all horizons of the AS soil, the highest oxic N₂O production rates occurred within 7 days from the beginning of Phase Oxid I (Fig. 3a, c, e, g). At the beginning of incubation, the N₂O production rates in the low lime and high lime treatments were only 0.3% and 0.15% in the Ap1 horizon (Fig. 3a), 77% and 57% in the Bg1 horizon (Fig. 3c) and 19% and 22% in the BC horizon (Fig. 3e) compared to those in the control treatment, respectively. In the C horizon, however, the N₂O production rates in the low lime and high lime treatments were both about 90% higher than those in the control (Fig. 3g).

In the non-AS soil, the oxic N₂O production rates in the Ap1, Bg1 and BC horizons were much lower than those in the AS soil in all treatments (Fig. 3b, d, f). A decreasing temporal pattern of N₂O production rates and decreasing effects of lime additions were observed in Ap and C horizons (Fig. 3b, h), whereas the patterns and effects were variable in the Bg1 and BC horizons (Fig. 3d, f).

In the Ap1, Bg1 and BC horizons of the AS soil, the cumulative N₂O production was significantly higher in the control than in the lime treatments during Phase Oxid I ($p < 0.05$) (Table 2). The amounts of cumulative N₂O production in the low lime and high lime treatments were only 2.7% and 1.8% in the Ap1 horizon, 62% and 50% in the Bg1 horizon, and 64% and 66% in the BC horizon, respectively, compared to those in the control treatment (Table 2). In the C horizon, however, the cumulative N₂O production in the low lime and

high lime treatments was 136% and 208% higher compared with the control, respectively (Table 2). Significant differences in the cumulative N₂O production were observed between all horizons ($p<0.05$). The cumulative N₂O production in the Ap1 horizon was always higher compared to all other horizons ($p<0.05$), followed by that in the C horizon in limed treatments. The N₂O production in the BC horizon was generally higher than that in the Bg1 horizon (Table 2).

In the non-AS soil, lime treatments significantly decreased cumulative N₂O production in the Ap1, Bg1 and C horizons as compared to the control ($p<0.05$) (Table 2). The low and high lime treatments decreased the amounts of cumulative N₂O production by 89% and 87% in the Ap1 horizon, by 51% and 55% in the Bg1 horizon, and by 92% and 94% in the C horizon, respectively, while in the BC horizon, they were 13% and 20% higher than in the control (Table 2). Significant differences in the cumulative N₂O production were observed between all horizons ($p<0.05$), with the rates decreasing in the order of Ap1 > C > Bg1 > BC horizon in all treatments. Nevertheless, in each respective horizon and treatment, the cumulative N₂O production in the AS soil was always larger, and in most cases even several times larger, than that in the non-AS soil (Table 2).

In both AS and non-AS soil, the NO₃⁻-N content decreased in the Ap1 and Bg1 horizons and increased in the BC and C horizons in all treatments during the oxic incubation (Table S3). In the AS soil, NH₄⁺-N increased with time in all horizons and treatments, whereas in the non-AS soil, NH₄⁺-N increased in the Ap1, Bg1 and C horizons but decreased in the BC horizon (Table S3).

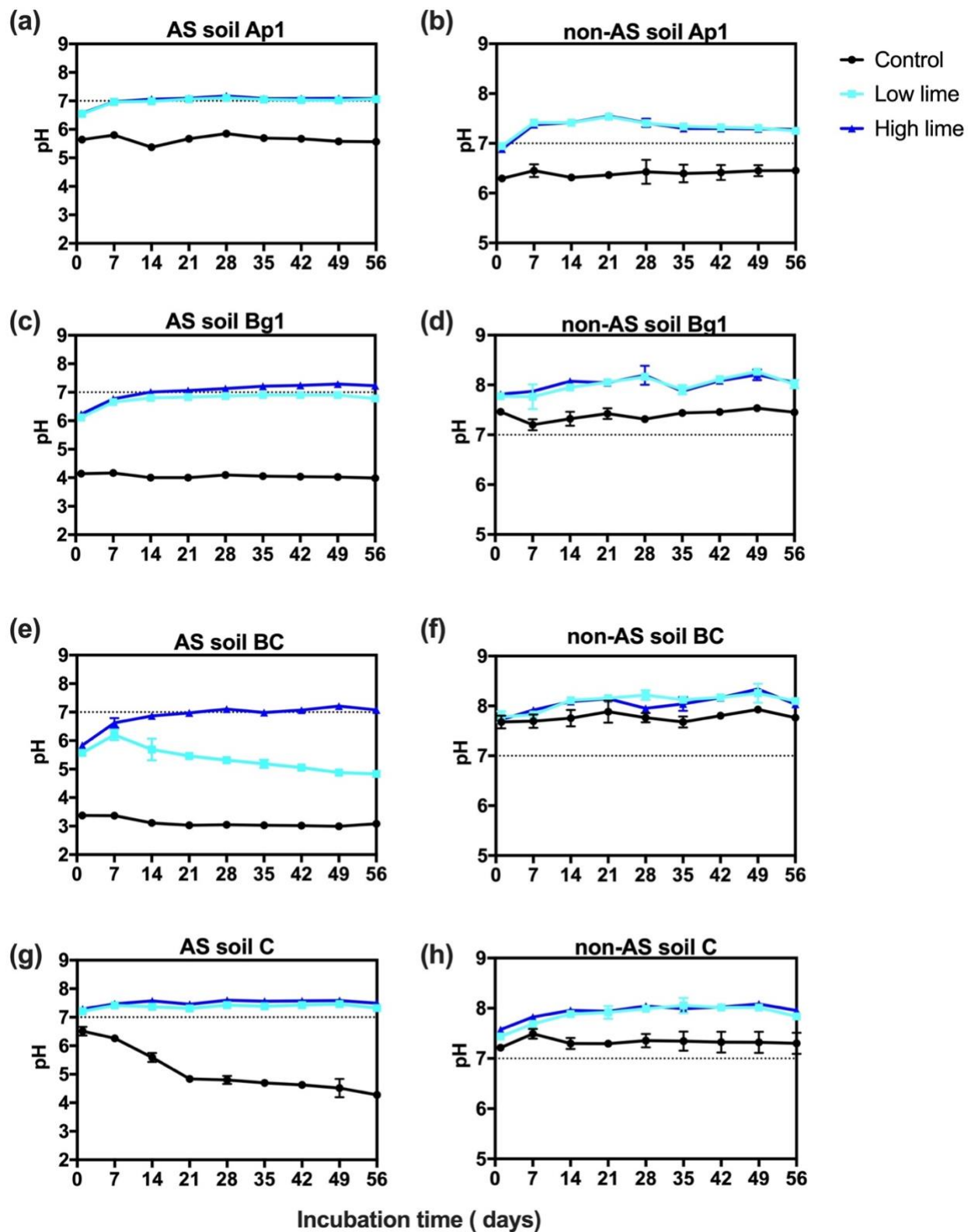


Fig. 2. Temporal variation of pH in the AS and non-AS soils at the Ap1 (a, b), at the Bg1 (c, d), at the BC (e, f), and at the C (g, h) horizons during Phase Oxid I (56 days). Values are the means and their standard errors (n=4).

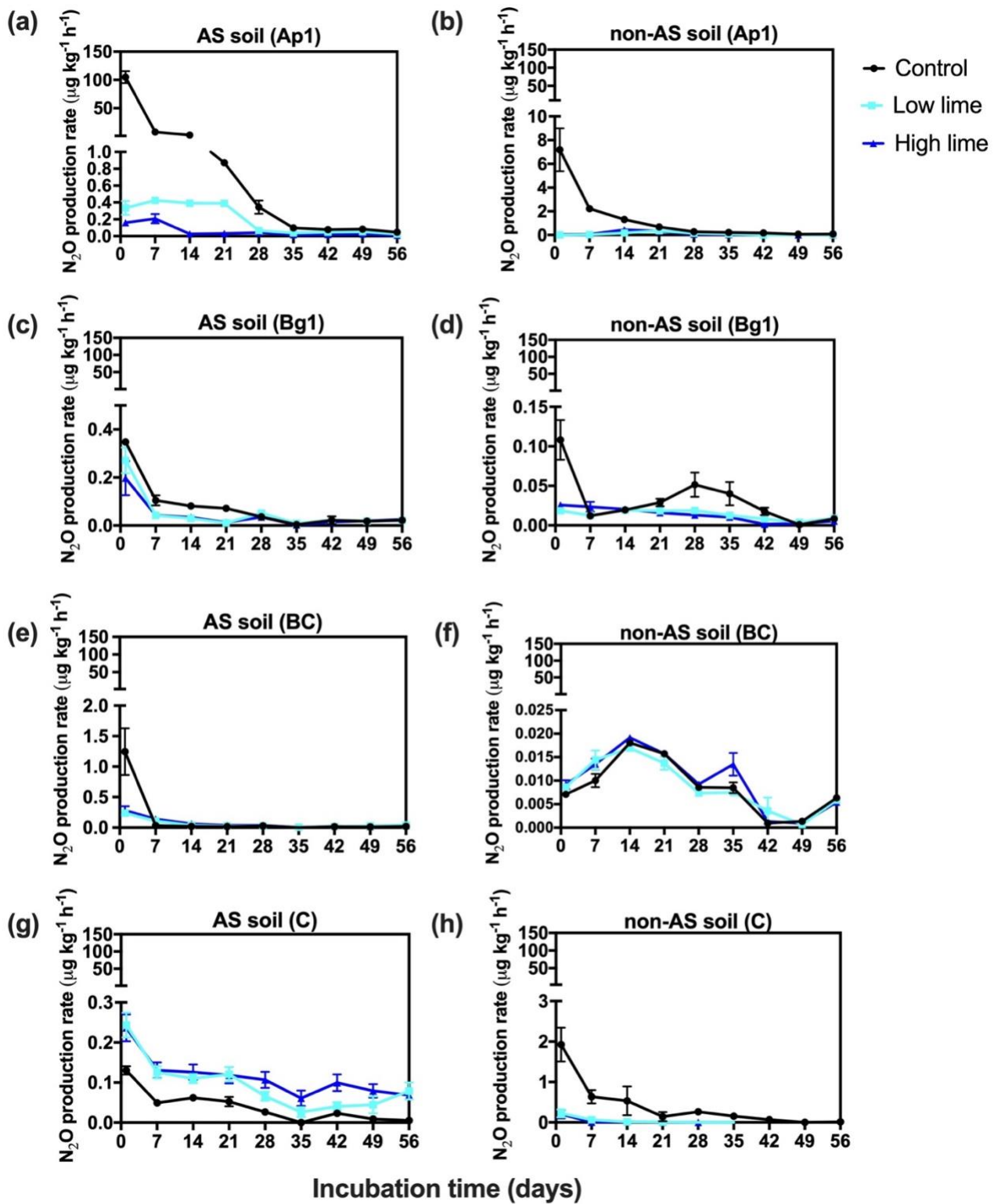


Fig. 3. Oxic N_2O production rate in the Ap1 (a, b), Bg1 (c, d), BC (e, f) and C (g, h) horizons in the AS and non-AS soils during Phase Oxid I (56 days). Values are means and their standard errors (n=4).

Table 2. Cumulative N₂O production^a and CO₂ production^a in different lime treatments and horizons of AS and non-AS soils during Phase Oxid I (56 days) (µg N₂O-N kg⁻¹)

Soil	GHG	Horizon	Control	Low lime	High lime
AS soil	N ₂ O production	Ap1	9452.4 ^{aA}	256.4 ^{bA}	171.7 ^{cA}
		Bg1	80.9 ^{aC}	50.0 ^{bD}	40.8 ^{cD}
		BC	117.1 ^{aB}	74.4 ^{bC}	76.9 ^{bC}
		C	46.7 ^{cD}	111.8 ^{bB}	142.2 ^{aB}
Non-AS soil		Ap1	1320.6 ^{aA}	140.6 ^{cA}	167.2 ^{bA}
		Bg1	35.6 ^{aC}	17.5 ^{bC}	16.2 ^{bC}
		BC	11.1 ^{bD}	12.5 ^{aD}	13.3 ^{aD}
		C	431.9 ^{aB}	35.4 ^{bB}	26.7 ^{cB}
AS soil	CO ₂ production	Ap1	636.0 ^{bA}	977.6 ^{aA}	675.8 ^{bA}
		Bg1	116.6 ^{cB}	314.3 ^{aC}	255.1 ^{bC}
		BC	71.7 ^{bC}	160.0 ^{aD}	142.4 ^{aD}
		C	144.9 ^{bB}	482.5 ^{aB}	419.6 ^{aB}
Non-AS soil		Ap1	693.1 ^{aA}	639.4 ^{bA}	678.4 ^{aA}
		Bg1	21.8 ^{cC}	41.3 ^{aC}	30.6 ^{bC}
		BC	5.1 ^{bD}	16.5 ^{aD}	16.8 ^{aD}
		C	57.7 ^{5cB}	83.3 ^{aB}	74.4 ^{bB}

Different small letters within each row indicate significant differences between the lime treatments. Different capital letters within each column of N₂O production and CO₂ production in the the AS soil and non-AS soil, respectively, represent significant differences between different soil horizons (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$).

3.2 Oxid CO₂ production during Phase Oxid I

In all horizons of the AS soil, the CO₂ production rate during Phase Oxid I was much lower in unlimed soils than in limed soils (Fig. 4a, c, e, g). The CO₂ production rate in the lime treatments soils decreased significantly during the first 14 days and then decreased more slowly or stabilised in the Ap1, Bg and BC horizons (Fig. 4a, c, e). Following the initial decrease, CO₂ production rate in the C horizon increased slightly after day 14 (Fig. 4g). In the non-AS soil, the CO₂ production rate in the control treatment was lower than that in the low and high lime treatments in the Bg1, BC and C horizons, especially during the first weeks of incubation (Fig. 4d, f, h), whereas the CO₂ production in the Ap1 horizon was similar in all treatments. The CO₂ production rate was much higher in the AS soil than that in the non-AS soil (Fig. 4).

In the AS soil, lime treatments in most cases significantly increased cumulative CO₂ production compared to the control ($p < 0.05$) (Table 2). As compared to the control treatment, the cumulative CO₂ production in the low and high lime treatments were 50% and 6% higher in the Ap1 horizon, and 170% and 120% higher in the Bg1 horizon, 120% and 100% higher in the BC horizon, as well as 230% and 190% higher in the C

horizon, respectively (Table 2). Significant differences in the amount of cumulative CO₂ production were observed between all horizons at a given treatment ($p<0.05$), with the production rates decreasing in the order of Ap1>C>Bg1>BC (Table 2).

In the Bg1, BC and C horizons of non-AS soil, significantly higher cumulative CO₂ production was observed in the limed treatments compared with the control ($p<0.05$), whereas liming did not increase CO₂ production in the Ap1 horizon (Table 2). As compared with the control treatment, the amounts of cumulative CO₂ production were 90% and 40% higher in the Bg1 horizon, 220% and 230%-fold higher in the BC horizon, and 40% and 30% higher in the C horizon, respectively (Table 2). The cumulative CO₂ production was significantly different between all horizons at a given treatment, with the amounts decreasing in the order of Ap1>C>Bg1>BC (Table 2). There was much higher cumulative CO₂ production in the Bg1, BC and C horizons of AS soil compared to the respective horizons of the non-AS soil at a given treatment (Table 2).

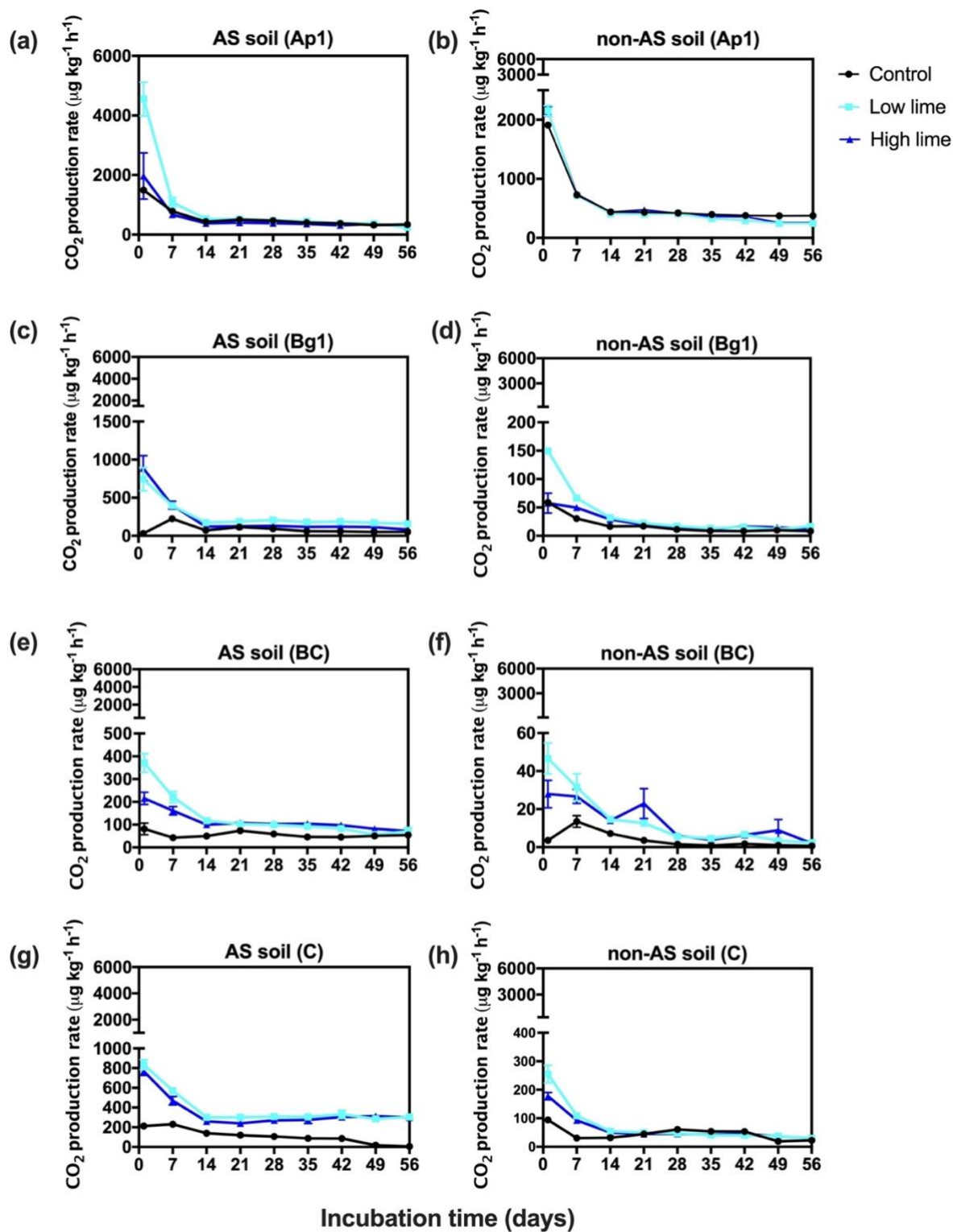


Figure. 4. Oxidic CO₂ production rate in Ap1 (a, b), Bg1 (c, d), BC (e, f) and C (g, h) horizons in the AS and non-AS soils during Phase Oxidic I (56 days). Values are means and their standard errors (n=4).

3.3 Anoxic N₂O production, total denitrification and mineral N during Phase Anoxic II

In the AS soil, significant differences in cumulative N₂O production were observed between all horizons ($p<0.05$) (Table 3). The low lime and high lime treatments decreased cumulative N₂O production by 86% and 94% in the Ap1 horizon, by 91% and 78% in the Bg1 horizon, but increased it in the BC and C horizons by a factor of 3 and 2, respectively (Table 3).

The lime treatments significantly increased total denitrification (N₂O+N₂ production) in all horizons of the AS soil, with denitrification rate always increasing in the order of control < low lime treatment < high lime treatment ($p<0.05$) (Table 3). The total rate of denitrification (N₂O+N₂) of low lime and high lime treatments were 0.9 and 1.7 times higher in the Ap1 horizon, 6 and 9 times higher in the Bg1 horizon, 1.4 and 4.7 times higher in the BC horizon, and 28 and 64 times higher in the C horizon, respectively, compared to that in the control treatment (Table 3). Total denitrification (N₂O+N₂) in the Ap1 horizon was significantly higher than in all other horizons in all treatments in both AS and non-AS soils ($p<0.05$) (Table 3).

In the non-AS soil, lime treatments significantly decreased cumulative N₂O production in all horizons ($p<0.05$) (Table 3). As compared to the control treatment, the cumulative N₂O production under low and high lime treatments were only 34% and 14% in the Ap1 horizon, 31% and 33% in the Bg1 horizon, 37% and 24% in the BC horizon, as well as 43% and 81% in the C horizon, respectively (Table 3).

Significant differences in total denitrification (N₂O+N₂) were observed between the control and lime treatments of the non-AS soil ($p<0.05$) (Table 3). As compared with the control treatment, total denitrification (N₂O+N₂) in the low and high lime treatments were 140% and 150% higher in the Ap1 horizon, and 30% and 80% higher in the C horizon. In the Bg1 and BC horizons, however, the lime treatments decreased total denitrification or had no effect (Table 3). Cumulative N₂O production and total denitrification (N₂O+N₂) were significantly higher in the Ap1 horizon compared with all other horizons in all treatments ($p<0.05$) (Table 3).

NO₃⁻-N content decreased during Phase Anoxic II in all treatments and horizons of AS and non-AS soils regardless of C₂H₂ addition (Table S4). In the AS soil, NH₄⁺-N content mostly increased in all treatments and horizons both with and without C₂H₂ (Table S4). In the non-AS soil, NH₄⁺-N content generally decreased in the Ap1 and Bg1 horizons and increased in the BC and C horizons in all treatments regardless of C₂H₂ addition (Table S4).

Table 3. Cumulative N₂O production^a, total denitrification^a and product ratio of denitrification^a in the different lime treatments and horizons of AS and non-AS soils during Phase Anoxic II (72 hr)

AS soil	Horizon	Control	Low lime	High lime
Cumulative N ₂ O production (μg N ₂ O-N kg ⁻¹)	Ap1	183.9 ^{aA}	25.4 ^{bA}	11.8 ^{cB}
	Bg1	74.1 ^{aB}	6.7 ^{cB}	16.3 ^{bA}
	BC	3.1 ^{cC}	5.3 ^{bB}	18.8 ^{aA}
	C	0.8 ^{bD}	1.2 ^{cC}	2.1 ^{aC}
Total denitrification (N ₂ O + N ₂) (μg N ₂ O-N kg ⁻¹)	Ap1	2345 ^{cA}	4343 ^{bA}	6206 ^{aA}
	Bg1	365 ^{cB}	2544 ^{bB}	3786 ^{aB}
	BC	117 ^{cC}	283 ^{bD}	667 ^{aD}
	C	15 ^{cD}	435 ^{bC}	975 ^{aC}
Product Ratio of Denitrification ((N ₂ O/N ₂ O+N ₂))	Ap1	0.08 ^{aA}	0.005 ^{bB}	0.002 ^{cC}
	Bg1	0.20 ^{aB}	0.003 ^{bC}	0.004 ^{bB}
	BC	0.03 ^{aC}	0.02 ^{bA}	0.03 ^{aA}
	C	0.05 ^{aC}	0.002 ^{bC}	0.002 ^{bC}
Non-AS soil		Control	Low lime	High lime
Cumulative N ₂ O production (μg N ₂ O-N kg ⁻¹)	Ap1	156.1 ^{aA}	53.1 ^{bA}	22.3 ^{cA}
	Bg1	24.9 ^{aC}	7.7 ^{bC}	8.3 ^{bB}
	BC	35.8 ^{aB}	13.3 ^{bB}	8.7 ^{cB}
	C	5.6 ^{aD}	2.4 ^{bD}	4.5 ^{aC}
Total denitrification (N ₂ O + N ₂) (μg N ₂ O-N kg ⁻¹)	Ap1	1150 ^{cA}	2714 ^{bA}	2896 ^{aA}
	Bg1	375 ^{aB}	268 ^{bB}	362 ^{aB}
	BC	77 ^{aC}	34 ^{bC}	82 ^{aC}
	C	20 ^{cD}	27 ^{bD}	36 ^{aD}
Product Ratio of Denitrification (N ₂ O/N ₂ O+N ₂)	Ap1	0.14 ^{aC}	0.02 ^{bC}	0.008 ^{cC}
	Bg1	0.07 ^{aD}	0.03 ^{bC}	0.02 ^{cC}
	BC	0.47 ^{aA}	0.40 ^{aA}	0.11 ^{bA}
	C	0.28 ^{aB}	0.09 ^{bB}	0.13 ^{bA}

Different small letters within each row represent significant differences between the lime treatments. Different capital letters within each column represent significant differences between different soil horizons (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$).

3.4 Anoxic CO₂ production during Phase Anoxic II

In the AS soil, lime treatments significantly increased cumulative CO₂ production in all horizons ($p < 0.05$) (Table S7). Compared to the control treatment, cumulative CO₂ production in the low lime and high lime treatment was 9% and 12% higher in the Ap1 horizon, 140% and 160% higher in the Bg1 horizon, 28% and 33% higher in the BC horizon, and 90% and 80% higher in the C horizon, respectively (Table S7).

In the non-AS soil, lime treatments significantly increased cumulative CO₂ production in the Bg1 and C horizons ($p<0.05$), but no significant increases were observed in the Ap1 and BC horizons (Table S7). Compared to the control treatment, cumulative CO₂ production in the low and high lime treatments were 26% and 23% higher in the Bg1 horizon, and 70% and 50% higher in the C horizon, respectively (Table S7). The cumulative CO₂ production in the Ap1 horizon was significantly higher than in all other horizons in both AS and non-AS soils (Table S7).

3.5 Oxic and anoxic GHG production based on CO₂-eq

Increasing soil pH by liming caused opposite but varied effects on oxic and anoxic GHG production in the different soils and horizons of our study: 1) enhanced reduction of N₂O to N₂ by liming clearly decreased the product ratio of denitrification N₂O/ (N₂O + N₂) and resulted in the decreased net production of N₂O, and 2) the increase CO₂ and N₂O production indicated that liming probably increased microbial activity and denitrification. Therefore, liming raised soil pH which caused a reduction of N₂O/ (N₂O+N₂) and resulted in decreased (net) production of N₂O. During Phase Oxic I, total GHG production (N₂O + CO₂ as CO₂ eq) in the lime treatments was significantly lower than that in the unlimed control treatment only in the Ap1 horizon of AS soil ($p<0.05$) (Fig. 5a). In the non-AS soil, total GHG production was not significantly different between treatments in most horizons ($p>0.05$) (Fig. 5c), but liming significantly decreased the proportion of N₂O in GHG production in most horizons at both sites ($p<0.05$) (Fig. 5e, g).

During Phase Anoxic II, GHG production (as CO₂ eq) in the lime treatments was significantly lower than that in the unlimed control treatment in the Ap1 horizon of AS soil (Fig. 5b) and in the Ap1, BC horizons of the non-AS soil (Fig. 5d) ($p<0.05$). Liming significantly decreased the proportion of N₂O in the total GHG production in the Ap1, Bg1 horizons of AS soil (Fig. 5f) and all horizons of the non-AS soil (Fig. 5h).

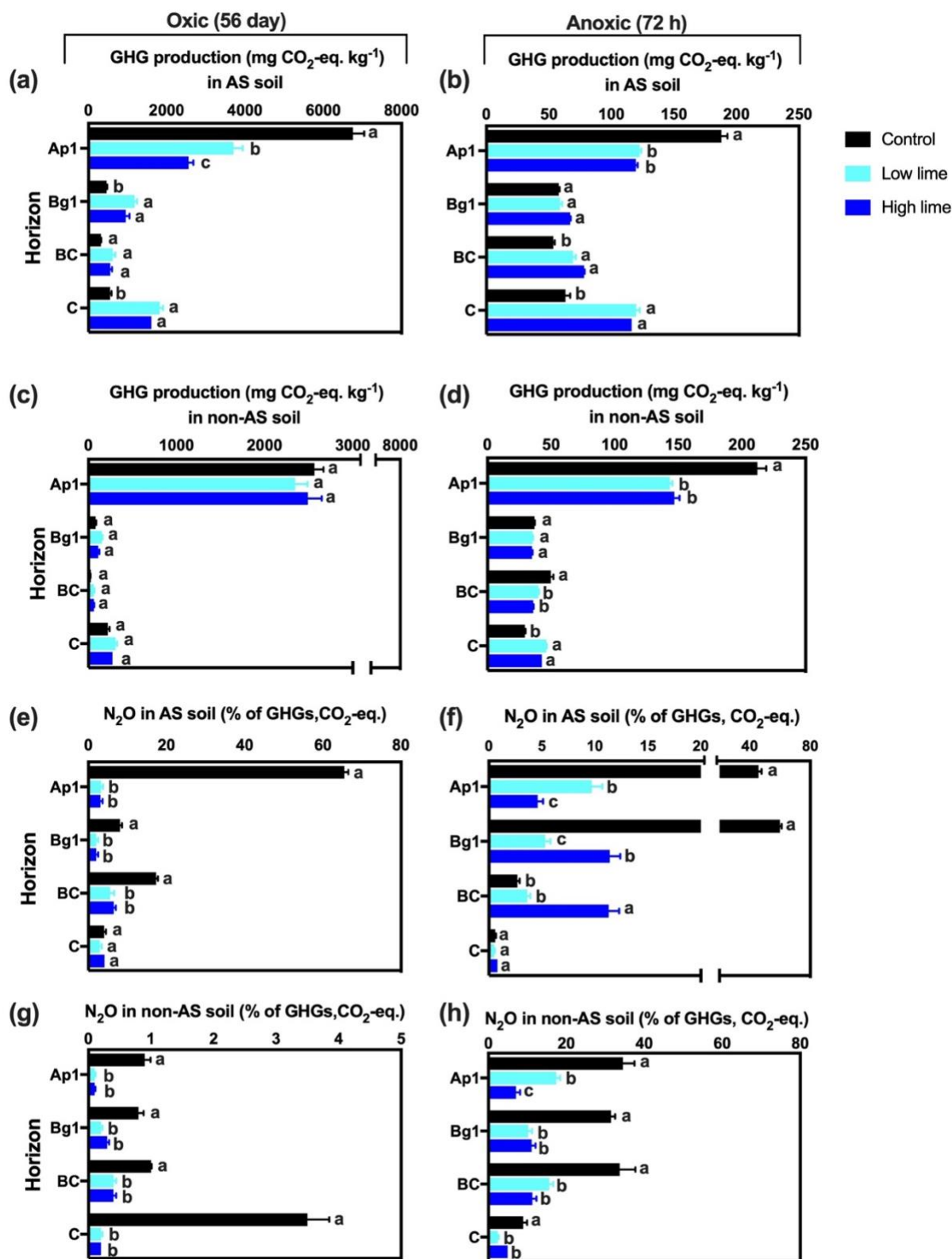


Figure 5. GHG production (N₂O+CO₂) in AS and non-AS soils (a, c) and proportion of N₂O in GHG production (CO₂-eq.) in AS and non-AS soils (e, g) during Phase Oxic I (56 d). GHG production (N₂O+CO₂) in AS and non-AS soils (b, d) and proportion of N₂O in GHG production (CO₂-eq.) in AS and non-AS soils (f, h) during Phase Anoxic I (72 h). Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$). The whiskers denote the standard error of mean.

4. Discussion

4.1 Effects of liming on the oxic production of N₂O

Liming of soil to pH 7 or above clearly decreased the cumulative N₂O production in the Ap1, Bg1, BC horizons of the AS soil and in the Ap1, Bg1 and C horizons of the non-AS soil. Such results suggest that acidity represents a constraint on the reduction of N₂O to N₂ in both soils (Liu et al., 2014), as N₂O is known to dominate over N₂ as a product of denitrification in acidic conditions (Qu et al., 2014; Šimek et al., 2002; Thomsen et al., 1994). In agreement with this, high soil pH is known to stimulate the activity of N₂O reductase for a more rapid conversion of N₂O to N₂ (Guo et al., 2014). Liu et al. (2014) observed that low soil pH prevented reduction of N₂O mainly by inhibiting the assembly of functional N₂O reductase. On the other hand, increasing pH generally enhances microbial activity and nitrogen cycling in soil and thus increase N₂O produced by nitrification and denitrification. For instance, Nugroho et al. (2007) found that liming (CaCO₃) of acid soils (pH 3.8) can stimulate the growth of ammonium-oxidizing bacteria and nitrifying activity in an acid pine forest soil.

Contrary to other AS soil horizons, liming was inefficient in reducing the N₂O production in the C horizon of the AS subsoil even when the pH was high. In the field, this horizon contains potential AS soil material that is nearly always inundated with water in reduced conditions and with abundant amounts of sulfide minerals. As expected, the oxidation of sulfides in the unlimed C horizon decreased the pH from 6.5 to 4.3 during the oxic incubation in this study, but in the limed treatments, the pH always remained high.

In the BC horizon of the AS soil, there was similar acidification observed during the oxic incubation, but with a less pronounced decrease in pH compared with the C horizon. The oxidation of sulfides had clearly resulted in very low soil pH values before the incubation.

In the unlimed control soil, there was no added lime that could neutralize the acidity from the oxidation of the sulfides. In principle, the decreasing soil pH during oxic incubation could have inhibited the reduction of N₂O and thus promoted the net production of N₂O over N₂ denitrification, especially in the C horizon of the AS soil. Nevertheless, any contributions from such acidification-induced N₂O production were likely more than counterbalanced by the loss of microbial activity and related N₂O production. This view is supported by the high response of both N₂O and CO₂ production to liming.

The decreasing N₂O production rate with time in all horizons and treatments of the AS soil during Phase Oxic I was probably due to the gradual depletion of NO₃⁻-N. Organic matter and nutrients might become limited over time during the incubation as it is consumed by the microbes during the incubation. In the Ap1 and Bg1 horizon, the decrease in NO₃⁻-N in the Ap1 and Bg1 horizons during the Phase Oxic I can be

attributed to either denitrification or immobilization of N into the microbial biomass as there was no leaching from the incubation vessels. Denitrification is the most likely mechanism involved as WPFS of 70% is generally considered high enough to favour denitrification in anoxic microsites of soil. On the other hand, immobilization involves the conversion of inorganic nitrogen (NO_3^- -N and NH_4^+ -N) into organic forms of cellular components, such as proteins and amino sugars (Brady and Weil, 2016). Liming boosted microbial activity, as shown by an increase in the CO_2 production in the limed AS soil horizons at the beginning of Phase Oxidic I. Therefore, the enhanced microbial growth could have caused immobilization of NO_3^- -N as well. However, immobilization of N to microbial biomass did not cause net depletion of NH_4^+ -N in soil as the net ammonification and net N mineralisation during Phase Oxidic I were positive, most likely due to high decomposition rate of organic matter in oxic conditions.

In the BC and C horizons of AS soil, the pool of NO_3^- -N was not depleted but increased. The initial NH_4^+ -N in the BC and C horizons were very high and the large increases in NH_4^+ -N in all horizons during Phase Oxidic I indicated mineralization of organic N to NH_4^+ . Oxic conditions promote oxidation of NH_4^+ to NO_3^- by nitrification. This suggests that nitrification could have produced a significant amount of NO_3^- -N with N_2O as a by-product. Nevertheless, the fact that liming significantly decreased N_2O production suggests that the pH-sensitive N_2O reductase enzyme had a more important role, and that the N_2O was likely produced in anoxic hotspots by coupled nitrification and denitrification (Šimek et al., 2011).

The AS soil had a much higher cumulative N_2O production compared with the non-AS soil in all horizons, which can be attributed to its higher contents of NO_3^- -N and NH_4^+ -N (Paasonen-Kivekäs and Yli-Halla, 2005). Recent studies have indicated larger N_2O emissions from AS soil than from non-AS mineral soils in Finland (Šimek et al., 2011; Šimek et al., 2014; Yli-Halla et al., 2020) and Australia (Galbally et al., 2010; Macdonald et al., 2008). Our results agree with the view that NO_3^- -N and NH_4^+ -N are important factors affecting oxic N_2O production and emissions from AS soils through nitrification and denitrification.

4.2 Effects of liming on the anoxic production of N_2O production and denitrification

Lime treatments decreased the anoxic production of N_2O in the Ap1 and Bg1 horizons of the AS soil, and in all horizons of the non-AS soil. Conversely, in all horizons of the AS soil, the total denitrification ($\text{N}_2\text{O}+\text{N}_2$) in the lime treatments was always significantly higher than that in the respective unlimed soil horizon, but in the non-AS soil this was the case only in the Ap1 horizon. Liming had raised the soil pH to the range of 7.0-8.0 at which the total denitrification ($\text{N}_2\text{O}+\text{N}_2$) is generally considered to be highest (Van Cleemput et al., 1975). In addition, earlier findings suggest that even if total denitrification activity increases, the amount of N_2O produced relative to N_2 decreases with increasing soil pH (Šimek and Cooper, 2002).

Soil pH controls the composition of the denitrifying microbial community. Low soil pH also limits the availability of organic C and mineral N to denitrifying bacteria (Bakken et al., 2012; McMillan et al., 2016). The effects of pH on the $\text{N}_2\text{O}/\text{N}_2$ ratio of denitrification has been explained by the pH-sensitivity of the enzyme N_2O reductase that is inhibited at low pH (Liu, 2010; Qu et al., 2014; Šimek et al., 2002; Thomsen et al., 1994). The lower product ratios of $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ in most lime treated horizons of AS soil support the view that high soil pH stimulated the activity of N_2O -reductase (Čuhel and Šimek, 2011). Similarly, Liu et al. (2010) showed a strong negative correlation between soil pH and the product ratio $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ within a pH range of 4-7 of long-term lime experiments (CaCO_3) in peat and clay loam soil in western Norway.

Nevertheless, an exception to the rule were the BC and C horizons of the AS soil, where liming proved inefficient in decreasing the product ratio and anoxic N_2O production. As a consequence, liming increased both anoxic N_2O production and total denitrification in these deep horizons.

Irrespective of the experimental treatment, the cumulative N_2O production and total denitrification ($\text{N}_2\text{O}+\text{N}_2$) in a given horizon of AS soil were always higher than those in the respective horizon of non-AS soil (Table 3). This can be attributed to the higher total N and initial mineral N (NO_3^- -N and NH_4^+ -N) contents in the AS soil horizons compared with the non-AS soil. Large amounts of bioavailable N are known to favour denitrification and enhance N_2O and N_2 emissions under anaerobic condition. Earlier studies on N_2O in AS soils have indicated that the occurrence of large amounts of NO_3^- -N and NH_4^+ -N in AS soils can cause significant release of N_2O under anaerobic conditions (Čuhel and Šimek, 2011; Denmead et al., 2010; Denmead et al., 2011).

4.3 Effects of liming on the oxic and anoxic production of CO_2

Liming significantly increased the cumulative CO_2 production compared with unlimed AS soil in both oxic and anoxic conditions. The carbonate from lime (CaCO_3) can neutralize the acidic soil and convert the carbonate to CO_2 . Page et al. (2009) and Grover et al. (2017) also reported that raising the soil pH with the dissolution of lime can concurrently contribute to the release of CO_2 from soils. In our study, nearly all added lime had reacted in soil by the end of the oxic and anoxic incubations, as the fractional conversion of carbonates always exceeded 90% (Table S2), but still even the largest differences in the total cumulative CO_2 -C production between the limed and control treatment (about 340 mg kg^{-1}) were only a small fraction of the amount of added carbonate C (1500 or 3000 mg kg^{-1}). Thus, during the incubation, much of the dissolved carbonate must have remained in the soil. In the lime treatments, most of the added carbonates have probably remained in porewater as dissolved bicarbonate, which is the dominant carbonate species in the circumneutral pH range.

Lime addition also increased the availability of organic carbon and nitrogen to the microbes which were initially limited by low soil pH in the AS soil (Zelles et al., 1990). Lime increased the biological activity in soil and therefore the rates of soil CO₂ respiration as in other studies (Badalucco et al., 1992; Biasi et al., 2008). In the non-AS soil, however, liming did not significantly increase the cumulative CO₂ production as the initial pH of non-AS soil was already above 6.3 in all horizons.

The cumulative CO₂ production in the AS soil was higher than in the non-AS soil in oxic conditions. This can be attributed to the several-fold larger organic carbon pools in the AS soil horizons as compared with the respective non-AS soil horizons (Table 1). The CO₂ production was highest in the Ap1 horizon, decreased rapidly with soil depth in the Bg1 and BC horizons, but then increased again in the C horizon. This confirms the trend observed in an earlier study in Finnish soils (Šimek et al., 2011). The abundant carbon stocks in the top horizon (Ap1) and deep horizon (C) serve as substrate for enhanced microbial growth and respiration under oxic conditions. Respiration is usually higher in soils rich in organic matter. This agrees with many early studies where higher amounts of organic carbon in soil increased production of CO₂ in soil (Bruce et al., 1997; Gallardo and Schlesinger, 1994). The prerequisite for the high rate of respiration include an active microbial community and abundant amount of easily decomposable organic matter. In the AS soil, microbial activity was generally limited by acidity, as the CO₂ production was increased by liming in nearly all AS soil horizons.

4.4 Effects of liming on the total GHG production based on CO₂-eq

In terms of CO₂ eq, liming caused a net reduction of GHG production only in the Ap1 horizons of both soils, even if liming nearly always decreased the proportion of N₂O in GHG production, excluding the C horizon and anoxic BC horizon in AS soil. Conversely, liming of acid subsoil horizons often increased GHG production.

The results suggest that liming can successfully reduce GHG production in AS soils by pH mitigation, provided that topsoil dominates the GHG production of soil profile. Nevertheless, even if liming of acid AS subsoil horizons can reduce the proportion of N₂O in GHG production, it seems less efficient in reducing the total GHG production and involves the risk of increasing the GHG production by enhanced microbial respiration and denitrification. In the non-AS subsoils, high initial pH probably reduced the effects of liming.

In the BC horizon of AS soil, liming concomitantly increased anoxic GHG production and the proportion of N₂O in GHG production. This result differs from all other horizons and may suggest a contribution of some

different mechanisms of GHG production as compared with other horizons. It is noted that in earlier studies, the highest anoxic N₂O production of all AS subsoil horizons was found in the BC horizon (Šimek et al., 2014). The mechanisms involved are worthy of detailed study in the future.

According to this study, the contribution of unlimed subsoil horizons to the total GHG production seemed generally small. This seems fortunate in practice, as it is easier to mitigate the GHG production by liming the topsoil than subsoil. However, the generalization of results to the field is not as simple as that for reasons outlined below.

In our incubations, we used mechanically disturbed soil samples at constant soil moisture status (70% WFPS) and at a higher temperature than typical in the field. The moisture status and temperature were selected so as to have optimal conditions for oxic N₂O production and for its mitigation by liming. In the field, however, soil moisture content varies with time and generally increases with depth. The degree of saturation may often exceed WFPS 70% already in the BC horizon and approaches saturation at the C horizon of AS soil. This increases the contribution of subsoil horizons to total GHG production in the soil profile. On the other hand, the field temperature in the subsoil horizons is much lower than the room temperature in this study, which is likely reflected in correspondingly slower microbial activity and GHG production in the field.

Moreover, in the incubation experiment, a relatively large amount of lime was added and mixed into a small amount of soil as a suspension so as to let it react efficiently and increase the impacts of lime in soil. In the field, lime suspension can be added into a structured subsoil through subsurface drains (Wu et al., 2015). Such lime will only contact the surfaces of the largest macropores and cracks in the subsoil. The efficiency of such liming on CO₂ and N₂O production in different soil horizons and the contributions of different soil horizons to GHG emissions *in-situ* remain topics for future research.

CH₄ is a third potentially important GHG that is globally relevant, but in our study, it is less significant because large CH₄ emissions from AS soils have not been reported in the field and because no significant CH₄ emissions were observed in our incubation study. During Phase Oxidic I, soil was expectedly a sink rather than a source of CH₄. During Phase Anoxic II, the relatively short incubation time (72 h) probably contributed to fact that the CH₄ production, if any, was very small compared with N₂O and CO₂ production.

5. Conclusions

We determined the effects of liming on N₂O and CO₂ production, total denitrification (N₂O+N₂) and the

product ratio of denitrification in different soil horizons of AS and non-AS soil by carrying out incubations at 70% WFPS in oxic and anoxic conditions. Liming effectively increased soil pH to 7 in all horizons in both soils. Liming decreased N₂O production in the Ap1, Bg1 and BC horizons in oxic conditions and in the Ap1 and Bg1 horizons in anoxic conditions in the AS soil. However, liming was not effective in reducing N₂O production in the C horizon in oxic and anoxic conditions, and in the BC horizon in anoxic conditions. However, the product ratio N₂O/(N₂O+N₂) of denitrification decreased with liming-induced pH change in both AS and non-AS soils in anoxic conditions. Lime treatments increased the total anoxic denitrification (N₂O+N₂) in all horizons of the AS soil. The higher cumulative production of N₂O and CO₂ in the horizons of the AS soil in oxic and anoxic conditions as compared to the respective non-AS soil horizons agreed well with their higher total carbon and nitrogen contents. Lime addition enhanced CO₂ production in the AS soil. Significant lime-induced reductions in the total GHG production as CO₂-eq were observed only in the Ap1 horizon of AS (oxic and anoxic) and non-AS (anoxic) soils. The results suggest that liming of the subsoil would not effectively decrease GHG emissions due to the increased CO₂ production and denitrification. In the future, long-term field studies are needed to evaluate the potential of liming of different soil horizons as a mitigating tool for N₂O production and facilitating the reduction of the product ratio N₂O/(N₂O+N₂) *in-situ*. At the same time, the viability of lime as a mitigation strategy for GHG emissions should also account for the increased CO₂ emissions connected with the lime application in agricultural land.

Acknowledgements

This study was supported by Finnish National Agency of Education granting an EDUFI fellowship with a full scholarship for the research visit of Ms. Chang Xu to the University of Helsinki (Sep 2019 – Mar 2020, EDUFI TM-19-11085). The research was carried out in the framework of FACCE ERA-GAS MAGGE-pH project (<https://www.eragas.eu/en/eragas/Research-projects/MAGGE-pH.htm>, <https://www.researchgate.net/project/Mitigating-Agricultural-Greenhouse-Gas-Emissions-by-improved-pH-management-of-soils-MAGGE-pH>).

References

- Amundson, R.G., Davidson, E.A., 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *Journal of Geochemical Exploration* 38, 13-41.
- Andriesse, W., Mensvoort, M.E.F.v., 2006. Acid sulfate soils: distribution and extent, In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. CRC Press, Boca Raton, FL, pp. 14–19.
- Astrom, M., Spiro, B., 2000. Impact of isostatic uplift and ditching of sulfidic sediments on the hydrochemistry of major and trace elements and sulfur isotope ratios in streams, Western Finland. *Environmental Science & Technology* 34, 1182.
- Backlund, K., Boman, A., Fröjdö, S., Astrom, M., 2005. An analytical procedure for determination of sulphur species and isotopes in boreal acid sulphate soils and sediments. *Agricultural and Food Science* 14, 70-82.
- Badalucco, L., Grego, S., Dell'Orco, S., Nannipieri, P., 1992. Effect of liming on some chemical, biochemical, and microbiological properties of acid soils under spruce (*Picea abies* L.). *Biology and Fertility of Soils* 14, 76-83.
- Bakken, L.R., Bergaust, L., Liu, B., Frostegård, A., 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N₂O emissions from soils. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 367, 1226.
- Bateman, E.J., Baggs, E.M., 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biology and Fertility of Soils* 41, 379-388.
- Biasi, C., Lind, S.E., Pekkarinen, N.M., Huttunen, J.T., Shurpali, N.J., Hyvönen, N.P., Repo, M.E., Martikainen, P.J., 2008. Direct experimental evidence for the contribution of lime to CO₂ release from managed peat soil. *Soil biology & biochemistry* 40, 2660-2669.
- Boman, A., Åström, M., Fröjdö, S., 2008. Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide—The role of artificial drainage. *Chemical Geology* 255, 68-77.
- Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.
- Brady, N.C., Weil, R.R., 2016. *The nature and properties of soils*, Fifteenth edition ed. Upper Saddle River, N.J. : Prentice Hall, Upper Saddle River, N.J.
- Bruce, A.H., Elisabeth, A.H., Robert, B.J., Chapin, F.S., Harold, A.M., Christopher, B.F., 1997. The fate of carbon in grasslands under carbon dioxide enrichment. *Nature* 388, 576.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Johnston, S.G., Hocking, R.K., 2008. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* 253, 64-73.
- Cavigelli, M.A., Robertson, G.P., 2001. Role of denitrifier diversity in rates of nitrous oxide consumption in a terrestrial ecosystem. *Soil biology & biochemistry* 33, 297-310.
- Colbourn, P., Dowdell, R.J., 1984. Denitrification in field soils. *Plant and Soil* 76, 213-226.

- Čuhel, J., Šimek, M., 2011. Proximal and distal control by pH of denitrification rate in a pasture soil. *Agriculture, Ecosystems & Environment* 141, 230-233.
- Dalhem, K., Engblom, S., Stén, P., Österholm, P., 2019. Subsurface hydrochemical precision treatment of a coastal acid sulfate soil. *Applied Geochemistry* 100, 352-362.
- Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. *Global Change Biology* 4, 217-227.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides. *BioScience* 50, 667-680.
- Denmead, O.T., Macdonald, B.C.T., Bryant, G., Naylor, T., Wilson, S., Griffith, D.W.T., Wang, W.J., Salter, B., White, I., Moody, P.W., 2010. Emissions of methane and nitrous oxide from Australian sugarcane soils. *Agricultural and Forest Meteorology* 150, 748-756.
- Denmead, O.T., Macdonald, B.C.T., White, I., Bryant, G., 2011. Gaseous Nitrogen Losses from Coastal Acid Sulfate Soils: A Short-Term Study. *Pedosphere* 21, 197-206.
- Dobbie, K.E., Smith, K.A., 2001. The effects of temperature, water-filled pore space and land use on N₂O emissions from an imperfectly drained gleysol. *European Journal of Soil Science* 52, 667-673.
- Esala, M.J., 1995. Changes in the extractable ammonium- and nitrate-nitrogen contents of soil samples during freezing and thawing. *Communications in Soil Science and Plant Analysis* 26, 61-68.
- Galbally, I.E., Meyer, M.C.P., Wang, Y.-P., Smith, C.J., Weeks, I.A., 2010. Nitrous oxide emissions from a legume pasture and the influences of liming and urine addition. *Agriculture, Ecosystems & Environment* 136, 262-272.
- Gallardo, A., Schlesinger, W.H., 1994. Factors limiting microbial biomass in the mineral soil and forest floor of a warm-temperate forest. *Soil Biology and Biochemistry* 26, 1409-1415.
- Gatland, J.R., Santos, I.R., Maher, D.T., Duncan, T.M., Erler, D.V., 2014. Carbon dioxide and methane emissions from an artificially drained coastal wetland during a flood: Implications for wetland global warming potential. *Journal of Geophysical Research: Biogeosciences* 119, 1698-1716.
- Grover, S.P., Butterly, C.R., Wang, X., Tang, C., 2017. The short-term effects of liming on organic carbon mineralisation in two acidic soils as affected by different rates and application depths of lime. *Biology and Fertility of Soils* 53, 431-443.
- Guo, X., Xueming, Y., Drury, C.F., Reynolds, W.D., Fan, R., 2014. The extent of soil drying and rewetting affects nitrous oxide emissions, denitrification, and nitrogen mineralization.(Report). *Soil Science Society of America Journal* 78, 194.
- Högfors-Rönholm, E., Christel, S., Dalhem, K., Lillhonga, T., Engblom, S., Österholm, P., Dopson, M., 2018. Chemical and microbiological evaluation of novel chemical treatment methods for acid sulfate soils. *Science of The Total Environment* 625, 39-49.

- Inubushi, K., Naganuma, H., Kitahara, S., 1996. Contribution of denitrification and autotrophic and heterotrophic nitrification to nitrous oxide production in andosols. *Biology and Fertility of Soils* 23, 292-298.
- Johnston, S.G., Keene, A.F., Burton, E.D., Bush, R.T., Sullivan, L.A., 2012. Quantifying alkalinity generating processes in a tidally remediating acidic wetland. *Chemical Geology* 304-305, 106-116.
- Kowalchuk, G., Stephen, J., 2001. Ammonia-oxidizing bacteria: A model for molecular microbial ecology. *Annual Review of Microbiology* 55, 485-529.
- Liu, B., 2010. Denitrification gene pools, transcription and kinetics of NO, N₂O and N₂ production as affected by soil pH. *FEMS Microbiology Ecology* 72, 407-417.
- Liu, B., Frostegård, Å., Bakken, L.R., 2014. Impaired reduction of N₂O to N₂ in acid soils is due to a posttranscriptional interference with the expression of nosZ. *mBio* 5, e01383-e01314.
- Ljung, K., Maley, F., Cook, A., Weinstein, P., 2009. Acid sulfate soils and human health—A Millennium Ecosystem Assessment. *Environment International* 35, 1234-1242.
- Macdonald, B., Denmead, O., White, I., Wilson, S., 2008. Green house gas emissions from acid sulphate and non-acid sulphate soils, *Proceedings of the Joint Conference of the 6th International Acid Sulphate Soil Conference and the Acid Rock Drainage Symposium*. Guangdong Press Group, Guangzhou, pp. 126–131.
- Martikainen, P.J., de Boer, W., 1993. Nitrous oxide production and nitrification in acidic soil from a dutch coniferous forest. *Soil Biology and Biochemistry* 25, 343-347.
- McMillan, A.M.S., Pal, P., Phillips, R.L., Palmada, T., Berben, P.H., Jha, N., Saggar, S., Luo, J., 2016. Can pH amendments in grazed pastures help reduce N₂O emissions from denitrification? – The effects of liming and urine addition on the completion of denitrification in fluvial and volcanic soils. *Soil biology & biochemistry* 93, 90-104.
- Mokma, D., Yli-Halla, M., Hartikainen, H., 2000. Soils in a young landscape on the coast of southern Finland.
- Nadeem, S., Dörsch, P., Bakken, L.R., 2013. Autoxidation and acetylene-accelerated oxidation of NO in a 2-phase system: Implications for the expression of denitrification in ex situ experiments. *Soil Biology and Biochemistry* 57, 606-614.
- Nugroho, R.A., Röling, W.F.M., Laverman, A.M., Verhoef, H.A., 2007. Low Nitrification Rates in Acid Scots Pine Forest Soils Are Due to pH-Related Factors. *Microb Ecol* 53, 89-97.
- Paasonen-Kivekäs, M., Yli-Halla, M., 2005. A comparison of nitrogen and carbon reserves in acid sulphate and non acid sulphate soils in western Finland. *Agricultural and Food Science* 14, 57–69.
- Page, K.L., Allen, D.E., Dalal, R.C., Slattery, W., 2009. Processes and magnitude of CO₂, CH₄, and N₂O fluxes from liming of Australian acidic soils: a review. *Australian Journal of Soil Research* 47, 747-762.
- Parkin, T.B., Sexstone, A.J., Tiedje, J.M., 1985. Adaptation of Denitrifying Populations to Low Soil pH. *Applied and Environmental Microbiology* 49, 1053.

- Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, In: Dost, H. (Ed.), *Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils.* International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 13–20
- Poungparn, S., Komiyama, A., Tanaka, A., Sangtiew, T., Maknual, C., Kato, S., Tanapermpool, P., Patanaponpaiboon, P., 2009. Carbon dioxide emission through soil respiration in a secondary mangrove forest of eastern Thailand. *Journal of tropical ecology* 25, 393-400.
- Qu, Z., Wang, J., Almøy, T., Bakken, L.R., 2014. Excessive use of nitrogen in Chinese agriculture results in high $N_2O/(N_2O+N_2)$ product ratio of denitrification, primarily due to acidification of the soils. *Global Change Biology* 20, 1685-1698.
- Rayment, G.E., Lyons, D.J., 2011. *Soil chemical methods.* CSIRO, Melbourne, Australia.
- Rudaz, A.O., Wälti, E., Kyburz, G., Lehmann, P., Fuhrer, J., 1999. Temporal variation in N_2O and N_2 fluxes from a permanent pasture in Switzerland in relation to management, soil water content and soil temperature. *Agriculture, Ecosystems & Environment* 73, 83-91.
- Saggar, S., Jha, N., Deslippe, J., Bolan, N.S., Luo, J., Giltrap, D.L., Kim, D.G., Zaman, M., Tillman, R.W., 2013. Denitrification and $N_2O:N_2$ production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. *Science of The Total Environment* 465, 173-195.
- Samad, M.S., Biswas, A., Bakken, L.R., Clough, T.J., de Klein, C.A.M., Richards, K.G., Lanigan, G.J., Morales, S.E., 2016. Phylogenetic and functional potential links pH and N_2O emissions in pasture soils. *Scientific Reports* 6, 35990-35990.
- Schaufler, G., Kitzler, B., Schindlbacher, A., Skiba, U., Sutton, M.A., Zechmeister - Boltenstern, S., 2010. Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. *European Journal of Soil Science* 61, 683-696.
- Scott-Denton, L.E., Sparks, K.L., Monson, R.K., 2003. Spatial and temporal controls of soil respiration rate in a high-elevation, subalpine forest. *Soil biology & biochemistry* 35, 525-534.
- Šimek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science* 53, 345-354.
- Šimek, M., Jiřová, L., Hopkins, D.W., 2002. What is the so-called optimum pH for denitrification in soil? *Soil Biology and Biochemistry* 34, 1227-1234.
- Šimek, M., Virtanen, S., Křišťůfek, V., Simojoki, A., Yli-Halla, M., 2011. Evidence of rich microbial communities in the subsoil of a boreal acid sulphate soil conducive to greenhouse gas emissions. *Agriculture, Ecosystems & Environment* 140, 113-122.
- Šimek, M., Virtanen, S., Simojoki, A., Chroňáková, A., Elhottová, D., Křišťůfek, V., Yli-Halla, M., 2014. The microbial communities and potential greenhouse gas production in boreal acid sulphate, non-acid sulphate, and reedy sulphidic soils. *Science of The Total Environment* 466-467, 663-672.

- Staff., S.S., 2014. Keys to Soil Taxonomy, 12th ed. . USDA-Natural Resources Conservation Service, Washington, DC.
- Stevens, R.J., Laughlin, R.J., 1998. Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils. *Nutrient cycling in agroecosystems* 52, 131-139.
- Thomsen, J., K. , Torben, G., Raymond, P.C., 1994. Mass Spectrometric Studies of the Effect of pH on the Accumulation of Intermediates in Denitrification by *Paracoccus denitrificans*. *Appl Environ Microbiol* 60, 536-541.
- Van Cleemput, O., Patrick, W.H., McIlhenny, R.C., 1975. Formation of chemical and biological denitrification products in flooded soil at controlled pH and redox potential. *Soil Biology and Biochemistry* 7, 329-332.
- Wu, X., Sten, P., Engblom, S., Nowak, P., Österholm, P., Dopson, M., 2015. Impact of mitigation strategies on acid sulfate soil chemistry and microbial community. *The Science of the total environment* 526, 215.
- Xu, C., Wong, V.N.L., Reef, R.E., 2021. Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia. *Sci Total Environ* 763, 142949-142949.
- Yli-Halla, M., Virtanen, S., Regina, K., Österholm, P., Ehnvall, B., Uusi-Kämpä, J., 2020. Nitrogen stocks and flows in an acid sulfate soil. *Environmental Monitoring and Assessment* 192, 751-751.
- Yoshinari, T., Hynes, R., Knowles, R., 1977. Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. *Soil biology & biochemistry* 9, 177-183.
- Zelles, L., Stepper, K., Zsolnay, A., 1990. The effect of lime on microbial activity in spruce (*Picea abies* L.) forests. *Biology and Fertility of Soils* 9, 78-82.

Supplementary Materials:

1. Determination of carbonates

The carbonate content was measured and compared at the end of 56-day oxic (Phase Oxic I) and anoxic (Phase Anoxic III) incubations of the AS soil. For Phase Anoxic III incubation (Fig. S1), a separate set of 48 soil cores from AS soil were prepared as follows: 10 g of soil (dry weight basis) was packed into a 3.5-cm diameter, 12.5-cm high 120 mL glass bottles.

Two pre-tests were completed to determine the lime requirement in the Ap1, Bg1, BC and C horizons in the AS soil; 1) 15 mL of 0.05 M CaCO₃ solution was added to 10 g soil (dry mass basis) and 2) 15 mL of 0.1 M CaCO₃ solution was added to 10 g soil (dry mass basis). The lime requirement was obtained graphically from the curve describing pH as a function of CaCO₃ additions. Within 6 days, 15 mL of the 0.1 M CaCO₃ solution raised the soil pH to 7 in all horizons. Based on the pre-test, we added 10 mL of 0.125 M CaCO₃ as the low lime treatment, and 10 mL of 0.25 M CaCO₃ as the high lime treatment, into homogenized soils. At the beginning of Phase Anoxic III, the lime treatments were established in the same way as in Phase Oxic I by applying pure calcite (CaCO₃, EMSURE® Reag. Ph Eur) as low lime (12.5 mg g⁻¹) and high lime (25 mg g⁻¹) treatments to soil, and a control treatment was established with no added lime. This was based on two pre-tests.

These soil cores were incubated for 56 days under anaerobic conditions. The 48 glass bottles were capped with a butyl rubber septum, the headspace was evacuated and replaced with N₂, and the soils were incubated with the addition of extra MilliQ-ultrapure water (10 ml) to achieve anaerobic conditions.

Carbonates were measured at the end of incubation to determine the apparent fractional conversion of added carbonates (= the reacted proportion of added carbonates) in soil. Subsamples of soil were taken from bottles and oven-dried for 105 °C for 48h. Then, the dry soil samples were placed into a muffle furnace oven to remove organic matter at 550°C for 3h. Afterwards, a proxy for the carbonate C content in the inorganic residue was determined by Dumas combustion with a TCN-analyzer (Leco, CN828). All C in the inorganic residue was assumed to originate from CaCO₃. The apparent fractional conversion of added carbonates (F_L) (%) in the lime treatments was calculated using equation 1, where m_L is mass of end of carbonates in the lime treatment [g], m_c is mass of end of carbonates in the control treatment, m_a is the mass of added lime (CaCO₃).

$$F_L = \left(1 - \frac{m_L - m_c}{m_a}\right) \times 100\% \text{ (Equation 1)}$$

$$F_L = \left(1 - \frac{m_L - m_c}{m_a}\right) \times 100\% \text{ (Equation 1)}$$

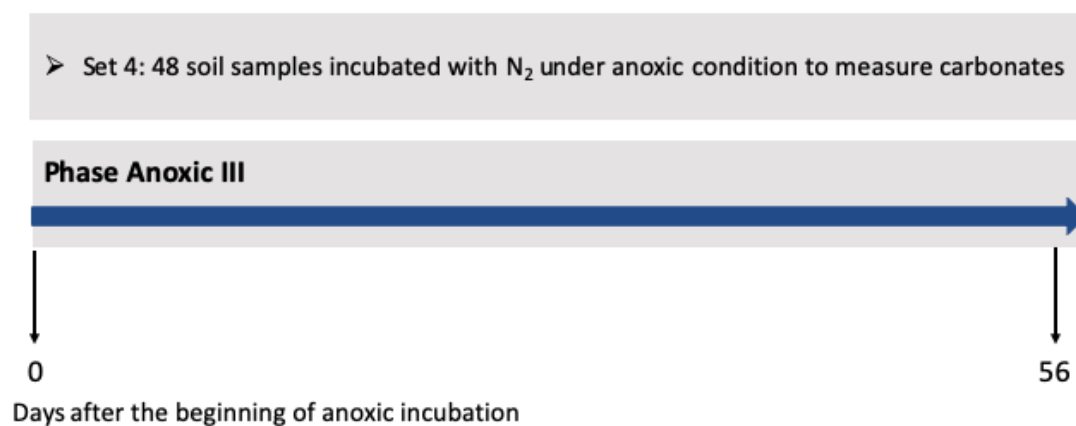


Fig.S1 Time sequence of the anoxic incubation (days 0 – 56). A total of 48 soil samples were incubated with 10 ml MQ water with N₂ under anoxic condition in the beginning of incubation (AS soil site x 4 horizons x 3 lime treatments x 4 replicates). The three lime treatments (CaCO₃) including unlimed control, low lime (12.5 mg g⁻¹) and high lime (25.0 mg g⁻¹) were applied in the beginning of the incubation.

2. Results

Soil carbonate content in the high lime treatment was higher than that in the low lime treatment in all horizons after Phase Oxidic I and Phase Anoxic III (Table S1). The fractional conversion of carbonates (F_L) was significantly higher in the low lime treatment than in the high lime treatment in the Ap1 during Phase Oxidic I and in the Bg1 during Phase Anoxic III ($p < 0.05$) (Table S2). Other differences in the F_L between low lime and high lime treatments were insignificant ($p > 0.05$) (Table S2). There was no significant difference in the fractional conversion of carbonates (F_L) between Phase Oxidic I and Phase Anoxic III in all treatments in all horizons ($p > 0.05$) (Table S2).

Tables S3 and S5 summarize the NO_3^- -N and NH_4^+ -N under lime treatments in different horizons in the AS soil and non-AS soil site during the Phase Oxidic I. Table S4 and S6 summarized the NO_3^- -N and NH_4^+ -N under lime treatments in different horizons in the AS soil and non-AS soil site during the Phase Anoxic II.

Fig. S2 summarized cumulative CO_2 production in AS and non-AS soils during Phase Anoxic II. Table S7 demonstrated the cumulative CO_2 production between the different lime treatments and horizons of AS and non-AS soils during Phase Anoxic II.

The cumulative N_2O production, cumulative $\text{N}_2\text{O} + \text{N}_2$ production and the $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ ratios during Phase Anoxic II (72 h) in the AS soil are shown in Fig. S2. In the AS soil, the largest cumulative anoxic N_2O production occurred in all treatments within the first 24 h of anoxia, followed by a decrease during the next 48 hr in the Ap1 and C horizons (Fig. S2a, j). In the Bg1 horizon, the cumulative N_2O production increased continuously over the 72 h duration of the incubation (Fig. S2d). In the BC horizon, the cumulative N_2O production in the lime treatments increased significantly during the first 48 hr, and then decreased towards the end of incubation at 72 h (Fig. S2g). The high lime treatment produced the largest cumulative $\text{N}_2\text{O} + \text{N}_2$ productions, indicating total denitrification, followed by the low lime treatment and control in all horizons (Fig. S2b, e, h, k). The product ratio of $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ decreased over the 72 h in all horizons and treatments (Fig. S2c, f, i, l). The product ratio of $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ in the control soil was higher than that in the lime treatments in the Ap1, Bg1 and C horizons (Fig. S2c, f, l).

The cumulative N_2O production, cumulative $\text{N}_2\text{O} + \text{N}_2$ production and the $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ ratios during Phase Anoxic II (72 h) in the non-AS soil were shown in Fig. S3. In the non-AS soil, the cumulative N_2O production increased over the 72-h duration of incubation in the Bg1, BC and C horizons (Fig. S3d, g, j), whereas a slight decrease was noticed in Ap1 after 48 h (Fig. S3a). Total denitrification ($\text{N}_2\text{O} + \text{N}_2$) increased in all horizons during the 72-h incubation (Fig. S3b, e, h, k). The product ratio of $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ in the control soil was higher than those in the lime treatments, and it decreased from 24h to 72h in all treatments and horizons (Fig. S3c, f, i, l).

Cumulative CO₂ production in the AS and non-AS soils during the Phase Anoxic II is shown in Fig. S4.

Table S1. Soil carbonate contents^a in AS soil site during Phase Oxidic I and Phase Anoxic III

Horizon		AS soil (Phase Oxidic I)			AS soil (Phase Anoxic III)		
		Control (g)	Low lime (g)	High lime (g)	Control (g)	Low lime (g)	High lime
Ap1	Start addition	0	0.125	0.25	0	0.125	0.25
	End	0.0031	0.0034	0.0049	0.0026	0.0029	0.0039
Bg1	Start addition	0	0.125	0.25	0	0.125	0.25
	End	0.0027	0.0028	0.0037	0.0023	0.0025	0.0044
BC	Start addition	0	0.125	0.25	0	0.125	0.25
	End	0.0019	0.0021	0.0031	0.0048	0.005	0.0056
C	Start addition	0	0.125	0.25	0	0.125	0.25
	End	0.0018	0.003	0.0042	0.0052	0.006	0.0071

^a The mass of carbonates as g (as CaCO₃) per a soil sample of 10 g (DM). Means \pm standard errors (n = 4).

Table S2. Fractional conversion of carbonate ^a (%) in the low and high lime treatments of AS soil during Phase Oxidic I and Phase Anoxic III

Horizons	Incubation	Low lime (%)	High lime (%)
Ap1	Phase Oxidic I	97.78 \pm 0.34 ^{aA}	93.72 \pm 0.15 ^{bA}
	Phase Anoxic III	97.75 \pm 0.48 ^{aA}	95.70 \pm 0.15 ^{aA}
Bg1	Phase Oxidic I	99.51 \pm 0.31 ^{aA}	96.72 \pm 0.13 ^{aA}
	Phase Anoxic III	98.98 \pm 0.35 ^{aA}	93.36 \pm 1.56 ^{bA}
BC	Phase Oxidic I	99.39 \pm 0.67 ^{aA}	96.09 \pm 0.34 ^{aA}
	Phase Anoxic III	98.88 \pm 0.13 ^{aA}	97.70 \pm 0.12 ^{aA}
C	Phase Oxidic I	92.56 \pm 0.89 ^{aA}	92.37 \pm 0.24 ^{aA}
	Phase Anoxic III	94.89 \pm 0.23 ^{aA}	93.76 \pm 0.34 ^{aA}

^a Means \pm standard errors (n = 4). The fractional conversion of carbonates represents the apparent relative mass loss (reacted part) of added carbonates in soil. Different small letters within each row denote significant differences between the lime treatments. Different capital letters within a given lime treatment and horizon denote significant differences between Phase Oxidic I and Phase Anoxic III (one-way ANOVA, Tukey test, p<0.05).

Table S3. Net changes of mineral N forms^a in the different lime treatments and horizons of AS soil and non-AS soils during Phase Oxid I (56 days) (N mg kg⁻¹)

Horizon	AS soil			Non-AS soil		
	Control	Low lime	High lime	Control	Low lime	High lime
a) $\Delta \text{NO}_3^- \text{-N}$						
Ap1	-16.8 ± 1.4	-15.2 ± 0.8	-15.9 ± 1.4	-16.5 ± 1.21	-15.5 ± 1.12	-14.6 ± 1.1
Bg1	-1.6 ± 0.7	-7.4 ± 0.2	-7.0 ± 0.2	-1.7 ± 0.05	-1.1 ± 0.004	-0.3 ± 0.03
BC	0.7 ± 0.07	0.6 ± 0.10	0.4 ± 0.1	0.6 ± 0.02	0.3 ± 0.04	1.3 ± 0.1
C	0.6 ± 0.02	0.6 ± 0.02	0.5 ± 0.01	0.2 ± 0.05	0.7 ± 0.02	0.6 ± 0.1
b) $\Delta \text{NH}_4^+ \text{-N}$						
Ap1	66.8 ± 3.8	83.2 ± 3.7	90.4 ± 0.4	39.2 ± 1.6	46.9 ± 2.04	53.6 ± 4.3
Bg1	11.6 ± 1.0	27.4 ± 1.2	15.0 ± 0.8	8.9 ± 1.4	6.1 ± 0.49	3.9 ± 0.05
BC	10.7 ± 1.1	10.6 ± 0.3	19.4 ± 1.1	-1.6 ± 0.1	-2.7 ± 0.06	-1.8 ± 0.2
C	7.7 ± 0.9	14.6 ± 1.5	7.9 ± 0.9	1.7 ± 0.3	1.9 ± 0.16	1.6 ± 0.1
c) $\Delta \text{N}_{\text{min}}$						
Ap1	50.1 ± 4.8	68.0 ± 4.5	74.5 ± 1.8	22.7 ± 1.8	31.4 ± 3.1	38.9 ± 5.4
Bg1	10.0 ± 1.7	20.0 ± 1.2	8.1 ± 0.9	7.1 ± 1.5	4.9 ± 0.5	3.6 ± 0.08
BC	11.4 ± 1.1	11.2 ± 1.3	19.8 ± 1.2	-0.9 ± 0.1	-2.4 ± 0.1	-0.4 ± 0.4
C	8.3 ± 0.9	15.2 ± 1.5	8.4 ± 0.9	2.1 ± 0.3	2.7 ± 0.1	2.2 ± 0.2

^a Means ± standard errors (n = 4). Difference between the N content at the end and before of Phase Oxid I. $\text{N}_{\text{min}} = \text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N}$

Table S4. Net changes of mineral N forms^a in the different lime treatments and horizons of AS and non-AS soils during Phase Anoxic II (72 h) (N mg kg⁻¹)

Horizon	AS soil			Non-AS soil		
	Control	Low lime	High lime	Control	Low lime	High lime
a) $\Delta \text{NO}_3^- \text{-N}$ (without C_2H_2)						
Ap1	-10.8 ± 0.3	-11.2 ± 0.5	-10.6 ± 0.1	-3.9 ± 0.2	-5.2 ± 0.4	-6.0 ± 1.2
Bg1	-1.7 ± 0.09	-0.04 ± 0.005	-0.1 ± 0.003	-0.8 ± 0.05	-1.2 ± 0.05	-2.79 ± 0.3
BC	-0.2 ± 0.02	-0.6 ± 0.03	-0.08 ± 0.003	-0.8 ± 0.09	-0.2 ± 0.02	-1.8 ± 0.05
C	-0.1 ± 0.01	-0.3 ± 0.03	-0.2 ± 0.02	-0.2 ± 0.02	-0.5 ± 0.03	-0.5 ± 0.02
b) $\Delta \text{NH}_4^+ \text{-N}$ (without C_2H_2)						
Ap1	4.7 ± 1.2	21.3 ± 1.1	52.6 ± 0.9	4.4 ± 0.05	-33.6 ± 1.4	-38.0 ± 3.1
Bg1	1.0 ± 2.0	5.6 ± 0.4	32.9 ± 0.04	-3.9 ± 0.8	-1.7 ± 0.09	-1.3 ± 0.05
BC	-1.0 ± 0.002	-2.1 ± 0.5	0.9 ± 0.1	0.7 ± 0.07	2.3 ± 0.4	1.3 ± 0.1
C	18.4 ± 0.2	16.9 ± 1.6	41.9 ± 1.1	3.7 ± 0.4	1.8 ± 0.1	2.8 ± 0.02
c) $\Delta \text{N}_{\text{min}}$ (without C_2H_2)						
Ap1	-6.1 ± 1.5	10.1 ± 1.6	41.9 ± 1.1	0.4 ± 0.03	-38.8 ± 1.8	-44.0 ± 4.2
Bg1	-0.8 ± 0.2	5.5 ± 0.4	32.7 ± 0.04	-4.7 ± 0.9	-2.8 ± 0.08	-4.1 ± 0.3
BC	-1.2 ± 0.02	-2.7 ± 0.5	0.9 ± 0.1	-0.01 ± 0.002	2.1 ± 0.4	-0.5 ± 0.05
C	18.3 ± 0.2	16.6 ± 1.7	41.6 ± 1.1	3.5 ± 0.4	1.2 ± 0.2	2.2 ± 0.03
d) $\Delta \text{NO}_3^- \text{-N}$ (with C_2H_2)						
Ap1	-10.9 ± 0.4	-11.7 ± 0.5	-11.1 ± 0.3	-4.0 ± 0.4	-3.8 ± 0.4	-5.5 ± 1.1
Bg1	-2.9 ± 0.7	-0.08 ± 0.001	-0.2 ± 0.2	-2.9 ± 0.4	-2.5 ± 0.07	-2.7 ± 0.06
BC	-0.4 ± 0.1	-0.6 ± 0.04	-0.1 ± 0.07	-0.8 ± 0.07	-0.5 ± 0.1	-1.4 ± 0.2
C	-0.2 ± 0.03	-0.4 ± 0.03	-0.3 ± 0.005	-0.1 ± 0.02	-0.6 ± 0.02	-0.5 ± 0.04
e) $\Delta \text{NH}_4^+ \text{-N}$ (with C_2H_2)						
Ap1	20.6 ± 0.6	37.8 ± 1.1	-5.8 ± 1.5	-19.4 ± 0.03	-26.6 ± 1.5	-32.7 ± 3.2
Bg1	3.2 ± 0.1	8.7 ± 0.4	41.9 ± 0.5	-1.2 ± 0.3	-1.9 ± 0.2	-1.7 ± 0.08
BC	3.8 ± 0.2	11.0 ± 0.6	11.6 ± 0.5	4.3 ± 0.3	3.2 ± 0.2	3.8 ± 0.4
C	25.2 ± 1.4	23.2 ± 2.5	6.9 ± 0.6	0.07 ± 0.01	2.1 ± 0.2	5.9 ± 0.3
f) $\Delta \text{N}_{\text{min}}$ (with C_2H_2)						
Ap1	9.7 ± 0.8	26.1 ± 0.5	-16.8 ± 1.8	-23.5 ± 0.4	-30.5 ± 1.6	-38.2 ± 4.3
Bg1	0.3 ± 0.07	8.6 ± 0.4	41.7 ± 0.2	-4.1 ± 0.7	-4.4 ± 0.2	-4.4 ± 0.1
BC	3.3 ± 0.4	10.3 ± 0.5	11.4 ± 0.4	3.5 ± 0.2	2.6 ± 0.1	2.4 ± 0.2
C	25.1 ± 1.4	22.7 ± 2.5	6.5 ± 0.6	-0.04 ± 0.005	1.5 ± 0.2	5.3 ± 0.2

^a Means ± standard errors (n = 4). Difference between the N content at the end and before of Phase Anoxic II. $\text{N}_{\text{min}} = \text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N}$

Table S5. Mineral N contents^a under lime treatments in different horizons in the AS soil and non-AS soil site at the end of the Phase Oxid I (N mg kg⁻¹)

Horizon		AS soil			Non-As soil		
		Control	Low lime	High lime	Control	Low lime	High lime
a) NO₃⁻-N							
Ap1	End	10.9 ± 0.5	12.6 ± 0.6	11.9 ± 0.2	4.3 ± 0.4	5.3 ± 0.4	6.1 ± 1.3
Bg1	End	6.1 ± 1.1	0.3 ± 0.006	0.7 ± 0.1	3.9 ± 0.7	4.6 ± 0.07	5.4 ± 0.5
BC	End	0.8 ± 0.2	0.7 ± 0.21	0.5 ± 0.01	2.7 ± 0.06	2.4 ± 0.01	3.4 ± 0.6
C	End	0.6 ± 0.03	0.6 ± 0.02	0.5 ± 0.01	0.4 ± 0.02	0.8 ± 0.02	0.7 ± 0.1
b) NH₄⁺-N							
Ap1	End	69.0 ± 5.6	85.3 ± 4.4	92.5 ± 0.1	41.0 ± 2.6	48.7 ± 2.5	55.4 ± 5.0
Bg1	End	15.4 ± 1.0	31.2 ± 2.2	18.8 ± 0.9	9.3 ± 2.3	6.5 ± 0.2	4.4 ± 0.07
BC	End	21.5 ± 0.8	21.3 ± 1.8	30.1 ± 3.1	1.9 ± 0.2	0.9 ± 0.1	1.8 ± 0.3
C	End	20.98 ± 0.4	27.8 ± 4.1	21.1 ± 1.4	2.0 ± 0.3	2.2 ± 0.2	1.8 ± 0.2
c) N_{min}							
Ap1	End	80.0 ± 6.0	97.9 ± 5.0	104.4 ± 0.3	45.3 ± 3.0	54.0 ± 2.9	61.5 ± 5.2
Bg1	End	21.5 ± 2.1	31.5 ± 2.2	19.5 ± 1.1	13.2 ± 3.0	11.1 ± 0.3	9.7 ± 0.5
BC	End	22.2 ± 1.0	22.0 ± 2.0	30.6 ± 3.1	4.7 ± 0.3	3.3 ± 0.1	5.2 ± 0.9
C	End	21.6 ± 0.4	28.4 ± 4.2	21.6 ± 1.4	2.3 ± 0.4	3.0 ± 0.2	2.6 ± 0.3

^a

Means ± standard errors (n = 4). N_{min} = NO₃⁻-N + NH₄⁺-N

Table S6. Mineral N contents^a under lime treatments in different horizons in the AS soil and non-AS soil site at the end of the Phase Anoxic II (N mg kg⁻¹)

Horizon		AS soil			Non-As soil		
		Control	Low lime	High lime	Control	Low lime	High lime
a) NO ₃ ⁻ -N (without C ₂ H ₂)							
Ap1	End	0.1 ± 0.02	1.4 ± 0.2	1.2 ± 0.01	0.34 ± 0.05	0.04 ± 0.005	0.08 ± 0.01
Bg1	End	4.3 ± 0.1	0.3 ± 0.04	0.6 ± 0.05	3.08 ± 0.52	3.40 ± 0.007	2.57 ± 0.32
BC	End	0.6 ± 0.01	0.1 ± 0.02	0.41 ± 0.009	1.97 ± 0.49	2.12 ± 0.003	1.63 ± 0.06
C	End	0.5 ± 0.02	0.3 ± 0.05	0.21 ± 0.05	0.19 ± 0.02	0.26 ± 0.03	0.19 ± 0.02
b) NH ₄ ⁺ -N (without C ₂ H ₂)							
Ap1	End	73.7 ± 2.9	106.6 ± 26.7	145.1 ± 2.0	45.5 ± 4.4	15.1 ± 2.6	17.4 ± 2.6
Bg1	End	16.4 ± 3.9	36.8 ± 3.1	51.7 ± 4.8	5.4 ± 0.7	4.8 ± 0.03	3.1 ± 0.07
BC	End	20.4 ± 3.1	19.1 ± 1.9	31.1 ± 2.7	2.7 ± 0.6	3.3 ± 0.5	3.1 ± 0.2
C	End	39.4 ± 0.4	44.8 ± 5.3	63.1 ± 0.3	5.7 ± 0.5	4.0 ± 0.09	4.7 ± 0.08
c) N _{min} (without C ₂ H ₂)							
Ap1	End	73.9 ± 3.0	108.1 ± 26.8	146.4 ± 2.0	45.8 ± 4.5	15.1 ± 2.6	17.5 ± 2.6
Bg1	End	20.7 ± 3.9	37.1 ± 3.2	52.3 ± 4.9	8.5 ± 1.2	8.1 ± 0.04	5.7 ± 0.4
BC	End	21.0 ± 3.2	19.3 ± 2.0	31.5 ± 2.8	4.7 ± 0.7	5.4 ± 0.4	4.7 ± 0.3
C	End	39.9 ± 0.4	45.1 ± 5.4	63.3 ± 0.4	5.9 ± 0.5	4.3 ± 0.1	4.8 ± 0.1
d) NO ₃ ⁻ -N (with C ₂ H ₂)							
Ap1	End	0.08 ± 0.01	0.8 ± 0.06	0.8 ± 0.07	0.2 ± 0.01	1.4 ± 0.08	0.5 ± 0.03
Bg1	End	3.1 ± 0.3	0.2 ± 0.07	0.5 ± 0.3	1.0 ± 0.03	2.0 ± 0.09	2.6 ± 0.08
BC	End	0.3 ± 0.05	0.05 ± 0.05	0.3 ± 0.08	1.9 ± 0.1	1.8 ± 0.2	2.1 ± 0.05
C	End	0.4 ± 0.06	0.2 ± 0.06	0.1 ± 0.01	0.2 ± 0.03	0.2 ± 0.03	0.2 ± 0.05
e) NH ₄ ⁺ -N (with C ₂ H ₂)							
Ap1	End	89.6 ± 5.8	123.1 ± 3.3	86.7 ± 3.1	21.6 ± 2.5	22.1 ± 0.5	22.6 ± 4.4
Bg1	End	18.6 ± 1.2	39.9 ± 1.1	60.7 ± 0.3	8.0 ± 0.7	4.6 ± 0.3	2.7 ± 0.7
BC	End	25.3 ± 1.1	32.3 ± 1.2	41.7 ± 3.8	6.3 ± 0.6	4.1 ± 0.3	5.6 ± 0.7
C	End	46.3 ± 2.2	51.1 ± 5.3	28.1 ± 2.8	2.1 ± 0.7	4.3 ± 0.5	7.7 ± 0.3
f) N _{min} (with C ₂ H ₂)							
Ap1	End	89.7 ± 5.8	124.0 ± 3.3	87.5 ± 3.0	21.8 ± 2.5	23.5 ± 0.5	23.2 ± 4.5
Bg1	End	21.7 ± 1.5	40.1 ± 1.2	61.3 ± 0.7	9.0 ± 0.7	6.6 ± 0.4	5.3 ± 0.8
BC	End	25.6 ± 1.1	32.4 ± 1.2	42.1 ± 3.9	8.2 ± 0.7	5.9 ± 0.5	7.6 ± 0.7
C	End	46.6 ± 2.2	51.2 ± 5.3	28.1 ± 2.8	2.3 ± 0.7	4.5 ± 0.5	7.9 ± 0.4

a

Means ± standard errors (n = 4). N_{min} = NO₃⁻-N + NH₄⁺-N

Table S7. Cumulative CO₂ production^a between the different lime treatments and horizons of AS and non-AS soils during Phase Anoxic II (72 h) (mg CO₂-C kg⁻¹)

Soil		Control	Low lime	High lime
AS soil	Ap1	27.8 ± 4.7 ^{bA}	30.2 ± 1.0 ^{aA}	31.1 ± 1.3 ^{aA}
	Bg1	6.3 ± 0.8 ^{bD}	15.2 ± 1.8 ^{aC}	16.2 ± 0.4 ^{aB}
	BC	14.2 ± 1.2 ^{bC}	18.2 ± 2.2 ^{aB}	18.9 ± 0.5 ^{aB}
	C	17.1 ± 3.9 ^{bB}	32.5 ± 2.9 ^{aA}	31.4 ± 2.7 ^{aA}
Non-AS soil	Ap1	37.9 ± 7.1 ^{aA}	32.3 ± 2.2 ^{bA}	37.2 ± 4.4 ^{aA}
	Bg1	6.9 ± 0.2 ^{bB}	8.7 ± 0.3 ^{aC}	8.5 ± 0.3 ^{aC}
	BC	9.0 ± 2.1 ^{aB}	9.2 ± 0.5 ^{aC}	8.7 ± 0.3 ^{aC}
	C	7.3 ± 0.5 ^{bB}	12.3 ± 0.3 ^{aB}	11.1 ± 0.2 ^{aB}

^a Means ± standard errors (n = 4). Different small letters within each row represent significant differences between the lime treatments. Different capital letters within each column represent significant differences between different soil horizons (one-way ANOVA, Tukey test, p<0.05).

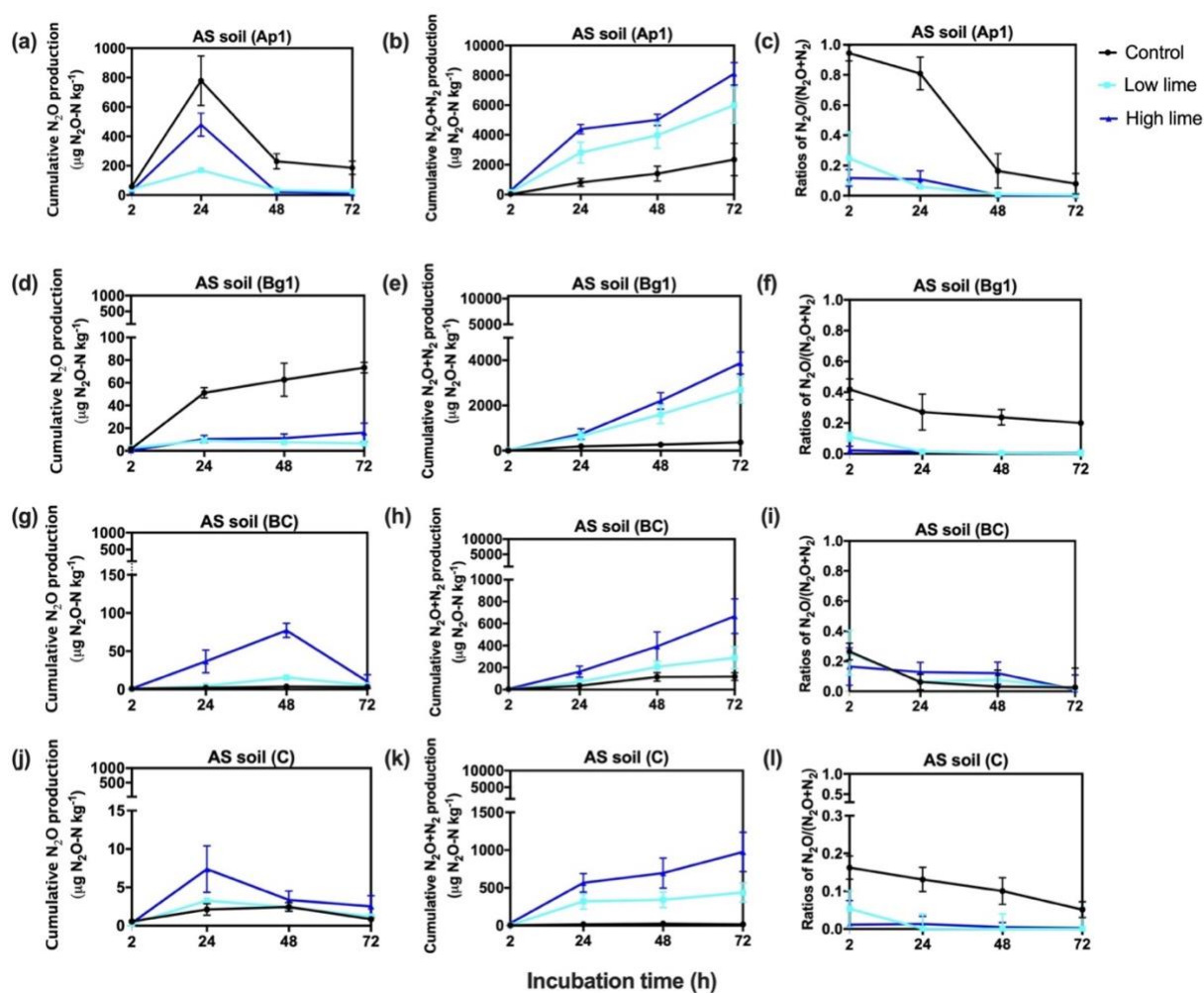


Figure. S2. Cumulative N_2O production, cumulative $\text{N}_2\text{O}+\text{N}_2$ production and the $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ ratios in Ap1 (a, b, c), Bg1 (d, e, f), BC (g, h, i) and C (j, k, l) horizons during Phase Anoxic II (72 h) in the AS soil. Vertical bars denote the standard error of mean ($n=4$).

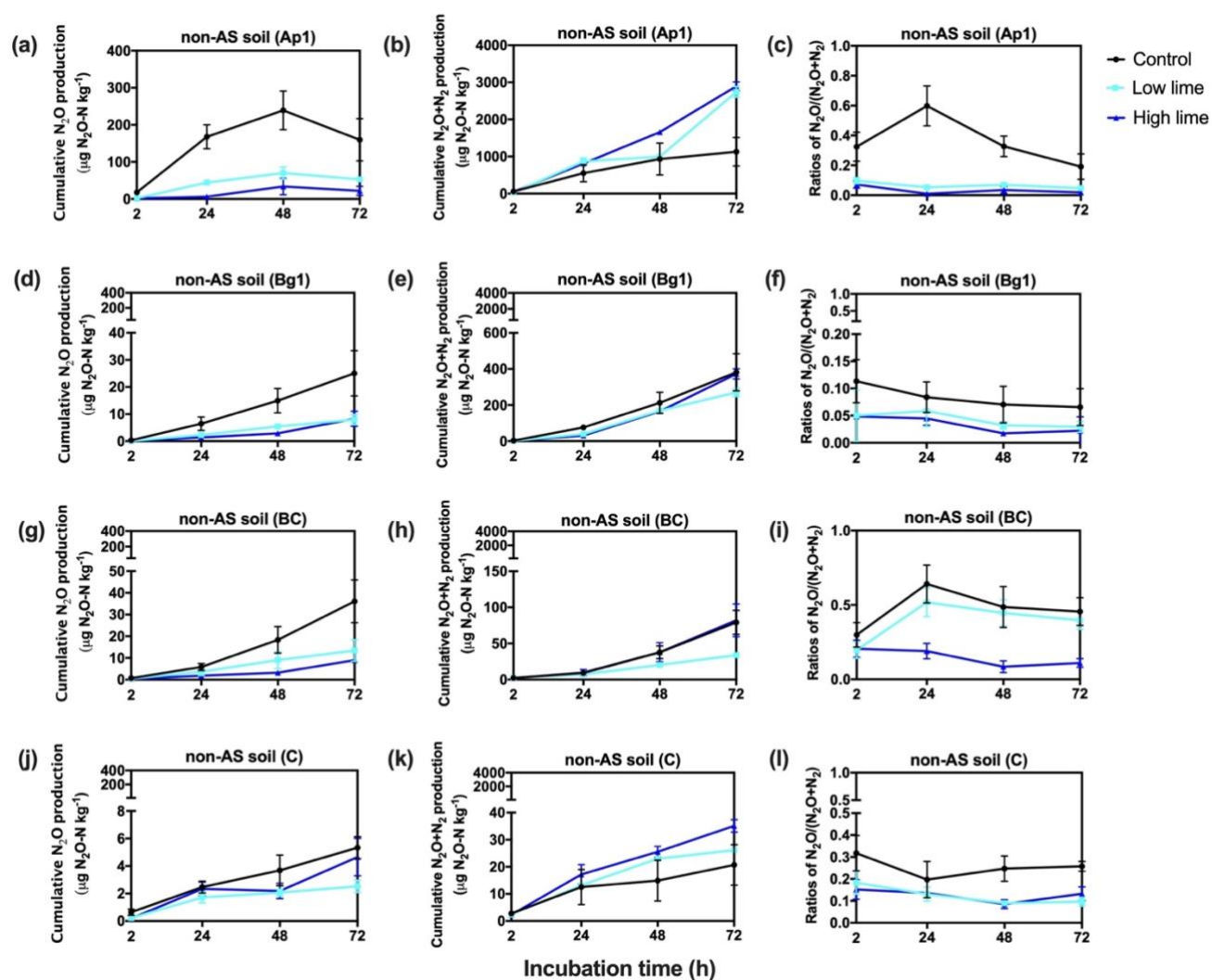


Figure. S3. Cumulative anoxic N_2O production, cumulative N_2O+N_2 production and the $N_2O/(N_2O+N_2)$ ratios in Ap1 (a, b, c), Bg1 (d, e, f), BC (g, h, i) and C (j, k, l) horizons during Phase Anoxic II (72 h) in the non-AS soil. Vertical bars denote the standard error of mean (n=4).

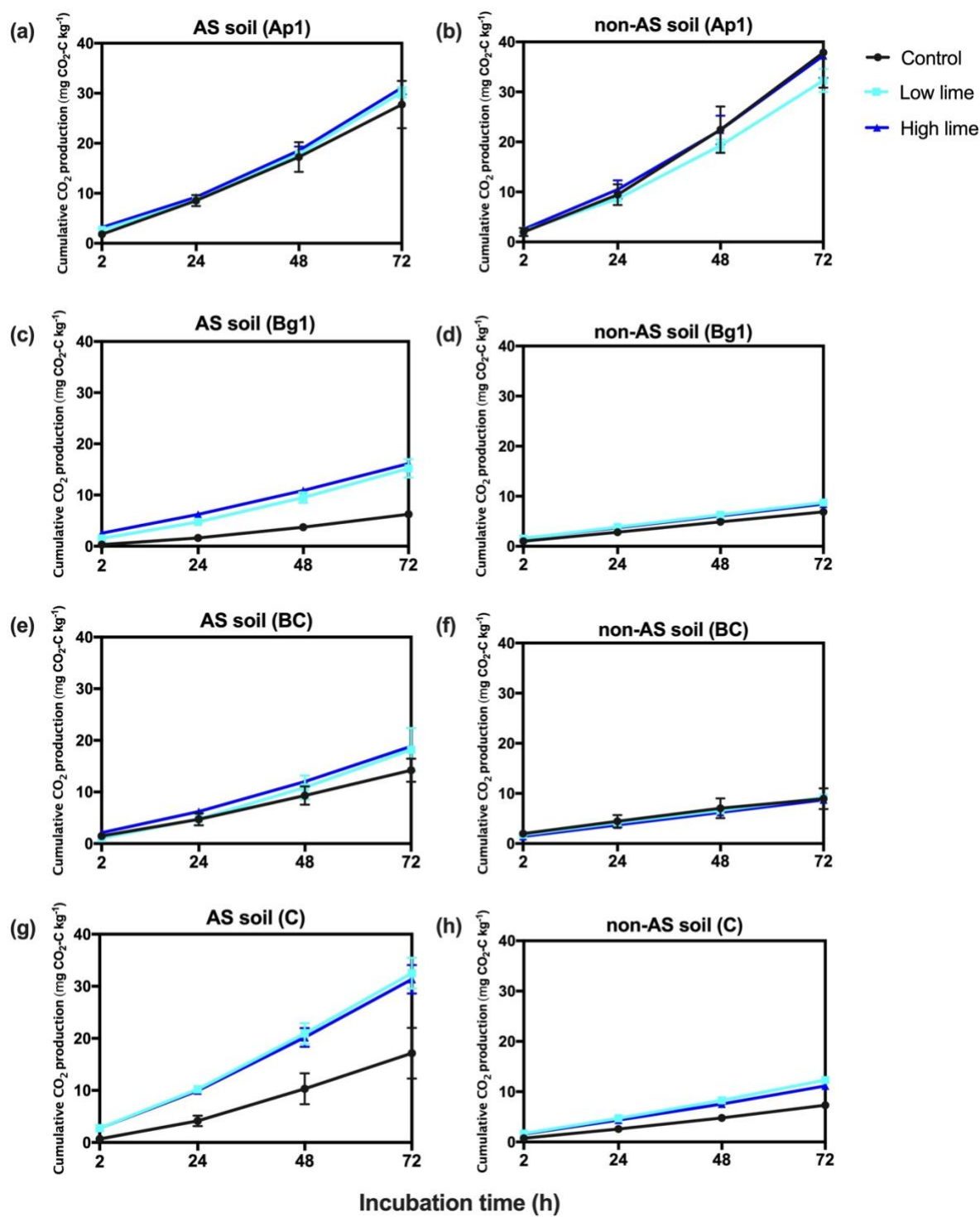


Figure. S4. Cumulative CO₂ production in Ap1 (a, b), Bg1 (c, d), BC (e, f) and C (g, h) horizons in the AS and non-AS soils during the Phase Anoxic II (72h). Values are means and standard errors of four replicates (n=4).

Chapter 5. Effect of lime and inundation on greenhouse gas emissions from temperate coastal wetlands in southern Australia

Effects of lime and inundation on greenhouse gas emissions from temperate coastal wetlands in southern Australia

Chang. Xu ^{1,2}, Vanessa N.L. Wong ¹

¹School of Earth, Atmosphere and Environment, Monash University, Wellington Road, Clayton, VIC 3800, Australia.

²Corresponding author: chang.xu@monash.edu

5.1 Abstract

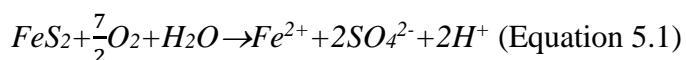
Coastal acid sulfate soils (ASS) contain large amounts of organic matter which can be potential sources of greenhouse gases (GHGs). Recent liming methods can reduce the acidity of ASS in the field. However, the effects of liming and inundation together on GHGs are still poorly known. We measured the effects of brackish water inundation and liming on GHGs from *Apium graveolens* (AG) in coastal wetland. The limed and non-limed soils were incubated under dry, flooded, and wet-dry cycles conditions of 14 d each for 42 days. CO₂, CH₄, and N₂O emissions were collected by closed chamber method and measured with gas chromatography. Based on CO₂-eq, the total GHG emissions were higher in limed soils than non-limed soils. Inundation decreased the total CO₂ and N₂O emissions and increased the CH₄ emissions. CH₄ was the dominant GHG in the total CO₂-eq emissions in the flooded treatment. Lime improved the soil pH and decreased titratable actual acidity (TAA), net acidity and heavy metals (Al, Fe, Mn) in most horizons under dry and wet-dry cycle treatments. The net acidity and heavy trace metals decreased following flooded treatment. Overall, the inundation and lime treatments can reduce the net acidity and trace metals in ASS. However, lime needs to carefully applied in coastal ASS due to the increased CO₂ emissions derived from the dissolution of CaCO₃.

Key words: coastal acid sulfate soils, lime, inundation, greenhouse gases, acidity

5.2 Introduction

Acid sulfate soils (ASS) are defined as soils or sediments containing oxidizable, or partly oxidized sulfide minerals (Melville and White, 1993; Pons, 1973). These sulfide minerals are mainly in the form of pyrite (FeS₂). Other forms of sulfide minerals include iron monosulfide (FeS) and greigite (Fe₃S₄) (Dent, 1986). The formation of iron sulphides in coastal environments generally requires sufficient Fe³⁺ iron from the sediments, SO₄²⁻ from seawater, organic matter and an anaerobic environment (Berner, 1984; Pons, 1973).

ASS is relatively harmless when in an undisturbed state, but when iron sulfides are disturbed and subsequently exposed to the atmosphere such as due to changes in water level, isostatic change of the lithosphere, or artificial drainage for agriculture, large quantities of sulfuric acid are released (Boman et al., 2010a; Burton et al., 2006b). Pyrite reacts with oxygen from the atmosphere and releases sulfuric acid according to the following reaction (Equation 5.1):



Fe^{2+} can then be oxidized to Fe^{3+} at low soil pH (<4), undergo hydrolysis and precipitate as ferric iron oxide and oxyhydroxide minerals such as goethite and ferrihydrite (Mosley et al., 2014b). Soil acidification can also release Al, Fe, Mn, Zn, Ni into rivers, groundwaters or in porewaters on the adjacent floodplain (Österholm and Åström, 2002; Simpson et al., 2010). Van den Berg et al. (1998) found that metal precipitation (Fe and Mn oxides) occurred when groundwater levels decreased and FeS_2 oxidized in an estuary in summer, with sulfate reduction occurring following inundation in winter. Burton et al. (2006d) also reported that iron sulfide oxidation and associated acidification contributed to the release of Fe, Al, As and other trace metals in estuarine sediments.

When CASS are subject to inundation, Fe^{3+} and SO_4^{2-} reduction processes are promoted (Burton et al., 2011; Johnston et al., 2014). The reductive processes can decrease acidity, produce alkalinity and stimulate the reformation of sulfidic minerals like FeS_2 and FeS (Keene et al., 2011; Powell and Martens, 2005). Johnston et al. (2009b) observed that there was a significant decrease in soil exchangeable acidity and increase in soil pH at the East Trinity wetland in Australia after tidal inundation.

Coastal acid sulfate soils (CASS) contain high organic carbon contents, particularly when they are under flooded conditions (Šimek et al., 2011). A large amount of organic matter in CASS can facilitate large emissions of CO_2 and CH_4 . The accumulation of mineral nitrogen can also lead to the release of N_2O (Allen et al., 2007; Livesley and Andrusiak, 2012). The GHG emissions in these coastal environments are mainly affected by the water table and organic matter content (Livesley and Andrusiak, 2012; Reddy and DeLaune, 2008). Following depletion of O_2 , anaerobic decomposition processes begin to dominate and follows the sequence of denitrification, Mn reduction, Fe^{3+} reduction, SO_4^{2-} reduction and methanogenesis (Ponnamperuma, 1972).

N_2O is produced in soils mainly by nitrification and denitrification (Davidson et al., 2000; Wrage et al., 2001). Nitrification is the microbial transformation of NH_4^+ to NO_3^- by ammonia oxidising bacteria under aerobic conditions, producing N_2O as a by-product (Kowalchuk and Stephen, 2001). Denitrification is the microbial transformation of NO_3^- to N_2 by denitrifying bacteria under anaerobic soil conditions, producing N_2O as an intermediate product (Knowles, 1982).

Soil pH has been considered an important variable of N transformations and affects the end product of denitrification. Bååth and Arnebrant (1994) found the soil pH had an impact on N₂O production as the pH could influence the availability of carbon source to the microbes. Previous studies have demonstrated that the ratio of N₂O/N₂ increased with decreased pH (Samad et al., 2016a; Šimek and Cooper, 2002). The explanation is that the low soil pH inhibited reduction of N₂O to N₂ by preventing the activity of the enzyme N₂O reductase (Šimek et al., 2002; Thomsen et al., 1994). Increased soil pH often stimulates the reduction of N₂O to N₂ due to the enhanced activity of N₂O reductase (Liu, 2010). The mitigation of acidity to decrease GHG emissions in CASS mainly focuses on two methods: 1) restricting the oxidation of sulfide minerals by keeping ASS permanently inundated to avoid acidity formation, or 2) neutralisation of acidity and lower the GHG emissions with the application of alkaline agents such as lime.

Lime treatments like calcium carbonate (CaCO₃) have been widely applied to manage acidity issues and reduce heavy metal mobilisation (Adams and Adams, 1983; Johnston et al., 2012). Dalhem et al. (2019) found that CaCO₃ can raise soil pH, lower acidity and lower the concentrations of Fe and Al in CASS in western Finland. Liming has also been proposed as a GHG mitigation strategy as increasing soil pH can reduce N₂O emissions (McMillan et al., 2016; Russenes et al., 2016). Earlier studies showed that limed soils can lower N₂O emissions because the increase in soil pH can stimulate the reduction of N₂O to N₂ by N₂O reductase, which is more sensitive at higher soil pH (Liu et al., 2014; Šimek and Cooper, 2002). Zaman et al. (2008) indicated liming may enhance denitrification while reducing the N₂O/N₂ product ratio in pasture soils while others have shown that lime can increase N₂O emissions (Higgins et al., 2013). Baggs et al. (2011) observed that the effect of liming was to stimulate both nitrification and denitrification and therefore increase the N₂O emissions from both.

The aim of this chapter is to identify the effects of lime addition and inundation treatments on greenhouse gas emissions (GHGs), net acidity and heavy metal mobility in a CASS environment.

5.3 Material and methods

5.3.1 Site description and sampling

The sampling site was the Aire River floodplain, which was located in the Otway Ranges to the west of Apollo Bay in south-western Victoria (38°47'43.1" S, 143°28'37" E), Australia. The Aire River is one of the largest rivers in south-western Victoria and enters the sea via a large estuarine lake complex west of Cape Otway. The Aire River estuary mouth is intermittently closed to the sea (CCMA, 2014). The Aire River region has an average annual rainfall of 894.8 mm, ranging from 41.6mm (February) to 106.4mm (July).

The mean annual temperature is 17.3°C varying from 13 °C (July) to 21.5°C (January) (Bureau of Meteorology (BOM), 2019).

The sampling site (38°46'01.6" S, 143°28'09.9" E; +3 m AHD) was grazed by cattle areas and drained by surface drains. The vegetation at the sites was dominated by *Paspalum distichum* which is a fast-growing grass. A total of 24 intact soil cores were collected from the top 20 cm of soil by pushing down a PVC tube (h= 40 cm, d=10 cm) sharpened at the bottom. All the plant material was removed from the soil surface by scalping prior to core collection. The cores were excavated and capped at the bottom, sealed with parafilm and plastic wrap for transport. The cores were kept cool at 4°C until analysis. Additional bulk soil from the 0-5 cm, 5-10 cm, and 10-20 cm soil layers from each site were sampled for characterisation, with one subsample placed in to a freezer at -80 °C, and one sub sample air-dried and sieved at 2 mm until further analysis (Rayment and Lyons, 2011).

5.3.2 Incubation Experiment

Three pre-tests were done to determine the lime requirement in the 0-5 cm, 5-10 cm and 10-20 cm soil depths; 1) 0.1 g CaCO₃ was added to 10 g soil (dry mass basis), 2) 0.2 g CaCO₃ was added to 10 g soil (dry mass basis) 3) 0.25 g CaCO₃ was added to 10 g soil (dry mass basis). All the lime was mixed with homogenized soils. The lime requirement was obtained graphically from the curve describing pH as a function of CaCO₃ additions over a 5 day treatment period. Within 5 days, 0.25 g CaCO₃ raised the 10g soil pH to 7 in all horizons. Based on the pre-test, we selected 0.25g CaCO₃/10g dry soil in the lime treatment.

Soils were incubated in the PVC tubes they were sampled in (d=10cm, h=40cm). The top 5 cm of field moist soils were amended with these doses of CaCO₃ which were incorporated into the soil under aerobic conditions for 2 days to stabilize the soil pH. The lime was added based on the weight of soil in the PVC tubes. The soils (with and without CaCO₃) were then incubated under dry, flooded, and wet-dry cycles conditions of 14 d each for a total of 42 days. The dry treatment had no water added and soil moisture content decreased under aerobic conditions. In the flooded treatment, the soils were flooded with Aire River water (Table. 5.1) which was maintained at 5 cm above the soil surface and the volume of the overlying Aire River water was 392.5 cm³ for the duration of the experiment. There were three wet-dry cycles. In the wet-dry cycle treatment, the soils had a starting water filled pore space (WFPS) of 100% (Equation 5.2 and 5.3) and were further incubated for 14 d, after which they were rewetted to 100% WFPS at the beginning of the second and third cycles. 100% WFPS in the soil cores were achieved by weighing the soil cores and adding Aire River water. All soil cores were incubated at a constant room temperature of 21 °C. There were four replicates for each treatment.

$$\text{WFPS} = (\theta/n)100 \text{ (Equation 5.2)}$$

where θ ($\text{m}^3 \text{m}^{-3}$) is volumetric soil water content and n ($\text{m}^3 \text{m}^{-3}$) is soil porosity, where

$$n = 1 - (\text{dry bulk density/average soil particle density}) \text{ (Equation 5.3)}$$

and an average soil particle density of 2.65 Mg m^{-3} was assumed.

GHG (CH_4 , CO_2 and N_2O) emissions of each soil core were collected at Day 1, 3, 6, 10, 13, 17, 20, 24, 27, 31, 34, 38, 42. We sampled the gas emissions at 0 and 10 min in duplicate after closing the chamber. Gas emissions were collected using a 25-ml gas-tight syringe (SGE, 25MDR-LL-GT) within 10 seconds and transferred into pre-evacuated 12-ml Exetainer[®] vials with silicon septa (Labco, UK). The GHG concentrations were measured using an Agilent 7890 gas chromatograph (GC). The flux rates, F_{CH_4} , F_{CO_2} , $F_{\text{N}_2\text{O}}$, were calculated using Equation 5.4 and 5.5. All CH_4 , CO_2 , N_2O flux rates were corrected for air temperature during the measurement and presented as $[\mu\text{g m}^{-2} \text{h}^{-1}]$

$$F_{\text{CH}_4 \text{ or } \text{CO}_2 \text{ or } \text{N}_2\text{O}} = \frac{b \times V_{\text{CH}} \times \text{MW} \times 60 \times 10^6}{A_{\text{CH}} \times \text{MV}_{\text{corr}} \times 10^9} \text{ (Equation 5.4)}$$

where A_{CH} is the basal area of the measuring chamber [m^2]; b is increase in concentration [ppb/min]; $\text{MW}_{\text{CH}_4\text{-C}}$ is the molecular weight of $\text{CH}_4\text{-C}$ [12g/mol]; $\text{MW}_{\text{CO}_2\text{-C}}$ is the molecular weight of $\text{CO}_2\text{-C}$ [12g/mol]; $\text{MW}_{\text{N}_2\text{O-N}}$ is the molecular weight of $\text{N}_2\text{O-N}$ [28g/mol]; MV_{corr} is the temperature-corrected molecular volume [m^3/mol]; V_{CH} is the volume of the measuring chamber [m^3].

$$\text{MV}_{\text{corr}} = 0.02241 \times \left(\frac{273.15 + T}{273.15} \right) \text{ (Equation 5.5)}$$

where MV_{corr} is as defined above; T is air temperature during the measurement [$^{\circ}\text{C}$]; 0.02241 m^3 is the molar volume of an ideal gas at 1 atm, 273.15.

The cumulative CH_4 , CO_2 and N_2O emissions ($\text{g m}^{-2} \text{d}^{-1}$) were calculated by the flux rate value ($\text{mg m}^{-2} \text{h}^{-1}$) of all sampling data during the incubation periods (42 days).

GHGs were then converted to CO_2 -equivalents ($\text{CO}_2\text{-eq}$) based on global warming potential of 25 for CH_4 and 298 for N_2O to compare the greenhouse gas impacts between the different inundation treatments.

Table 0.1 Soluble cation and anion concentrations in Aire River water

Site	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	NO_3^{-} (mg/L)	SO_4^{2-} (mg/L)
Aire River water	55.3	141.7	1227.5	1993.4	0.4	106.5

5.3.3 Soil Characterisation

The pH, Eh and soil water content in the treated cores were measured by Conductivity-TDS-Salinity pH-ORP-Temperature meter, platinum electrodes and HS2 Hydrosense II system (model CS 659), respectively at Day 1, 3, 6, 10, 13, 17, 20, 24, 27, 31, 34, 38, 42 during the incubation period. At the end of the incubation period, the 20 cm soil cores were divided into 0-5 cm, 5-10 cm and 10-20 cm soil depths and then destructively sampled for soil characterisation. The initial frozen soil samples were thawed under N₂ before soil characterisation. Soils were oven-dried at 85°C and lightly crushed and sieved to 2 mm. Soil pH, electrical conductivity (EC) were measured in 1:5 soil:water extracts (Rayment and Lyons, 2011). Soil pH and EC were measured using a Conductivity-TDS-Salinity pH-ORP-Temperature meter. Soluble cations (Ca, Cu, Fe, K, Na, Mg, Mn, Zn, Si, Al and Pb) in 1:5 soil:water extracts were measured by inductively coupled plasma - optical emission spectrometry (ICP-OES) (iCAP, 7000 series) at the start and end of the incubation. Dissolved N (NO₃⁻ and NH₄⁺) were analysed on a Lachat QC 8500 Flow Injection Analyser (FIA) at the start and end of the incubation. Soil moisture content and bulk density were determined by weight after drying at 105°C for 24 h at the start and end of the incubation. Soil organic carbon (SOC) and total nitrogen (TN) content were measured on dried (85°C) soil samples by high temperature combustion using a Perkin Elmer 2400 Series II CHNS/ O Analyzer at the start and end of the incubation. Soil particle size distribution were analysed by Beckman Coulter 13320 laser diffraction analysis after pretreatment with 10% H₂O₂ to remove organic matter.

Titrateable actual acidity (TAA) was measured at the start and end of the incubation. TAA was determined by titration with 0.25M NaOH in a 1:40 soil:1M KCl suspension (Ahern et al., 2004). Acid-neutralizing capacity (ANC) was analysed by titration with 0.25M NaOH to pH 4.0 on 1:25 soil:0.1M HCl suspensions (Rayment and Lyons, 2011).

Reduced inorganic sulfur (RIS) was measured based on a sequential extraction process (Burton et al., 2008b). Reduced inorganic sulfides mainly include acid volatile sulfide (AVS) and chromium reducible sulfur (CRS). Acid volatile sulfide (AVS; which quantifies monosulfide) was extracted by shaking 2 g of soil with 10 mL of 6 M HCl/0.1M ascorbic acid in gas tight 50 mL centrifuge tubes for 18 h. The evolved H₂S (g) was trapped in 3% Zn acetate in 2 M NaOH, and then quantified through iodometric titration with 0.025 M sodium thiosulfate. Pyrite-S is usually quantified as chromium reducible sulfur (CRS) and the method described in (Burton et al., 2008b) was used. CRS was extracted by shaking with acidified CrCl₂ solution for 48 h. The evolved H₂S (g) was trapped in 3% Zn acetate in 2M NaOH. The CRS was subsequently measured by iodometric titration with 0.025 M sodium thiosulfate. Samples were analyzed with four replicates.

Net acidity was calculated by acid–base accounting, which was to evaluate the potential for soils to generate acidity from sulfide oxidation and the neutralisation potential of the sediments (Ahern et al., 2004). Net acidity was calculated according to Equation 5.6 and expressed in $\text{mol H}^+ \text{ kg}^{-1}$

$$\text{Net acidity} = (\text{AVS} + \text{S}^0 + \text{CRS}) + \text{TAA} - (\text{ANC}/\text{FF}) \text{ (Equation 5.6)}$$

where a minimum fineness factor (FF) of 1.5 was applied.

5.4 Statistical analysis

One-way analysis of variance (ANOVA) in combination with a post-hoc Tukey test was conducted to detect significant difference in net change of NO_3^- , net change of NH_4^+ , net change of mineral N, cumulative gas emissions (CO_2 , CH_4 and N_2O), AVS and CRS between the dry, flooded and wet-dry cycle treatments ($p < 0.05$). A one-way analysis of variance (ANOVA) in combination with a post-hoc Tukey test was conducted to detect significant difference in NO_3^- , NH_4^+ , TAA, ANC, net acidity, trace metals between the lime treatments ($p < 0.05$). A one-way ANOVA was used to determine the significant differences in the net change in NO_3^- , NH_4^+ and mineral N, cumulative gas emissions (CO_2 , CH_4 and N_2O), AVS, CRS, Eh, soil water content between the non-limed soils and limed soils ($p < 0.05$).

5.5 Results

5.5.1 Soil pH, EC, redox potential, soil water content, SOC, TN and mineral N

The initial soil pH was around 5.5 in all soil depths. The initial soil EC was around 0.3 mS cm^{-1} and decreased with soil depth. The initial soil organic carbon (SOC) content was around 5% and decreased with soil depth. The initial total nitrogen (TN) was around 0.5% and decreased with soil depth (Table 5.2).

The target pH of 7 was reached in the limed treatment under flooded and wet-dry cycle treatments (Fig. 5.1b, c). Under the dry treatment, the pH reached 7 within 3 days of the beginning of experiment and decreased to 6.6 after lime addition while the pH decreased from 5.7 to 5.2 in the dry treatment in the non-limed soils (Fig. 5.1a). The pH consistently remained at 6 in the flooded treatment in the non-limed soil (Fig. 5.1b). In the wet-dry cycle treatment, the pH decreased from 6 to 5.7 on day 10 and increased to 5.9 at the end of the experimental period (Fig. 5.1c)

The Eh of the soil followed the fluctuating soil moisture conditions. There was no significant difference in Eh between the lime treatment and no lime treatment with all water table treatments ($p > 0.05$). The Eh in the

dry treatment increased from +230 mV to +295 mV in the non-limed soils and increased from +201 mV to +285 mV in the limed soil during the incubation period (Fig. 5.1d). In the flooded treatment, the Eh decreased from -118 mV to -205 mV and decreased from -166 mV to -206 mV in non-limed and limed soils respectively (Fig. 5.1e). When soils were subjected to the wet-dry cycle treatment, Eh oscillated between +140 and +278 mV in the non-limed soil and between +131 and +266 mV in the limed soil (Fig. 5.1f).

There were no significant differences in soil water content between limed and non-limed soils under dry, flooded and wet-dry cycle conditions ($p>0.05$) (Fig. 5.1g, h, i). In the dry treatment, soil water content decreased by 71.2%, 73.2% in the non-limed and limed soils, respectively, by the end of the treatment.

The soils remained saturated in the flooded treatment and the soil water content was 100% in both limed and non-limed soils (Fig. 5.1h). The wet-dry cycle treatment led to the soil water content fluctuating according to the cycles. In each wet-dry cycle treatment, soil water content decreased by 16.7% and 16.1% from the initial 100% on average in the non-limed and limed soils respectively, from flooded periods to drained periods (Fig. 5.1i).

The SOC decreased under all treatments compared with the initial value (Table 5.3) and indicated the decomposition of SOC occurred. Figure 5.2 shows the NO_3^- and NH_4^+ concentration at the end of the inundation treatments in both non-limed and limed soils. In the dry treatment, the NO_3^- concentrations significantly increased compared to the initial soils in both non-limed and limed soils ($p<0.05$). In the flooded and wet-dry cycle treatments, NH_4^+ concentrations significantly decreased compared to initial soils in both non-limed and limed soils ($p<0.05$). In the dry and wet-dry cycle treatments, the NO_3^- concentration in non-limed soil was higher than that in the limed soil in the 0-5 cm soil layer. Under the flooded treatment, the NH_4^+ concentrations in limed soils were higher than that in non-limed soil in the 0-5 cm and 10-20 cm soil layers.

The net change in NO_3^- concentrations in the non-limed soil was significantly higher than that in the limed soil under dry and wet-dry cycle treatments ($p<0.05$) (Table 5.4). The NH_4^+ concentration in limed soil increased following the flooded treatment in the 5-20 cm soil layer. The sequence of net change of NO_3^- concentration in water table treatment was dry treatment > wet-dry cycle treatment > flooded treatment. The net change in NH_4^+ concentrations in flooded treatment was significantly higher than that in the dry and wet-dry cycle treatments ($p<0.05$) (Table 5.4).

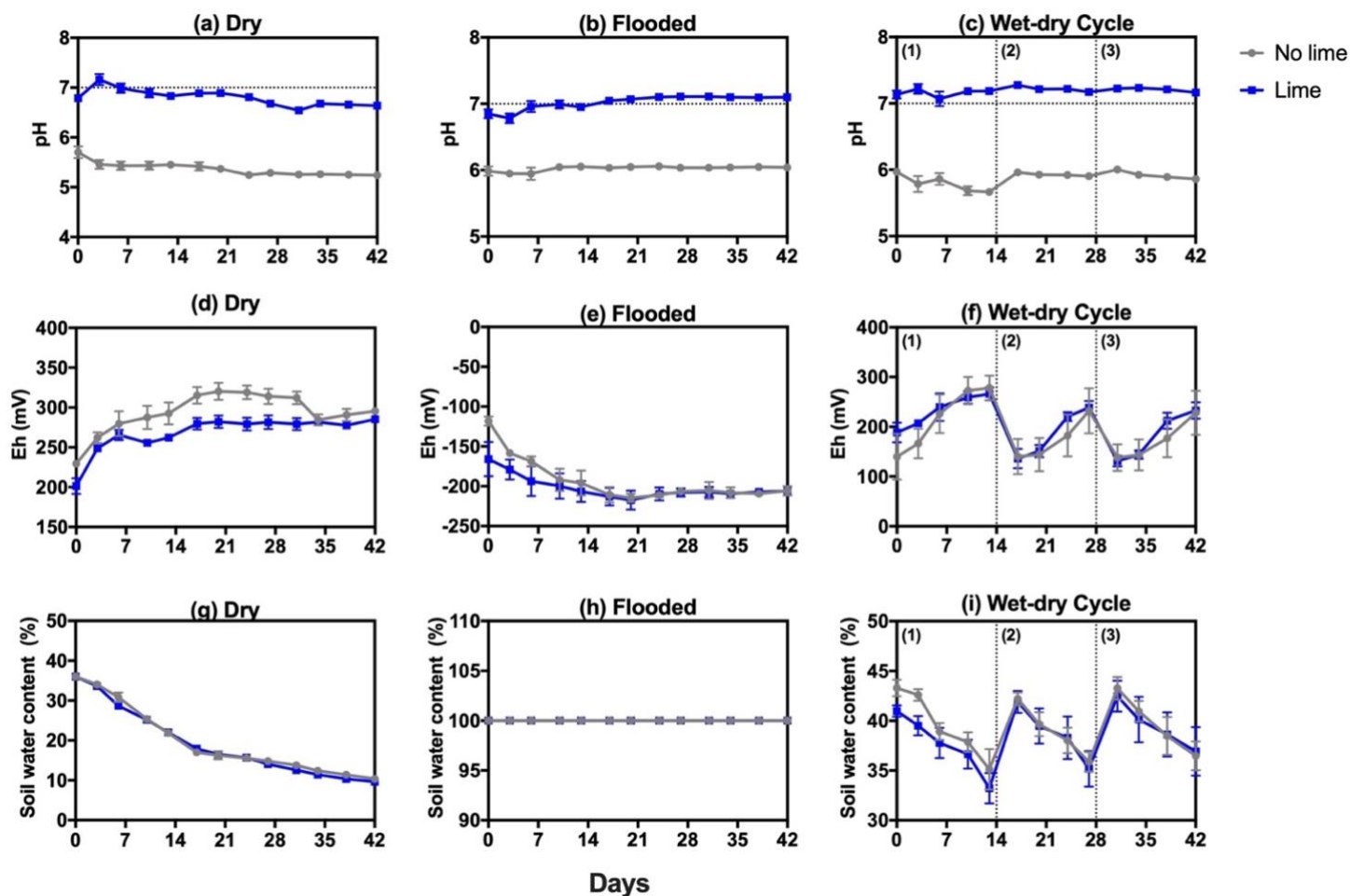


Fig. 0.1 Temporal variations under dry, flooded and wet-dry cycle treatments in pH (a, b, c), Eh (d, e, f), soil water content (g, h, i). Vertical bars denote standard error of means (n=4). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS

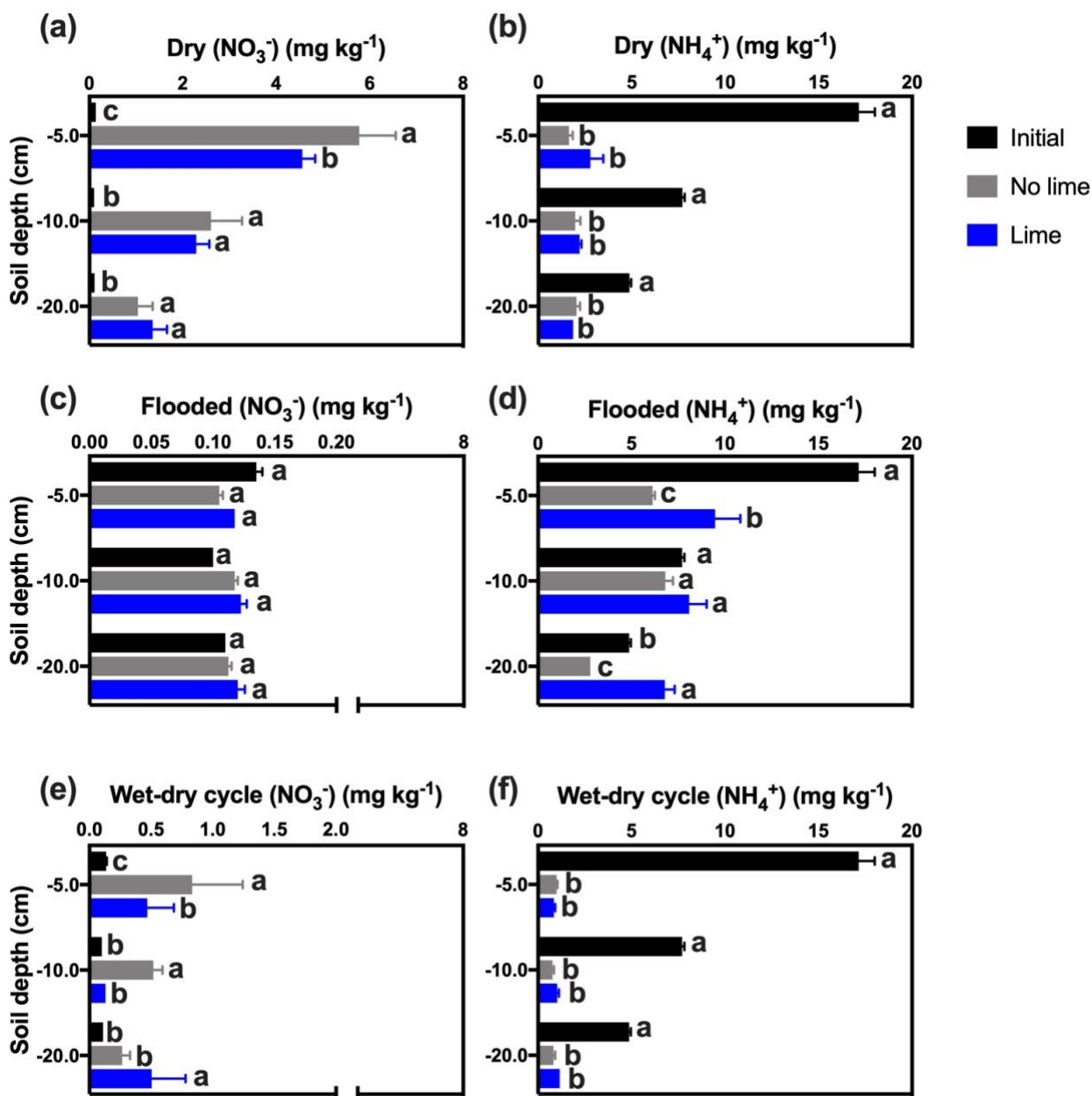


Fig. 0.2 NO_3^- and NH_4^+ concentration under the dry (a, b), flooded (c, d), wet-dry cycle (e, f) in both non-limed and limed soils. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$). Vertical bars denote standard error of means ($n = 4$).

Table 0.2 Physical and chemical characteristics of the soils

Depth (cm)	Sand (%)	Silt (%)	Clay (%)	pH	EC (mS cm ⁻¹)	Bulk Density (g cm ⁻³)	Soil water content (%)	SOC (%)	Total N (%)	C/N
0-5	0	83	17	5.64 ± 0.005	0.34 ± 0.003	0.74 ± 0.02	35.78 ± 0.93	4.99	0.46	10.91
5-10	0	78	22	5.38 ± 0.01	0.23 ± 0.001	0.83 ± 0.02	30.25 ± 0.42	4.56	0.43	10.73
10-20	0	79	21	5.47 ± 0.03	0.27 ± 0.001	0.91 ± 0.01	28.64 ± 0.64	3.19	0.30	10.63

Table 0.3 SOC and TN after dry, flooded and wet-dry cycle treatments in both non-limed and limed soils

Horizons			Dry	Flooded	Wet-dry Cycle
(cm)	Treatment		(%)	(%)	(%)
0-5	No lime	SOC	4.30	3.94	4.39
		N	0.41	0.38	0.41
		C/N	10.62	10.50	10.85
5-10		SOC	3.59	3.52	3.71
		N	0.33	0.32	0.34
		C/N	10.87	11.0	10.82
10-20		SOC	2.64	2.66	2.76
		N	0.25	0.24	0.25
		C/N	10.78	11.18	11.14
0-5	Lime	SOC	4.78	4.41	4.0
		N	0.39	0.35	0.34
		C/N	12.33	12.52	11.95
5-10		SOC	3.84	3.57	3.44
		N	0.36	0.36	0.33
		C/N	10.80	10.05	10.58
10-20		SOC	2.67	2.82	3.07
		N	0.24	0.26	0.29
		C/N	11.13	10.73	10.75

Table 0.4 Net changes of mineral N forms under different water level treatments in both non-limed and limed soils during the incubation (N mg kg⁻¹)

a) ΔNO_3^-				
Depth	Treatment	Dry	Flooded	Wet-dry cycle
0-5	No lime	5.65 ± 0.67^{aA}	-0.03 ± 0.001^{cA}	0.70 ± 0.05^{bA}
	Lime	4.43 ± 0.05^{aB}	-0.02 ± 0.001^{cA}	0.34 ± 0.04^{bB}
5-10	No lime	2.50 ± 0.03^{aA}	0.018 ± 0.001^{cA}	0.42 ± 0.03^{bA}
	Lime	2.19 ± 0.03^{aA}	0.023 ± 0.005^{bA}	0.03 ± 0.002^{bB}
10-20	No lime	0.93 ± 0.05^{aB}	0.003 ± 0.0005^{cB}	0.16 ± 0.03^{bB}
	Lime	1.25 ± 0.02^{aA}	0.01 ± 0.002^{cA}	0.40 ± 0.05^{bA}
b) ΔNH_4^+				
0-5	No lime	-15.51 ± 1.2^{bA}	-11.01 ± 1.1^{aB}	-16.16 ± 0.8^{bA}
	lime	-14.37 ± 1.4^{bA}	-7.67 ± 0.8^{aA}	-16.31 ± 1.2^{bA}
5-10	No lime	-5.73 ± 0.5^{bA}	-0.91 ± 0.05^{aB}	-6.94 ± 0.08^{bA}
	lime	-5.5 ± 0.6^{bA}	0.39 ± 0.04^{aA}	-6.68 ± 0.8^{bA}
10-20	No lime	-2.84 ± 0.3^{aA}	-2.09 ± 0.2^{aB}	-4.05 ± 0.5^{bA}
	lime	-3.0 ± 0.4^{bA}	1.91 ± 0.2^{aA}	-3.72 ± 0.5^{bA}
c) ΔN_{\min}				
0-5	No lime	-9.88 ± 1.2^{aA}	-11.05 ± 1.3^{aB}	-15.47 ± 1.8^{bA}
	lime	-9.95 ± 0.8^{aA}	-7.69 ± 0.7^{aA}	-15.98 ± 1.7^{bA}
5-10	No lime	-3.24 ± 0.5^{bA}	-0.90 ± 0.1^{aB}	-6.53 ± 0.05^{cA}
	lime	-3.32 ± 0.4^{bA}	0.40 ± 0.03^{aA}	-6.66 ± 0.5^{cA}
10-20	No lime	-1.92 ± 0.3^{aA}	-2.09 ± 0.3^{aB}	-3.90 ± 0.5^{bA}
	lime	-1.78 ± 0.1^{bA}	1.91 ± 0.2^{aA}	-3.32 ± 0.2^{bA}

^a Means \pm standard errors (n = 4). Difference between the N content at the end and before the incubation. $\text{N}_{\min} = \text{NO}_3^- + \text{NH}_4^+$. Different small letters within each row represent significant differences in mean value between the water table treatments (one-way ANOVA, Tukey test, $p < 0.05$). Different capital letters within each column represent significant differences in mean value between different lime treatments in ΔNO_3^- , ΔNH_4^+ and ΔN_{\min} respectively (t test, $p < 0.05$)

5.5.2 CO₂ emissions

The highest CO₂ flux in the dry treatment occurred on Day 24 with $118.3 (\pm 40.2) \text{ mg m}^{-2} \text{ h}^{-1}$ in the non-limed soils, and on Day 24 with $152.9 (\pm 38.4) \text{ mg m}^{-2} \text{ h}^{-1}$ in the limed soils (Fig. 5.3a). In the flooded treatments, the highest CO₂ flux occurred on Day 24 with $56.1 (\pm 8.1) \text{ mg m}^{-2} \text{ h}^{-1}$ in the non-limed soils and on Day 42 with $117.6 (\pm 25.6) \text{ mg m}^{-2} \text{ h}^{-1}$ in the limed soils (Fig. 5.3c). In the wet-dry cycle treatment, during the first 14 days of the first cycle, the CO₂ flux decreased from 61.8 to 58.8 $\text{mg m}^{-2} \text{ h}^{-1}$ on Day 6 and increased to 67.6 $\text{mg m}^{-2} \text{ h}^{-1}$ on Day 14 in the non-limed soils. During the second cycle, the CO₂ flux reached peak value on Day 3, then decreased in the non-limed soils (Fig. 5.3e). In the limed soils, the CO₂

flux increased from 55.7 to 87.3 mg m⁻² h⁻¹ on Day 6 and decreased to 77.2 mg m⁻² h⁻¹ during the first cycle and followed the same trend in the second and third cycle during the wet-dry cycle treatment (Fig. 5.3e).

The cumulative CO₂ emissions were significantly higher in the limed soils than non-limed soils in all inundation ($p<0.05$). The lime treatment increased the cumulative CO₂ emissions by 29.9%, 71.3%, 44.6% in the dry, flooded and wet-dry cycle treatments respectively compared to no lime treatment (Table 5.5). Significant differences in the cumulative CO₂ emissions were observed between different inundation treatments ($p<0.05$), with the amounts decreasing in the order of dry treatment > wet-dry cycle treatment > flooded treatment.

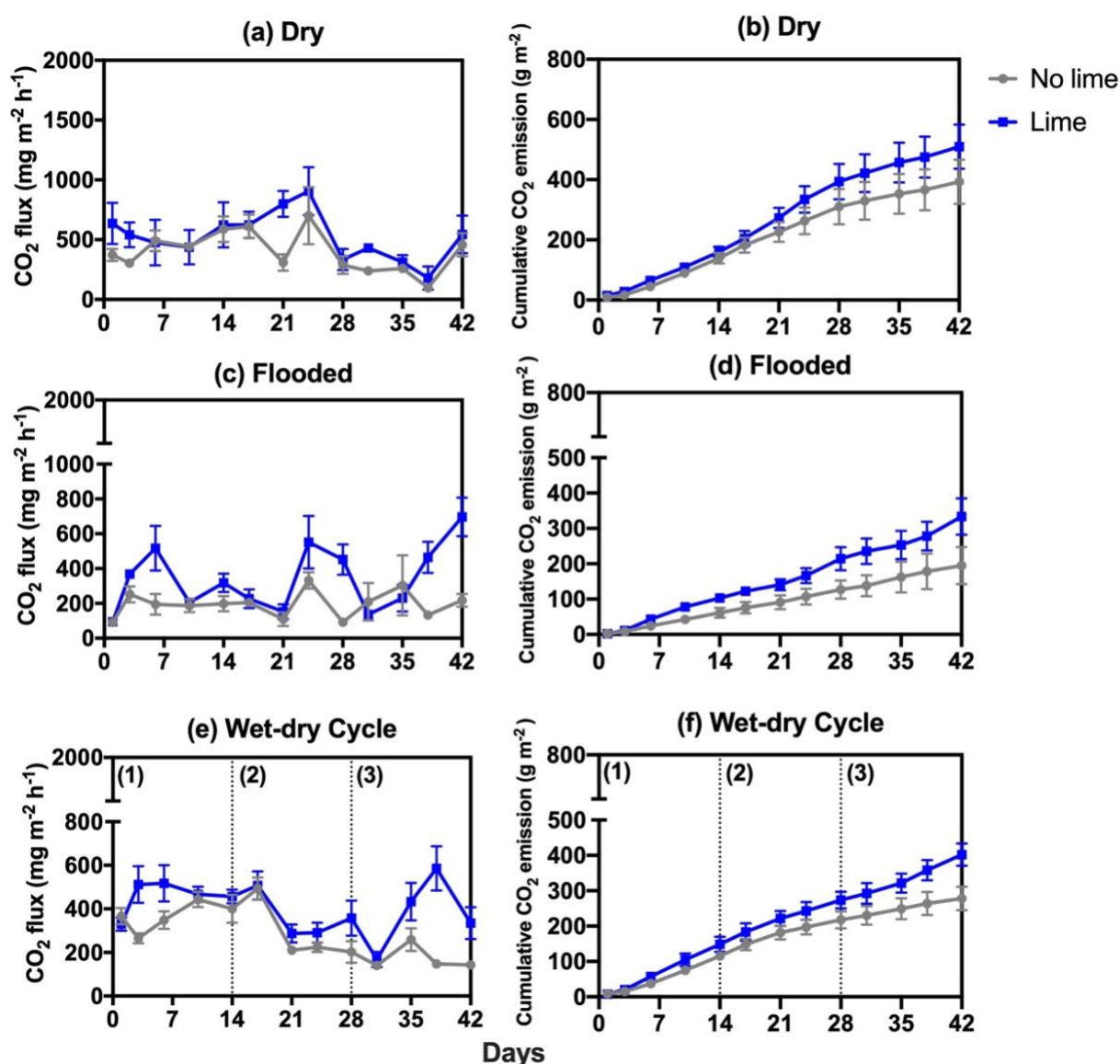


Fig. 0.3 Temporal variations of CO₂ flux and cumulative CO₂ emissions under the dry (a, b), flooded (c, d), and wet-dry cycle (e, f) treatments. Vertical bars denote standard error of means (n=4). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS.

Table 0.5 Cumulative CO₂, CH₄ and N₂O emission in both non-limed and limed soils during incubation periods

GHGs	Treatment	Dry (g m ⁻²)	Flooded (g m ⁻²)	Wet-dry cycle (g m ⁻²)
CO ₂	No lime	392.70 ± 73.64 ^{aB}	195.10 ± 52.67 ^{cB}	278.0 ± 33.60 ^{bB}
	Lime	509.60 ± 73.63 ^{aA}	333.8 ± 51.30 ^{cA}	402.20 ± 31.76 ^{bA}
CH ₄	No lime	0.27 ± 0.02 ^{cA}	62.20 ± 8.91 ^{aB}	1.76 ± 0.19 ^{bA}
	Lime	0.23 ± 0.03 ^{cA}	108.80 ± 9.35 ^{aA}	1.35 ± 0.13 ^{bA}
N ₂ O	No lime	0.30 ± 0.03 ^{aA}	0.19 ± 0.02 ^{bA}	0.39 ± 0.03 ^{aA}
	Lime	0.22 ± 0.02 ^{bB}	0.16 ± 0.01 ^{bA}	0.28 ± 0.04 ^{aB}

Values represent means of four replicates. Different small letters within each row represent significant differences in mean value between the water level treatments (one-way ANOVA, Tukey test, $p < 0.05$). Different capital letters within each column represent significant differences in mean value between different lime treatments in CO₂, CH₄ and N₂O respectively (t test, $p < 0.05$)

5.5.3 CH₄ emissions

In the dry treatment, CH₄ flux decreased from 1.7 to 0.004 mg m⁻² h⁻¹ in the non-limed soils and decreased from 0.9 to 0.008 mg m⁻² h⁻¹ in the limed soils (Fig. 5.4a). In the flooded treatment, CH₄ flux increased slowly from 0.3 to 1.1 mg m⁻² h⁻¹ in the first 6 days and then significantly increased from 10.2 mg m⁻² h⁻¹ on Day 10 to 151 mg m⁻² h⁻¹ to the end of incubation experiment in the non-limed soil. The lime treatment increased the CH₄ flux from 2.9 mg m⁻² h⁻¹ in the beginning to 328.5 mg m⁻² h⁻¹ on Day 35 and subsequently decreased to 95.2 mg m⁻² h⁻¹ at the end of experimental period (Fig. 5.4c). In the wet-dry cycle treatment, the peak value of CH₄ flux in the non-limed soil occurred on Day 6 with 4.3 mg m⁻² h⁻¹ and decreased to 0.4 mg m⁻² h⁻¹ to the end of the treatment. With the addition of lime, CH₄ flux in the beginning was 3.7 times higher than that in the non-limed soil. The CH₄ flux decreased from 6.1 mg m⁻² h⁻¹ on Day 1 to 0.4 mg m⁻² h⁻¹ to the end of the treatment in limed soil (Fig. 5.4e).

The cumulative CH₄ emissions were significantly higher in limed soils than non-limed soils in the flooded treatment ($p < 0.05$). There was no significant difference between non-limed and limed soils in the dry and wet-dry cycle treatments ($p > 0.05$). The cumulative CH₄ emissions were 0.75 time higher in limed soil compared to the non-limed soil in the flooded treatment (Table 5.5). There was a significant difference in the CH₄ emissions between different inundation treatments ($p < 0.05$), with the sequence of flooded treatment > wet-dry cycle treatment > dry treatment.

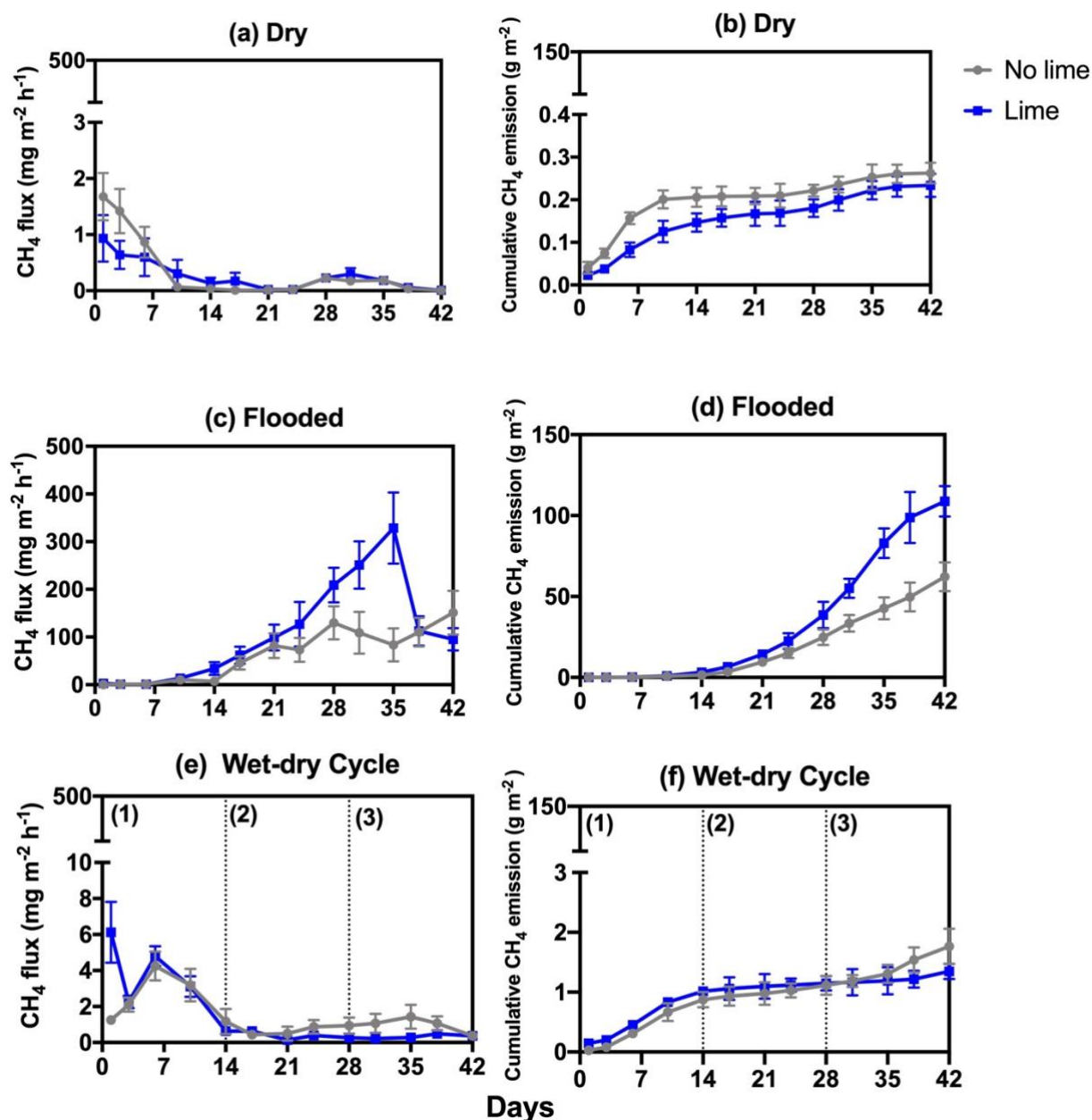


Fig. 0.4 Temporal variations of CH₄ flux and cumulative CH₄ emissions under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means (n=4). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS.

5.5.4 N₂O emissions

In the dry treatment, the N₂O flux increased from 0.36 to 0.41 mg m⁻² h⁻¹ on Day 17 and decreased to 0.09 mg m⁻² h⁻¹ at the end of the treatment in the non-limed soil. The lime treatment decreased the N₂O flux from 0.35 mg m⁻² h⁻¹ in the beginning to 0.07 mg m⁻² h⁻¹ on Day 42. The N₂O flux in the limed soil was lower than that in the non-limed soil during the whole incubation period (Fig. 5.5a). In the flooded treatment, the N₂O flux increased from 0.21 mg m⁻² h⁻¹ in the beginning to 0.38 mg m⁻² h⁻¹ on Day 17 and decreased to 0.08 mg m⁻² h⁻¹ in the end in the non-limed soil. The lime treatment decreased the N₂O flux from 0.2 to 0.06 mg m⁻² h⁻¹. In the wet-dry cycle treatment in the non-limed soil, the N₂O flux decreased from 0.45 to 0.35 mg m⁻² h⁻¹ and increased to 0.48 mg m⁻² h⁻¹ during the first wet-dry cycle, and decreased from 0.48 to 0.35 mg m⁻² h⁻¹ and increased to 0.47 mg m⁻² h⁻¹ during the second cycle, and decreased from 0.47 to 0.37 mg m⁻² h⁻¹ during the third cycle.

$^2 \text{ h}^{-1}$ and reached $0.43 \text{ mg m}^{-2} \text{ h}^{-1}$ during the third cycle (Fig. 5.5e). The lime treatment increased the N_2O flux from $0.23 \text{ mg m}^{-2} \text{ h}^{-1}$ in the beginning to $0.4 \text{ mg m}^{-2} \text{ h}^{-1}$ on Day 14 and subsequently decreased to $0.32 \text{ mg m}^{-2} \text{ h}^{-1}$ in the end (Fig. 5.5e).

The lime treatment significantly decreased the cumulative N_2O emissions compared with non-limed soils under the dry and wet-dry cycle treatments ($p < 0.05$). The lime treatment decreased cumulative N_2O emissions by 36% and 39% in the dry and wet-dry cycle treatments respectively compared to non-limed treatment (Table 5.5). There was no significant difference between limed soils and non-limed soils under flooded treatment ($p > 0.05$). The cumulative N_2O emissions were significantly higher in wet-dry cycle treatment than that in the flooded treatment in both limed and non-limed soils ($p < 0.05$) (Table 5.5).

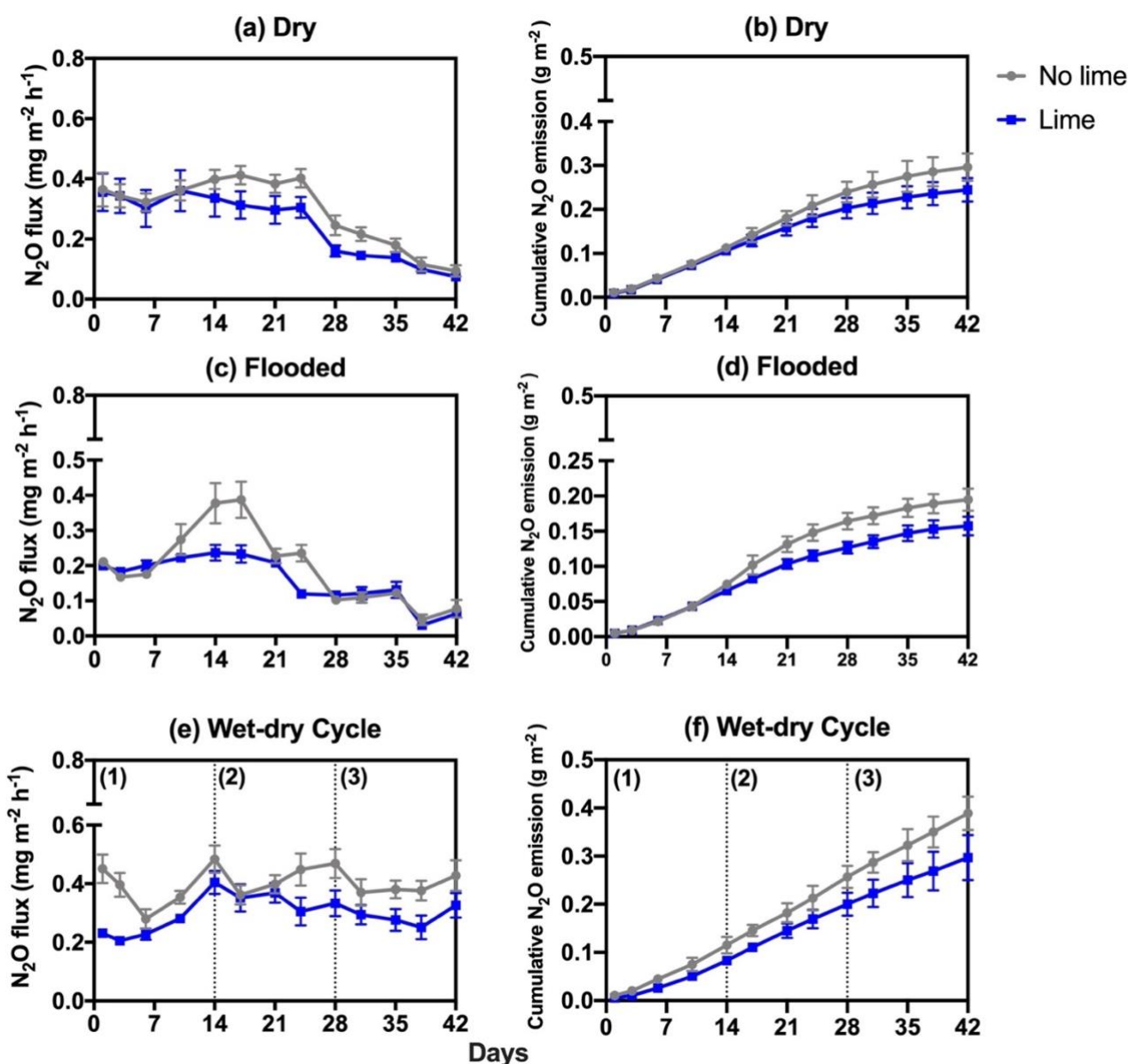


Fig. 0.5 Temporal variations of N_2O flux and cumulative N_2O emissions under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means (n=4). (1), (2), (3) represent three wet-dry cycles and started from 100% WFPS

5.5.5 Conversion to CO₂-eq

Based on the cumulative emissions shown in Table 5.5 and the global warming potential of 298 for N₂O and 25 for CH₄, GHGs were converted to CO₂-eq. The CO₂, CH₄ and N₂O emissions after conversion are shown in Table 5.6. Generally, the GHG emissions (kg CO₂-eq ha⁻¹ d⁻¹) in limed soils were 18.83%, 71.62%, 14.95 times higher under dry, flooded, wet-dry cycle treatments, respectively, compared with that in non-limed soils. The total GHG emissions (CO₂, CH₄ and N₂O) in non-limed and limed soils were 116.39 and 138.31 kg CO₂-eq ha⁻¹ d⁻¹ under the dry treatment, and were 430.17, 738.44 kg CO₂-eq ha⁻¹ d⁻¹ under the flooded treatment, and were 107.31, 123.66 kg CO₂-eq ha⁻¹ d⁻¹ under the wet-dry cycle treatment. In both non-limed and limed soils, CO₂ was the main GHG (80.33%, 87.72%), followed by N₂O (18.29%, 11.29%), and CH₄ (1.38%, 0.99%) in the dry treatment respectively. CH₄ comprised the main part of total CO₂-eq emissions in the flooded treatment (86.07%, 87.70%) in the non-limed and limed soils respectively. In the wet-dry cycle treatment, CO₂ was the main gas contributing to the global warming potential (61.68%, 77.44%), followed by N₂O (25.79%, 16.06%), and CH₄ (12.54%, 6.50%) in the non-limed and limed soils respectively.

Table 0.6 Cumulative CO₂, CH₄ and N₂O emission after converting to CO₂-eq

GHGs	Treatment	Dry (kg CO ₂ -eq ha ⁻¹ d ⁻¹)	Flooded (kg CO ₂ -eq ha ⁻¹ d ⁻¹)	Wet-dry cycle (kg CO ₂ -eq ha ⁻¹ d ⁻¹)
CO ₂	No lime	93.50 ± 17.53 ^{ab}	46.45 ± 12.54 ^{bb}	66.19 ± 8.00 ^{ab}
	Lime	121.33 ± 17.53 ^{aA}	79.48 ± 12.21 ^{cA}	95.76 ± 7.56 ^{bA}
CH ₄	No lime	1.61 ± 0.12 ^{cA}	370.24 ± 53.04 ^{ab}	13.45 ± 1.73 ^{bA}
	Lime	1.37 ± 0.18 ^{cA}	647.62 ± 55.65 ^{aA}	8.04 ± 0.77 ^{bA}
N ₂ O	No lime	21.29 ± 2.13 ^{aA}	13.48 ± 1.42 ^{bA}	27.67 ± 2.13 ^{aA}
	Lime	15.61 ± 1.42 ^{bb}	11.35 ± 0.71 ^{bA}	19.87 ± 2.84 ^{ab}

Values represent means of four replicates. Different small letters within each row represent significant differences in mean value between the water level treatments (one-way ANOVA, Tukey test, $p < 0.05$). Different capital letters within each column represent significant differences in mean value between different lime treatments in CO₂, CH₄ and N₂O (CO₂-eq) respectively (t test, $p < 0.05$)

5.5.6 AVS, CRS, TAA, ANC and Net acidity

AVS ranged from 0 to 27.5 $\mu\text{g/g}$ and CRS ranged from 37.27 to 187.04 $\mu\text{g/g}$ in the non-limed soils in the inundation treatments. AVS ranged from 0 to 15 $\mu\text{g/g}$ and CRS ranged from 18.26 to 146.83 $\mu\text{g/g}$ in the limed soils amongst all inundation treatments (Table 5.7). CRS was the dominant component of RIS.

Under the flooded treatment, significantly higher concentrations of CRS were found compared with other treatments in most soil depths in both limed and non-limed soils ($p < 0.05$) (Table 5.7). Under the dry treatment, significantly lower concentrations of CRS were found in all soil depths in both the limed and non-limed soils (Table 5.7).

Significantly higher concentrations of CRS were found in the non-limed soil compared to the limed soil under the dry treatment in the 0-20 m soil layer and in the wet-dry cycle treatment in the 0-10 cm soil layer ($p < 0.05$). However, the CRS concentration was significantly higher in the limed soil than the non-limed soil in the 10-20 cm soil layer under the flooded treatment ($p < 0.05$) (Table 5.7).

CRS was positively correlated with SOC in the non-limed soils ($p < 0.05$) and AVS was positively correlated with the C/N ratio in the limed soils ($p < 0.05$) (Table 5.8).

The TAA significantly increased in all the inundation treatments in the non-limed soil compared to the initial state ($p < 0.05$) (Fig. 5.6). The dry treatment had the highest TAA in the non-limed soil. The TAA in the dry, flooded and wet-dry cycle treatment was 5.8-11.2 times, 2.9-7.0 times, 2.9-7.7 times higher compared with the initial state respectively (Fig. 5.6a, d, g). TAA was not observed in the 0-5 cm soil layer in the limed soil in all inundation treatments, while ANC was only found in the 0-5 cm soil layer in the limed soil. There was no significant difference in TAA between non-limed and limed soils in the 10-20 cm layer in the flooded treatment ($p > 0.05$) (Fig. 5.6d).

The net acidity was negative in the 0-5 cm layer in limed soils in all inundation treatments (Fig. 5.6c, f, i). The net acidity in dry, flooded and wet-dry cycle treatment was 4.9-10.3 times, 2.5-3.9 times, 1.2-4.4 times higher compared with initial state respectively (Fig. 5.6c, f, i). Lime treatment significantly lowered the TAA and net acidity compared with non-limed treatment in all soil layers under dry and wet-dry cycle treatments ($p < 0.05$) (Fig. 5.6a, g, c, i).

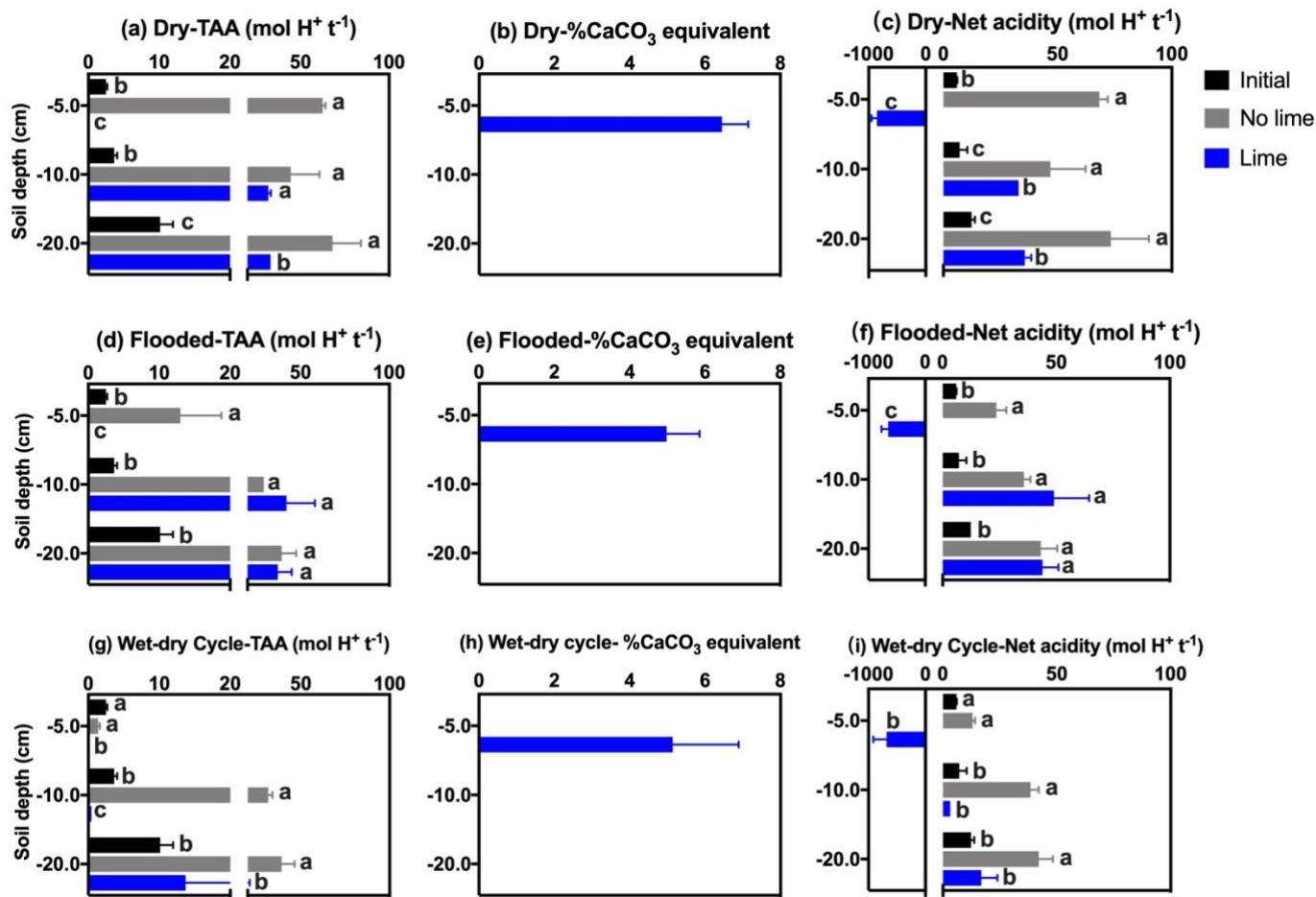


Fig. 0.6 TAA (Titratable actual acidity), acid neutralisation capacity (ANC) and net acidity under dry (a, b, c), flooded (d, e, f) and wet-dry cycle (g, h, i) treatments. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p < 0.05$; $n = 4$). Vertical bars denote standard error of means ($n=4$).

Table 0.7 AVS and CRS concentrations between treatments in different soil horizons in both non-limed and limed soils

Horizons (cm)	Treatment	RIS	Initial ($\mu\text{g/g}$)	Dry ($\mu\text{g/g}$)	Flooded ($\mu\text{g/g}$)	Wet-dry Cycle ($\mu\text{g/g}$)
0-5	No lime	AVS	0 ^{bA}	0 ^{bB}	27.5 \pm 3.7 ^{aA}	0 ^{bA}
	Lime		0 ^{bA}	7.5 \pm 1.5 ^{aA}	15 \pm 2.3 ^{aB}	0 ^{bA}
	No lime	CRS	105.24 \pm 20.3 ^{bA}	92.85 \pm 15.6 ^{bA}	142.89 \pm 18.5 ^{aA}	187.04 \pm 20.7 ^{aA}
	Lime		104.34 \pm 12.5 ^{bA}	44.29 \pm 5.3 ^{bB}	146.83 \pm 20.6 ^{aA}	20.17 \pm 3.4 ^{bB}
5-10	No lime	AVS	0 ^{bA}	0 ^{bA}	10 \pm 2.5 ^{aA}	0 ^{bA}
	Lime		0 ^{bA}	0 ^{aA}	0 ^{aB}	0 ^{aA}
	No lime	CRS	56.44 \pm 5.8 ^{bA}	37.27 \pm 3.6 ^{bA}	95.82 \pm 12.7 ^{aA}	111.90 \pm 14.6 ^{aA}
	Lime		54.45 \pm 4.6 ^{bA}	18.26 \pm 2.3 ^{cB}	110.37 \pm 12.3 ^{aA}	44.15 \pm 6.4 ^{bB}
10-20	No lime	AVS	0 ^{bA}	20 \pm 3.2 ^{aA}	0 ^{bA}	0 ^{bA}
	Lime		0 ^{bA}	5 \pm 1.3 ^{aB}	0 ^{bA}	0 ^{bA}
	No lime	CRS	56.06 \pm 7.8 ^{aA}	63.74 \pm 7.6 ^{aA}	62.58 \pm 5.8 ^{aB}	48.09 \pm 5.9 ^{aA}
	Lime		57.32 \pm 6.5 ^{aA}	35.82 \pm 3.4 ^{cB}	109.06 \pm 11.5 ^{aA}	50.34 \pm 4.7 ^{bA}

Values represent means of four replicates. Different small letters within each row represent significant differences in mean value between the water level treatments (one-way ANOVA, Tukey test, $p < 0.05$). Different capital letters within each column represent significant differences in mean value between different lime treatments in AVS and CRS respectively (t test, $p < 0.05$)

Table 0.8 Pearson correlation analysis between RIS (AVS and CRS) and soil parameters

Parameters	AVS		CRS	
	No lime	Lime	No lime	Lime
SOC	-0.087	0.53	0.72*	0.06
ΔSOC	0.38	-0.34	0.20	-0.14
C/N	-0.54	0.77*	-0.46	0.06

Pair sample size, $n=9$ for SOC, ΔSOC (initial-after treatment) and C/N in the soil layer (0-20 cm) after the dry, flooded and wet-dry cycle treatments in all sites.

* $p < 0.05$ correlations are significant

5.5.7 Trace metals and anions

Limed soils had significantly lower Al concentration compared to non-limed soils under flooded and wet-dry cycle conditions in all horizons ($p < 0.05$) (Fig. 5.7b, c) and in the 0-5 cm soil layer in the dry treatment ($p < 0.05$) (Fig. 5.7a). The Fe concentration in limed soils was significantly lower compared to non-limed soils under flooded and wet-dry cycle conditions in the 0-5 cm soil layer ($p < 0.05$) (Fig. 5.7e, f). The Mn concentration in limed soils was significantly lower compared to non-limed soils under dry and wet-dry cycle conditions in the 0-5 cm soil layer ($p < 0.05$) (Fig. 5.7g, i).

The Al and Fe concentrations increased significantly in the flooded treatment in the non-limed soils in all horizons ($p < 0.05$) (Fig. 5.7b, e). The Al and Fe concentration decreased significantly in the dry treatment in

non-limed soils in the 0-10 cm soil layer ($p<0.05$) (Fig. 5.7a, d). The Al concentration decreased significantly in limed soils compared with non-limed soils in the 0-20 cm soil layer under flooded and wet-dry cycle treatments ($p<0.05$). The Fe concentration decreased significantly in the limed soil compared to non-limed soil in the 0-5 cm soil layer under flooded and wet-dry cycle treatments ($p<0.05$).

The SO_4^{2-} concentration increased in the dry treatment in both limed and non-limed soils (Fig. 5.8a). In the flooded treatment, the SO_4^{2-} concentration decreased in both limed and non-limed soils (Fig. 5.8c). The $\text{Cl}^-/\text{SO}_4^{2-}$ increased following the flooded and wet-dry cycle treatments (Fig. 5.8d, f). Lower $\text{Cl}^-/\text{SO}_4^{2-}$ were observed in the 5-20 cm soil layer under the dry treatment (Fig. 5.8b).

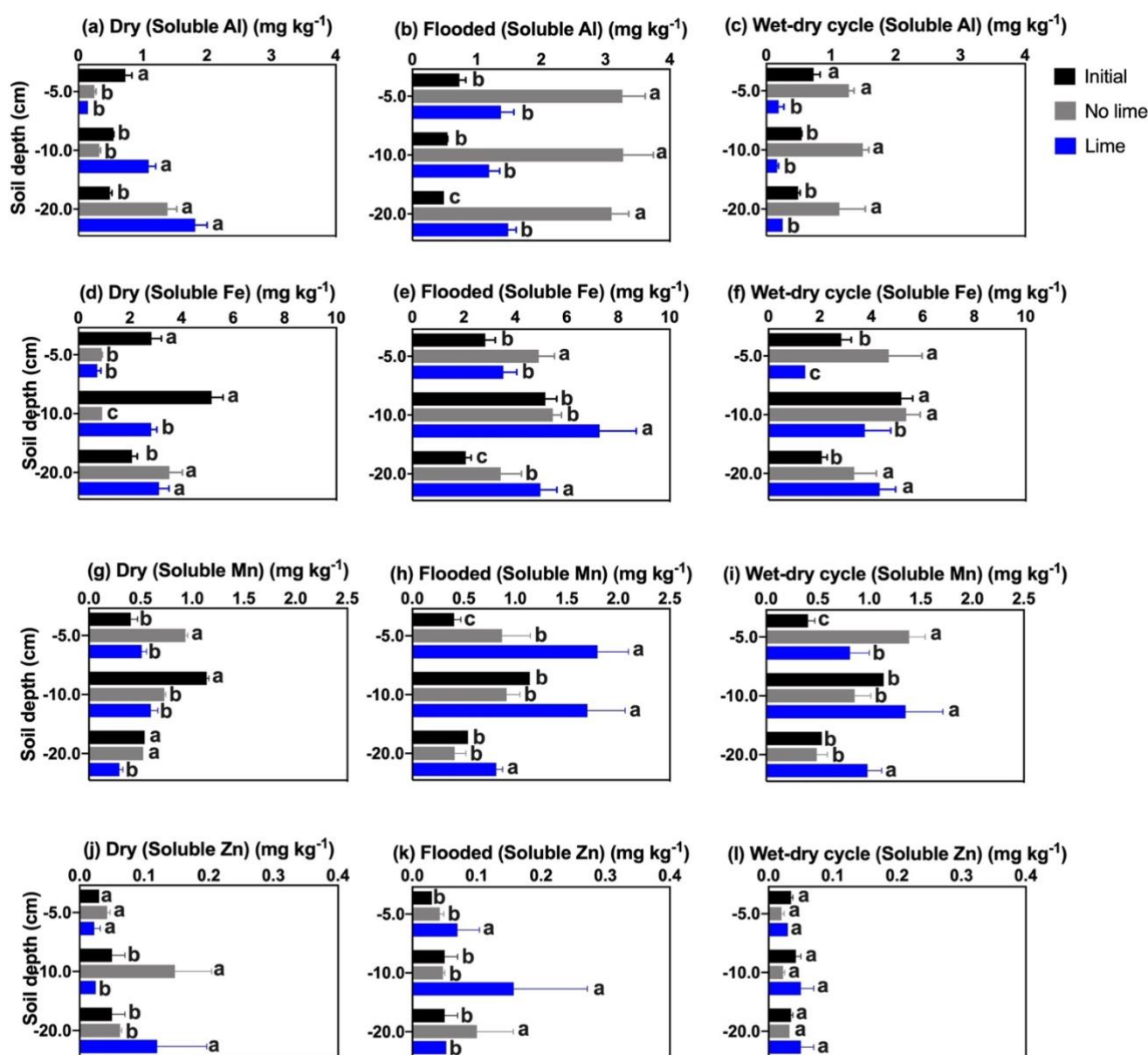


Fig. 0.7 Soluble trace metals Al, Fe, Mn, and Zn under dry (a, d, g, j), flooded (b, e, h, k) and wet-dry cycle (c, f, i, l) treatments. Different small letters within each horizon indicate significant differences between the lime treatments (one-way ANOVA, Tukey test, $p<0.05$; $n=4$). Vertical bars denote standard error of means ($n=4$)

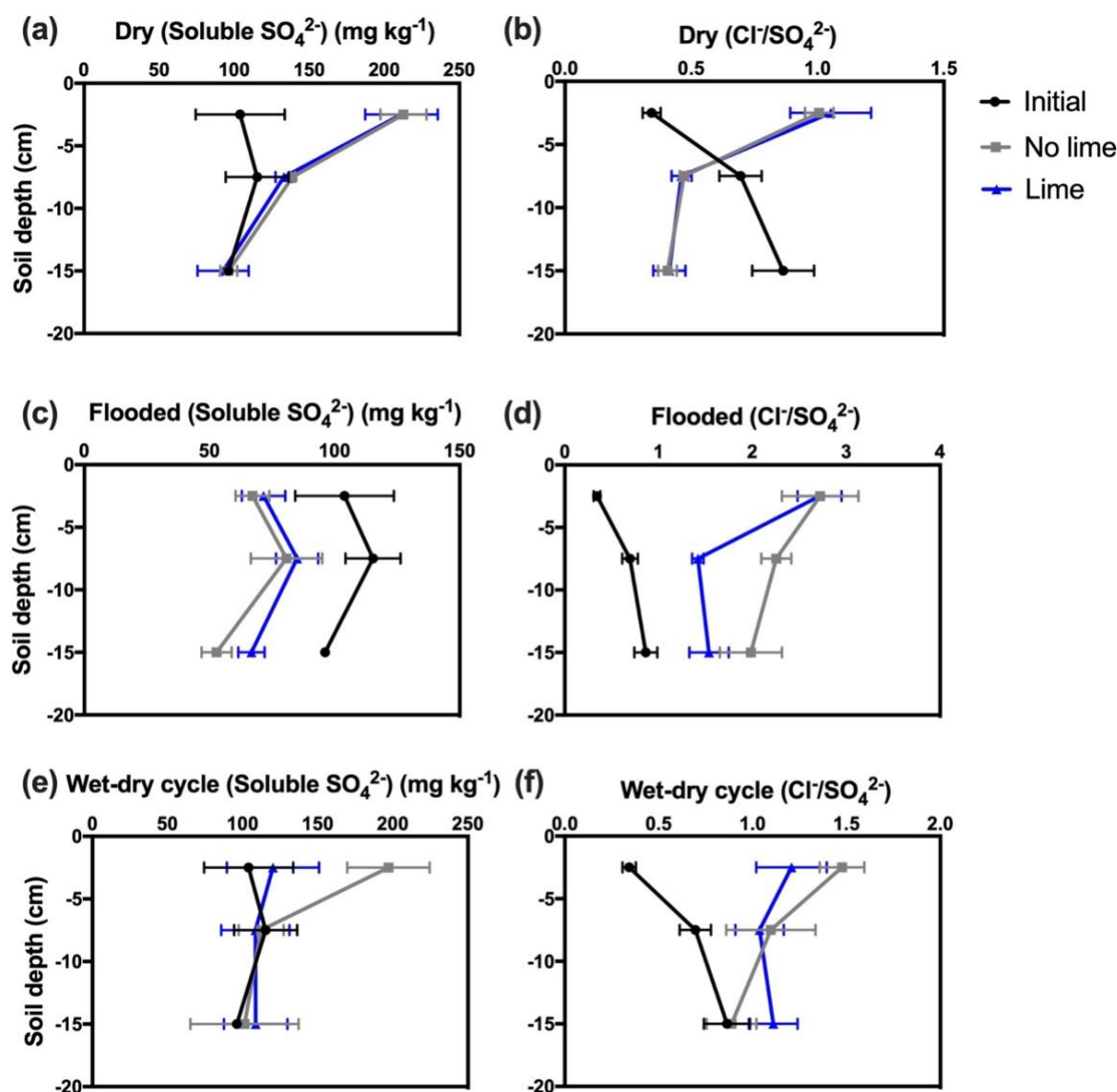


Fig. 0.8 Soluble SO₄²⁻ and Cl⁻/SO₄²⁻ under the dry (a, b), flooded (c, d), wet-dry cycle (e, f). Vertical bars denote standard error of means (n=4).

5.6. Discussion

5.6.1 Influence of lime and inundation on AVS, CRS and acidity

The oxidation of RIS species (in the form of FeS₂, FeS) under the dry treatment can promote the generation of acidity (Cook et al., 2000; Lin et al., 1995). TAA is used to estimate the pool of exchangeable H⁺ in ASS (McElnea et al., 2002) and significantly increased in the dry treatment. The oxidation of Fe²⁺ in the dry treatment can lead to hydrolysis and generation of H⁺ (Johnston et al., 2011), which can contribute to the increase in TAA.

TAA and net acidity in the flooded treatment was lower compared with the dry treatment in non-limed soils (Fig. 5.6). The flooded treatment changed the geochemical conditions of the soils and promoted reduction of

Fe^{3+} and SO_4^{2-} (Berner, 1984). These reductive reactions in flooded conditions can consumed acidity (White et al., 1997) and promote the reformation of iron sulfide minerals like FeS_2 and FeS (Hicks et al., 2003; Johnston et al., 2009a). These suggestions are supported by significantly higher concentrations of CRS observed under flooded conditions (Table 5.6). Inundated conditions also allow the conversion from FeS to FeS_2 which was also observed in the high concentrations of CRS (Rickard and Luther, 2007).

The addition of lime can increase the soil pH at the surface. The addition of lime neutralized the acidity in the soils and therefore decreased the TAA and net acidity under the dry and wet-dry cycle treatments. Wu et al. (2015) reported that CaCO_3 and $\text{Ca}(\text{OH})_2$ treatments could reduce the acidity in ASS in Finland. Wong et al. (2016b) found that lime addition can also neutralize the acidity in coastal floodplain soils in Australia.

5.6.2 Influence of lime and inundation on trace metals

The soluble Fe concentration decreased in the top horizon with lime addition. This might be due to the formation of Fe oxides causing the concentration of Fe to decrease under the lime treatment in the dry treatment. This may be due to oxidising conditions created in the dry treatment which then leads to the precipitation of Fe^{3+} in the soil and lower concentration of Fe (Dent and Pons, 1995; Virtanen et al., 2017). Dalhem et al. (2019) has previously described the stability of Fe can shift towards schwertmannite and iron oxides with a raised pH and consequently, the Fe concentrations are decreased. Mosley et al. (2014a) also observed that dissolved Fe can form amorphous Fe oxides when acidic drainage water mixes with alkaline river water. Also, the low concentration of soluble Fe in the flooded and wet-dry cycle treatments could be potentially due to the formation of FeS through the reaction of H_2S with Fe^{2+} . Under the flooded treatment, the increase in AVS and CRS in all soil depths (Table 5.7) and the decrease in SO_4^{2-} concentration (Fig. 5.8) suggested that the reformation of iron sulfide in both non-limed and limed soils had occurred.

The effect of lime can also be seen in the marked decrease in Al concentrations in all horizons in the flooded and wet-dry cycle treatments (Fig. 5.7b, c). This was expected because the solubility of Al is strongly pH dependent and an increase in soil pH in the surface layer can lead to the hydrolysis and precipitation of Al hydroxides (Dalhem et al., 2019). Hogfors-Ronnholm et al. (2018) demonstrated that CaCO_3 was the best mitigation method to lower metal release from ASS.

5.6.3 CO₂ emissions

Soil CO_2 emissions are produced due to the decomposition of soil organic matter and plant root respiration (Amundson and Davidson, 1990). Soil pH affects CO_2 emissions as microbial activity is influenced by soil pH (Oertel et al., 2016). Jugsujinda et al. (1996) observed that CO_2 emissions increased with increasing soil pH in ASS. The carbonate from the added lime (CaCO_3) can neutralize the acidity in the non-limed soil to

produce CO₂ (West and McBride, 2005). Hamilton et al. (2007) concluded that use of lime in agriculture can also act as a source of CO₂.

Lime addition significantly increased the cumulative CO₂ emissions compared with non-limed soil in all inundation treatments. Liming can increase the availability of organic carbon to microbes which are most likely initially limited by low soil pH, and this therefore leads to increased SOC mineralisation (Grover et al., 2017; Rousk et al., 2009). Aciego Pietri and Brookes (2008) observed that an increase in pH up to 7 with added CaCO₃ improved soil microbial biomass function in an arable soil in the UK, confirming the significance of a neutral pH to stimulate microbial biomass growth and mineralization of soil organic matter. Fuentes et al. (2006) also found that higher respiration rates from limed soil compared to non-limed soils, which were attributed to neutral soil pH. Therefore, the additional CO₂ emissions in limed soils are from both lime dissolution and organic matter mineralisation.

Significantly higher cumulative CO₂ emissions were observed in the dry treatment and wet-dry cycle treatments compared with the flooded treatment. This is because dry treatment and dry periods of wet-dry cycle treatment led to oxic conditions and increased soil respiration, promoting higher cumulative CO₂ emissions (Hirota et al., 2007; Liu et al., 2013). Yang et al. (2013) observed that the CO₂ emissions were significantly higher under oxic conditions at lowest water table positions in a freshwater marsh.

5.6.4 CH₄ emissions

CH₄ is produced by decomposition of organic matter under highly reducing conditions (Bartlett et al., 1987; Keller and Stallard, 1994; Moore and Roulet, 1993). Liming significantly increased the cumulative CH₄ emissions compared to non-limed soils in the flooded treatment. The pH value has effects on CH₄ emissions because methanogenesis only proceeds at a high rate when the pH is maintained in the neutral range (Jones et al., 1987; Wang et al., 1993; Zinder, 1994). Most methanogenic bacteria function in a pH range between 6.7 and 7.4, but optimally at pH 7.0-7.2 and the rate of CH₄ production may decrease if the pH is lower than 6.1 or higher than 8.3 (Bitton, 1994; Lay et al., 1997). Murakami et al. (2005) observed that liming increased CH₄ emissions in acid peat soils because the decomposition of organic matter was enhanced under limed condition and therefore increased substrate supply for methanogenic microorganisms.

The flooded treatment had significantly higher cumulative CH₄ emissions compared to the dry and wet-dry cycle treatments. The Eh in the flooded treatment in the study was around -200 mV and the CH₄ flux increased significantly after 10 days' incubation. CH₄ is produced by methanogenesis when Eh < -150 mV (Jugsujinda et al., 1996) so we can assume that methanogenesis is the main gas pathway under the flooded condition.

5.6.5 N_2O emission

Lower cumulative N_2O emissions were observed in the limed soils compared with non-limed soils in all inundation treatments (Table 5.5). This might be attributed to the lower conversion of NH_4^+ to NO_3^- and lower nitrifying activity in limed soils. NH_4^+ is quickly consumed and converted to NO_3^- under aerobic conditions and the increase in NO_3^- can indicate nitrifying activity under the dry treatment and dry periods of the wet-dry cycle treatment. Neutral soil pH can promote the activity of N_2O reductase and stimulate the conversion of N_2O to N_2 (Bakken et al., 2012; Galbally et al., 2010). In the non-limed soil, the soil pH was around 5.5 in our study. Low soil pH in the dry treatment during oxic conditions promoted the production of N_2O because N_2O reductase is not sensitive at lower soil pH values. Wang et al. (2018) also found that low soil pH can increase N_2O emissions, indicating that liming can be used as a tool to mitigate N_2O emissions.

N_2O was produced by nitrification in the dry treatment and the dry period of the wet-dry cycle treatment. This is because the dry treatment significantly increased the NO_3^- concentration and decreased NH_4^+ concentration in both non-limed and limed soils. The flooded treatment decreased NO_3^- in both non-limed and limed soil in the 0-5 cm layer because of denitrification as NO_3^- is reduced to N_2O or N_2 under anoxic conditions. The cumulative N_2O emission was highest in the wet-dry cycle treatment compared to the dry and flooded treatments. This is because during the wet-dry cycle treatment, NH_4^+ was most likely oxidized to NO_3^- in the dry periods by nitrification and then NO_3^- was then likely reduced to N_2O or N_2 by denitrification. The initial WFPS was 100% during flooded periods of wet-dry cycle treatment, which can promote N_2O production. Davidson (1993) also observed that the dominant source was N_2O when WFPS > 60% during denitrification under anaerobic conditions.

5.6.6 Influence of lime and inundation on GHG emissions

The total GHG emissions after CO_2 -eq conversion in limed soils were higher compared with non-limed soils under all inundation treatments. Even though lime addition decreased N_2O emissions, CO_2 emissions increased in all inundation treatments and increased CH_4 emissions in the flooded treatment. When considering lime as a GHG mitigation tool, we also need to consider CO_2 , CH_4 and N_2O emissions together. Lime enhanced CO_2 emissions because the lime can react with the acid in the soil to form CO_2 . Abalos et al. (2020) also indicated that liming can increase CO_2 emissions and decrease N_2O emissions in Denmark.

Based on CO_2 -eq, the decreasing order of the total GHG emissions in both non-limed and limed soils were flooded treatment > dry treatment > wet-dry cycle treatment. This is because CH_4 comprised the primary GHG of total CO_2 -eq emissions in the flooded treatment.

5.7 Conclusion

Based on CO₂-eq, the total GHG emissions were higher in limed soils than non-limed soils. This is because lime increased CO₂ emissions in all inundation treatments and increased CH₄ emissions in the flooded treatment. Overall, liming as a mitigation strategy for GHG emissions should consider the increased CO₂ and CH₄ emissions and water table fluctuations in coastal wetlands even though lime can decrease N₂O emissions. Inundation decreased the total CO₂ and N₂O emissions and increased the CH₄ emissions. This is because CH₄ was the dominant GHG in the total CO₂-eq emissions in the flooded treatment. Lime raised the pH of soil, mitigated net acidity and heavy metals (Al, Fe, Mn) in most horizons under dry and wet-dry cycle treatments. The flooded treatment lowered TAA and net acidity compared with the dry treatment. The TAA and net acidity, heavy trace metals decreased following flooded treatment. Thus, inundation is an effective method to reduce the acidity and heavy metals in this study.

5.8 References

- Abalos, D., Liang, Z., Dörsch, P., Elsgaard, L., 2020. Trade-offs in greenhouse gas emissions across a liming-induced gradient of soil pH: Role of microbial structure and functioning. *Soil biology & biochemistry* 150, 108006.
- Aciego Pietri, J.C., Brookes, P.C., 2008. Relationships between soil pH and microbial properties in a UK arable soil. *Soil biology & biochemistry* 40, 1856-1861.
- Adams, T.M., Adams, S.N., 1983. The effects of liming and soil pH on carbon and nitrogen contained in the soil biomass. *The Journal of agricultural science* 101, 553.
- Ahern, C.R., Blunden, B., Sullivan, L.A., McElnea, A.E., 2004. Soil sampling handling, preparation and storage, In: Ahern, C.R., McElnea, A.E., Sullivan, L.A. (Eds.), *Acid Sulfate Soils Laboratory Methods Guidelines*. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.
- Allen, D.E., Dalal, R.C., Rennenberg, H., Meyer, R.L., Reeves, S., Schmidt, S., 2007. Spatial and temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments and the atmosphere. *Soil Biology and Biochemistry* 39, 622-631.
- Amundson, R.G., Davidson, E.A., 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *Journal of Geochemical Exploration* 38, 13-41.
- Bååth, E., Arnebrant, K., 1994. Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. *Soil biology & biochemistry* 26, 995-1001.
- Baggs, E.M., 2011. Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction. *Current Opinion in Environmental Sustainability* 3, 321-327.
- Bakken, L.R., Bergaust, L., Liu, B., Frostegård, A., 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N₂O emissions from soils. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 367, 1226.
- Bartlett, K., Bartlett, D., Harriss, R., Sebacher, D., 1987. Methane emissions along a salt marsh salinity gradient. *Biogeochemistry* 4, 183-202.
- Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochimica et Cosmochimica Acta* 48, 605-615.
- Bitton, G., 1994. *Wastewater microbiology*. New York : Wiley-Liss, New York.
- Boman, A., Fröjdö, S., Backlund, K., Aström, M.E., 2010. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.
- Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochimica et Cosmochimica Acta* 75, 3434-3451.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006a. Fractionation and extractability of sulfur, iron and trace elements in sulfidic sediments. *Chemosphere* 64, 1421-1428.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006b. Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica Acta* 70, 5455-5468.
- Burton, E.D., Sullivan, L.A., Bush, R.T., Johnston, S.G., Keene, A.F., 2008. A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* 23, 2759-2766.

- CCMA, 2014. Corangamite Waterway Strategy 2014- 2022, https://issuu.com/gsdm/docs/waterway_strategy_2014-22.
- Cook, F.J., Hicks, W., Gardner, E.A., Carlin, G.D., Froggatt, D.W., 2000. Export of Acidity in Drainage Water from Acid Sulphate Soils. *Marine Pollution Bulletin* 41, 319-326.
- Dalhem, K., Engblom, S., Stén, P., Österholm, P., 2019. Subsurface hydrochemical precision treatment of a coastal acid sulfate soil. *Applied Geochemistry* 100, 352-362.
- Davidson, E.A., 1993. Soil Water Content and the Ratio of Nitrous Oxide to Nitric Oxide Emitted from Soil, In: Oremland, R.S. (Ed.), *Biogeochemistry of Global Change: Radiatively Active Trace Gases Selected Papers from the Tenth International Symposium on Environmental Biogeochemistry*, San Francisco, August 19–24, 1991. Springer US, Boston, MA, pp. 369-386.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides. *BioScience* 50, 667-680.
- Dent, D., 1986. Acid sulphate soils: a baseline for research and development. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.
- Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263-276.
- Fuentes, J.P., Bezdicek, D.F., Flury, M., Albrecht, S., Smith, J.L., 2006. Microbial activity affected by lime in a long-term no-till soil. *Soil & tillage research* 88, 123-131.
- Galbally, I.E., Meyer, M.C.P., Wang, Y.-P., Smith, C.J., Weeks, I.A., 2010. Nitrous oxide emissions from a legume pasture and the influences of liming and urine addition. *Agriculture, Ecosystems & Environment* 136, 262-272.
- Grover, S.P., Butterly, C.R., Wang, X., Tang, C., 2017. The short-term effects of liming on organic carbon mineralisation in two acidic soils as affected by different rates and application depths of lime. *Biology and Fertility of Soils* 53, 431-443.
- Hamilton, S.K., Kurzman, A.L., Arango, C., Jin, L., Robertson, G.P., 2007. Evidence for carbon sequestration by agricultural liming. *Global Biogeochem. Cycles* 21, GB2021-n/a.
- Hicks, W., Fitzpatrick, R., Bowman, G., 2003. MANAGING COASTAL ACID SULFATE SOILS: THE EAST TRINITY EXAMPLE.
- Higgins, S., Laughlin, R.J., Watson, C.J., 2013. Antecedent effect of lime on nitrous oxide and dinitrogen emissions from grassland soils. *Nutrient cycling in agroecosystems* 95, 219-229.
- Hirota, M., Senga, Y., Seike, Y., Nohara, S., Kunii, H., 2007. Fluxes of carbon dioxide, methane and nitrous oxide in two contrastive fringing zones of coastal lagoon, Lake Nakaumi, Japan. *Chemosphere* 68, 597-603.
- Högfors-Rönholm, E., Christel, S., Dalhem, K., Lillhonga, T., Engblom, S., Österholm, P., Dopson, M., 2018. Chemical and microbiological evaluation of novel chemical treatment methods for acid sulfate soils. *Science of The Total Environment* 625, 39-49.
- Johnston, S.G., Burton, E.D., Aaso, T., Tuckerman, G., 2014. Sulfur, iron and carbon cycling following hydrological restoration of acidic freshwater wetlands. *Chemical Geology* 371, 9-26.
- Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., Smith, D., Martens, M.A., McElnea, A.E., Ahern, C.R., Powell, B., Stephens, L.P., Wilbraham, S.T., van Heel, S., 2009a. Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coastal and Shelf Science* 81, 257-266.
- Johnston, S.G., Keene, A.F., Burton, E.D., Bush, R.T., Sullivan, L.A., 2012. Quantifying alkalinity generating processes in a tidally remediating acidic wetland. *Chemical Geology* 304-305, 106-116.

- Johnston, S.G., Keene, A.F., Bush, R.T., Burton, E.D., Sullivan, L.A., Smith, D., McElnea, A.E., Martens, M.A., Wilbraham, S., 2009b. Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* 149, 335-346.
- Johnston, S.G., Keene, A.F., Bush, R.T., Sullivan, L.A., Wong, V.N.L., 2011. Tidally driven water column hydro-geochemistry in a remediating acidic wetland. *Journal of Hydrology* 409, 128-139.
- Jones, W.J., Nagie, D.P.J., Whitman, W.B., 1987. Methanogens and the diversity of archaeobacteria. *Microbiol Rev* 51, 135-177.
- Jugsujinda, A., Delaune, R., Lindau, C., Sulaeman, E., Pezeshki, S., 1996. Factors controlling carbon dioxide and methane production in acid sulfate soils. *An International Journal of Environmental Pollution* 87, 345-355.
- Keene, A.F., Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., McElnea, A.E., Ahern, C.R., Powell, B., 2011. Effects of hyper-enriched reactive Fe on sulfidisation in a tidally inundated acid sulfate soil wetland. *Biogeochemistry* 103, 263-279.
- Keller, M., Stallard, R.F., 1994. Methane emission by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research: Atmospheres* 99, 8307-8319.
- Knowles, R., 1982. Denitrification. *Microbiological Reviews* 46, 43-70.
- Kowalchuk, G., Stephen, J., 2001. Ammonia-oxidizing bacteria: A model for molecular microbial ecology. *Annual Review of Microbiology* 55, 485-529.
- Lay, J.-J., Li, Y.-Y., Noike, T., 1997. Influences of pH and moisture content on the methane production in high-solids sludge digestion. *Water research (Oxford)* 31, 1518-1524.
- Lin, C., Melville, M.D., Hafer, S., 1995. Acid sulphate soil-landscape relationships in an undrained, tide-dominated estuarine floodplain, Eastern Australia. *Catena (Giessen)* 24, 177-194.
- Liu, B., 2010. Denitrification gene pools, transcription and kinetics of NO, N₂O and N₂ production as affected by soil pH. *FEMS Microbiology Ecology* 72, 407-417.
- Liu, B., Frostegård, Å., Bakken, L.R., 2014. Impaired reduction of N₂O to N₂ in acid soils is due to a posttranscriptional interference with the expression of nosZ. *mBio* 5, e01383-e01314.
- Liu, Y., Wan, K.-Y., Tao, Y., Li, Z.-G., Zhang, G.-S., Li, S.-L., Chen, F., 2013. Carbon dioxide flux from rice paddy soils in central China: effects of intermittent flooding and draining cycles. *PloS one* 8, e56562.
- Livesley, S.J., Andrusiak, S.M., 2012. Temperate mangrove and salt marsh sediments are a small methane and nitrous oxide source but important carbon store. *Estuarine, Coastal and Shelf Science* 97, 19-27.
- McElnea, A.E., Ahern, C.R., Menzies, N.W., 2002. The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* 40, 1133-1157.
- McMillan, A.M.S., Pal, P., Phillips, R.L., Palmada, T., Berben, P.H., Jha, N., Sagggar, S., Luo, J., 2016. Can pH amendments in grazed pastures help reduce N₂O emissions from denitrification? – The effects of liming and urine addition on the completion of denitrification in fluvial and volcanic soils. *Soil biology & biochemistry* 93, 90-104.
- Melville, M., White, I., Lin, C., 1993. The origins of acid sulphate soils, In: Bush, R (ed.). *Proceedings of the National Conference on Acid Sulphate Soils (Coolangatta, NSW: June 24-25, 1993)*. CSIRO Australia/NSW Agriculture/Tweed Shire Council.
- Moore, T.R., Roulet, N.T., 1993. Methane flux: Water table relations in northern wetlands. *Geophysical Research Letters* 20.

- Mosley, L.M., Fitzpatrick, R.W., Palmer, D., Leyden, E., Shand, P., 2014a. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. *Sci Total Environ* 485-486, 281-291.
- Mosley, L.M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., W. Fitzpatrick, R., 2014b. Acidification of floodplains due to river level decline during drought. *J Contam Hydrol* 161, 10-23.
- Murakami, M., Furukawa, Y., Inubushi, K., 2005. Methane production after liming to tropical acid peat soil. *Soil science and plant nutrition (Tokyo)* 51, 697-699.
- Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., Erasmí, S., 2016. Greenhouse gas emissions from soils—A review. *Chemie der Erde - Geochemistry* 76, 327-352.
- Österholm, P., Åström, M., 2002. Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. *Applied Geochemistry* 17, 1209-1218.
- Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils, In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 29-96.
- Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, In: Dost, H. (Ed.), *Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils*. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 13–20.
- Powell, B., Martens, M., 2005. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar Pollut Bull* 51, 149-164.
- Rayment, G.E., Lyons, D.J., 2011. *Soil chemical methods*. CSIRO, Melbourne, Australia.
- Reddy, K.R., DeLaune, R.D., 2008. *Biogeochemistry of Wetlands: Science and Applications*. Baton Rouge: CRC Press, Baton Rouge.
- Rickard, D., Luther, G.W., 2007. Chemistry of Iron Sulfides. *Chem. Rev* 107, 514-562.
- Rousk, J., Brookes, P.C., Baath, E., 2009. Contrasting Soil pH Effects on Fungal and Bacterial Growth Suggest Functional Redundancy in Carbon Mineralization. *Appl Environ Microbiol* 75, 1589-1596.
- Russenes, A.L., Korsæth, A., Bakken, L.R., Dörsch, P., 2016. Spatial variation in soil pH controls off-season N₂O emission in an agricultural soil. *Soil Biology and Biochemistry* 99, 36-46.
- Samad, M.D.S., Ambarish, B., Lars, R.B., Timothy, J.C., Cecile, A.M.D.K., Karl, G.R., Gary, J.L., Sergio, E.M., 2016. Phylogenetic and functional potential links pH and N₂O emissions in pasture soils. *Scientific Reports* 6.
- Šimek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science* 53, 345-354.
- Šimek, M., Jiřová, L., Hopkins, D.W., 2002. What is the so-called optimum pH for denitrification in soil? *Soil Biology and Biochemistry* 34, 1227-1234.
- Šimek, M., Virtanen, S., Křišťůfek, V., Simojoki, A., Yli-Halla, M., 2011. Evidence of rich microbial communities in the subsoil of a boreal acid sulphate soil conducive to greenhouse gas emissions. *Agriculture, Ecosystems & Environment* 140, 113-122.
- Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B.M., Spadaro, D.A., Mosley, L., 2010. Climate-driven mobilisation of acid and metals from acid sulfate soils. *Marine and Freshwater Research* 61, 129-138.

- Thomsen, J., K., Torben, G., Raymond, P.C., 1994. Mass Spectrometric Studies of the Effect of pH on the Accumulation of Intermediates in Denitrification by *Paracoccus denitrificans*. *Appl Environ Microbiol* 60, 536-541.
- Van den Berg, G.A., Loch, J.P.G., Winkels, H.J., 1998. Effect of Fluctuating Hydrological Conditions on the Mobility of Heavy Metals in Soils of a Freshwater Estuary in the Netherlands. *Water, air, and soil pollution* 102, 377-388.
- Virtanen, S., Puustinen, M., Yli-Halla, M., 2017. Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate soil fields – based on soil redox potential and pH measurements. *Geoderma* 308, 252-259.
- Wang, Y., Guo, J., Vogt, R.D., Mulder, J., Wang, J., Zhang, X., 2018. Soil pH as the chief modifier for regional nitrous oxide emissions: New evidence and implications for global estimates and mitigation. *Glob Chang Biol* 24, e617-e626.
- Wang, Z.P., DeLaune, R.D., Patrick, W.H., Jr, Masscheleyn, P.H., 1993. Soil Redox and pH Effects on Methane Production in a Flooded Rice Soil. *Soil Science Society of America Journal*.
- West, T.O., McBride, A.C., 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. *Agriculture, Ecosystems & Environment* 108, 145-154.
- White, I., Melville, M.D., Wilson, B.P., Sammut, J., 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management* 5, 55-72.
- Wong, V.N.L., McNaughton, C., Pearson, A., 2016. Changes in soil organic carbon fractions after remediation of a coastal floodplain soil. *Journal of Environmental Management* 168, 280-287.
- Wrage, N., Velthof, G., van Beusichem, M., Oenema, O., 2001. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry* 33, 1723-1732.
- Wu, X., Sten, P., Engblom, S., Nowak, P., Österholm, P., Dopson, M., 2015. Impact of mitigation strategies on acid sulfate soil chemistry and microbial community. *The Science of the total environment* 526, 215.
- Yang, J., Liu, J., Hu, X., Li, X., Wang, Y., Li, H., 2013. Effect of water table level on CO₂, CH₄ and N₂O emissions in a freshwater marsh of Northeast China. *Soil Biology and Biochemistry* 61, 52-60.
- Zaman, M., Nguyen, M., Saggar, S., 2008. N sub(2)O and N sub(2) Emissions from Pasture and Wetland Soils with and Without Amendments of Nitrate, Lime and Zeolite Under Laboratory Condition. *Australian Journal of Soil Research* 46, 526-526.
- Zinder, S.H., 1994. *Physiological Ecology of Methanogens*. Boston, MA: Springer US, Boston, MA, pp. 128-206.

Chapter 6. Discussion and concluding remarks

6.1 General discussion

In ASS, large amounts of organic matter and interconnected reactions of sulfur and nitrogen make them potential sources of GHGs. In recent years, there has been an increase in studies identifying the GHGs derived from large areas of ASS (Denmead et al., 2011; Šimek et al., 2014). ASS are often found in low lying areas globally, including tropical coastal areas, estuarine floodplains and mangrove marshes, which provide waterlogged environments for pyrite formation (Dent and Pons, 1995).

The Australian studies (chapter 2, 3 and 5) described how coastal wetlands are highly vulnerable to inundation due to sea level rise and storm surge events. The intermittent tidal (wet-dry) cycles in coastal wetlands can cause variations in the watertable, affecting decomposition of organic matter which transforms SOC and N and therefore affects GHGs (Liu et al., 2017; Yang et al., 2017). Wet-dry cycles also occur over longer time periods due to seasonal changes from precipitation, storm surge events and seasonal flooding (Livesley and Andrusiak, 2012). When coastal wetlands are inundated, the depletion of O₂ results in a predictable sequence of anaerobic processes which follows the sequence: denitrification, Mn reduction, Fe(III) reduction, SO₄²⁻ reduction and methanogenesis (Ponnamperuma, 1972). Under anaerobic conditions, organic matter can undergo anaerobic microbial respiration to produce CH₄. This study has demonstrated that CH₄ was the main gas contributing to global warming based on CO₂-eq when ASS was inundated or subjected to wet-dry cycle conditions. CH₄ production occurred under strict anaerobic conditions (Dutaur and Verchot, 2007). This study also found that the CO₂ flux and N₂O flux were higher when the soils were drained compared to the flooded periods in wet-dry cycle treatments. The drained periods in the wet-dry cycle treatment led to enhanced O₂ penetration and promoted aerobic respiration and therefore enhanced the CO₂ flux compared with flooded periods in all sites. Wet-dry cycles also allow O₂ penetration into the soil during dry periods and NH₄⁺ was converted to NO₃⁻ by nitrification, thus enhancing N₂O flux.

CO₂ and N₂O comprised a small part of total CO₂-eq emissions under anaerobic conditions (Chapter 2). The low N₂O emissions in inundated soils may be caused by 1) reduction of NO₃⁻ to N₂ by denitrifiers under reducing conditions (Ruser et al., 2006); 2) the layer of surface water acting as a diffusion barrier and preventing emissions diffusing from the soil to the atmosphere; or 3) the low NO₃⁻ concentration which limits the denitrification process.

When ASS were drained and oxidized due to either natural processes such as coastal regression, isostatic land uplift (Boman et al., 2010a), or through human actions such as drainage of coastal areas for agriculture (Burton et al., 2006a; Mathew et al., 2001), the decomposition of organic matter was accelerated and CO₂ is produced (Tobias and Neubauer, 2019). This study has also found that when the soils were under dry

conditions, CO₂ comprised the principle part of total CO₂-eq emissions. N₂O was the second largest gas contributing to global warming under dry condition mainly due to nitrification processes because of the conversion from NH₄⁺ to NO₃⁻.

Vegetation type in ASS influence GHG emissions by providing different quantities and qualities of SOC and N. The C/N ratio in soils is used to determine the potential decomposability of organic matter (Bai et al., 2005). This research demonstrated that *Phragmites australis* had the highest CO₂ and CH₄ emissions compared to other sites because it had the highest SOC compared to other sites and the C/N ratio is comparatively lower compared to the *Leptospermum lanigerum* site. This promotes higher decomposition rates in the *Phragmites australis* site. This study also suggests that *Apium graveolens* and *Paspalum distichum* sites can be easily be decomposed compared to *Leptospermum lanigerum* species sites due to the lower C/N ratios in ASS environments.

When ASS was disturbed or exposed to the atmosphere by lowering of water tables, acidification of soil and water will occur and lead to the release of heavy metals (Boman et al., 2010b; Grealish et al., 2014). This study demonstrated that drying can cause the oxidation of sulfide minerals, acidification and increase dissolved trace metals. However, inundation of ASS by oceanic water or freshwater can improve water quality because of the neutralization of soil acidity by reduction reactions of Fe³⁺ and SO₄²⁻ (Johnston et al., 2014; Johnston et al., 2012). This research has shown that brackish water inundation prevented further oxidation of RIS and is an effective mitigation method to reduce net acidity in coastal ASS environments.

In Finland, almost all fields need artificial drainage before they can be properly cultivated. Lime is widely used to increase the soil pH (Dalhem et al., 2019; Wu et al., 2015). However, declining rates of liming can result in gradual lowering of soil pH and enhanced N₂O emissions. In the Finnish study (Chapter 4), the results indicated that addition of lime (CaCO₃) can increase the soil pH to neutral conditions and reduce N₂O emissions in most horizons. The total GHG production based on CO₂-eq in the lime treatments was significantly lower than that in the non-limed control treatment in surface soils of ASS.

Less attention has been paid to the effects of lime addition on GHGs in ASS in Australia. This study determined whether the lime treatment was effective in reducing GHGs in coastal areas in Australia even though the formation of ASS is different compared to their formation in Finland (Chapter 5). The results showed lime addition decreased N₂O emissions but increased CO₂ emissions and CH₄ emissions in all inundation treatments. Total GHG emissions based on CO₂-eq conversion in limed soils were higher compared with non-limed soils under all inundation treatments in temperate coastal wetlands in Australia. This is in contrast to what was found in the Finnish study.

Overall, our results demonstrated that GHGs were mainly affected by SOC, mineral N, soil pH and inundation in ASS. Lime treatment and inundation strategies are two practical methods to remediate ASS as they can improve soil pH, reduce soil acidification and transport of trace metals. From the incubation experiments applied in Finland and Australia, it is suggested that lime treatment should be carefully applied to reduce emissions, because there might be additional CO₂ emissions produced when the lime neutralizes the acidity produced.

6.2 Future research

Generally, liming reduced GHG emissions based on CO₂-eq in ASS in Finland, provided that topsoil dominated the GHG production of the soil profile. However, it was less efficient in reducing the total GHG emissions in subsoils in Finland due to enhanced microbial respiration and denitrification. Australian soils had higher GHG emissions based on CO₂-eq with lime addition in all horizons compared with non-limed soils. The liming had different effects on GHG emissions between Finland and Australia. The mineral N contents (NH₄⁺-N and NO₃⁻-N) in Australian ASS was generally lower than that in the Finnish ASS. The N₂O emission only contributed to small proportion in the total GHG emissions in the Australian ASS. However, the N₂O emission contributed to large proportion in the total GHG emission in the top horizon in the Finnish ASS. Therefore, even though liming decreased N₂O emissions in Australian ASS, the higher GHG emissions in limed soils were due to enhanced CO₂ emissions. The efficiency of liming on GHG emissions in different soil horizons were also different in Finland. Therefore, the contributions of different soil horizons to GHG emissions in the field remain topics for future research.

Further field-based studies should consider the different environmental factors like soil temperature, diurnal and seasonal variations, tides, storms, rainfall together affecting GHG emissions over longer periods of time in ASS. Incubation experiments in Chapters 2, 3, 4, and 5 were undertaken in a controlled environment which analysed the effects of specific treatments on GHG emissions. Scaling up these experiments in to the field to measure the GHG emissions at a landscape scale among different vegetation types when the floodplain is subjected to cyclical inundation will better represent the effects due to sea level rise and storm surge events.

In our study, adding lime to soils increased CO₂ emissions when the lime neutralized the acidity in ASS in the closed system. In the open system, the acid generated in ASS might be exported through groundwater

flow. Therefore, how the CO₂ emissions affected by adding lime in the natural soils for longer periods of time needs to be identified in the future.

In this study, a lab-based closed chamber method was applied to measure GHG flux. The results from chamber method deliver data at the scale of a soil core (0.5-5m²) (Reimann et al., 2009). At an ecosystem scale, the fluxes of energy, matter and organisms are important drivers (Limberger et al., 2017). CO₂ and CH₄ flux contribute to ecosystem flux and can provide insights into how climate change affects the carbon budget at an ecosystem scale (Baldocchi, 2003; Xiao et al., 2011). However, in the field, GHG fluxes are the result of decomposition of organic matter and interactions with inundation and biological activity. Tower-based approaches such as eddy covariance provide quasi-continuous measurement of gas exchange at the ecosystem scale and can quantify GHG flux over larger areas (McNicol et al., 2017). The whole ecosystem CH₄ and CO₂ flux can be measured using eddy covariance flux tower (Teh et al., 2011). N₂O flux can be measured using the static flux chamber approach. Eddy covariance flux tower is a micrometeorological method, which uses vertical turbulence to analyse the gas exchange between soil surface and atmosphere in terms of gas, energy, and momentum (Vesala et al., 2006). The eddy covariance technique can be applied to measure continuous carbon flux and incorporate areas up to the medium local scale (5-50 km²) (Myklebust et al., 2008; Reimann et al., 2009). Therefore, to scale up the effects of inundation on carbon cycling and GHG emissions over the floodplain with different vegetation types from this study, closed chamber methods and eddy covariance flux towers should be coupled to identify the floodplain fluxes at an ecosystem level.

In ASS, sulfur cycling is also an important biogeochemical process and necessary for sulfate reduction, pyrite formation, heavy metal transport and atmospheric sulfur emissions (SO₂ and H₂S) (Luther et al., 1986). SO₂ and H₂S are significant pollutants and can change the acid-base chemistry of the atmosphere, playing an important role in the global sulfur cycle. van Breemen et al. (1993) and Macdonald et al. (2004b) suggested that large potential acidity stores in pyritic sediments can be a source of SO₂. Kinsela et al. (2011) demonstrated that drained ASS are potentially large sources of biogenic H₂S and SO₂ and found SO₂ fluxes were closely related to surface soil temperatures and moisture content, while H₂S was emitted regardless of these factors. Studies on H₂S and SO₂ have been widely conducted in wetlands. However, the studies about biogenic S emissions (H₂S and SO₂) from ASS are lacking. Sulfur is an important redox element under natural conditions and can also undergo different biogeochemical transformations under different soil pH and redox potentials. Thus, this is a gap in our understanding of emissions from ASS environments.

In this study, the GHG emissions from coastal wetlands and agriculture land were measured. In the future, evaluating GHG emissions and soil organic carbon from other types of wetlands, such as restored and drained wetlands and peatlands in ASS environments is important to understand the mechanisms and

implications in a changing climate and with changing land-use. The data and knowledge generated from the research can aid the policy-makers for GHG accounting purposes. The research will improve assessment approaches about wetlands under different land-uses in ASS environments and provide support to climate mitigation and adaptation plans.

6.3 Conclusions

The overall aim of this thesis was to determine the GHGs in ASS from coastal wetlands due to sea level rise in Australia and from agricultural land due to the post-glacial rebound by isostatic uplift in Finland. The results will assist land managers in remediating ASS using lime treatments and inundation strategies.

The thesis had the following objectives:

Objective 1: Identify the effects of inundation on GHGs under controlled conditions in coastal acid sulfate soils (CASS) with sea level rise with different vegetation types in southern Australia.

Chapter 2 addressed this objective by assessing the effects of inundation caused by sea level fluctuations and sea level rise with climate change on GHGs. Soil cores from different vegetation types in the floodplain were incubated under dry, flooded and wet-dry cycle treatments. During the dry treatment, CO₂ is the dominant GHG while CH₄ dominates in flooded conditions. Under the wet-dry cycle treatment, CH₄ was the main gas contributing to global warming, followed by CO₂ and N₂O. In addition, treatments with *Phragmites australis* had higher global warming potential based on CO₂-eq compared with other vegetation types like rushes, pastures, woody vegetation due to the higher organic matter.

Objective 2: Identify the effect of inundation on soil chemistry in CASS with different vegetation types in southern Australia.

Chapters 3 and 5 addressed this objective by assessing the effects of inundation caused by sea level fluctuation and sea level rise on soil chemistry, including RIS in terms of AVS and CRS, potential acidity and trace metals (Fe, Al, Mn, Zn, Ni). The flooded treatment significantly increased AVS and CRS in most soil depths. The highest net acidity occurred in the dry treatment and lowest net acidity was observed following the flooded treatment in most soil depths. Brackish water inundation provides a mechanism to prevent further oxidation of RIS and can be an effective tool to reduce acidity by forming or reforming

pyrite in temperate ASS environments. These results highlighted that inundation could be considered when planning remediation approaches for ASS.

Objective 3: Determine the effect of lime (CaCO_3) addition on GHGs (N_2O and CO_2) and the product ratio of denitrification $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ in ASS and non-ASS under aerobic and anaerobic conditions in boreal agricultural land and coastal wetland

Chapters 4 and 5 addressed this objective by identifying the effects of lime treatments on GHG emissions from ASS. Low soil pH in ASS inhibits the reduction of N_2O to N_2 and leads to N_2O becoming the more dominant GHG. Low soil pH limits the availability of organic C and mineral N to denitrifying bacteria. Lime decreased N_2O due to the conversion from N_2O to N_2 via N_2O reductase during denitrification. The product ratio of $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ in the limed soils was lower than non-limed soils in most horizons. Chapters 4 and 5 applied lime to ASS from Finnish agricultural land and an Australian coastal wetland and observed that lime (CaCO_3) can reduce the N_2O emissions, but also increased CO_2 emissions due to the dissolution of CaCO_3 and the increased SOC mineralization. In Chapter 4, lime can also increase the total denitrification product ($\text{N}_2\text{O}+\text{N}_2$) because lime addition increased the availability of organic carbon and nitrogen to the microbes which were initially limited by low soil pH in the ASS. Therefore, mitigating GHG emissions by liming of soils in the field should be done with caution due to concurrently increased CO_2 emissions and denitrification.

Objective 4: Identify the effects of lime (CaCO_3) and inundation on GHGs and potential acidity in a coastal wetland soil in southern Australia.

Chapter 5 addressed this objective by examining the inundation and lime treatments on RIS, TAA, net acidity, trace metals (Fe, Al, Mn, Zn, Ni) in a coastal wetland in Australia. The highest net acidity occurred in the dry treatment. Inundation can reduce acidity by forming or reforming pyrite in ASS. The lime added to the pasture soils raised the soil pH effectively. Liming neutralized the acidity in the soils and therefore decreased net acidity. Lime addition generally decreased Al and Fe concentrations in most horizons because the increase in soil pH can lead to the precipitation of Al and Fe minerals.

In general, this study showed that SOC, mineral N, water levels, soil pH together can affect GHG emissions in ASS from coastal wetlands in Australia and agricultural land in Finland. CH_4 was the main gas contributing to global warming potential based on CO_2 -eq when ASS was inundated while CO_2 was the largest contributor of total CO_2 -eq emissions when ASS were in dry conditions. Lime treatments are widely used to remediate drained ASS for agriculture. Lime addition was effective in improving soil pH, decreasing

N₂O emissions and N₂O/(N₂O+N₂), but the increased CO₂ and CH₄ emissions contribute to higher global warming potential based on CO₂-eq with liming. Overall, the inundation and lime strategies can reduce the net acidity and trace metals in ASS if they are oxidized and can assist land managers to remediate ASS. However, lime treatment needs to be carefully applied due to the increased CO₂ emissions derived from the dissolution of CaCO₃. Also, the inundation treatment might lead to higher global warming potential due to the dominant CH₄ emissions.

6.4 References

- Abalos, D., Liang, Z., Dörsch, P., Elsgaard, L., 2020. Trade-offs in greenhouse gas emissions across a liming-induced gradient of soil pH: Role of microbial structure and functioning. *Soil biology & biochemistry* 150, 108006.
- Aciego Pietri, J.C., Brookes, P.C., 2008. Relationships between soil pH and microbial properties in a UK arable soil. *Soil biology & biochemistry* 40, 1856-1861.
- Adams, T.M., Adams, S.N., 1983. The effects of liming and soil pH on carbon and nitrogen contained in the soil biomass. *The Journal of agricultural science* 101, 553.
- Ahern, C.R., Blunden, B., Sullivan, L.A., McElnea, A.E., 2004. Soil sampling handling, preparation and storage, In: Ahern, C.R., McElnea, A.E., Sullivan, L.A. (Eds.), *Acid Sulfate Soils Laboratory Methods Guidelines*. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia.
- Allen, D.E., Dalal, R.C., Rennenberg, H., Meyer, R.L., Reeves, S., Schmidt, S., 2007. Spatial and temporal variation of nitrous oxide and methane flux between subtropical mangrove sediments and the atmosphere. *Soil Biology and Biochemistry* 39, 622-631.
- Amundson, R.G., Davidson, E.A., 1990. Carbon dioxide and nitrogenous gases in the soil atmosphere. *Journal of Geochemical Exploration* 38, 13-41.
- Andersson, S., Nilsson, S.I., 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil biology & biochemistry* 33, 1181-1191.
- Andriessse, W., Mensvoort, M.E.F.v., 2006. Acid sulfate soils: distribution and extent, In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. CRC Press, Boca Raton, FL, pp. 14–19.
- Arakaki, T., Morse, J.W., 1993. Coprecipitation and adsorption of Mn(II) with mackinawite (FeS) under conditions similar to those found in anoxic sediments. *Geochimica et Cosmochimica Acta* 57, 9-14.
- Armstrong, J., Armstrong, W., 2001. Rice and Phragmites: effects of organic acids on growth, root permeability, and radial oxygen loss to the rhizosphere. *Am J Bot* 88, 1359-1370.
- Astrom, M., Bjorklund, A., 1995. Impact of acid sulfate soils on stream water geochemistry in western Finland. *Journal of Geochemical Exploration* 55, 163-170.
- Astrom, M., Spiro, B., 2000. Impact of isostatic uplift and ditching of sulfidic sediments on the hydrochemistry of major and trace elements and sulfur isotope ratios in streams, Western Finland. *Environmental Science & Technology* 34, 1182.
- Bååth, E., Arnebrant, K., 1994. Growth rate and response of bacterial communities to pH in limed and ash treated forest soils. *Soil biology & biochemistry* 26, 995-1001.

- Backlund, K., Boman, A., Fröjdö, S., Åström, M., 2005. An analytical procedure for determination of sulphur species and isotopes in boreal acid sulphate soils and sediments. *Agricultural and Food Science* 14, 70-82.
- Badalucco, L., Grego, S., Dell'Orco, S., Nannipieri, P., 1992. Effect of liming on some chemical, biochemical, and microbiological properties of acid soils under spruce (*Picea abies* L.). *Biology and Fertility of Soils* 14, 76-83.
- Baggs, E.M., 2011. Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction. *Current Opinion in Environmental Sustainability* 3, 321-327.
- Baggs, E.M., Smales, C.L., Bateman, E.J., 2010. Changing pH shifts the microbial sources as well as the magnitude of N₂O emission from soil. *Biology and Fertility of Soils* 46, 793-805.
- Bai, J., Ouyang, H., Deng, W., Zhu, Y., Zhang, X., Wang, Q., 2005. Spatial distribution characteristics of organic matter and total nitrogen of marsh soils in river marginal wetlands. *Geoderma* 124, 181-192.
- Bakken, L.R., Bergaust, L., Liu, B., Frostegård, A., 2012. Regulation of denitrification at the cellular level: a clue to the understanding of N₂O emissions from soils. *Philosophical transactions of the Royal Society of London. Series B, Biological sciences* 367, 1226.
- Baldocchi, D.D., 2003. Assessing the eddy covariance technique for evaluating carbon dioxide exchange rates of ecosystems: past, present and future. *Global Change Biology* 9, 479-492.
- Bartlett, K., Bartlett, D., Harriss, R., Sebach, D., 1987. Methane emissions along a salt marsh salinity gradient. *Biogeochemistry* 4, 183-202.
- Bateman, E.J., Baggs, E.M., 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biology and Fertility of Soils* 41, 379-388.
- Beek, K.J., Blokhuis, W.A., Driessen, P.M., Van Breemen, N., Brinkman, R., Pons, L.J., 1980. Problem soils: their reclamation and management, In: Alterra, L., Wageningen, NL (Eds.), *Land Reclamation and Water Management, Developments, Problems and Challenges*. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 43-72.
- Beringer, J., Livesley, S.J., Randle, J., Hutley, L.B., 2013. Carbon dioxide fluxes dominate the greenhouse gas exchanges of a seasonal wetland in the wet-dry tropics of northern Australia. *Agricultural and Forest Meteorology* 182-183, 239-247.
- Berner, R.A., 1984. Sedimentary pyrite formation: An update. *Geochimica et Cosmochimica Acta* 48, 605-615.
- Bethke, C.M., 2007. *Geochemical and Biogeochemical Reaction Modeling*. Cambridge: Cambridge University Press, Cambridge.
- Biasi, C., Lind, S.E., Pekkarinen, N.M., Huttunen, J.T., Shurpali, N.J., Hyvönen, N.P., Repo, M.E., Martikainen, P.J., 2008. Direct experimental evidence for the contribution of lime to CO₂ release from managed peat soil. *Soil biology & biochemistry* 40, 2660-2669.
- Bitton, G., 1994. *Wastewater microbiology*. New York : Wiley-Liss, New York.
- Blodau, C., Peiffer, S., 2003. Thermodynamics and organic matter: constraints on neutralization processes in sediments of highly acidic waters. *Applied Geochemistry* 18, 25-36.
- Boman, A., Åström, M., Fröjdö, S., 2008. Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide—The role of artificial drainage. *Chemical Geology* 255, 68-77.
- Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010a. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.

- Boman, A., Fröjdö, S., Backlund, K., Åström, M.E., 2010b. Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. *Geochimica et Cosmochimica Acta* 74, 1268-1281.
- Brady, N.C., Weil, R.R., 2016. The nature and properties of soils, Fifteenth edition ed. Upper Saddle River, N.J. : Prentice Hall, Upper Saddle River, N.J.
- Bruce, A.H., Elisabeth, A.H., Robert, B.J., Chapin, F.S., Harold, A.M., Christopher, B.F., 1997. The fate of carbon in grasslands under carbon dioxide enrichment. *Nature* 388, 576.
- Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochimica et Cosmochimica Acta* 75, 3434-3451.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006a. Elemental sulfur in drain sediments associated with acid sulfate soils. *Applied Geochemistry* 21, 1240-1247.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006b. Fractionation and extractability of sulfur, iron and trace elements in sulfidic sediments. *Chemosphere* 64, 1421-1428.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006c. Reduced Inorganic Sulfur Speciation in Drain Sediments from Acid Sulfate Soil Landscapes. *Environmental Science & Technology* 40, 888-893.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006d. Sedimentary iron geochemistry in acidic waterways associated with coastal lowland acid sulfate soils. *Geochimica et Cosmochimica Acta* 70, 5455-5468.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Hocking, R.K., Mitchell, D.R.G., Johnston, S.G., Fitzpatrick, R.W., Raven, M., McClure, S., Jang, L.Y., 2009. Iron-Monosulfide Oxidation in Natural Sediments: Resolving Microbially Mediated S Transformations Using XANES, Electron Microscopy, and Selective Extractions. *Environmental Science & Technology* 43, 3128-3134.
- Burton, E.D., Bush, R.T., Sullivan, L.A., Johnston, S.G., Hocking, R.K., 2008a. Mobility of arsenic and selected metals during re-flooding of iron- and organic-rich acid-sulfate soil. *Chemical Geology* 253, 64-73.
- Burton, E.D., Sullivan, L.A., Bush, R.T., Johnston, S.G., Keene, A.F., 2008b. A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Applied Geochemistry* 23, 2759-2766.
- Bush, R.T., Fyfe, D., Sullivan, L.A., 2004. Occurrence and abundance of monosulfidic black ooze in coastal acid sulfate soil landscapes. *Australian Journal of Soil Research* 42, 609.
- Cavigelli, M.A., Robertson, G.P., 2001. Role of denitrifier diversity in rates of nitrous oxide consumption in a terrestrial ecosystem. *Soil biology & biochemistry* 33, 297-310.
- CCMA, 2014. Corangamite Waterway Strategy 2014- 2022, https://issuu.com/gsdm/docs/waterway_strategy_2014-22.
- Chanton, J.P., Arkebauer, T.J., Harden, H.S., Verma, S.B., 2002. Diel variation in lacunal CH₄ and CO₂ concentration and $\delta^{13}\text{C}$ in *Phragmites australis*. *Biogeochemistry* 59, 287-301.
- Chen, G.C., Tam, N.F.Y., Ye, Y., 2010. Summer fluxes of atmospheric greenhouse gases N₂O, CH₄ and CO₂ from mangrove soil in South China. *Science of The Total Environment* 408, 2761-2767.
- Cheng, X., Peng, R., Chen, J., Luo, Y., Zhang, Q., An, S., Chen, J., Li, B., 2007. CH₄ and N₂O emissions from *Spartina alterniflora* and *Phragmites australis* in experimental mesocosms. *Chemosphere* 68, 420-427.
- Colbourn, P., Dowdell, R.J., 1984. Denitrification in field soils. *Plant and Soil* 76, 213-226.

- Cook, F.J., Hicks, W., Gardner, E.A., Carlin, G.D., Froggatt, D.W., 2000. Export of Acidity in Drainage Water from Acid Sulphate Soils. *Marine Pollution Bulletin* 41, 319-326.
- Creeper, N., Fitzpatrick, R., Shand, P., 2013. The occurrence of inland acid sulphate soils in the floodplain wetlands of the Murray-Darling Basin, Australia, identified using a simplified incubation method. *Soil Use Manage* 29, 130-139.
- Čuhel, J., Šimek, M., 2011. Proximal and distal control by pH of denitrification rate in a pasture soil. *Agriculture, Ecosystems & Environment* 141, 230-233.
- Dalal, R., Allen, D., 2008. TURNER REVIEW No. 18. Greenhouse gas fluxes from natural ecosystems. *Australian Journal of Botany* 56, 369-407.
- Dalhem, K., Engblom, S., Stén, P., Österholm, P., 2019. Subsurface hydrochemical precision treatment of a coastal acid sulfate soil. *Applied Geochemistry* 100, 352-362.
- Davidson, E.A., 1992. Sources of Nitric Oxide and Nitrous Oxide following Wetting of Dry Soil. *Soil Science Society of America Journal* 56, 95-102.
- Davidson, E.A., 1993. Soil Water Content and the Ratio of Nitrous Oxide to Nitric Oxide Emitted from Soil, In: Oremland, R.S. (Ed.), *Biogeochemistry of Global Change: Radiatively Active Trace Gases Selected Papers from the Tenth International Symposium on Environmental Biogeochemistry, San Francisco, August 19–24, 1991*. Springer US, Boston, MA, pp. 369-386.
- Davidson, E.A., Belk, E., Boone, R.D., 1998. Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. *Global Change Biology* 4, 217-227.
- Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides. *BioScience* 50, 667-680.
- Denmead, O.T., Macdonald, B.C.T., Bryant, G., Naylor, T., Wilson, S., Griffith, D.W.T., Wang, W.J., Salter, B., White, I., Moody, P.W., 2010. Emissions of methane and nitrous oxide from Australian sugarcane soils. *Agricultural and Forest Meteorology* 150, 748-756.
- Denmead, O.T., Macdonald, B.C.T., White, I., Bryant, G., 2011. Gaseous Nitrogen Losses from Coastal Acid Sulfate Soils: A Short-Term Study. *Pedosphere* 21, 197-206.
- Dent, D., 1986. Acid sulphate soils: a baseline for research and development. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands.
- Dent, D.L., Pons, L.J., 1995. A world perspective on acid sulphate soils. *Geoderma* 67, 263-276.
- Desai, A.R., Moorcroft, P.R., Bolstad, P.V., Davis, K.J., 2007. Regional carbon fluxes from an observationally constrained dynamic ecosystem model: Impacts of disturbance, CO₂ fertilization, and heterogeneous land cover. *Journal of Geophysical Research: Biogeosciences* 112, n/a-n/a.
- Dobbie, K.E., Smith, K.A., 2001. The effects of temperature, water-filled pore space and land use on N₂O emissions from an imperfectly drained gleysol. *European Journal of Soil Science* 52, 667-673.
- Dutaur, L., Verchot, L.V., 2007. A global inventory of the soil CH₄ sink. *Global Biogeochemical Cycles* 21, n/a-n/a.
- Edén, P., Auri, J., Rankonen, E., Martinkauppi, A., Österholm, P., Beucher, A., 2012. Mapping acid sulfate soils in Finland: methods and results, 7th International Acid Sulfate Soil Conference, Vaasa, Finland 2012 - Towards Harmony between Land Use and the Environment, pp. 31-33.
- Esala, M.J., 1995. Changes in the extractable ammonium- and nitrate-nitrogen contents of soil samples during freezing and thawing. *Communications in Soil Science and Plant Analysis* 26, 61-68.

- Evangelou, V.P., Zhang, Y.L., 1995. A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Critical reviews in environmental science and technology* 25, 141-199.
- Fältmarsch, R., Astrom, M., Vuori, K.-M., 2008. Environmental risks of metals mobilised from acid sulphate soils in Finland: A literature review. *Boreal Environment Research* 13, 444-456.
- Fanning, D.S., Burch, S.N., 2000. Coastal acid sulfate soils, In: R.I.Barnhisel (Ed.), *Reclamation of drastically disturbed lands*. ASA,CSSA, and SSSA, Madison,WI, pp. 921-937.
- Fanning, D.S., Rabenhorst, M.C., Burch, S.N., Islam, K.R., Tangren, S.A., 2002. Sulfides and sulfates, In: Dixon, J.B., Schulze, D.G., Daniels, W.L. (Eds.), *Soil mineralogy with environmental applications*. Soil Science Society of America, Madison, WI, pp. 229–260.
- Fioretto, A., Di Nardo, C., Papa, S., Fuggi, A., 2005. Lignin and cellulose degradation and nitrogen dynamics during decomposition of three leaf litter species in a Mediterranean ecosystem. *Soil biology & biochemistry* 37, 1083-1091.
- Firestone, M.K., Firestone, R.B., Tiedje, J.M., 1980. Nitrous oxide from soil denitrification: factors controlling its biological production. *Science (New York, N.Y.)* 208, 749.
- Fitzpatrick, R., J. Davies, P., P. Thomas, B., Merry, R., Fotheringham, D., Hicks, W., L. Barnett, E., 2002. Properties, distribution and environmental hazards of South Australian coastal acid sulfate soils.
- Fitzpatrick, R., Marvanek, S., Powell, B., Grealish, G., 2010. Atlas of Australian Acid Sulfate Soils: recent developments and future priorities, In: Gilkes, R.J., Prakongkep, N. (Eds.), *Proceedings: 19th World Congress of Soil Science. Soil solutions for a changing world*. CSIRO, Brisbane, Australia, pp. 24-27.
- Fitzpatrick, R.W., Fritsch, E., Self, P.G., 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes: V. Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* 69, 1-29.
- Fuentes, J.P., Bezdicek, D.F., Flury, M., Albrecht, S., Smith, J.L., 2006. Microbial activity affected by lime in a long-term no-till soil. *Soil & tillage research* 88, 123-131.
- Galbally, I.E., Meyer, M.C.P., Wang, Y.-P., Smith, C.J., Weeks, I.A., 2010. Nitrous oxide emissions from a legume pasture and the influences of liming and urine addition. *Agriculture, Ecosystems & Environment* 136, 262-272.
- Gallardo, A., Schlesinger, W.H., 1994. Factors limiting microbial biomass in the mineral soil and forest floor of a warm-temperate forest. *Soil Biology and Biochemistry* 26, 1409-1415.
- Gao, B., Ju, X., Su, F., Meng, Q., Oenema, O., Christie, P., Chen, X., Zhang, F., 2014. Nitrous oxide and methane emissions from optimized and alternative cereal cropping systems on the North China Plain: A two-year field study. *Sci Total Environ* 472, 112-124.
- Garbuio, F.J., Jones, D.L., Alleoni, L.R.F., Murphy, D.V., Caires, E.F., 2011. Carbon and Nitrogen Dynamics in an Oxisol as Affected by Liming and Crop Residues under No - Till. *Soil Science Society of America Journal* 75, 1723-1730.
- Gatland, J.R., Santos, I.R., Maher, D.T., Duncan, T.M., Erler, D.V., 2014. Carbon dioxide and methane emissions from an artificially drained coastal wetland during a flood: Implications for wetland global warming potential. *Journal of Geophysical Research: Biogeosciences* 119, 1698-1716.
- Grealish, G.J., Fitzpatrick, R.W., Shand, P., 2014. Regional distribution trends and properties of acid sulfate soils during severe drought in wetlands along the lower River Murray, South Australia: Supporting hazard assessment. *Geoderma Regional* 2-3, 60-71.
- Green, R., Waite, T.D., Melville, M.D., 2007. Treatment of Acid Sulfate Soil Drainage By Direct Application of Alkaline Reagents. *Water, air, and soil pollution* 178, 59-68.

- Grover, S.P., Butterly, C.R., Wang, X., Tang, C., 2017. The short-term effects of liming on organic carbon mineralisation in two acidic soils as affected by different rates and application depths of lime. *Biology and Fertility of Soils* 53, 431-443.
- Guo, X., Xueming, Y., Drury, C.F., Reynolds, W.D., Fan, R., 2014. The extent of soil drying and rewetting affects nitrous oxide emissions, denitrification, and nitrogen mineralization.(Report). *Soil Science Society of America Journal* 78, 194.
- Hall, J.M., Paterson, E., Killham, K., 1998. The effect of elevated CO₂ concentration and soil pH on the relationship between plant growth and rhizosphere denitrification potential. *Global Change Biology* 4, 209-216.
- Hamilton, S.K., Kurzman, A.L., Arango, C., Jin, L., Robertson, G.P., 2007. Evidence for carbon sequestration by agricultural liming. *Global Biogeochem. Cycles* 21, GB2021-n/a.
- Hicks, W., Fitzpatrick, R., Bowman, G., 2003. MANAGING COASTAL ACID SULFATE SOILS: THE EAST TRINITY EXAMPLE.
- Hicks, W.S., Bowman, G.M., Fitzpatrick, R.W., 2009. Effect of season and landscape position on the aluminium geochemistry of tropical acid sulfate soil leachate. *Australian Journal of Soil Research* 47, 137-153.
- Higgins, S., Laughlin, R.J., Watson, C.J., 2013. Antecedent effect of lime on nitrous oxide and dinitrogen emissions from grassland soils. *Nutrient cycling in agroecosystems* 95, 219-229.
- Hirota, M., Senga, Y., Seike, Y., Nohara, S., Kunii, H., 2007. Fluxes of carbon dioxide, methane and nitrous oxide in two contrastive fringing zones of coastal lagoon, Lake Nakaumi, Japan. *Chemosphere* 68, 597-603.
- Hirota, M., Tang, Y., Hu, Q., Hirata, S., Kato, T., Mo, W., Cao, G., Mariko, S., 2004. Methane emissions from different vegetation zones in a Qinghai-Tibetan Plateau wetland. *Soil Biology and Biochemistry* 36, 737-748.
- Högfors-Rönholm, E., Christel, S., Dalhem, K., Lillhonga, T., Engblom, S., Österholm, P., Dopson, M., 2018. Chemical and microbiological evaluation of novel chemical treatment methods for acid sulfate soils. *Science of The Total Environment* 625, 39-49.
- Holmer, M., Nielsen, S.L., Nielsen, 1997. Sediment sulfur dynamics related to biomass-density patterns in *Zostera marina* (eelgrass) beds. *Marine ecology. Progress series (Halstenbek)* 146, 163-171.
- Im, S., Mostafa, A., Kim, D.-H., 2021. Use of citric acid for reducing CH₄ and H₂S emissions during storage of pig slurry and increasing biogas production: Lab- and pilot-scale test, and assessment. *The Science of the total environment* 753, 142080-142080.
- Inglett, K., Inglett, P., Reddy, K., Osborne, T., 2012. Temperature sensitivity of greenhouse gas production in wetland soils of different vegetation. *An International Journal* 108, 77-90.
- Inubushi, K., Naganuma, H., Kitahara, S., 1996. Contribution of denitrification and autotrophic and heterotrophic nitrification to nitrous oxide production in andosols. *Biology and Fertility of Soils* 23, 292-298.
- IPCC, 2007. Changes in Atmospheric Constituents and in Radioactive Forcing, *Climate Change: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Isbell, R.F.a., 2016. The Australian soil classification, Second edition. ed. Clayton, Vic. CSIRO Publishing.
- Jayalath, N., Fitzpatrick, R., Mosley, L.M., Marschner, P., 2021. Addition of wheat straw to acid sulfate soils with different clay contents reduces acidification in two consecutive submerged-moist cycles. *Geoderma* 385, 114892.
- Jayalath, N., Fitzpatrick, R.W., Mosley, L., Marschner, P., 2016. Type of organic carbon amendment influences pH changes in acid sulfate soils in flooded and dry conditions. *Journal of soils and sediments* 16, 518-526.

- Jiao, Z., Hou, A., Shi, Y., Huang, G., Wang, Y., Chen, X., 2006. Water Management Influencing Methane and Nitrous Oxide Emissions from Rice Field in Relation to Soil Redox and Microbial Community. *Communications in Soil Science and Plant Analysis* 37, 1889-1903.
- Johnston, S.G., Burton, E.D., Aaso, T., Tuckerman, G., 2014. Sulfur, iron and carbon cycling following hydrological restoration of acidic freshwater wetlands. *Chemical Geology* 371, 9-26.
- Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., Smith, D., Martens, M.A., McElnea, A.E., Ahern, C.R., Powell, B., Stephens, L.P., Wilbraham, S.T., van Heel, S., 2009a. Changes in water quality following tidal inundation of coastal lowland acid sulfate soil landscapes. *Estuarine, Coastal and Shelf Science* 81, 257-266.
- Johnston, S.G., Keene, A.F., Burton, E.D., Bush, R.T., Sullivan, L.A., 2012. Quantifying alkalinity generating processes in a tidally remediating acidic wetland. *Chemical Geology* 304-305, 106-116.
- Johnston, S.G., Keene, A.F., Bush, R.T., Burton, E.D., Sullivan, L.A., Smith, D., McElnea, A.E., Martens, M.A., Wilbraham, S., 2009b. Contemporary pedogenesis of severely degraded tropical acid sulfate soils after introduction of regular tidal inundation. *Geoderma* 149, 335-346.
- Johnston, S.G., Keene, A.F., Bush, R.T., Sullivan, L.A., Wong, V.N.L., 2011. Tidally driven water column hydro-geochemistry in a remediating acidic wetland. *Journal of Hydrology* 409, 128-139.
- Johnston, S.G., Slavich, P.G., Hirst, P., 2005. Changes in surface water quality after inundation of acid sulfate soils of different vegetation cover. *Australian Journal of Soil Research* 43, 1-12.
- Johnston, S.G., Slavich, P.G., Sullivan, L.A., Hirst, P., 2003. Artificial drainage of floodwaters from sulfidic backswamps: effects on deoxygenation in an Australian estuary. *Marine and Freshwater Research* 54, 781-795.
- Jones, W.J., Nagie, D.P.J., Whitman, W.B., 1987. Methanogens and the diversity of archaeobacteria. *Microbiol Rev* 51, 135-177.
- Joukainen, S., Yli-Halla, M., 2003. Environmental impacts and acid loads from deep sulfidic layers of two well-drained acid sulfate soils in western Finland. *Agriculture, Ecosystems & Environment* 95, 297-309.
- Jugsujinda, A., Delaune, R., Lindau, C., Sulaeman, E., Pezeshki, S., 1996. Factors controlling carbon dioxide and methane production in acid sulfate soils. *An International Journal of Environmental Pollution* 87, 345-355.
- Karimian, N., Johnston, S.G., Burton, E.D., 2017. Effect of cyclic redox oscillations on water quality in freshwater acid sulfate soil wetlands. *Science of The Total Environment* 581-582, 314-327.
- Karimian, N., Johnston, S.G., Burton, E.D., 2018. Iron and sulfur cycling in acid sulfate soil wetlands under dynamic redox conditions: A review. *Chemosphere* 197, 803-816.
- Keene, A.F., Johnston, S.G., Bush, R.T., Sullivan, L.A., Burton, E.D., McElnea, A.E., Ahern, C.R., Powell, B., 2011. Effects of hyper-enriched reactive Fe on sulfidisation in a tidally inundated acid sulfate soil wetland. *Biogeochemistry* 103, 263-279.
- Keller, M., Stallard, R.F., 1994. Methane emission by bubbling from Gatun Lake, Panama. *Journal of Geophysical Research: Atmospheres* 99, 8307-8319.
- Kinsela, A.S., Denmead, O.T., Macdonald, B.C.T., Melville, M.D., Reynolds, J.K., White, I., 2011. Field-based measurements of sulfur gas emissions from an agricultural coastal acid sulfate soil, eastern Australia. *Soil Research* 49, 471-480.
- Knowles, R., 1982. Denitrification. *Microbiological Reviews* 46, 43-70.
- Kolbl, A., Marschner, P., Fitzpatrick, R., Mosley, L., Kogel-Knabner, I., 2017. Linking organic matter composition in acid sulfate soils to pH recovery after re-submerging. *Geoderma* 308, 350-362.

- Kowalchuk, G., Stephen, J., 2001. Ammonia-oxidizing bacteria: A model for molecular microbial ecology. *Annual Review of Microbiology* 55, 485-529.
- Lamontagne, S., Hicks, W.S., Fitzpatrick, R.W., Rogers, S., 2006. Sulfidic materials in dryland river wetlands. *Marine and Freshwater Research* 57, 775-788.
- Lasorsa, B., Casas, A., 1996. A comparison of sample handling and analytical methods for determination of acid volatile sulfides in sediment. *Marine Chemistry* 52, 211-220.
- Lay, J.-J., Li, Y.-Y., Noike, T., 1997. Influences of pH and moisture content on the methane production in high-solids sludge digestion. *Water research (Oxford)* 31, 1518-1524.
- Leifeld, J., 2018. Distribution of nitrous oxide emissions from managed organic soils under different land uses estimated by the peat C/N ratio to improve national GHG inventories. *Science of The Total Environment* 631-632, 23-26.
- Levinson, A.A., 1968. *Oceans (Foundations of Earth Science Series)* : Karl K. Turekian: Prentice-Hall, New York, 1968. Elsevier Ltd, pp. 1367-1368.
- Limberger, R., Birtel, J., Farias, D.d.S., Matthews, B., 2017. Ecosystem flux and biotic modification as drivers of metaecosystem dynamics. *Ecology* 98, 1082-1092.
- Lin, C., Melville, M.D., Hafer, S., 1995. Acid sulphate soil-landscape relationships in an undrained, tide-dominated estuarine floodplain, Eastern Australia. *Catena (Giessen)* 24, 177-194.
- Lin, Z., Herbert Jr, R.B., 1997. Heavy metal retention in secondary precipitates from a mine rock dump and underlying soil, Dalarna, Sweden. *Environmental geology (Berlin)* 33, 1-12.
- Ling, Y.-C., Bush, R., Grice, K., Tulipani, S., Berwick, L., Moreau, J.W., 2015. Distribution of iron- and sulfate-reducing bacteria across a coastal acid sulfate soil (CASS) environment: implications for passive bioremediation by tidal inundation. *Frontiers in Microbiology* 6, 624.
- Liu, B., 2010. Denitrification gene pools, transcription and kinetics of NO, N₂O and N₂ production as affected by soil pH. *FEMS Microbiology Ecology* 72, 407-417.
- Liu, B., Frostegård, Å., Bakken, L.R., 2014. Impaired reduction of N₂O to N₂ in acid soils is due to a posttranscriptional interference with the expression of nosZ. *mBio* 5, e01383-e01314.
- Liu, X., Ruecker, A., Song, B., Xing, J., Conner, W.H., Chow, A.T., 2017. Effects of salinity and wet–dry treatments on C and N dynamics in coastal-forested wetland soils: Implications of sea level rise. *Soil Biology and Biochemistry* 112, 56-67.
- Liu, Y., Wan, K.-Y., Tao, Y., Li, Z.-G., Zhang, G.-S., Li, S.-L., Chen, F., 2013. Carbon dioxide flux from rice paddy soils in central China: effects of intermittent flooding and draining cycles. *PloS one* 8, e56562.
- Livesley, S.J., Andrusiak, S.M., 2012. Temperate mangrove and salt marsh sediments are a small methane and nitrous oxide source but important carbon store. *Estuarine, Coastal and Shelf Science* 97, 19-27.
- Ljung, K., Maley, F., Cook, A., Weinstein, P., 2009. Acid sulfate soils and human health—A Millennium Ecosystem Assessment. *Environment International* 35, 1234-1242.
- Luther, r.G.W., Church, T.M., Scudlark, J.R., Cosman, M., 1986. Inorganic and Organic Sulfur Cycling in Salt-Marsh Pore Waters. *Science* 232, 746-749.
- Macdonald, B., Denmead, O., White, I., Wilson, S., 2008. Green house gas emissions from acid sulphate and non-acid sulphate soils, *Proceedings of the Joint Conference of the 6th International Acid Sulphate Soil Conference and the Acid Rock Drainage Symposium*. Guangdong Press Group, Guangzhou, pp. 126–131.

- Macdonald, B.C.T., Denmead, O.T., White, I., Melville, M.D., 2004a. Natural sulfur dioxide emissions from sulfuric soils. *Atmospheric Environment* 38, 1473-1480.
- Macdonald, B.C.T., Smith, J., Keene, A.F., Tunks, M., Kirtseva, A., White, I., 2004b. Impacts of runoff from sulfuric soils on sediment chemistry in an estuarine lake. *Sci Total Environ* 329, 115-130.
- Marín-Muñiz, J.L., Hernández, M.E., Moreno-Casasola, P., 2015. Greenhouse gas emissions from coastal freshwater wetlands in Veracruz Mexico: Effect of plant community and seasonal dynamics. *Atmospheric Environment* 107, 107-117.
- Martikainen, P.J., de Boer, W., 1993. Nitrous oxide production and nitrification in acidic soil from a dutch coniferous forest. *Soil Biology and Biochemistry* 25, 343-347.
- Mathew, E.K., Panda, R.K., Nair, M., 2001. Influence of subsurface drainage on crop production and soil quality in a low-lying acid sulphate soil. *Agricultural Water Management* 47, 191-209.
- McClaugherty, C., Berg, B., 1987. Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition *Pedobiologia* 30, 101-112.
- McElnea, A.E., Ahern, C.R., Menzies, N.W., 2002. The measurement of actual acidity in acid sulfate soils and the determination of sulfidic acidity in suspension after peroxide oxidation. *Australian Journal of Soil Research* 40, 1133-1157.
- McMillan, A.M.S., Pal, P., Phillips, R.L., Palmada, T., Berben, P.H., Jha, N., Saggar, S., Luo, J., 2016. Can pH amendments in grazed pastures help reduce N₂O emissions from denitrification? – The effects of liming and urine addition on the completion of denitrification in fluvial and volcanic soils. *Soil biology & biochemistry* 93, 90-104.
- McNicol, G., Sturtevant, C.S., Knox, S.H., Dronova, I., Baldocchi, D.D., Silver, W.L., 2017. Effects of seasonality, transport pathway, and spatial structure on greenhouse gas fluxes in a restored wetland. *Glob Chang Biol* 23, 2768-2782.
- Megonigal, J.P., Schlesinger, W.H., 1997. Enhanced CH₄ Emissions from a Wetland Soil Exposed to Elevated CO₂. *Biogeochemistry* 37, 77-88.
- Melville, M., White, I., Lin, C., 1993. The origins of acid sulphate soils, In: Bush, R (ed.). *Proceedings of the National Conference on Acid Sulphate Soils* (Coolangatta, NSW: June 24-25, 1993). CSIRO Australia/NSW Agriculture/Tweed Shire Council.
- Minh, L.Q., Tuong, T.P., van Mensvoort, M.E.F., Bouma, J., 1998. Soil and water table management effects on aluminum dynamics in an acid sulphate soil in Vietnam. *Agriculture, Ecosystems & Environment* 68, 255-262.
- Mokma, D., Yli-Halla, M., Hartikainen, H., 2000. Soils in a young landscape on the coast of southern Finland.
- Moore, T.R., Roulet, N.T., 1993. Methane flux: Water table relations in northern wetlands. *Geophysical Research Letters* 20.
- Morse, J.W., Luther, G.W., 1999. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochimica et Cosmochimica Acta* 63, 3373-3378.
- Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. *Environ Sci Technol* 38, 131A-136A.
- Mosley, L.M., Fitzpatrick, R.W., Palmer, D., Leyden, E., Shand, P., 2014a. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. *Sci Total Environ* 485-486, 281-291.

- Mosley, L.M., Palmer, D., Leyden, E., Cook, F., Zammit, B., Shand, P., Baker, A., W. Fitzpatrick, R., 2014b. Acidification of floodplains due to river level decline during drought. *J Contam Hydrol* 161, 10-23.
- Mosley, L.M., Zammit, B., Jolley, A.-M., Barnett, L., Fitzpatrick, R., 2014c. Monitoring and assessment of surface water acidification following rewetting of oxidised acid sulfate soils. *Environ Monit Assess* 186, 1-18.
- Murakami, M., Furukawa, Y., Inubushi, K., 2005. Methane production after liming to tropical acid peat soil. *Soil science and plant nutrition (Tokyo)* 51, 697-699.
- Myklebust, M.C., Hipps, L.E., Ryel, R.J., 2008. Comparison of eddy covariance, chamber, and gradient methods of measuring soil CO₂ efflux in an annual semi-arid grass, *Bromus tectorum*. *Agricultural and Forest Meteorology* 148, 1894-1907.
- Nadeem, S., Dörsch, P., Bakken, L.R., 2013. Autoxidation and acetylene-accelerated oxidation of NO in a 2-phase system: Implications for the expression of denitrification in ex situ experiments. *Soil Biology and Biochemistry* 57, 606-614.
- Nordstrom, D.K., 1982. Aqueous Pyrite Oxidation and the Consequent Formation of Secondary Iron Minerals, In: Kittrick, D.F.a.L.H. (Ed.), *Acid Sulfate Weathering*. Soil Science Society of America, pp. 37-56.
- Nugroho, R.A., Röling, W.F.M., Laverman, A.M., Verhoef, H.A., 2007. Low Nitrification Rates in Acid Scots Pine Forest Soils Are Due to pH-Related Factors. *Microb Ecol* 53, 89-97.
- Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., Erasmi, S., 2016. Greenhouse gas emissions from soils—A review. *Chemie der Erde - Geochemistry* 76, 327-352.
- Osterholm, P., Astrom, M., 2004. Quantification of current and future leaching of sulfur and metals from Boreal acid sulfate soils, western Finland. *Australian Journal of Soil Research* 42, 547-551.
- Österholm, P., Åström, M., 2002. Spatial trends and losses of major and trace elements in agricultural acid sulphate soils distributed in the artificially drained Rintala area, W. Finland. *Applied Geochemistry* 17, 1209-1218.
- Paasonen-Kivekäs, M., Yli-Halla, M., 2005. A comparison of nitrogen and carbon reserves in acid sulphate and non acid sulphate soils in western Finland. *Agricultural and Food Science* 14, 57–69.
- Page, K.L., Allen, D.E., Dalal, R.C., Slattery, W., 2009. Processes and magnitude of CO₂, CH₄, and N₂O fluxes from liming of Australian acidic soils: a review. *Australian Journal of Soil Research* 47, 747-762.
- Parkin, T.B., Sexstone, A.J., Tiedje, J.M., 1985. Adaptation of Denitrifying Populations to Low Soil pH. *Applied and Environmental Microbiology* 49, 1053.
- Payne, M.K., Stolt, M.H., 2017. Understanding sulfide distribution in subaqueous soil systems in southern New England, USA. *Geoderma* 308, 207-214.
- Peiffer, S., Behrends, T., Hellige, K., Larese-Casanova, P., Wan, M., Pollok, K., 2015. Pyrite formation and mineral transformation pathways upon sulfidation of ferric hydroxides depend on mineral type and sulfide concentration. *Chemical Geology* 400, 44-55.
- Ponnamperuma, F.N., 1972. The Chemistry of Submerged Soils, In: Brady, N.C. (Ed.), *Advances in Agronomy*. Academic Press, pp. 29-96.
- Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils, In: Dost, H. (Ed.), *Acid Sulphate Soils. Proceedings of the International Symposium on Acid Sulphate Soils*. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, pp. 13–20
- Poungparn, S., Komiyama, A., Tanaka, A., Sangtiew, T., Maknual, C., Kato, S., Tanapermpool, P., Patanaponpaiboon, P., 2009. Carbon dioxide emission through soil respiration in a secondary mangrove forest of eastern Thailand. *Journal of tropical ecology* 25, 393-400.

- Powell, B., Martens, M., 2005. A review of acid sulfate soil impacts, actions and policies that impact on water quality in Great Barrier Reef catchments, including a case study on remediation at East Trinity. *Mar Pollut Bull* 51, 149-164.
- Qu, Z., Wang, J., Almøy, T., Bakken, L.R., 2014. Excessive use of nitrogen in Chinese agriculture results in high $N_2O/(N_2O+N_2)$ product ratio of denitrification, primarily due to acidification of the soils. *Global Change Biology* 20, 1685-1698.
- Rabenhorst, M.C., Fanning, D.S., 2006. Acid sulfate soils: problems, In: Lal, R. (Ed.), *Encyclopedia of Soil Science*. CRC Press, Boca Raton, FL, pp. 19–22.
- Rabot, E., Hénault, C., Cousin, I., 2016. Effect of the soil water dynamics on nitrous oxide emissions. *Geoderma* 280, 38-46.
- Ram, R., Kalnins, C., Pownceby, M.I., Ehrig, K., Etschmann, B., Spooner, N., Brugger, J., 2021a. Selective radionuclide co-sorption onto natural minerals in environmental and anthropogenic conditions. *J Hazard Mater* 409, 124989-124989.
- Ram, R., Morrisroe, L., Etschmann, B., Vaughan, J., Brugger, J., 2021b. Lead (Pb) sorption and co-precipitation on natural sulfide, sulfate and oxide minerals under environmental conditions. *Minerals engineering* 163, 106801.
- Rampant, P., Croatto, B.A., 2003. Acid sulfate soil hazard maps : guidelines for coastal Victoria. Department of Primary Industries.
- Rayment, G.E., Lyons, D.J., 2011. *Soil chemical methods*. CSIRO, Melbourne, Australia.
- Reddy, K.R., DeLaune, R.D., 2008. *Biogeochemistry of Wetlands: Science and Applications*. Baton Rouge: CRC Press, Baton Rouge.
- Reimann, C., Matschullat, J., Birke, M., Salminen, R., 2009. Arsenic distribution in the environment: The effects of scale. *Applied Geochemistry* 24, 1147-1167.
- Reth, S., Reichstein, M., Falge, E., 2005. The effect of soil water content, soil temperature, soil pH-value and the root mass on soil CO₂ efflux – A modified model. *Plant and Soil* 268, 21-33.
- Rickard, D., 1997. Kinetics of pyrite formation by the H₂S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: The rate equation. *Geochimica et Cosmochimica Acta* 61, 115-134.
- Rickard, D., Luther, G.W., 2007. Chemistry of Iron Sulfides. *Chem. Rev* 107, 514-562.
- Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS). *Marine Chemistry* 97, 141-197.
- Ritsema, C., Groenenberg, J., 1993. Pyrite Oxidation, Carbonate Weathering, and Gypsum Formation in a Drained Potential Acid Sulfate Soil.
- Rousk, J., Brookes, P.C., Baath, E., 2009. Contrasting Soil pH Effects on Fungal and Bacterial Growth Suggest Functional Redundancy in Carbon Mineralization. *Appl Environ Microbiol* 75, 1589-1596.
- Rudaz, A.O., Wälti, E., Kyburz, G., Lehmann, P., Fuhrer, J., 1999. Temporal variation in N₂O and N₂ fluxes from a permanent pasture in Switzerland in relation to management, soil water content and soil temperature. *Agriculture, Ecosystems & Environment* 73, 83-91.
- Ruser, R., Flessa, H., Russow, R., Schmidt, G., Buegger, F., Munch, J.C., 2006. Emission of N₂O, N₂ and CO₂ from soil fertilized with nitrate: effect of compaction, soil moisture and rewetting. *Soil Biology and Biochemistry* 38, 263-274.
- Russenes, A.L., Korsath, A., Bakken, L.R., Dörsch, P., 2016. Spatial variation in soil pH controls off-season N₂O emission in an agricultural soil. *Soil Biology and Biochemistry* 99, 36-46.

- Saggar, S., Jha, N., Deslippe, J., Bolan, N.S., Luo, J., Giltrap, D.L., Kim, D.G., Zaman, M., Tillman, R.W., 2013. Denitrification and N₂O:N₂ production in temperate grasslands: Processes, measurements, modelling and mitigating negative impacts. *Science of The Total Environment* 465, 173-195.
- Samad, M.D.S., Ambarish, B., Lars, R.B., Timothy, J.C., Cecile, A.M.D.K., Karl, G.R., Gary, J.L., Sergio, E.M., 2016a. Phylogenetic and functional potential links pH and N₂O emissions in pasture soils. *Scientific Reports* 6.
- Samad, M.S., Biswas, A., Bakken, L.R., Clough, T.J., de Klein, C.A.M., Richards, K.G., Lanigan, G.J., Morales, S.E., 2016b. Phylogenetic and functional potential links pH and N₂O emissions in pasture soils. *Scientific Reports* 6, 35990-35990.
- Sammut, J., White, I., Melville, M., 1994. Stratification in acidified coastal floodplain drains. *Wetlands (Australia)*, 49-64.
- Sammut, J., White, I., Melville, M.D., 1996. Acidification of an estuarine tributary in eastern Australia due to drainage of acid sulfate soils. *Marine and Freshwater Research* 47, 669-684.
- Schaufler, G., Kitzler, B., Schindlbacher, A., Skiba, U., Sutton, M.A., Zechmeister - Boltensstern, S., 2010. Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. *European Journal of Soil Science* 61, 683-696.
- Scott-Denton, L.E., Sparks, K.L., Monson, R.K., 2003. Spatial and temporal controls of soil respiration rate in a high-elevation, subalpine forest. *Soil biology & biochemistry* 35, 525-534.
- Senbayram, M., Budai, A., Bol, R., Chadwick, D., Marton, L., Gündogan, R., Wu, D., 2019. Soil NO₃⁻ level and O₂ availability are key factors in controlling N₂O reduction to N₂ following long-term liming of an acidic sandy soil. *Soil biology & biochemistry* 132, 165-173.
- Šimek, M., Cooper, J.E., 2002. The influence of soil pH on denitrification: progress towards the understanding of this interaction over the last 50 years. *European Journal of Soil Science* 53, 345-354.
- Šimek, M., Jiřová, L., Hopkins, D.W., 2002. What is the so-called optimum pH for denitrification in soil? *Soil Biology and Biochemistry* 34, 1227-1234.
- Šimek, M., Virtanen, S., Křiřtůfek, V., Simojoki, A., Yli-Halla, M., 2011. Evidence of rich microbial communities in the subsoil of a boreal acid sulphate soil conducive to greenhouse gas emissions. *Agriculture, Ecosystems & Environment* 140, 113-122.
- Šimek, M., Virtanen, S., Simojoki, A., Chroňáková, A., Elhottová, D., Křiřtůfek, V., Yli-Halla, M., 2014. The microbial communities and potential greenhouse gas production in boreal acid sulphate, non-acid sulphate, and reedy sulphidic soils. *Science of The Total Environment* 466-467, 663-672.
- Simpson, S.L., Fitzpatrick, R.W., Shand, P., Angel, B.M., Spadaro, D.A., Mosley, L., 2010. Climate-driven mobilisation of acid and metals from acid sulfate soils. *Marine and Freshwater Research* 61, 129-138.
- Sohlenius, G., Öborn, I., 2004. Geochemistry and partitioning of trace metals in acid sulphate soils in Sweden and Finland before and after sulphide oxidation. *Geoderma* 122, 167-175.
- Staff., S.S., 2014. Keys to Soil Taxonomy, 12th ed. . USDA-Natural Resources Conservation Service, Washington, DC.
- Stevens, R.J., Laughlin, R.J., 1998. Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils. *Nutrient cycling in agroecosystems* 52, 131-139.
- Sullivan, L., Bush, R., 2000. The behaviour of drain sludge in acid sulfate soil areas: Some implication for acidification and waterways management, In: Slavich, P. (Ed.),

- Proceedings of a workshop on remediation and assessment of broadacre acid sulfate soils. NSW Agriculture, Wollongbar, Australia, pp. 43-48.
- Sullivan., L.A., Clay., C., Ward., N.J., Baker., A.K.M., Shand, P., 2018. National Acid Sulfate Soils Guidance - A synthesis, In: Resources, t.D.o.A.a.W. (Ed.), Australia.
- Sun, Q.-Q., Shi, K., Damerell, P., Whitham, C., Yu, G.-H., Zou, C.-L., 2013. Carbon dioxide and methane fluxes: Seasonal dynamics from inland riparian ecosystems, northeast China. *Science of The Total Environment* 465, 48-55.
- Teh, Y.A., Silver, W.L., Sonnentag, O., Detto, M., Kelly, M., Baldocchi, D.D., 2011. Large Greenhouse Gas Emissions from a Temperate Peatland Pasture. *Ecosystems (New York)* 14, 311-325.
- Thomsen, J., K., Torben, G., Raymond, P.C., 1994. Mass Spectrometric Studies of the Effect of pH on the Accumulation of Intermediates in Denitrification by *Paracoccus denitrificans*. *Appl Environ Microbiol* 60, 536-541.
- Tobias, C., Neubauer, S.C., 2019. Chapter 16 - Salt Marsh Biogeochemistry—An Overview, In: Perillo, G.M.E., Wolanski, E., Cahoon, D.R., Hopkinson, C.S. (Eds.), *Coastal Wetlands*. Elsevier, pp. 539-596.
- Tong, C., Huang, J., Hu, Z., Jin, Y., 2013. Diurnal Variations of Carbon Dioxide, Methane, and Nitrous Oxide Vertical Fluxes in a Subtropical Estuarine Marsh on Neap and Spring Tide Days. *Journal of the Coastal and Estuarine Research Federation* 36, 633-642.
- Tong, C., Wang, W.-Q., Zeng, C.-S., Marrs, R., 2010. Methane (CH₄) emission from a tidal marsh in the Min River estuary, southeast China. *Journal of Environmental Science and Health, Part A* 45, 506-516.
- van Breemen, N., 1993. Environmental aspects of acid sulphate soils, In: Dent, D., Mensvoort, M.v. (Eds.), *Selected papers of the Ho Chi Minh City symposium on acid sulphate soils*, pp. 391-402.
- Van Cleemput, O., Patrick, W.H., McIlhenny, R.C., 1975. Formation of chemical and biological denitrification products in flooded soil at controlled pH and redox potential. *Soil Biology and Biochemistry* 7, 329-332.
- Van den Berg, G.A., Loch, J.P.G., Winkels, H.J., 1998. Effect of Fluctuating Hydrological Conditions on the Mobility of Heavy Metals in Soils of a Freshwater Estuary in the Netherlands. *Water, air, and soil pollution* 102, 377-388.
- van Spanning, R.J.M., Richardson, D.J., Ferguson, S.J., 2007. Chapter 1 - Introduction to the Biochemistry and Molecular Biology of Denitrification. Elsevier B.V, pp. 3,I-20,II.
- Vann, C., Patrick Megonigal, J., 2003. Elevated CO₂ and water depth regulation of methane emissions: Comparison of woody and non-woody wetland plant species. *Biogeochemistry* 63, 117-134.
- Vesala, T., Huotari, J., Rannik, Ü., Suni, T., Smolander, S., Sogachev, A., Launiainen, S., Ojala, A., 2006. Eddy covariance measurements of carbon exchange and latent and sensible heat fluxes over a boreal lake for a full open-water period. *J. Geophys. Res* 111, D11101-n/a.
- Virtanen, S., Puustinen, M., Yli-Halla, M., 2017. Oxidation of iron sulfides in subsoils of cultivated boreal acid sulfate soil fields – based on soil redox potential and pH measurements. *Geoderma* 308, 252-259.
- Virtanen, S., Simojoki, A., Hartikainen, H., Yli-Halla, M., 2014. Response of pore water Al, Fe and S concentrations to waterlogging in a boreal acid sulphate soil. *Sci Total Environ* 485-486, 130-142.
- Virtasalo, J.J., Osterholm, P., Kotilainen, A.T., Astrom, M.E., 2020. Enrichment of trace metals from acid sulfate soils in sediments of the Kvarken Archipelago, eastern Gulf of Bothnia, Baltic Sea. *Biogeosciences* 17, 6097-6113.

- Wang, Y., Guo, J., Vogt, R.D., Mulder, J., Wang, J., Zhang, X., 2018. Soil pH as the chief modifier for regional nitrous oxide emissions: New evidence and implications for global estimates and mitigation. *Glob Chang Biol* 24, e617-e626.
- Wang, Z.P., DeLaune, R.D., Patrick, W.H., Jr, Masscheleyn, P.H., 1993. Soil Redox and pH Effects on Methane Production in a Flooded Rice Soil. *Soil Science Society of America Journal*.
- Webster, J.R., Benfield, E.F., 1986. Vascular Plant Breakdown in Freshwater Ecosystems. *Annual Review of Ecology and Systematics* 17, 567-594.
- West, T.O., McBride, A.C., 2005. The contribution of agricultural lime to carbon dioxide emissions in the United States: dissolution, transport, and net emissions. *Agriculture, Ecosystems & Environment* 108, 145-154.
- Westrich, J.T., Berner, R.A., 1984. The Role of Sedimentary Organic Matter in Bacterial Sulfate Reduction: The G Model Tested. *Limnology and Oceanography* 29, 236-249.
- Whalen, S.C., 2005. Biogeochemistry of Methane Exchange between Natural Wetlands and the Atmosphere. *Environmental Engineering Science* 22, 73-94.
- White, I., Melville, M., Macdonald, B., Quirk, R., Hawken, R., Tunks, M., Buckley, D., Beattie, R., Williams, J., Heath, L., 2007. From conflicts to wise practice agreement and national strategy: cooperative learning and coastal stewardship in estuarine floodplain management, Tweed River, eastern Australia. *Journal of Cleaner Production* 15, 1545-1558.
- White, I., Melville, M.D., Wilson, B.P., Sammut, J., 1997. Reducing acidic discharges from coastal wetlands in eastern Australia. *Wetlands Ecology and Management* 5, 55-72.
- Wong, V.N.L., Cheetham, M.D., Bush, R.T., Sullivan, L.A., Ward, N.J., 2016a. Accumulation of sulfidic sediments in a channelised inland river system, southern Australia. *Marine and Freshwater Research* 67, 1655-1666.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Bush, R.T., Sullivan, L.A., Slavich, P.G., 2010. Seawater causes rapid trace metal mobilisation in coastal lowland acid sulfate soils: Implications of sea level rise for water quality. *Geoderma* 160, 252-263.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Bush, R.T., Sullivan, L.A., Slavich, P.G., 2013. Seawater-induced mobilization of trace metals from mackinawite-rich estuarine sediments. *Water Res* 47, 821-832.
- Wong, V.N.L., Johnston, S.G., Burton, E.D., Hirst, P., Sullivan, L.A., Bush, R.T., Blackford, M., 2015. Seawater inundation of coastal floodplain sediments: Short-term changes in surface water and sediment geochemistry. *Chemical Geology* 398, 32-45.
- Wong, V.N.L., McNaughton, C., Pearson, A., 2016b. Changes in soil organic carbon fractions after remediation of a coastal floodplain soil. *Journal of Environmental Management* 168, 280-287.
- Wrage, N., Velthof, G., van Beusichem, M., Oenema, O., 2001. Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biology and Biochemistry* 33, 1723-1732.
- Wu, X., Sten, P., Engblom, S., Nowak, P., Österholm, P., Dopson, M., 2015. Impact of mitigation strategies on acid sulfate soil chemistry and microbial community. *The Science of the total environment* 526, 215.
- Xiao, J., Zhuang, Q., Law, B.E., Baldocchi, D.D., Chen, J., Richardson, A.D., Melillo, J.M., Davis, K.J., Hollinger, D.Y., Wharton, S., Oren, R., Noormets, A., Fischer, M.L., Verma, S.B., Cook, D.R., Sun, G., McNulty, S., Wofsy, S.C., Bolstad, P.V., Burns, S.P., Curtis, P.S., Drake, B.G., Falk, M., Foster, D.R., Gu, L., Hadley, J.L., Katul, G.G., Litvak, M., Ma, S., Martin, T.A., Matamala, R., Meyers, T.P., Monson, R.K., Munger, J.W., Oechel, W.C., Paw, U.K.T., Schmid, H.P., Scott, R.L., Starr, G., Suyker, A.E., Torn, M.S., 2011. Assessing net ecosystem carbon exchange of U.S. terrestrial ecosystems by integrating eddy covariance flux measurements and satellite observations. *Agricultural and Forest Meteorology* 151, 60-69.

- Xu, C., Wong, V.N.L., Reef, R.E., 2021. Effect of inundation on greenhouse gas emissions from temperate coastal wetland soils with different vegetation types in southern Australia. *Sci Total Environ* 763, 142949-142949.
- Xu, X., Zou, X., Cao, L., Zhamangulova, N., Zhao, Y., Tang, D., Liu, D., 2014. Seasonal and spatial dynamics of greenhouse gas emissions under various vegetation covers in a coastal saline wetland in southeast China. *Ecological Engineering* 73, 469-477.
- Yang, J., Liu, J., Hu, X., Li, X., Wang, Y., Li, H., 2013. Effect of water table level on CO₂, CH₄ and N₂O emissions in a freshwater marsh of Northeast China. *Soil Biology and Biochemistry* 61, 52-60.
- Yang, W.-B., Yuan, C.-S., Tong, C., Yang, P., Yang, L., Huang, B.-Q., 2017. Diurnal variation of CO₂, CH₄, and N₂O emission fluxes continuously monitored in-situ in three environmental habitats in a subtropical estuarine wetland. *Marine Pollution Bulletin* 119, 289-298.
- Yau, C.C., Wong, V.N.L., Kennedy, D.M., 2016. Soil chemistry and acidification risk of acid sulfate soils on a temperate estuarine floodplain in southern Australia. *Soil Research* 54.
- Yli-Halla, M., Virtanen, S., Regina, K., Österholm, P., Ehnvall, B., Uusi-Kämppe, J., 2020. Nitrogen stocks and flows in an acid sulfate soil. *Environmental Monitoring and Assessment* 192, 751-751.
- Yoshinari, T., Hynes, R., Knowles, R., 1977. Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. *Soil biology & biochemistry* 9, 177-183.
- Yuan, C., Mosley, L.M., Fitzpatrick, R., Marschner, P., 2015. Amount of organic matter required to induce sulfate reduction in sulfuric material after re-flooding is affected by soil nitrate concentration. *J Environ Manage* 151, 437-442.
- Zaman, M., Nguyen, M., 2010. Effect of lime or zeolite on N₂O and N₂ emissions from a pastoral soil treated with urine or nitrate-N fertilizer under field conditions. *Agriculture, Ecosystems & Environment* 136, 254-261.
- Zaman, M., Nguyen, M., Saggar, S., 2008. N sub(2)O and N sub(2) Emissions from Pasture and Wetland Soils with and Without Amendments of Nitrate, Lime and Zeolite Under Laboratory Condition. *Australian Journal of Soil Research* 46, 526-526.
- Zaman, M., Nguyen, M.L., Matheson, F., Blennerhassett, J.D., Quin, B.F., 2007. Can soil amendments (zeolite or lime) shift the balance between nitrous oxide and dinitrogen emissions from pasture and wetland soils receiving urine or urea-N? *Australian Journal of Soil Research* 45, 543-553.
- Zelles, L., Stepper, K., Zsolnay, A., 1990. The effect of lime on microbial activity in spruce (*Picea abies* L.) forests. *Biology and Fertility of Soils* 9, 78-82.
- Zhang, Y., Wang, L., Xie, X., Huang, L., Wu, Y., 2013. Effects of invasion of *Spartina alterniflora* and exogenous N deposition on N₂O emissions in a coastal salt marsh. *Ecological Engineering* 58, 77-83.
- Zinder, S.H., 1994. *Physiological Ecology of Methanogens*. Boston, MA: Springer US, Boston, MA, pp. 128-206.
- Ziska, L.H., Moya, T.B., Wassmann, R., Namuco, O.S., Lantin, R.S., Aduna, J.B., Abao Jr, E., Bronson, K.F., Neue, H.U., Olszyk, D., 1998. Long-term growth at elevated carbon dioxide stimulates methane emission in tropical paddy rice. *Global Change Biology* 4, 657-665.