The Metropolitan Water Reclamation District of Greater Chicago

WELCOME

TO THE JULY EDITION

OF THE 2011

M&R SEMINAR SERIES

BEFORE WE BEGIN

- **SILENCE CELL PHONES & PAGERS**
- **QUESTION AND ANSWER SESSION WILL FOLLOW PRESENTATION**
- **SEMINAR SLIDES WILL BE POSTED ON MWRD WEBSITE AT (www. MWRD.org)**
- Home Page $\Rightarrow$ (Public Interest) $\Rightarrow$ more public interest $\Rightarrow$ M&R Seminar Series $\Rightarrow$ 2011 Seminar Series

Professor Kartik Chandran

Ph.D. (Environmental Engineering) University of Connecticut
B.S. (Chemical Engineering) Indian Institute of Technology

Present Associate Professor, Department of Earth and Environmental Engineering, Columbia University

2005- 2010 Assistant Professor, Department of Earth and Environmental Engineering, Columbia University

2004 Research Associate, Virginia Polytechnic Institute and State University

2001- 2004 Research Technical Associate, Chief Engineer's Research Group, Metcalf & Eddy

Research Interests

- Environmental microbiology, microbial N- cycling,
- sustainable sanitation and wastewater treatment,
- global climate impacts of engineered wastewater treatment practice
- microbial ecology of engineered biological waste and water treatment reactors
- elucidation of microbial biochemical degradation pathways

Selected activities and honors

- Water Environment Research Foundation Paul L. Busch Award (2010)
- AEESP accompanying keynote lecture at WEFTEC, New Orleans, LA (2010)
- Nominated to the Board of Trustees, Water Environment Federation (2010)
- National Science Foundation Early Faculty Career Development Award, CAREER (2009)
- Visiting Professor, Delft University of Technology, hosted by Prof. Mark van Loosdrecht,
- National Research Council, National Academies of Science Summer Faculty Fellowship award, hosted by the United States Environmental Protection Agency Headquarters, Cincinnati, OH, (Summer 2007).

Wastewater treatment and climate change

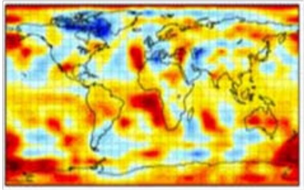
Inventories and mechanisms of biogenic nitrous oxide

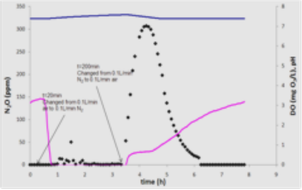
Kartik Chandran

Columbia University

Metropolitan Water Reclamation District of Greater Chicago

July 29th, 2011





Wastewater tmt. derived GHG

Table 8-1: Emissions from Waste (Tg CO_2 Eq.)

Gas/Source	1990	1995	2000	2001	2002	2003	2004	2005	2006
CH_4	**172.9**	**169.1**	**146.7**	**143.0**	**145.5**	**151.0**	**148.1**	**149.0**	**151.1**
Landfills	149.6	144.0	120.8	117.6	120.1	125.6	122.6	123.7	125.7
Wastewater Treatment	23.0	24.3	24.6	24.2	24.1	23.9	24.0	23.8	23.9
Composting	0.3	0.7	1.3	1.3	1.3	1.5	1.6	1.6	1.6
N_2O	**6.6**	**7.7**	**8.9**	**9.2**	**9.0**	**9.3**	**9.6**	**9.7**	**9.9**
Domestic Wastewater Treatment	6.3	6.9	7.6	7.8	7.6	7.7	7.8	8.0	8.1
Composting	0.4	0.8	1.4	1.4	1.4	1.6	1.7	1.7	1.8
Total	**179.6**	**176.8**	**155.6**	**152.1**	**154.5**	**160.3**	**157.7**	**158.7**	**161.0**

Note: Totals may not sum due to independent rounding.

From denitrification in anoxic or non-aerated zones

This is equivalent to 900,000 passenger cars added each year

Source: USEPA GHG Sources and Sinks Inventory, 2008

Domestic wastewater N_2O emission estimates

$$N_2O_{TOTAL} = N_2O_{PLANT} + N_2O_{EFFLUENT}$$

$$N_2O_{PLANT} = N_2O_{NIT/DENIT} + N_2O_{WOUT\ NIT/DENIT}$$

$$N_2O_{NIT/DENIT} = [(US_{POPND}) \times EF_2 \times F_{IND\text{-}COM}] \times 1/10\text{^}9$$

$$N_2O_{WOUT\ NIT/DENIT} = \{[(US_{POP} \times WWTP) - US_{POPND} \times F_{IND\text{-}COM}] \times EF_1\} \times 1/10\text{^}9$$

$$N_2O_{EFFLUENT} = \{[(US_{POP} \times Protein \times F_{NPR} \times F_{NON\text{-}CON} \times F_{IND\text{-}COM}) - N_{SLUDGE}] \times EF_3 \times 44/28\} \times 1/10\text{^}6$$

- **EF1=3.2 g N_2O/PE/year**
- **EF2=7.0 g N_2O/PE/year**
- **EF3= 0.005 kg N_2O -N/kg sewage-N produced**

Source: USEPA GHG Sources and Sinks Inventory, 2008

This presentation focuses on

- N_2O emissions from different wastewater treatment process configurations

- Insights to molecular phenomena linked with N_2O and NO production in *N. europaea*

- Impact of partial nitrification OR organic carbon source on N_2O production via denitrification

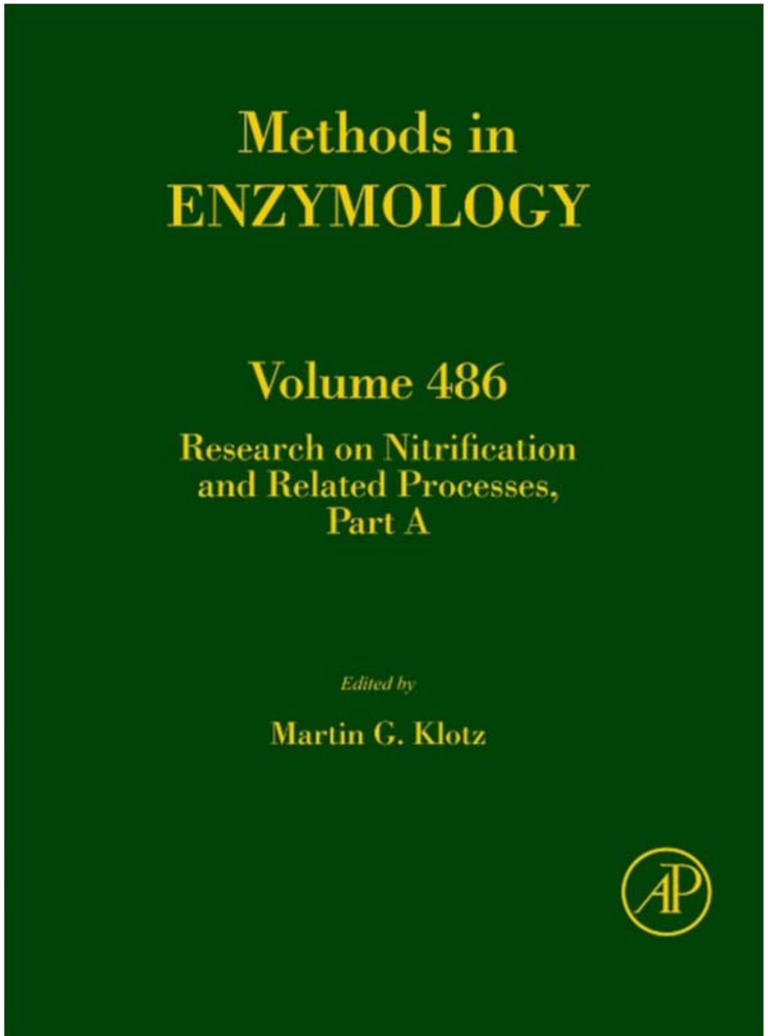
Role of nitrification and denitrification in N_2O emissions

N_2O production mainly
High N_2O emission expected

N_2O production and consumption
Low N_2O emission expected

- Based on known mechanisms, significantly higher emissions from aerated zones expected
- How does this influence the way we have been thinking about N_2O emissions from WWTPs?

Development of a standardized protocol for measurement



Chandran, 2011

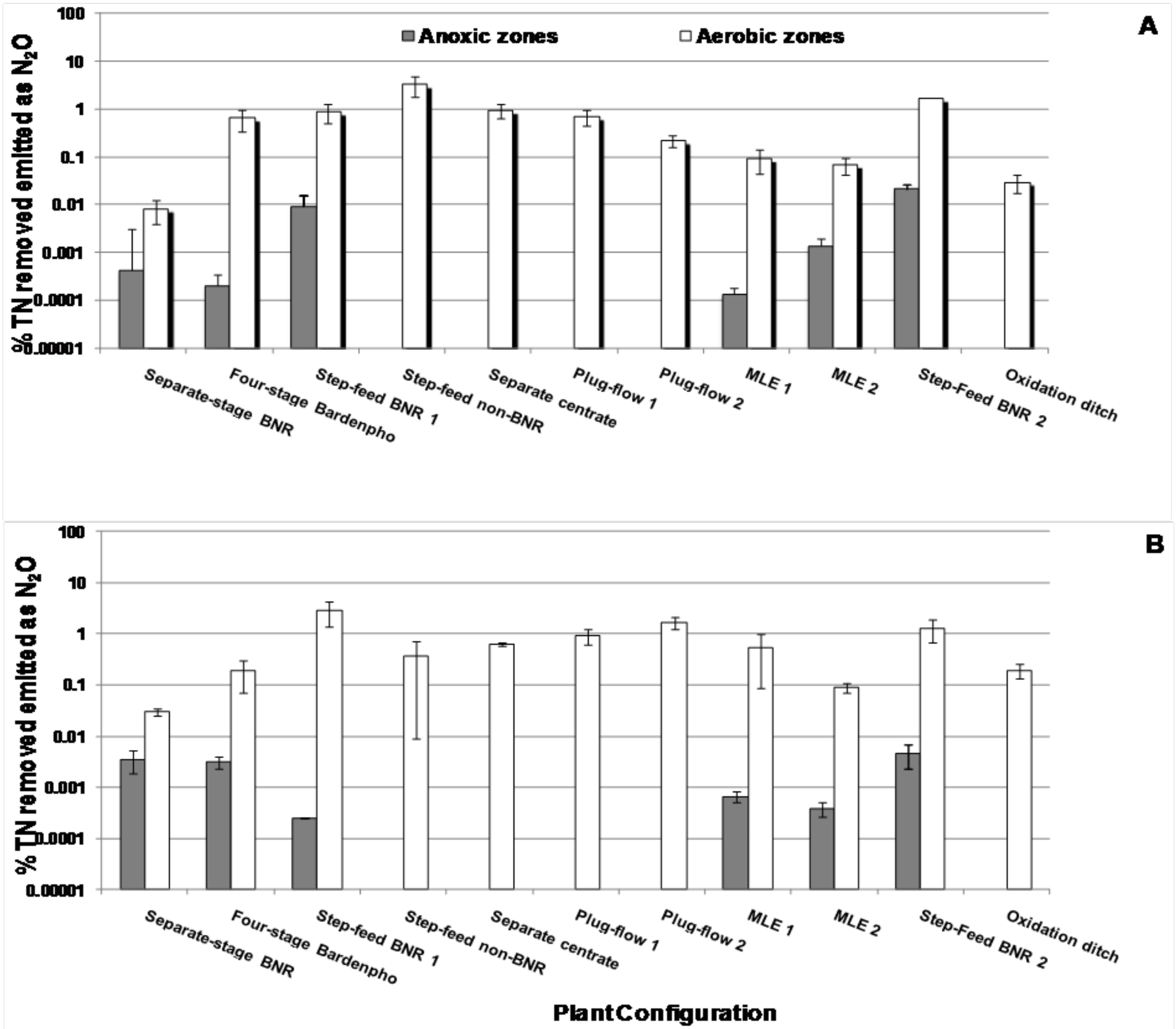
- Protocol has been reviewed by US EPA and is now being implemented nationwide
- Shared with other teams around the globe via GWRC

Summary of emissions

Plant Configuration	Temp(°C)	Avg. reactor influent TK N load (g-N/day)	Avg. reactor effluent TN load (g-N/day)	Q (MGD)	% influent TKN emitted as N_2O	% removed TKN emitted as N_2O	Emission factor (g N_2O/PE/yr)
Separate-stage BNR	15 ± 0.48	1.8 x 10^6	3.6 x 10^5	23	0.03 ± 0.00	0.03 ± 0.01	1.2 ± 0.18
	23 ± 0.28	2.3 x 10^6	4.3 x 10^5	27	0.01 ± 0.00	0.01 ± 0.00	0.28 ± 0.13
Four-stage Bardenpho	14 ± 0.26	8.6 x 10^5	1.7 x 10^5	7.8	0.16 ± 0.10	0.19 ± 0.12	9.8 ± 6.1
	23 ± 0.20	7.4 x 10^5	7.6 x 10^4	8.1	0.60 ± 0.29	0.66 ± 0.32	33 ± 16
Step-feed BNR 1	19 ± 0.22	3.1 x 10^6	1.4 x 10^6	29	1.6 ± 0.83	2.9 ± 1.5	92 ± 47
	25 ± 0.28	2.9 x 10^6	9.4 10^5	30	0.62 ± 0.27	0.90 ± 0.39	33 ± 14
Step-feed non-BNR	17 ± 0.12	8.6 x 10^6	4.4 x 10^6	71	0.18 ± 0.18	0.37 ± 0.36	13 ± 13
	26 ± 0.81	8.9 x 10^6	4.2 x 10^6	93	1.8 ± 0.79	3.3 ± 1.5	97 ± 43
Separate centrate	30 ± 2.3	8.8 x 10^6	5.5 x 10^6	2.0	0.24 ± 0.02	0.63 ± 0.06	590 ± 53
	34 ± 0.32	8.5 x 10^6	4.2 x 10^6	1.6	0.54 ± 0.16	0.96 ± 0.32	1600 ± 500
Plug-flow 1	11 ± 0.20	1.8 x 10^6	1.0 x 10^6	18	0.40 ± 0.14	0.92 ± 0.32	23 ± 7.9
	23 ± 0.46	1.8 x 10^6	7.3 x 10^5	15	0.41 ± 0.14	0.70 ± 0.24	28 ± 9.6
Plug-flow 2	11 ± 0.41	6.3 x 10^5	4.0 x 10^5	8.7	0.62 ± 0.15	1.7 ± 0.41	26 ± 6.4
	22 ± 0.58	6.6 x 10^5	4.0 x 10^5	6.6	0.09 ± 0.03	0.22 ± 0.06	5.0 ± 1.4
MLE 1	22 ± 0.28	7.3 x 10^5	1.3 x 10^5	4.0	0.44 ± 0.37	0.54 ± 0.45	47 ± 39
	26 ± 1.8	6.8 x 10^5	1.9 x 10^5	4.0	0.07 ± 0.04	0.09 ± 0.05	6.8 ± 3.5
MLE 2	21 ± 0.72	5.9 x 10^5	1.2 x 10^5	3.3	0.07 ± 0.02	0.09 ± 0.02	7.4 ± 1.7
	26 ± 0.17	6.9 x 10^5	1.5 x 10^5	4.1	0.06 ± 0.02	0.07 ± 0.03	5.4 ± 2.0
Step-feed BNR 2	29 ± 0.18	2.2 x 10^6	2.9 x 10^5	14	1.5 ± 0.02	1.7 ± 0.02	140 ± 1.2
Oxidation ditch	14 ± 0.58	3.7 x 10^5	1.8 x 10^5	3.3	0.10 ± 0.03	0.19 ± 0.06	6.1 ± 1.9
	19 ± 0.58	3.9 x 10^5	4.3 x 10^4	3.4	0.03 ± 0.01	0.03 ± 0.01	1.8 ± 0.77
Step-feed BNR 3	20 ± 1.8	4.5 x 10^6	7.3 x 10^5	40	0.14 ± 0.02	0.17 ± 0.03	9.3 ± 1.5
	24 ± 0.78	7.8 x 10^6	8.6 x 10^5	57	0.05 ± 0.03	0.06 ± 0.03	4.1 ± 2.2

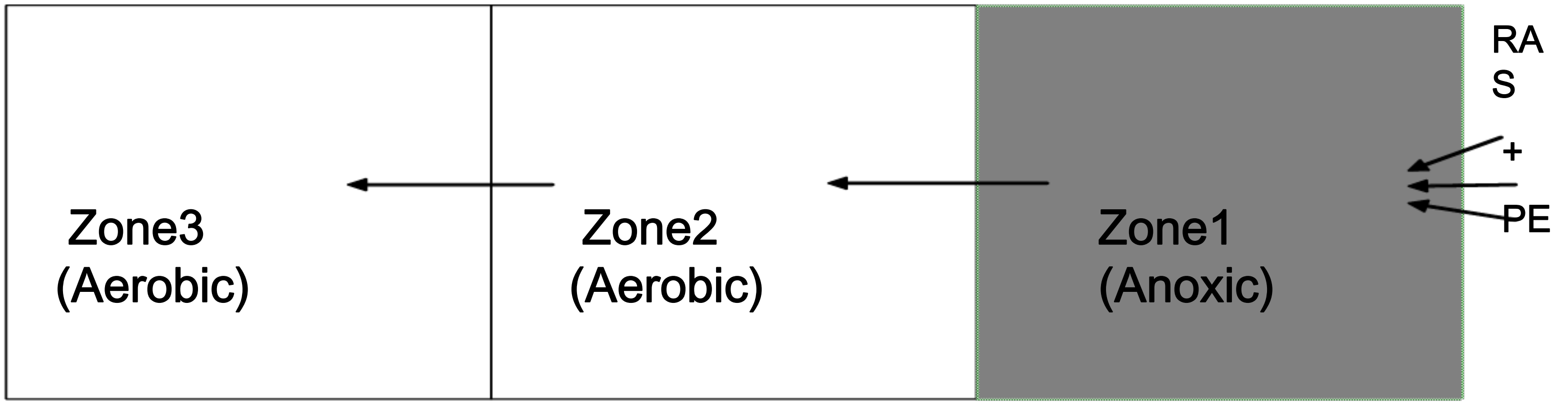
However, these do not convey the complete picture

Relative emissions from aerated and non-aerated zones



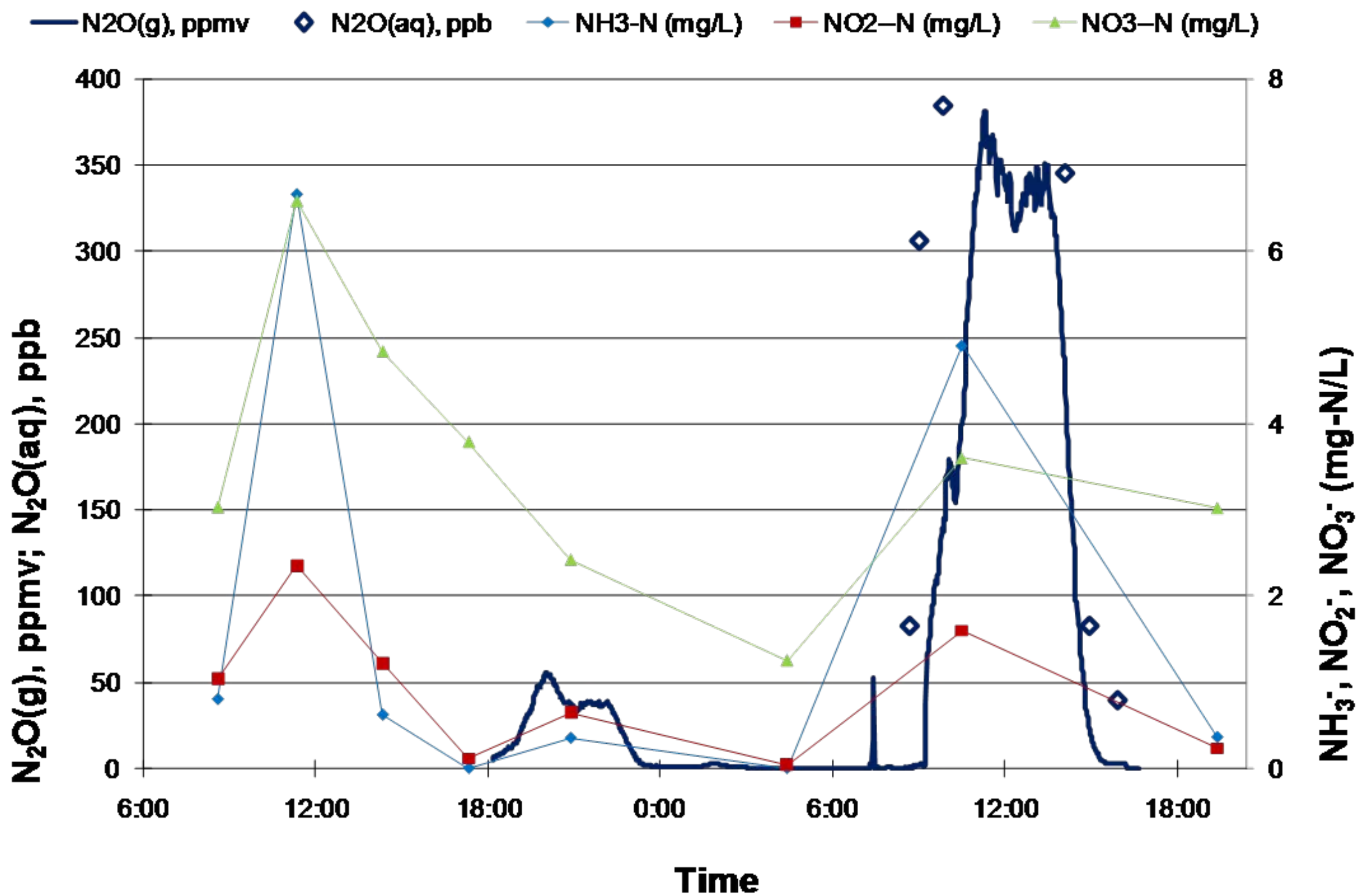
- Aerated zones contributed more to emissions than non-aerated zones

Spatial variability in N_2O emissions



Ammonia(ppm-N)	1.5 ±0.71	11.5 ±4.95	14
Nitrite (ppm-N)	0	0.003 ±0.001	0.002 ±0.003
Nitrate (ppm-N)	10.15 ±0.21	2.65 ±0.35	0.85 ±0.07
DO (mg-O_2/L)	4.2	2.3	0.1
ORP (mV)	55.9	-10	-172
pH	7.1	7.12	7.02
Temp (℃)	29.5	29.3	29.1
Aqueous N_2O (ppb-N_2O)	572.55	192.16	54.9
Gaseous N_2O (ppm-N_2O)	22.8 ±0.67	16.47 ±0.27	1.46 ±0.14

Diurnal variability in N_2O emissions

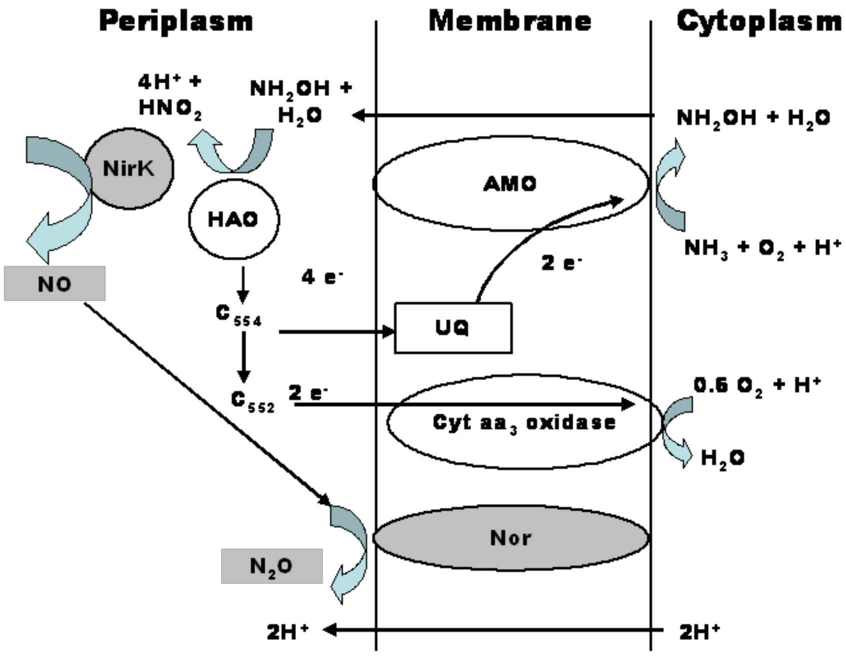


- Significant diurnal variability in N_2O(g) and N_2O (l) conc. in aerobic zones
- Near perfect correlation with diurnal NH_3, NO_2^- and NO_3^- conc.

Summary

- High-degree of variability in emissions observed
- N_2O emissions from aerobic zones were consistently higher than from anoxic zones
- Based on multivariate regression and data mining
  - High ammonia, nitrite and DO conc. positively correlated with N_2O fluxes
  - High DO and nitrite conc. together correlated positively with N_2O fluxes
- N_2O emissions are related to inadequate design and operation of BNR processes
  - There is no conflict between water quality and air quality, rather they go hand in hand
  - N_2O emissions can be used as an indicator of process upsets

What are the mechanisms linked to N_2O and NO generation by nitrifying bacteria?



Hypotheses

- Anoxic conditions stimulate the co- expression of *nirK* and *norB* in *N. europaea* and thus, NO and N_2O production.

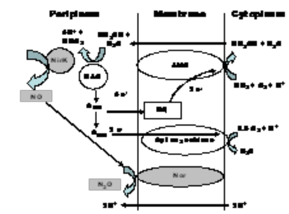
- Upon *recovery* back to aerobic conditions, the trends are reversed.

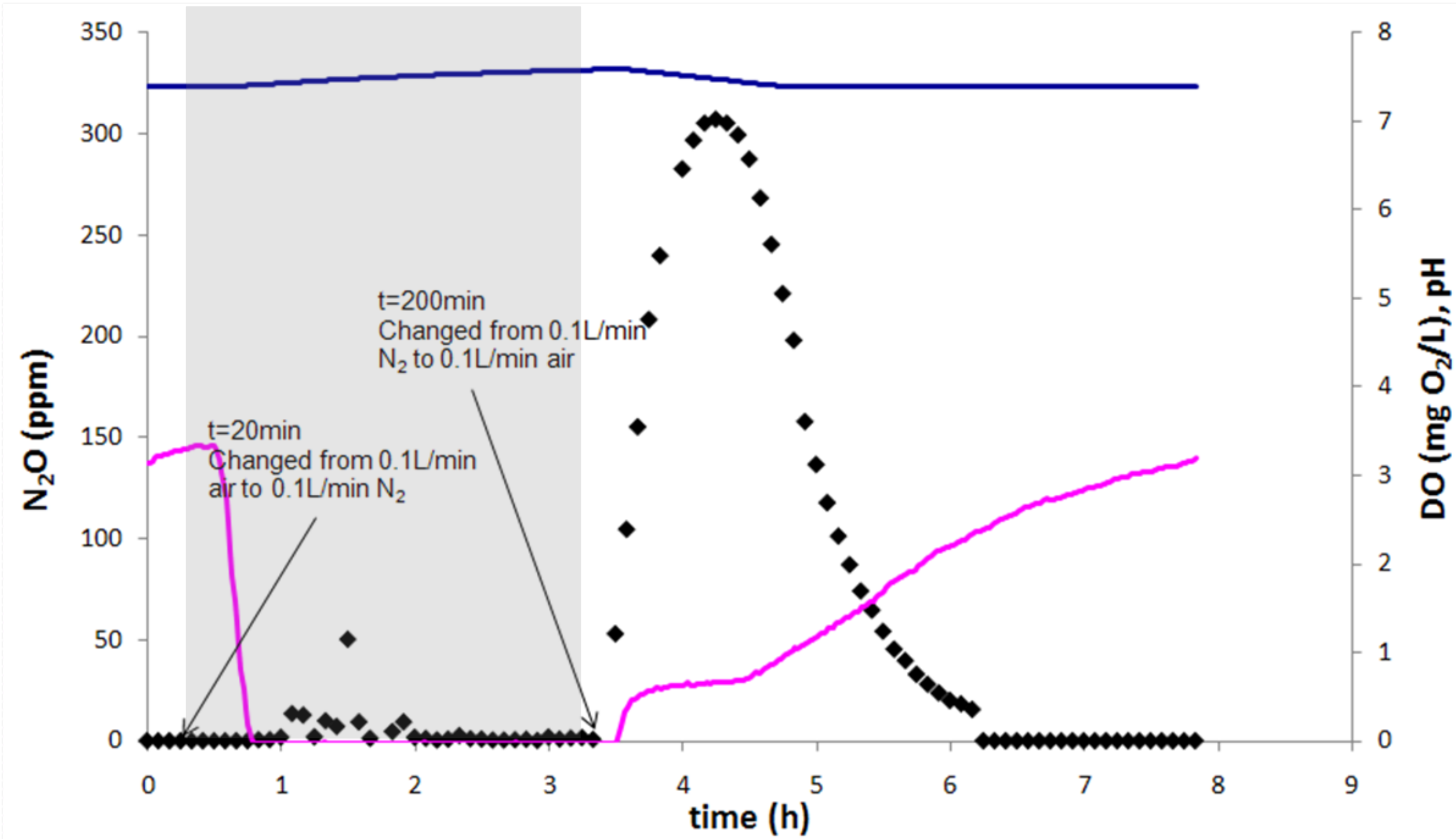
Yu et al., 2010

Chemostat operation

- V=4L
- HRT=SRT=2.2d
- Transient anoxic period = 48h, followed by about 80 h recovery
- $S_{nh,o}$ = 280 mg-N/L at steady state
- $S_{nh,o}$=28, 140, 280 mg-N/L during transient state
  - To determine the impact of S_{nh} accumulation on response and recovery

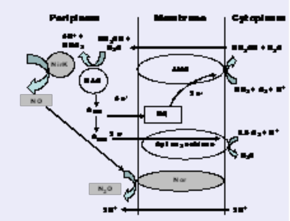
Short term change in DO-Nitrification

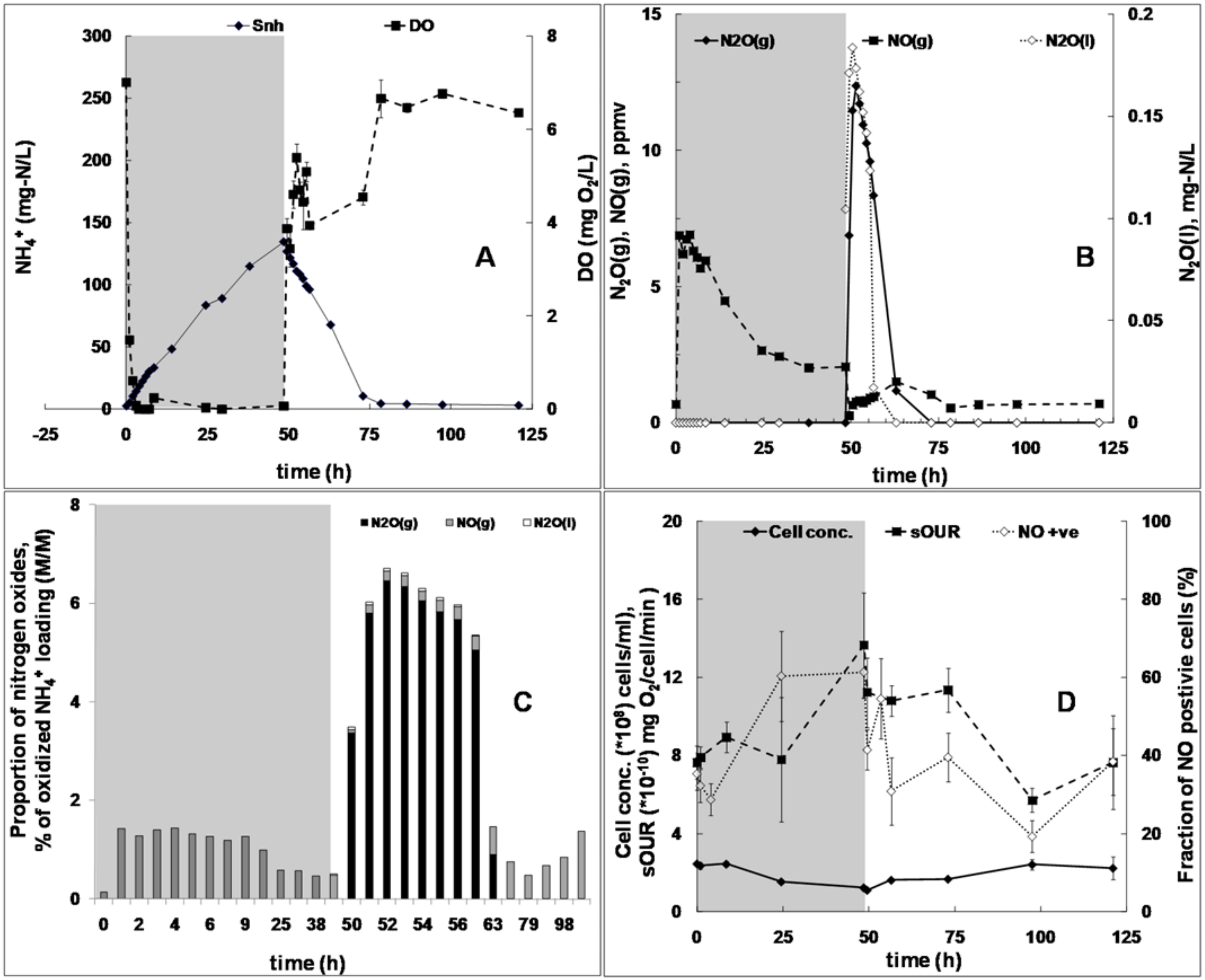




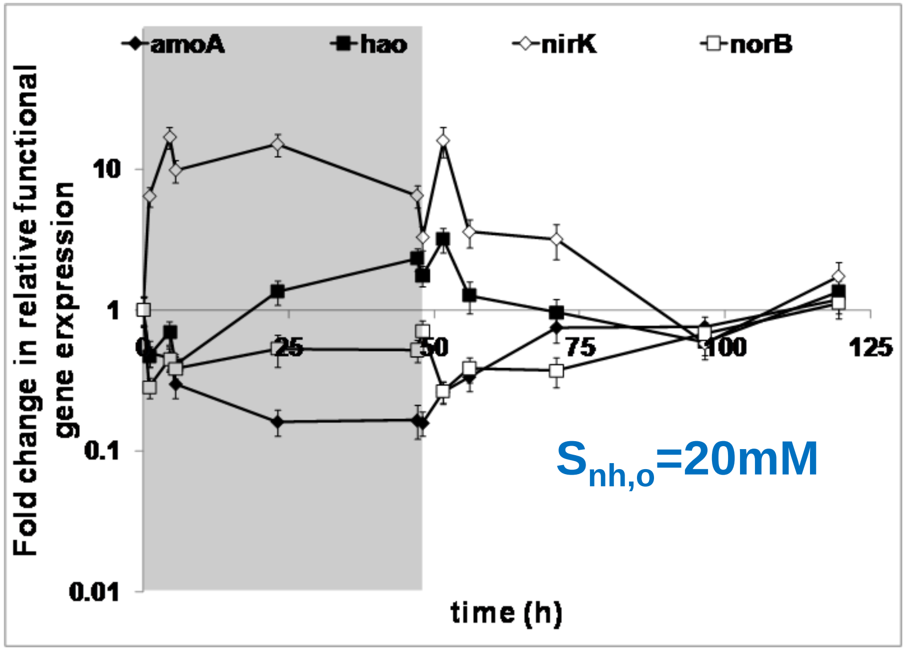
- N_2O production is directional
  - Manifestation of recovery response

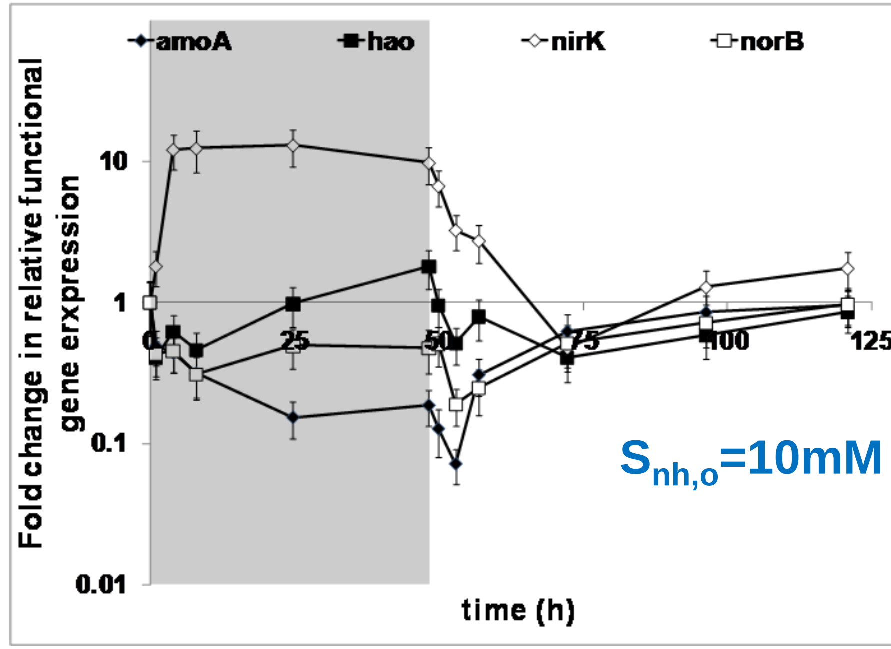
Short term change in DO-Nitrification

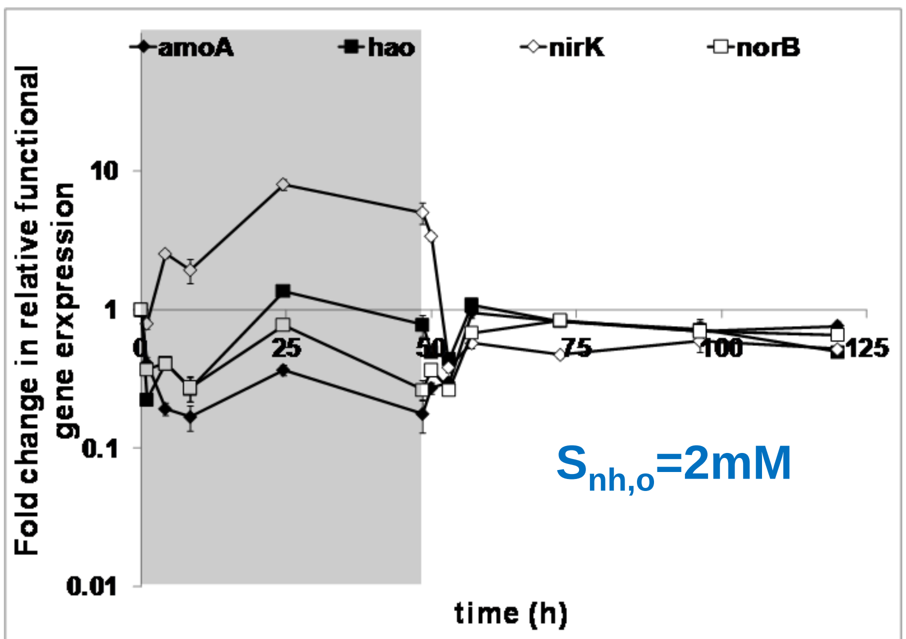




Yu et al., 2010

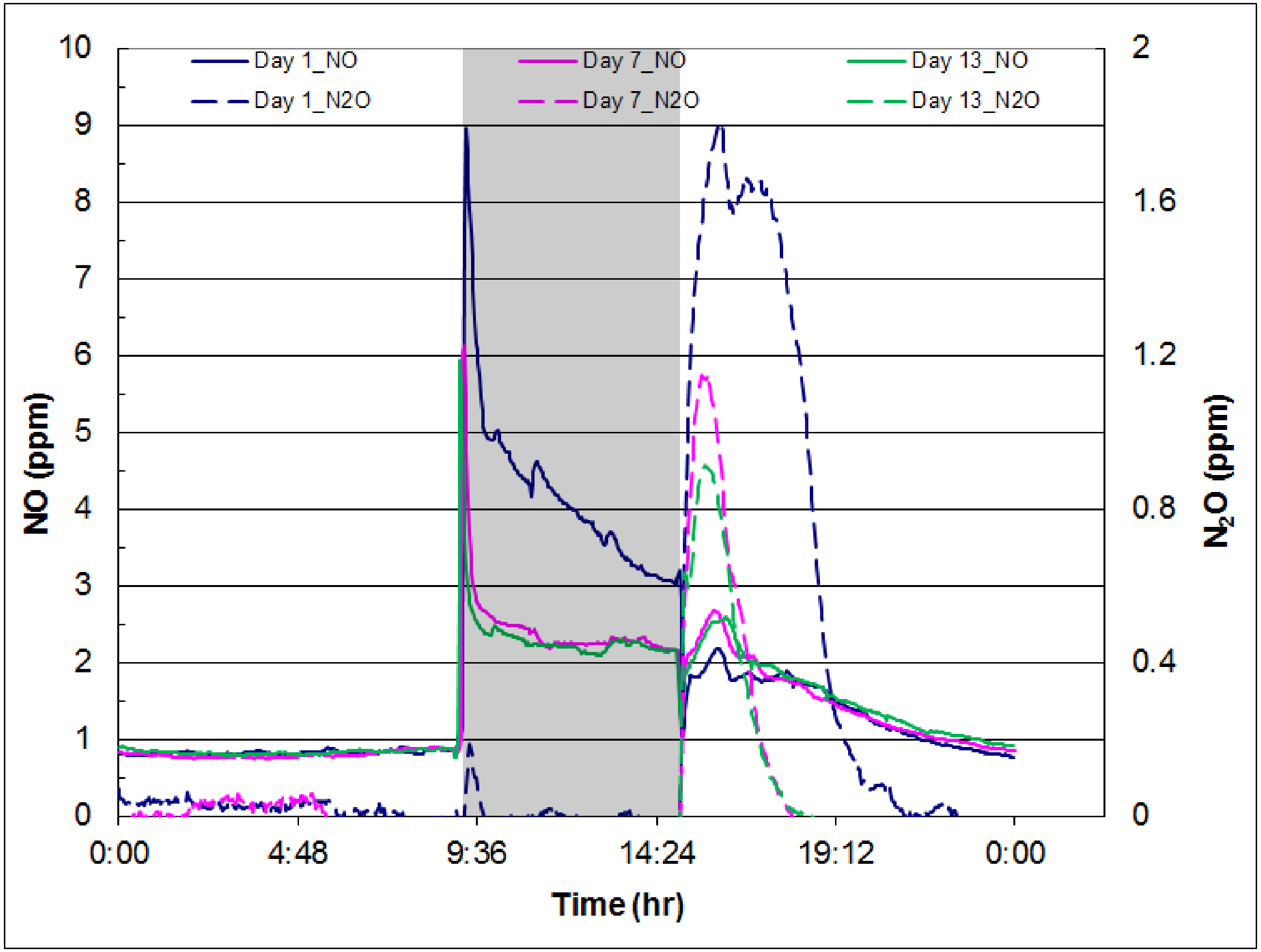






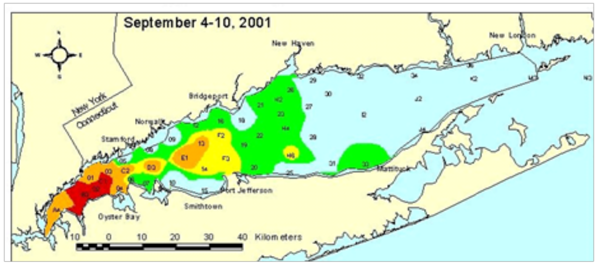
- Nitrite reductase was by far the most responsive to anoxic-oxic cycling
  - *nirK* ➔ NO
- nirK and norB are not co-expressed
- Gene level imbalances are linked to process level N_2O inventories

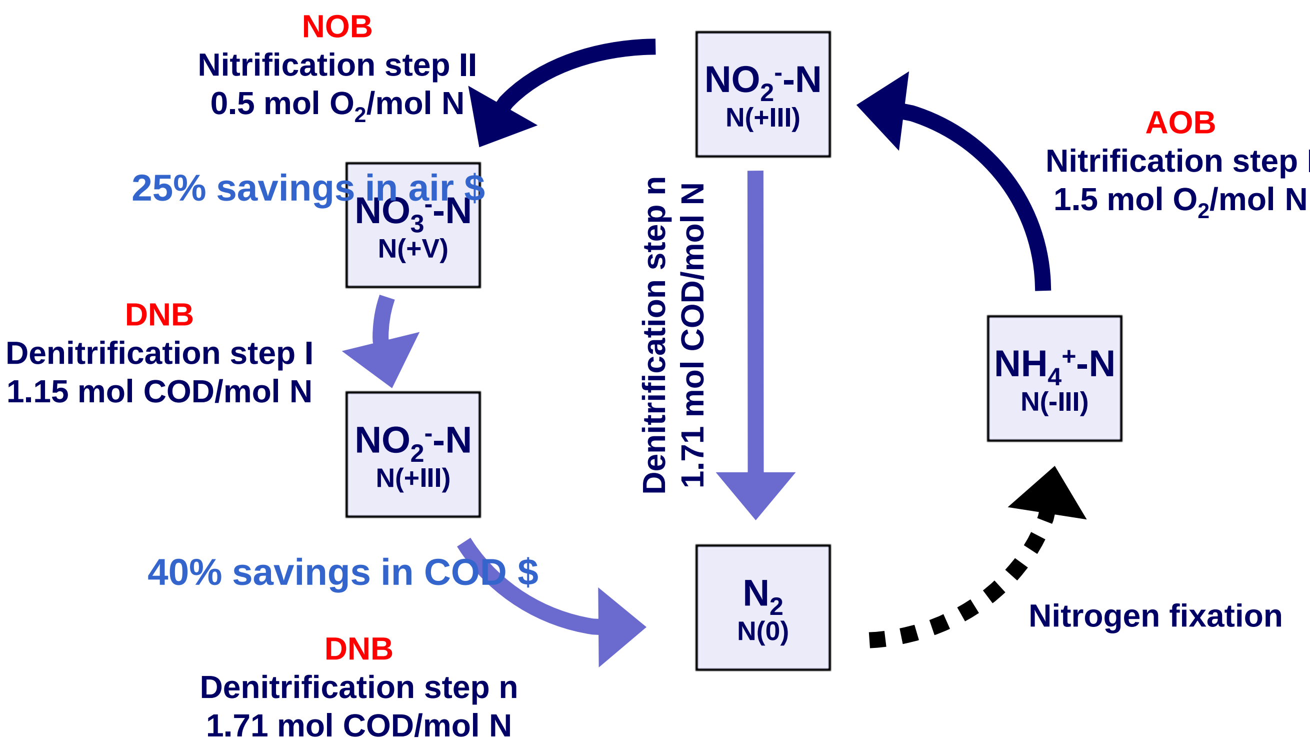
Adaptation to repeated anoxic-oxic cycling



The quest for cost effective BNR

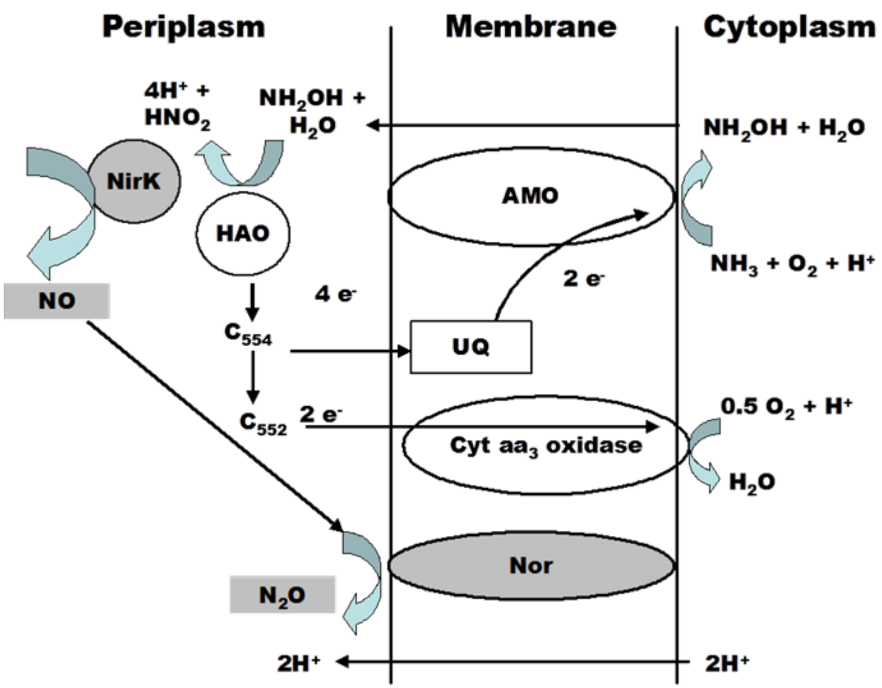
Engineering microbial communities





Factors correlating with N_2O emissions from nitrification

- **Known triggers for N_2O from nitrification**
  - High nitrite concentrations
  - Low DO concentrations and cycling from anoxic to oxic conditions
  - High ammonia concentration transients



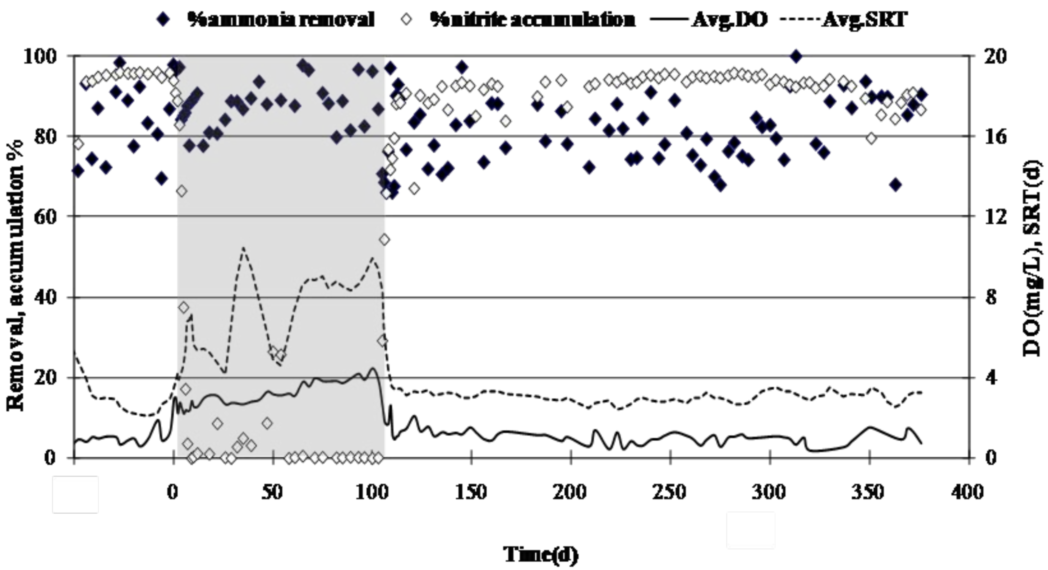
Ahn et al., 2011

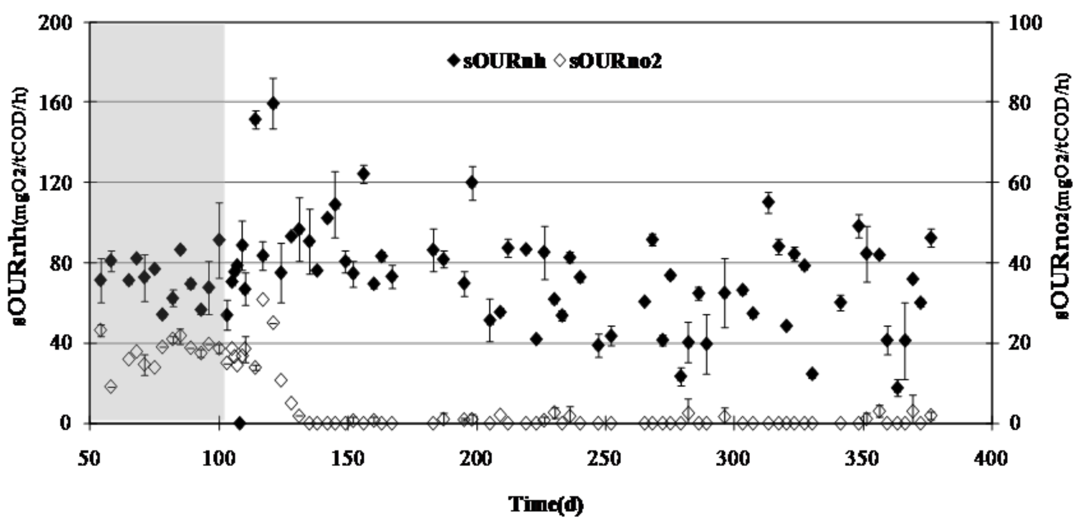
Do we need to re-think partial nitrification based N-removal strategies?

Reactor Operation

- V=11.18 d, HRT=1.1 d, pH=7.5 ± 0.1, T=21^{o}C
- Pre-study partial-nitrification phase
  - SRT = 3d, DO = 1.5 ± 0.87 mg O_2/L
- Full-nitrification phase
  - SRT= 8d, DO = 3.8 ± 0.38 mg O_2/L, 104 days
- Partial-nitrification phase
  - SRT= 3d, DO = 1.1 ± 0.38 mg O_2/L, 273 days

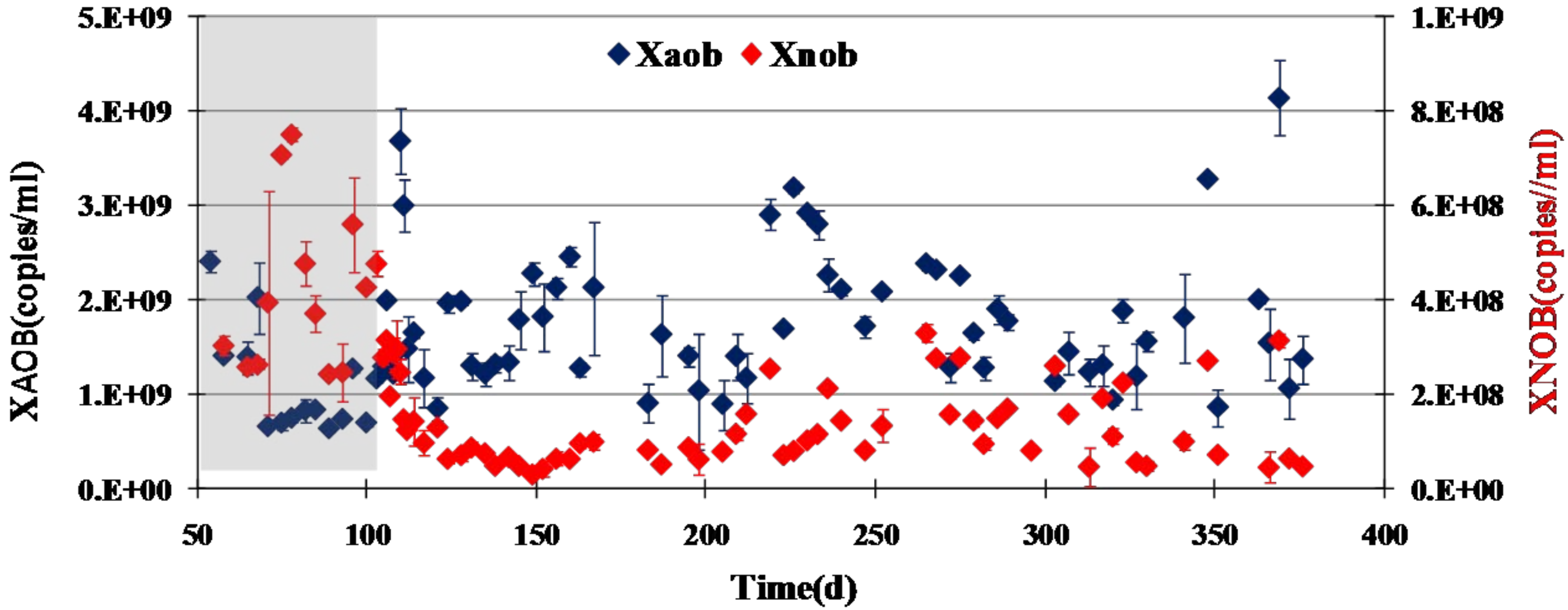
Performance and kinetics





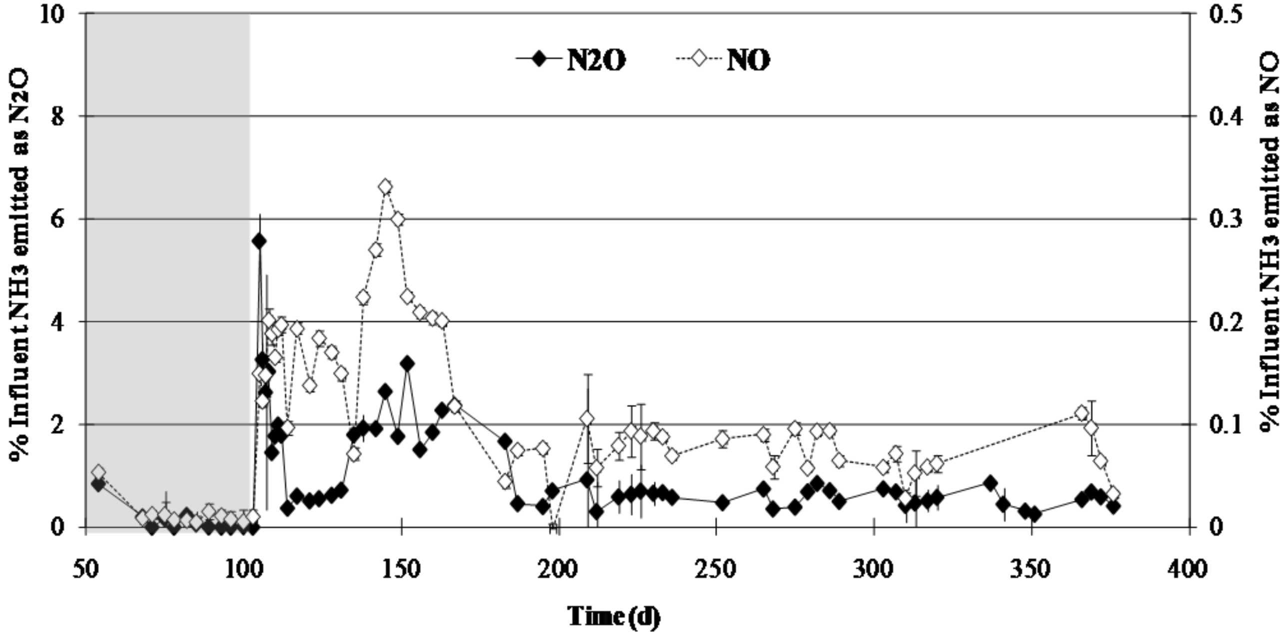
- Rapid change in N-speciation upon changing operating conditions
- Significant decrease in NOB kinetics during PN
- No change in AOB kinetics

Impact of changing operating conditions on microbial ecology



- PN mode led to significant washout of NOB
- No change in dominant AOB speciation
  - *Nitrosomonas europaea and eutropha* dominant AOB in both phases (not shown)

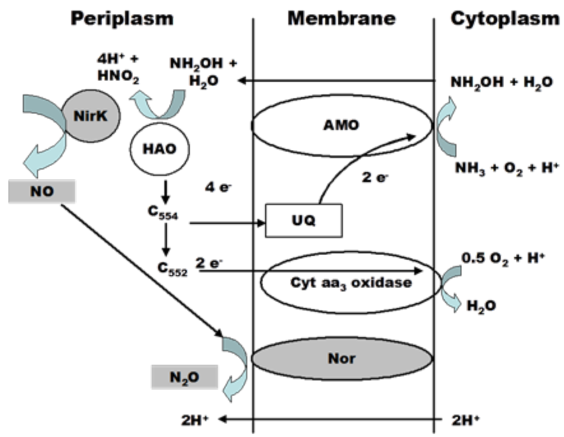
Impact on N_2O and NO emissions

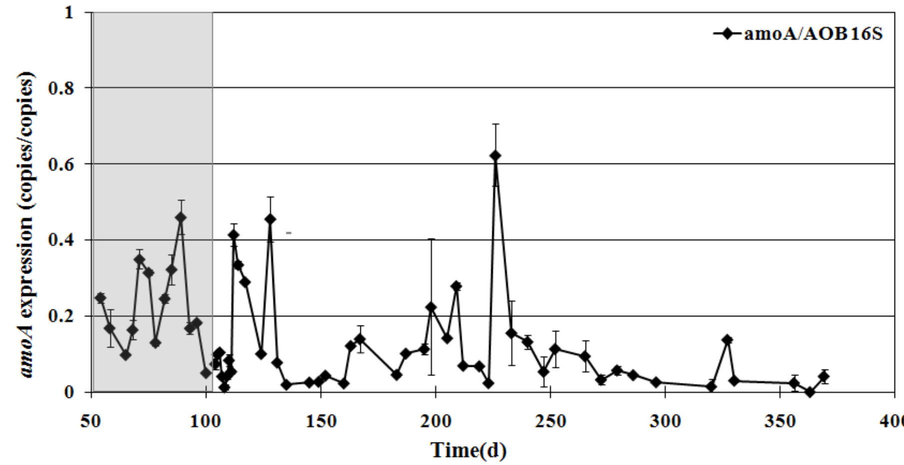


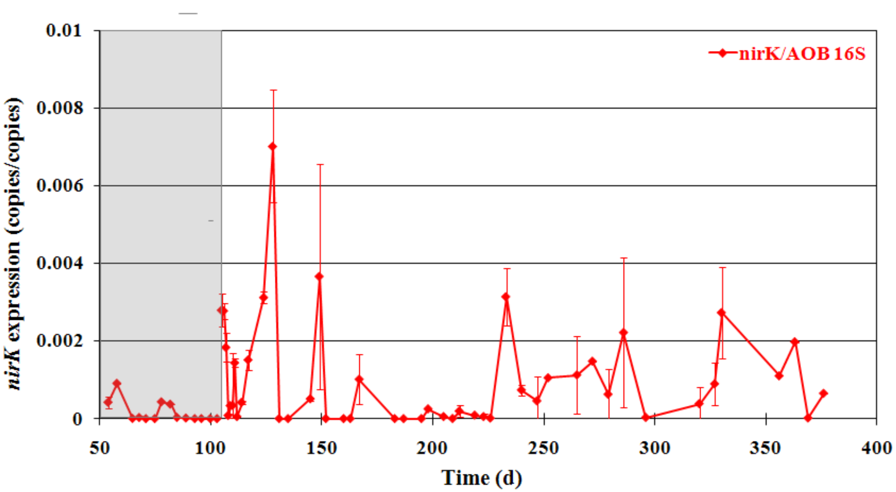
- Highest emissions observed just after switch from full nitrification to partial nitrification
  - However, emissions during PN were not sustained – subsided and stabilized after 80 days
  - Stabilized emissions during PN still statistically higher than during FN ($\alpha=0.05$)

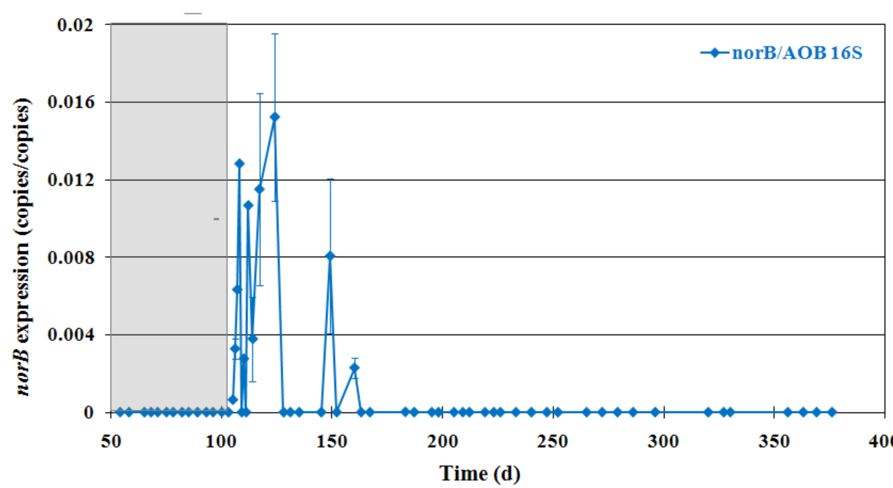
Why does PN result in higher emissions?

Insights from gene expression profiles









- The switch from FN to PN resulted in spikes in expression of *nirK* and *norB*
  - *nirK* ➔ NO *norB* ➔ N_2O
- Good agreement between gene expression and chemical profiles

Summary

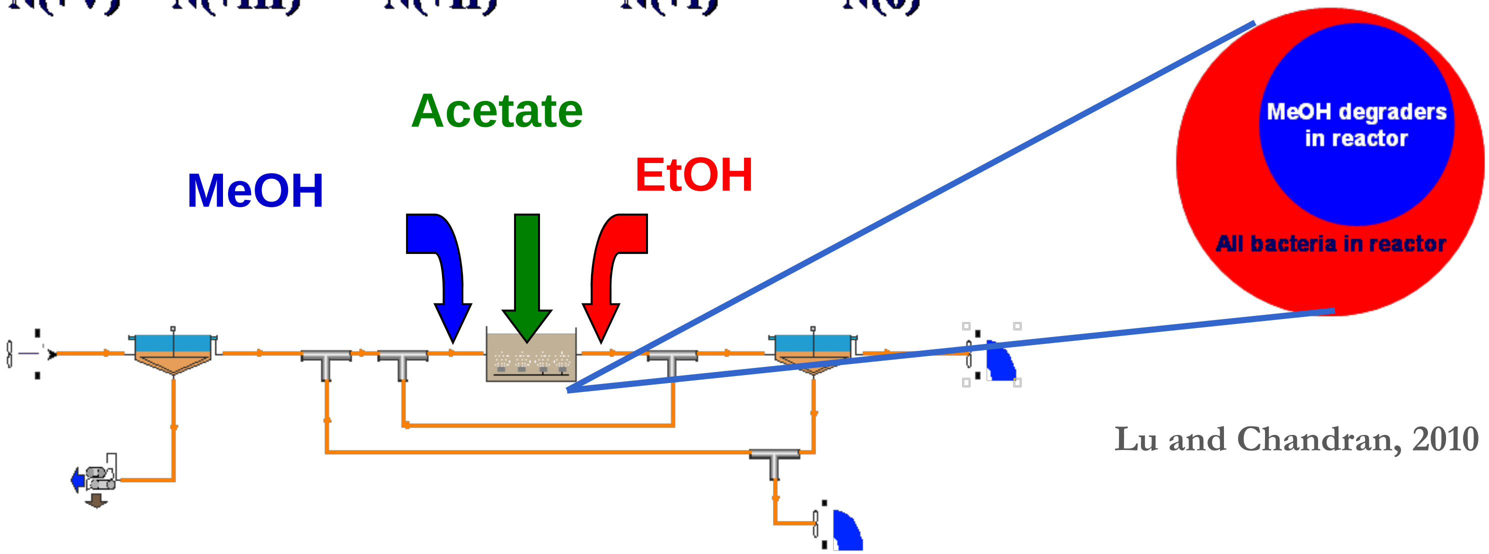
- Statistically higher emissions of N_2O and NO during PN than during FN
- Highest emissions close to the point of switching modes from FN to PN
  - *Gaseous* emissions observed even after rapid change in *aqueous* N-speciation
- Spikes in gaseous emissions were linked to spikes in expression of genes coding for their production in AOB (*nirK* and *norB*)
  - Microbes tend to adapt!

To put matters in perspective

- PN offers significant benefits in terms of lower operating costs
  – Nitrification as well as downstream removal via denitrification or anammox
- Higher N_2O emissions from PN operation for treating streams such as centrate and leachate represents an optimization challenge
- Additional analyses such as LCA could be useful in decision making on a case-specific and site-specific basis
  – Poor performance remains a bigger factor for higher emissions

Role of different electron donors on N_2O and NO emissions

NaR	NiR	NOR	N_2OR	
NO_3^- -------	NO_2^- -------	NO ↑ -------	N_2O ↑ -------	N_2 ↑
N(+V)	N(+III)	N(+II)	N(+I)	N(0)



Lu and Chandran, 2010

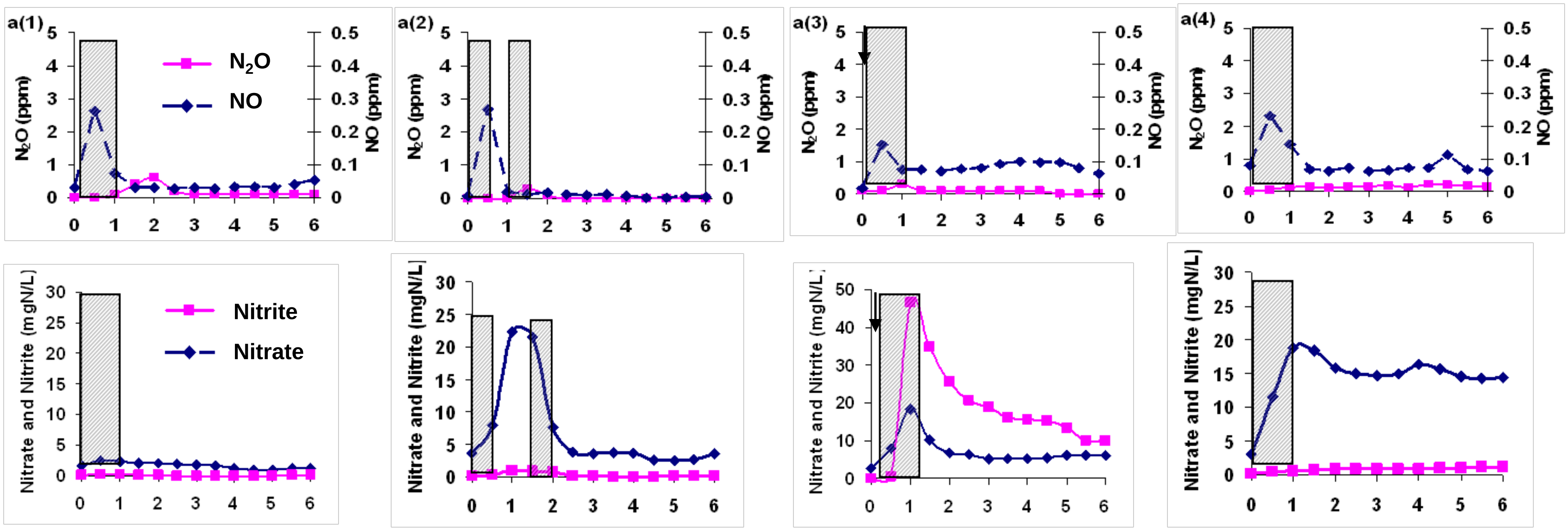
- Different electron donors give rise to different μ_{max} and K_S for denitrification on
  - Response to different transient stressors needs to be systematically studied
  - Different susceptibilities ➔ different emissions?

Experimental setup

- Transient stressors
  - **Organic carbon limitation** COD:N = 2.5 : 1
  - **Exposure to high nitrite concentration spike:** 50mg-N/L
  - **Oxygen Inhibition**
    DO = 2-3 mg/L, 5-6 mg/L, 7-9 mg/L
- USEPA reviewed gas phase monitoring protocol

Impact on methanol based denitrification

Steady State | **Carbon Limitation** | **Nitrite Pulse** | **High DO ($7\text{-}9 mgO_2/L$)**



- Minimal N_2O and NO emissions
  - COD limitation: transient NO_3^- accumulation
  - NO_2^- pulse: transient NO_3^- accumulation
  - High DO: permanent NO_3^- accumulation

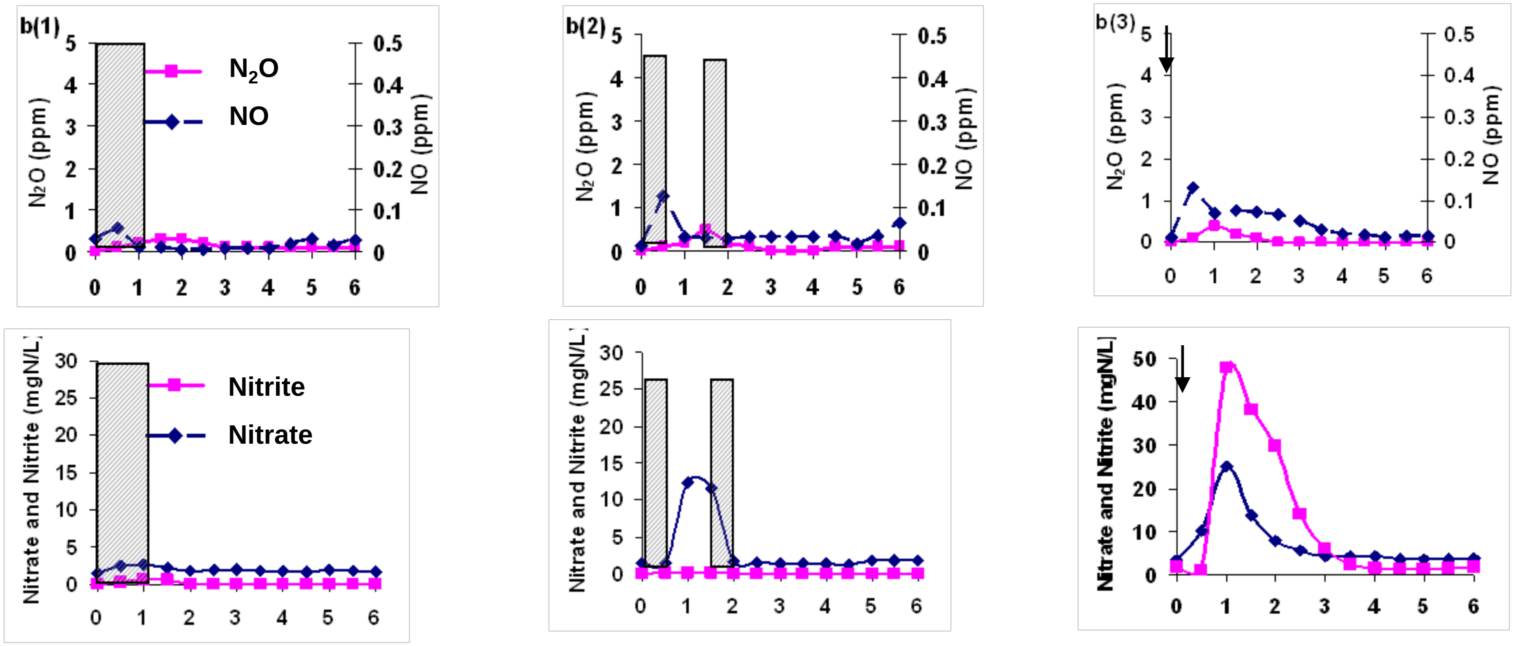
Lu and Chandran, 2010

Impact on ethanol based denitrification (I)

Steady State

Carbon Limitation

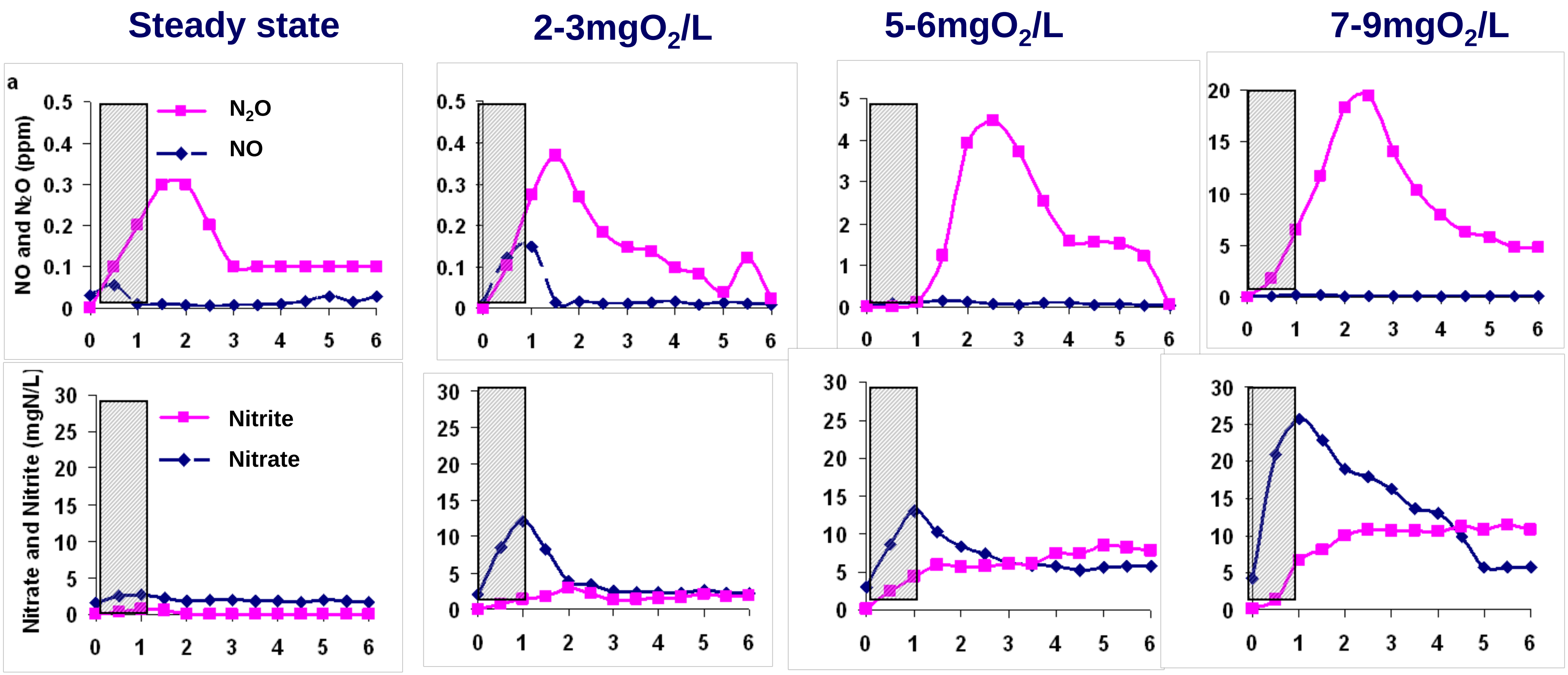
Nitrite Pulse (50mgN/L)



- Minimal N_2O and NO emissions with transient and finite peaks
  - COD limitation: transient NO_3^- accumulation
  - NO_2^- pulse: transient NO_3^- and NO_2^- accumulation

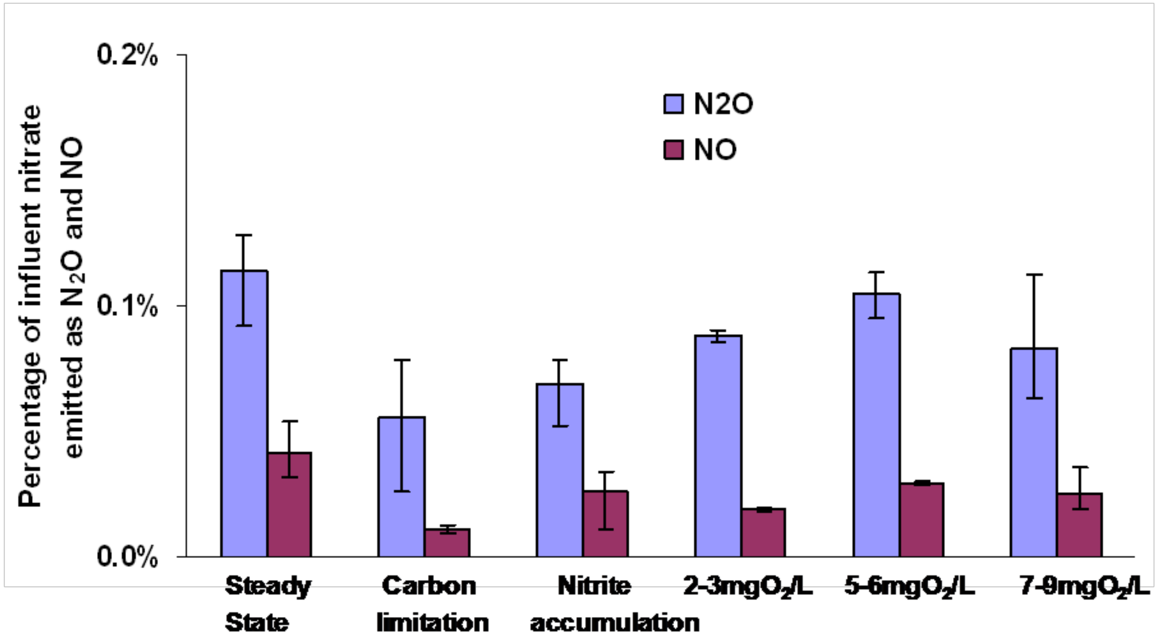
Lu and Chandran, 2010

Impact on ethanol based denitrification (II)



- N_2O and NO emissions increased with DO concentration
- N_2O emission peak: correlated with peak NO_3^- concentration
- Transient accumulation of NO_3^- : increased with DO concentration
- Permanent accumulation of NO_2^- : increased with DO concentration

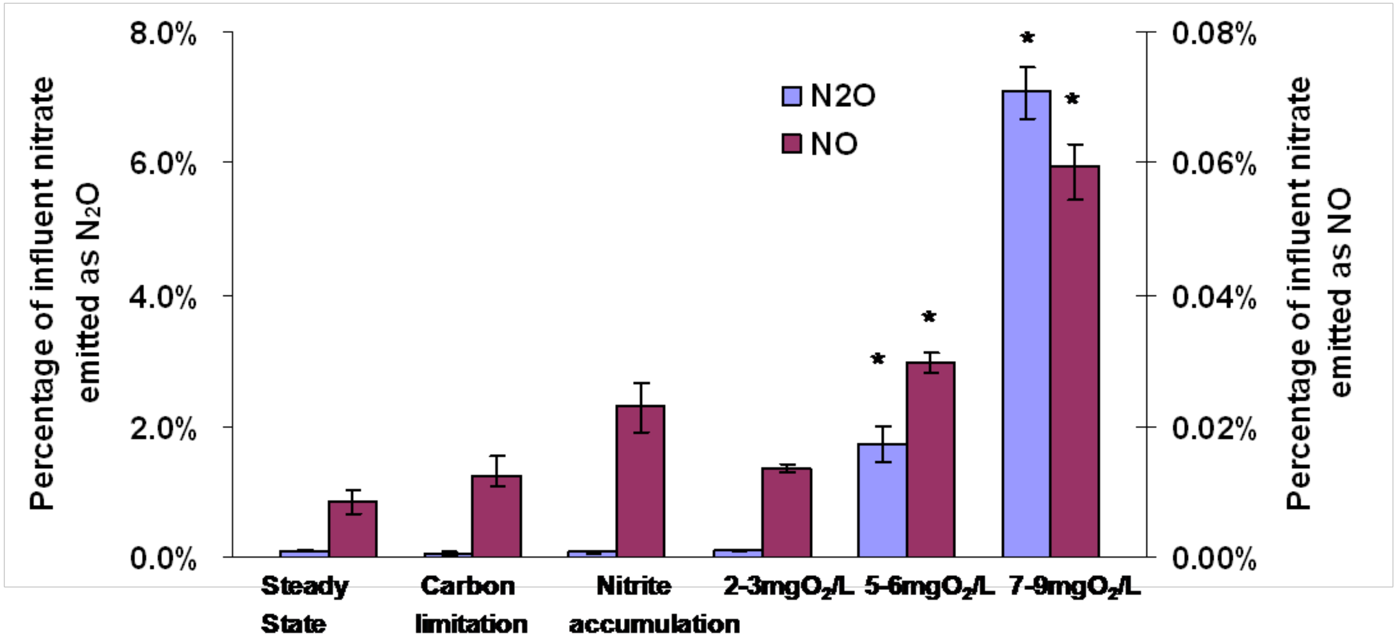
Gas emissions from methanol-denitrification



- Approximately 0.12% and 0.05% of influent NO_3^--N load converted to N_2O and NO, respectively at steady state
- Statistically similar emissions in
  - Control, carbon limitation, NO_2^--N exposure, O_2 inhibition

Lu and Chandran, 2010

Gas emissions from ethanol-denitrification



- Approximately 0.10% and 0.01% of influent NO_3^--N load converted to N_2O and NO, respectively at steady state
- Statistically similar emissions in
  - Control, carbon limitation, NO_2^--N exposure
- Significantly higher N_2O and or NO emissions at DO > 5mg O_2/L

Lu and Chandran, 2010

Implications

- Emissions related to denitrification are dependent upon the organic C-sources used
  - the microbial ecology and kinetics thus fostered
  - relative susceptibility and tolerance to stressors
- Organic C-limitation and nitrite toxicity played a minor role in emissions from both methanol and ethanol
  - Partial inhibition resulted in N_2O emissions (ethanol)
  - Higher inhibition led to low emission (methanol)

Implications for pre-anoxic zone sizing

- Ethanol bleed out to aerobic zone can result in N_2O and NO emissions

- Lower emissions expected during similar methanol bleed out

Summary of observations

- Started with one or two emission factors in 2008
- N_2O emissions related to recovery from stress response of nitrifying bacteria
  - Similar patterns observed at full-scale
  - Attributed to an imbalance between the expression of specific pathways in AOB
- Next: Based on mechanisms, develop BNR strategies to minimize both *aqueous* and *gaseous* N discharges

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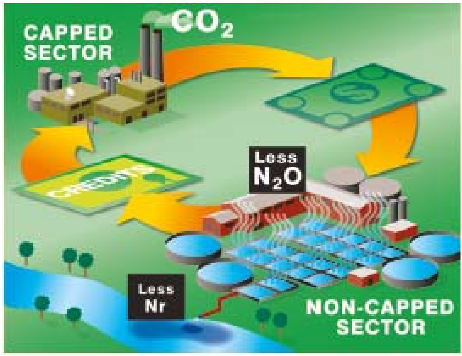

Emissions Credits: Opportunity To Promote Integrated Nitrogen Management in the Wastewater Sector

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