

NITROUS OXIDE AND GAS TRANSFER IN FULL-SCALE ACTIVATED SLUDGE BASINS

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INTRODUCTION

Nitrous oxide (N_2O) potent greenhouse gas, ozone depleting
265-298x CO_2 100-year global warming potential
Wastewater treatment ~3% of anthropogenic N_2O

BNR emits 0.03-5.6 % influent nitrogen as N_2O . Pathways include:
Nitrifier denitrification
Hydroxylamine (NH_2OH) oxidation
Incomplete heterotrophic denitrification

Measuring N_2O production difficult
 N_2O probes available but uncommon, do not give off-gas concentration
Gas measurements uncommon in most WWTPs

Interest in modelling N_2O production
Use models to estimate gas concentration from dissolved N_2O
Reliable estimates = understanding & reducing carbon footprint



THESIS OBJECTIVES

Primary goals:

- Study production and off-gas of N_2O in Viikinmäki activated sludge basins
- Measure and compare N_2O transfer and oxygen transfer

Secondary goals:

- Assess depth variability of N_2O at Viikinmäki



LITERATURE REVIEW

Nitrous Oxide Transfer from Wastewater:

- Kosonen, 2013 – long-term study of N_2O production at Viikinmäki
 - Local and plant-wide N_2O emissions
- Blomberg, 2016 – model N_2O production at Viikinmäki
 - liquid probes and plant-wide emissions
- Baresel et al., 2016 – liquid probes & plant-wide emissions at Käppala
- Foley et al., 2010 – spot measurements with liquid probes and emissions grab samples for gas chromatograph analysis, 7 plants in Australia

Oxygen Transfer in Wastewater:

- ASCE, 1996 - established standard method for testing oxygen transfer
- Jiang et al., 2017 – compare O_2 transfer with wastewater quality (COD)
- Hamborg et al., 2010 – compare liquid mass transfer coefficients of O_2 , CO_2 , and N_2O in water

Novel Research:

- Limited studies using N_2O probes alongside local N_2O emissions
- No prior simultaneous studies of N_2O and O_2 transfer



BACKGROUND

Gas Transfer:

$$\frac{\partial C}{\partial t} = K_L a * (C_L - C^*) - r \quad [1]$$

- Gas concentration in wastewater with negligible reactions:

$$\frac{\partial C_G}{\partial t} = (\alpha) * K_L a * (C_L - \frac{C_G}{H}) \quad [2]$$

- Assume well-mixed vertically, integrate. Substitute time for the approximate bubble detention time V_R/Q_A :

$$C_{G,out} = C_{G,in} * e^{-\frac{(\alpha)*K_L a * V_R}{H * Q_A}} + H C_L * \left(1 - e^{-\frac{(\alpha)*K_L a * V_R}{H * Q_A}}\right) \quad [3]$$

- Henry's H and $K_L a$ temperature dependent
 - adjusted with Van't Hoff and Arrhenius equations
- Proposed N_2O empirical $K_L a$ equations (Foley et al, 2010):

$$K_L a_F^* = \left(\frac{D_R}{D_L}\right)^{-0.49} * (34500 * v_g)^{0.86} \quad [4]$$

BACKGROUND

Oxygen Transfer Rate & Efficiency:

- Standard oxygen transfer rate (SOTR) and actual oxygen transfer rate (AOTR or OTR) in mass/time:

$$SOTR = K_L a_{20} * C_{s,20} * V * 10^{-3} \quad [5]$$

$$AOTR = SOTR * \alpha * F * \left(\frac{\beta C_{S,T,H} - C_L}{C_{s,20}} \right) * 1.024^{(T-20[^\circ C])} \quad [6]$$

- SOTR: clean water, standard conditions, AOTR: actual conditions
- Oxygen transfer efficiency is a measure of the percent oxygen uptake from aeration:

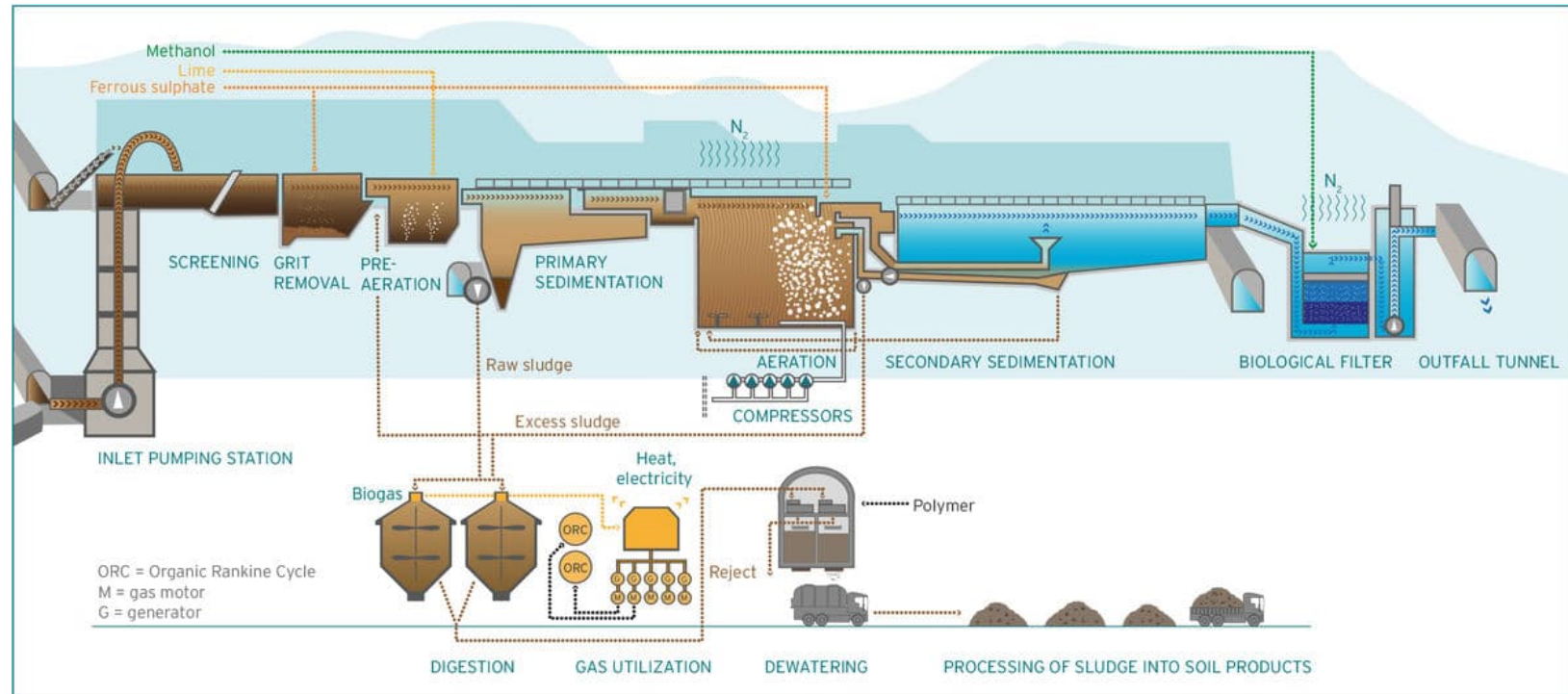
$$OTE = \frac{OTR}{W_{O_2}} \sim \frac{O_{2,in} - O_{2,out}}{O_{2,in}} \quad [7]$$

$$OTR = (\alpha) * K_L a * (C^* - C_L) * V \quad [8]$$

LOCATION

Viikinmäki Wastewater Treatment Plant:

- Fully enclosed, continuous gas sampling since 2012
- Fully automated, online measurements of many wastewater parameters
- Previous N₂O studies at Viikinmäki:
 - Average N₂O emission of 0-80 ppm
 - Significantly increased N₂O emissions during this study: 30-300 ppm



Viikinmäki wastewater treatment train (HSY, 2015)

MATERIALS & METHODS:

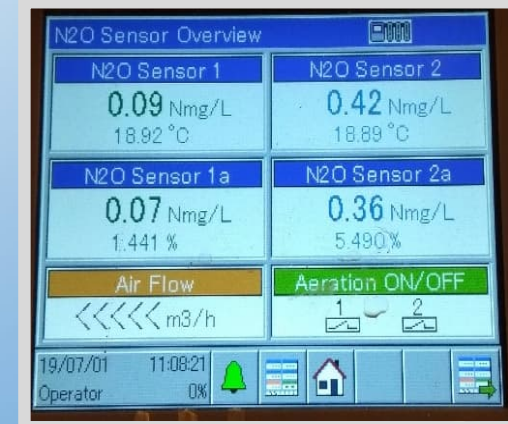
Depth Profile

Materials

- Ruttner sampler device
- Unisense N₂O probe (Clark-type microsensor)
- pH probe

Methods

- Test performed twice: 2 April and 1 July 2019
- N₂O probe and Ruttner lowered to set distance
 - 2 April: 3 & 5m, successive measurements
 - 1 July: 1, 3, & 5m, concurrent duplicate measurements
- Compared values from Unisense Environment display, online data



MATERIALS & METHODS:

Gas Transfer

Materials

- Floating hood and/or Alphasampler connected to:
 - Gasmet FT-IR analyser
 - AMI oxygen analyser
 - Extech hot wire thermos-anemometer
- Unisense and DO probes for dissolved N_2O , O_2

Methods

- Line 5: 7.-13.5.2019 ; Line 9: 13.-20.5.2019
- Simultaneous gas measurements: zones 4, 5, and 6
- Hood near Unisense probes to compare gas, liquid measurements



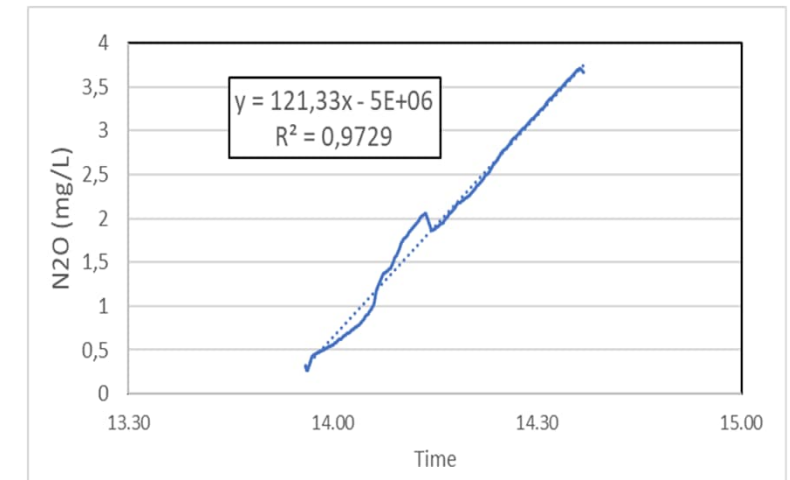
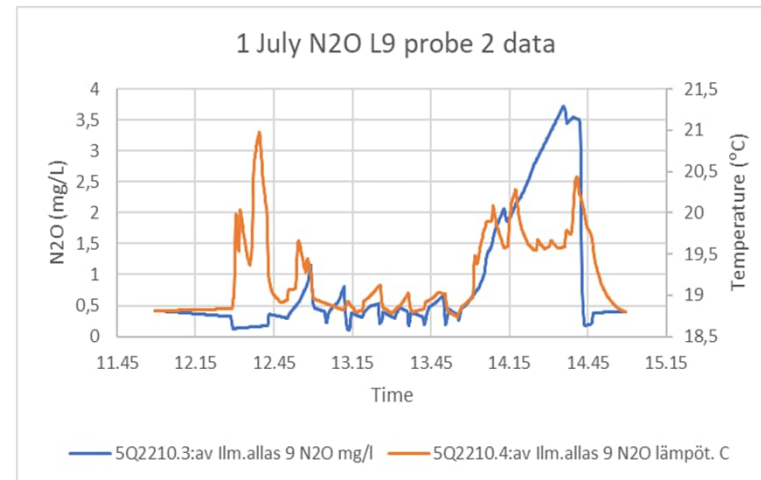
RESULTS

Vertical Profile:

- Minimal N₂O and pH variability (<10%) within 5 m

Date and location	Depth ¹	Ambient N ₂ O reading ²	Ruttner N ₂ O reading ²
2 April, line 5 zone 4	3 m	0.11 mg/L	0.10 mg/L
	5 m	0.10 mg/L	0.09 mg/L
1 July, line 9 zone 6	1 m	0.36 mg/L	*
	3 m	0.37 mg/L	*
	5 m	0.39 mg/L	*

- Method unsuitable for >5 m depths
 - Alternate method necessary to fully confirm well-mixed assumption
- July 1 N₂O production rate of 5.06 mg/L/h



RESULTS

Oxygen Transfer:

- Daily variation in OTE & OTR
- Higher OTE and lower flowrates in later zones

Date	Position ¹	Airflow (m ³ /h)	OTE (%)	OTR (kg/h)	$\alpha K_L a$ (1/h)
7-May	5.5A	1186	27.3	82.7	3.9
8-May	5.5C	1188	29.1	88.4	4.0
8-May	5.5B	1182	28.7	86.7	4.0
8-May	5.5A	1193	25.9	79.0	3.6
9-May	5.6	513	28.7	37.6	1.7
9-May	5.5D	1110	31.3	88.8	3.8
10-May	5.4/5 ²	1639	13.9	58.2	2.6
10-May	5.5A	1391	22.1	78.6	3.4
13-May	5.6	541	31.5	43.5	1.9
13-May	5.5B	1037	31.2	82.7	3.6
14-May	9.4A	1370	15.1	52.9	2.4
16-May	9.4A	1636	14.1	59.0	2.7
16-May	9.4 α	1636	12.4	51.8	2.4
17-May	9.6	835	24.1	51.4	2.3

$\alpha K_L a$ range of 1.6-4.0

- Average zone airflow used for calculations
 - Alphameter hood airflow much lower, small tubing = pressure loss

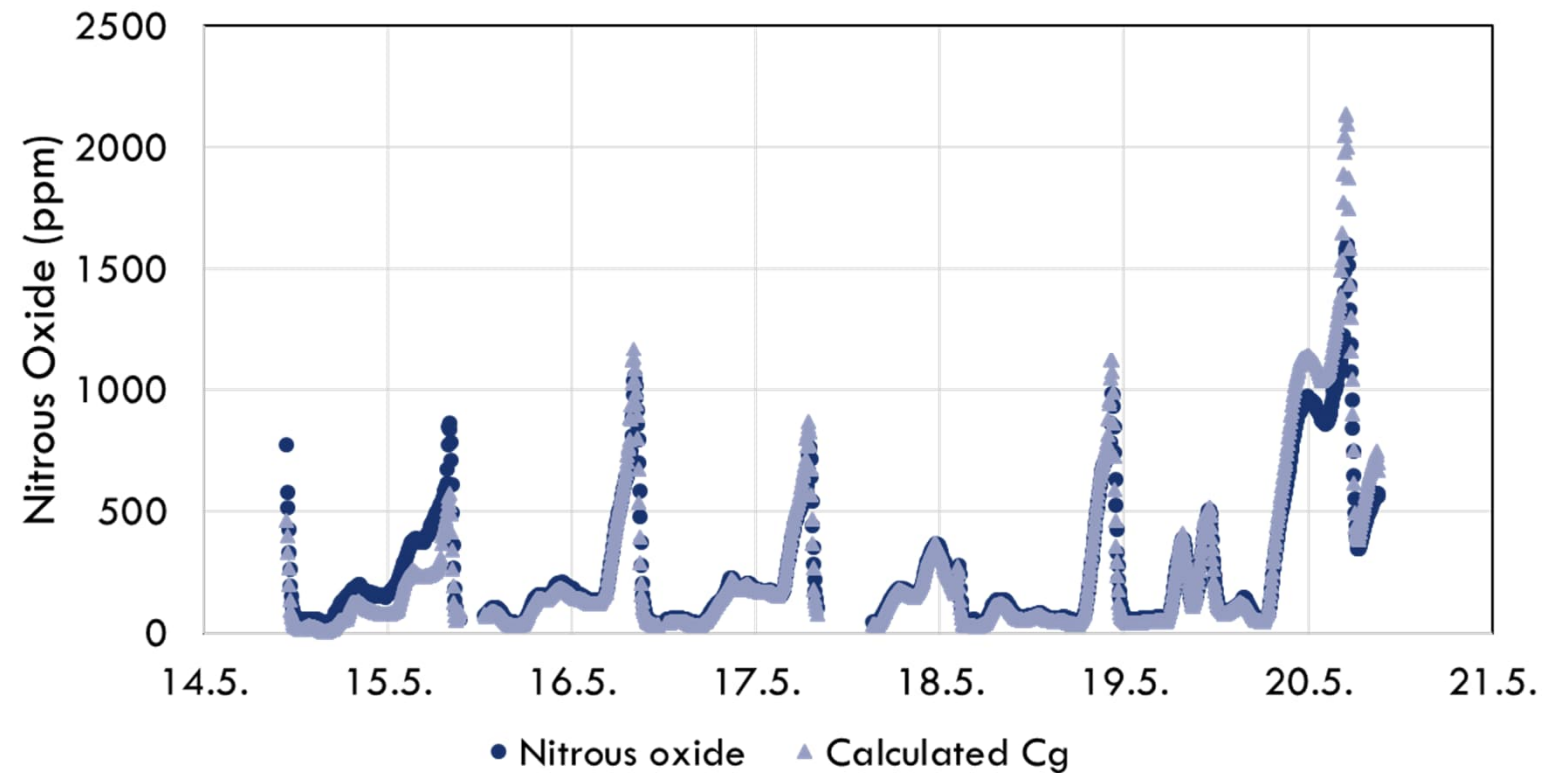


RESULTS

Nitrous Oxide Transfer:

- Clear correlation off-gas & probe N_2O concentrations
- Average $\alpha K_L a$ 1.6-2 h^{-1}
 - Foley Equation $K_L a$ 0.2-0.5 h^{-1} , α : 2.5-4

Calculated vs. Measured N_2O



- Underestimates at start of week, overestimates at end of week
 - wastewater composition changes daily

DISCUSSION

Sources of Uncertainty:

- Probes: communication error, drift, biofilm
- Gasmeter FT-IR: noise, malfunctions, inaccuracies
- Calculations: use of incorrect values or assumptions

Sensitivity Analysis:

- Wish to assess impact of uncertainties
- Baresel et al., 2016: dissolved N_2O errors largest impact on calculated off-gas N_2O
 - Compared to errors in depth, temperature, reactor area



DISCUSSION

Study Shortcomings:

- Short time, small volume of data to draw conclusions
- Vertical sampling human error: probe not at equilibrium at each depth, depths inconsistent, incomplete analysis

Unfinished Work:

- Sensitivity analysis
- Compare local and plant-wide values
- Analyse logged oxygen transfer data



CONCLUSIONS

- Exact variation with depth inconclusive, but insignificant within first 5 meters
- Oxygen transfer daily and flow-based variation
 - Flow-based expected, daily caused by water quality?
- N₂O probes useful for estimation of off-gas
 - Limitations on application at different plants
- Combination of probe data, air flow can be used to assess effects of operational changes on N₂O production



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THANK YOU

QUESTIONS?

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