

Modelling of nitrous oxide emissions from an A2/O process treating municipal wastewater

Theoni M. Massara^{1,2}, Albert Guisasola³, Evina Katsou^{1,2}, Juan Antonio Baeza³

¹Department of Mechanical, Aerospace and Civil Engineering, Brunel University London, Uxbridge Campus, Middlesex, UB8 3PH, Uxbridge, UK.

²Institute of Environment, Health and Societies, Brunel University London, Uxbridge Campus, Middlesex, UB8 3PH, Uxbridge, UK.

³Departament d'Enginyeria Química, Biològica i Ambiental, Escola d'Enginyeria, Universitat Autònoma de Barcelona, Cerdanyola del Vallés (Barcelona), 08193, Barcelona, Spain.

Corresponding author: Theoni M. Massara

E-mail: Theoni.Massara@brunel.ac.uk

Abstract: Nitrous oxide (N₂O) is a greenhouse gas significantly contributing to the greenhouse effect and potentially generated during the biological nutrient removal in wastewater treatment plants (WWTPs). The 3 possible microbial pathways for the N₂O production are the incomplete hydroxylamine oxidation, the nitrifier denitrification and the heterotrophic denitrification. The first two, both followed by Ammonia Oxidising Bacteria (AOB), are considered as the most important N₂O production mechanisms. In this work, a modified version of the IWA ASM2d model expanded to describe nitrification and 4-step denitrification was combined with a 2-pathway model describing N₂O production by AOB. The ultimate goal was the development of a mathematical tool predicting the N₂O emissions out of municipal wastewater treatment data. Although low dissolved oxygen (DO) is applied to decrease the energy requirements in WWTPs, our model estimates that low DO (<1.8 mgL⁻¹) combined with a high influent ammonium (NH₄⁺) concentration (>20.0 mgL⁻¹) are conditions working to the advantage of partial nitrification and triggering N₂O production through the nitrifier denitrification pathway.

Keywords: N₂O, ASM2d, A2/O, DO, AOB

Introduction

In wastewater treatment, biological nutrient removal processes constitute a potential hotspot for the generation of greenhouse gases (i.e. carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O)). CH₄ and N₂O have a global warming potential which is, respectively, 25 and 265 times higher than the one of CO₂ in a 100-year period (IPCC, 2013). As a consequence, N₂O production and emission are research topics of great interest considering N₂O's big contribution to the greenhouse effect. The IWA Activated Sludge Models (ASM) (Henze *et al.*, 2000) are a widely used tool for the description of nitrogen (N) and phosphorus (P) removal in wastewater treatment plants (WWTPs). However, they do not include N₂O production and quantification.

Past studies have investigated the microbial pathways for N₂O production and suggested the following three: nitrifier denitrification, incomplete hydroxylamine oxidation and heterotrophic denitrification. The first two are activated by ammonia oxidising bacteria (AOB). Amongst these three mechanisms, the two AOB-related ones are regarded as the principal N₂O production routes. The aim of this work was to integrate a detailed prediction of the N₂O production and emission in the model-based description of full-scale WWTPs performing COD, N and P removal.

Material and Methods

An ASM2d model including nitrification and 4-step denitrification (expanded from Guerrero *et al.*, 2011) was coupled with a 2-pathway model for N₂O emissions by AOB developed by Pocquet *et al.* (2016). Table 1 shows the 38 processes included in our model.

The kinetic model was developed in MATLAB for an anaerobic/anoxic/oxic (A2/O) configuration. The influent composition data were typical wastewater values from the municipal WWTP of Manresa (Catalonia, Spain) (more info on the Manresa WWTP available in Machado *et al.*, 2014). The maximum emission factor, defined as the percentage of N transformed to N₂O with respect to the total N-amount in the influent, was calculated for each scenario under steady-state operation. At this point, it shall be underlined that the percentage of N transformed to N₂O included both the N₂O in the effluent (i.e. dissolved N₂O) in addition to the amount of the produced N₂O which was transformed into gas; stripping was modelled, too. Steady-state was achieved by simulating the WWTP with constant influent composition for a period of 200 d.

Results and Conclusions

The first aim was to determine the effect of changing conditions on the N₂O emission factor. This involved simulating the fluctuation of the following: dissolved oxygen (DO) concentration in the aerobic reactor, influent ammonium (NH₄⁺) concentration, influent COD values, influent flow rate, internal recycling ratio. The second target was to test the impact of different sets of kinetic parameters for the growth and the decay of the AOB and NOB (Nitrite Oxidising Bacteria) populations. The first set was taken from the study of Hiatt and Grady (2008) and the second from Jubany *et al.* (2009). In spite of the different absolute values of the two parameter sets, the trials for different fluctuating conditions revealed similar trends for both parameter groups. In terms of effect on the N₂O emission factor, the DO and the influent NH₄⁺ concentration appeared as the most crucial factors.

The combined effect of aerobic DO and influent NH₄⁺ on the N₂O emission factor under the AOB parameters of Hiatt and Grady (2008) is presented in this abstract. The DO tested range of concentration was 0.01-4.0 mgL⁻¹; influent NH₄⁺ concentration was tested for values from 10.0 to 40.0 mgL⁻¹. According to the results, NH₄⁺ was not oxidised and nitrification did not occur for DO < 0.8 mgL⁻¹. The maximum N₂O emission factor was 27.2% as a combination of DO around 1.1 mgL⁻¹ along with the highest influent NH₄⁺ concentration tested (40.0 mgL⁻¹). A general observation is that the highest emission factors appeared within the range of 1.0 < DO < 1.8 mgL⁻¹ (Figure 1). The latter suggests that full nitrification did not happen in the low DO environment. Thus, partial nitrification (NH₄⁺ oxidation to nitrite (NO₂⁻)) occurred and, then, N₂O was generated via the nitrifier denitrification pathway. The DO increase from 1.8 mgL⁻¹ and onwards enhanced nitrification. As a consequence, the accumulation of NO₂⁻ decreased and less N₂O was produced through the nitrifier denitrification pathway. After that, the N₂O emission factor followed a decreasing trend reaching approximately the value of 2.0% at the higher DO concentrations. All things considered, the developed model estimates that DO < 1.8 mgL⁻¹ combined with a high influent NH₄⁺ concentration (>20.0 mgL⁻¹) favour partial nitrification and induce N₂O production through the nitrifier denitrification pathway. In one hand, low DO conditions are a way to reduce the energy requirements during the biological N-removal in wastewaters with low COD content. On the other hand, our results show that partial nitrification is possible under these conditions. Hence, the high N₂O emissions which are likely occur will be possibly translated into an overall carbon footprint beyond the desired limits.

Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie (grant agreement No 645769). T.M. Massara is also grateful to the Natural Environment Research Council (NERC) of the UK for the 4-year full PhD studentship. J.A. Baeza and A. Guisasola are members of the GENOCOV research group (Grup de Recerca Consolidat de la Generalitat de Catalunya, 2014 SGR 1255).

References

- Guerrero, J., Guisasola, A., Baeza, J.A. (2011) 'The nature of the carbon source rules the competition between PAO and denitrifiers in systems for simultaneous biological nitrogen and phosphorus removal', *Water Research*, 45, pp. 4793–4802.
- Henze, M., Gujer, W., Mino, T., van Loosdrecht, M. (2000) 'Activated Sludge Models ASM1, ASM2, ASM2d and ASM3', IWA Publishing, London, UK.
- Hiatt, W. C., Grady, C. P. L. (2008) 'An Updated Process Model for Carbon Oxidation, Nitrification, and Denitrification', *Water Environment Research*, 80 (11), pp. 2145-2156.
- IPCC (2013) 'Climate Change 2013: the physical science basis', Cambridge University Press, Cambridge, UK.
- Jubany, I., Lafuente, J., Baeza, J. A., Carrera, J. (2009) 'Total and stable washout of nitrite oxidizing bacteria from a nitrifying continuous activated sludge system using automatic control based on Oxygen Uptake Rate measurements', *Water Research*, 43 (11), pp. 2761-2772.
- Machado, V.C., Lafuente, J., Baeza, J.A. (2014) 'Activated sludge model 2d calibration with full-scale WWTP data: comparing model parameter identifiability with influent and operational uncertainty', *Bioprocess and Biosystems Engineering*, 37, pp. 1271-1287.
- Pocquet, M., Wu, Z., Queinnec, I., Sperandio, M. (2016) 'A two pathway model for N₂O emissions by ammonium oxidizing bacteria supported by the NO/N₂O variation', *Water Research*, 88, pp. 948-959.

Table 1. List of the 38 processes included in our ASM2d model for 4-step nitrification-denitrification combined with a 2-pathway model for N₂O production by AOB.

Hydrolysis processes	P1	Aerobic hydrolysis	Phosphorus-accumulating organisms (PAOs): XPAO	P20	Anoxic storage of XPP (2 nd step: NO ₂ ⁻)	
	P2	Anoxic hydrolysis (1 st step: NO ₃ ⁻)		P21	Aerobic growth of XPAO	
	P3	Anoxic hydrolysis (2 nd step: NO ₂ ⁻)		P22	Anoxic growth of XPAO (NO ₃ ⁻ →NO ₂ ⁻)	
	P4	Anaerobic hydrolysis		P23	Anoxic growth of XPAO: (NO ₂ ⁻ →NO)	
Heterotrophic organisms: XH	P5	Aerobic growth on SF		Nitrifying Organisms	P24	Anoxic growth of XPAO: (NO→N ₂ O)
	P6	Aerobic growth on SA			P25	Anoxic growth of XPAO: (N ₂ O→N ₂)
	P7	Denitrification on SF (NO ₃ ⁻ →NO ₂ ⁻)			P26	Lysis of XPAO
	P8	SF: Anoxic growth of heterotrophs (NO ₂ ⁻ →NO)			P27	Lysis of XPP
	P9	SF: Anoxic growth of heterotrophs (NO→N ₂ O)			P28	Lysis of XPHA
	P10	SF: Anoxic growth of heterotrophs (N ₂ O→N ₂)			P29	NH ₃ oxidation to NH ₂ OH with oxygen consumption
	P11	Denitrification on SA (NO ₃ ⁻ →NO ₂ ⁻)			P30	NH ₂ OH oxidation to NO coupled with oxygen reduction (XAOB growth here)
	P12	SA: Anoxic growth of heterotrophs (NO ₂ ⁻ →NO)			P31	NO oxidation to NO ₂ ⁻ coupled with oxygen reduction
	P13	SA: Anoxic growth of heterotrophs (NO→N ₂ O)			P32	NO reduction to N ₂ O coupled with the NH ₂ OH oxidation to NO ₂ ⁻
	P14	SA: Anoxic growth of heterotrophs (N ₂ O→N ₂)			P33	HNO ₂ reduction to N ₂ O coupled with NH ₂ OH oxidation to NO ₂ ⁻
Phosphorus-accumulating organisms (PAOs): XPAO	P15	Fermentation		P34	Aerobic growth of XNOB	
	P16	Lysis		P35	Lysis AOB	
	P17	Storage of XPHA	P36	Lysis NOB		
	P18	Aerobic storage of XPP	P37	Precipitation		
	P19	Anoxic storage of XPP (1 st step: NO ₃ ⁻)	Precipitation of P with Fe(OH)3	P38	Redissolution	

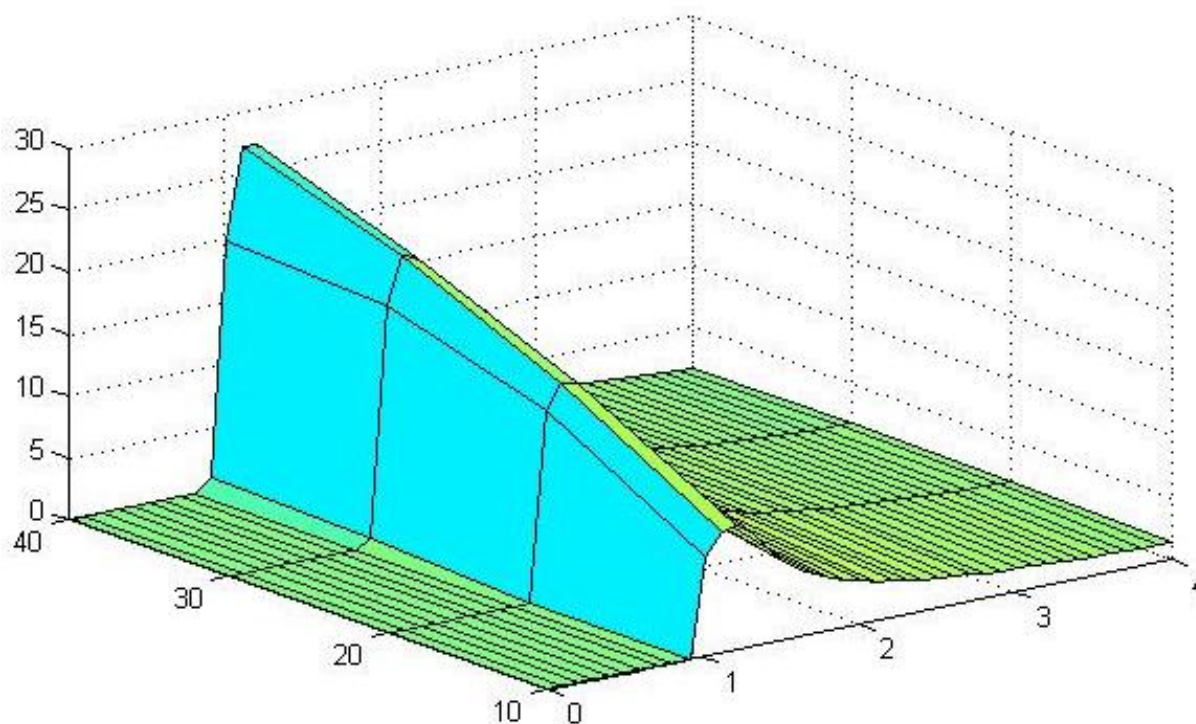


Figure 1. Combined effect of applying different DO and influent NH_4^+ concentration on the N_2O emission factor. Parameters for the growth and the decay of the AOB (Ammonia Oxidising Bacteria) and NOB (Nitrite Oxidising Bacteria) were taken from Hiatt and Grady (2008).