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Unwanted mainstream nitritation–denitritation causing massive N₂O emissions in a continuous activated sludge process

A. Kuokkanen, K. Blomberg, A. Mikola and M. Heinonen

ABSTRACT

Nitrous oxide emissions can contribute significantly to the carbon footprint of municipal wastewater treatment plants even though emissions from conventional nitrogen removal processes are assumed to be moderate. An increased risk for high emissions can occur in connection with process disturbances and nitrite (NO₂⁻) accumulation. This work describes the findings at a large municipal wastewater treatment plant where the levels of NO₂⁻ in the activated sludge process effluent were spontaneously and strongly increased on several activated sludge lines which was suspected to be due to shortcut nitrogen removal that stabilized for several months. The high NO₂⁻ levels were linked to a dramatic increase in nitrous oxide (N₂O) emissions. As much as over 20% of the daily influent nitrogen load was emitted as N₂O. These observations indicate that highly increased NO₂⁻ levels can occur in conventional activated sludge processes and result in high nitrous oxide emissions. They also raise questions concerning the risk of increased greenhouse gas (GHG) emissions of the nitritation–denitritation processes – although the uncontrolled nature of the event described here must be taken into consideration – and underline the importance of continuous monitoring and control of N₂O emissions.

Key words | activated sludge process, GHG, N₂O, nitritation–denitritation, nitrous oxide, NO₂⁻

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HIGHLIGHTS

- NO₂⁻ can play a significant role in N₂O emissions also in conventional activated sludge processes.
- Variations in NO₂⁻ levels can explain poorer than expected negative correlation between total nitrogen removal and N₂O.
- Nitritation-denitritation can stabilize for a long period also in conditions that do not typically promote it.
- Monitoring N₂O emissions is crucial in operating nitritation–denitritation processes.

INTRODUCTION

Nitrous oxide (N₂O), a gas formed in varying amounts in nitrogen transformations and wastewater treatment, strongly promotes global warming (IPCC 2013). N₂O emissions have been recognized as major contributors to the carbon footprint of municipal wastewater treatment

plants (WWTPs) in a study of 16 Scandinavian treatment plants (Gustafsson & Tumlin 2013). In a long-term study by Daelman *et al.* (2013), 75% of a treatment plant's carbon footprint was due to direct N₂O emissions. At the Viikinmäki WWTP, the measured direct N₂O emissions were calculated to contribute over 60% of the total carbon footprint (Mölsä 2019).

Shortcut nitrogen removal processes have been thoroughly investigated in recent years due to energy and

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chemical savings they offer. Highly varying N₂O emission factors have been observed in nitritation–denitritation processes (Vasilaki *et al.* 2019; Li *et al.* 2020). In addition to differences between processes, emissions can vary in single processes in different process conditions. In a study by Peng *et al.* (2017), the N₂O emission factors in a nitritation–denitritation process treating co-digested pig slurry centrate could be decreased from 17 to 0.12% by the choice of aeration and feeding strategies. Vasilaki *et al.* (2020) observed N₂O emissions varying from 1.3 to 19% of the influent NH₄-N load on a SCENA-process which combines nitritation–denitritation and biological phosphorus removal.

Currently, altogether three pathways have been identified as contributing to N₂O production in a wastewater environment. Two pathways for N₂O production in nitrification – the hydroxylamine pathway and the nitrifier denitrification pathway – have been recognized and either one or both can be used to model processes, depending on the process conditions, such as NO₂⁻ and DO (Peng *et al.* 2015). In heterotrophic denitrification N₂O is an intermediate and can therefore be consumed or accumulated. Elevated N₂O emissions are typically linked to various different factors such as low dissolved oxygen (DO), high nitrite (NO₂⁻) or nitrous acid concentration, varying NH₄⁺ concentrations, low chemical oxygen demand (COD) alternating anoxic and aerobic conditions and abrupt changes (Vasilaki *et al.* 2019) as different operational conditions promote different pathways.

Earlier studies at the Viikinmäki WWTP have shown large variations of N₂O emissions (Kosonen *et al.* 2016). Some level of correlation of emissions with total nitrogen removal in AS has been observed but the earlier, lower peak values have remained unexplained (Blomberg *et al.* 2017). Based on a study of the denitrifying filters at the Viikinmäki WWTP (Heinonen *et al.* 2014), the activated sludge (AS) process was identified as the main source of N₂O emissions, and a modelling study of the N₂O emissions produced in the AS (Blomberg *et al.* 2018) supported these observations. While NO₂⁻ is recognized as an important factor in N₂O emissions at WWTP's (Kampschreur *et al.* 2009), the NO₂-N concentrations are normally assumed to be negligible in continuous municipal AS processes, where the temperature range, sludge retention time (SRT), loading rate and oxygen levels promote full nitrification. Peng & Zhu (2006) reviewed various control technologies in promoting nitritation–denitritation and suggest controlling pH and DO, as many of the other possible control measures require sequencing operation, high temperature (>25 °C) or high ammonia load, none of which occur at the Viikinmäki WWTP during normal operation.

This article presents long-term monitoring data of comprehensive N₂O emissions at a municipal WWTP and describes two spontaneous and prolonged periods of nitritation–denitritation in a process that normally performs full nitrification and denitrification.

The role of NO₂⁻ in N₂O emissions and the causes of initialization and stabilization of nitritation–denitritation are evaluated. Even though more questions than answers are presented concerning the original causes triggering the nitritation–denitritation, the authors advocate that the observed phenomena, based on long-term and comprehensive full-scale WWTP data, are a valuable addition to studies on understanding and mitigating the N₂O emissions in wastewater treatment.

MATERIALS AND METHODS

WWTP characteristics

All data presented are from on-line measurements and laboratory analyses at the Viikinmäki municipal WWTP in Helsinki, Finland, which has a population equivalent (PE) of over one million. The treatment plant is situated underground with all exhaust air from the wastewater treatment process passing through one exhaust air pipe enabling the measurement of total N₂O emissions.

Viikinmäki WWTP is a conventional AS plant with a mechanical pre-treatment, seven primary settling lines and nine AS lines (lines 1–9) and ten post-denitrifying filters. The AS lines are pre-denitrifying, comprising anoxic and aerobic zones and nitrate recirculation (100–300% of influent flow). Phosphorus removal is based on chemical precipitation with ferrous sulfate. Calcium hydroxide is used for pH control in AS and methanol is used as a carbon source in the post-denitrifying filters.

Each 11,500 m³ AS line is divided into six equally sized zones. The aerated volume of each line is controlled automatically to optimize ammonia and total nitrogen removal. The first zone is anoxic, zones 2 and 3 can be mixed or aerated, controlled by on-line ammonia measurement in zone 6, and zones 4–6 are aerated. The oxygen set-points can be constant or controlled by ammonia measurement in zone 6. Each AS line has a separate return sludge recirculation (approximately 70% of influent flow), but excess sludge is pumped to the beginning of the process and removed in the primary settling and there can thus be some exchange of bacteria between the AS lines.

The treatment plant has mesophilic digestion of sludge. 15–20% of reject waters from sludge centrifuges, equivalent to 300 kg NH₄⁺-N/d, are treated in a pilot deammonification moving bed biofilm (MBBR) process (ANITAMox™). The treated reject water is normally led to primary settling line 1, where the wastewater flows mainly to AS line 1 and partly to AS line 2. The untreated reject water is distributed equally to all treatment lines.

Viikinmäki WWTP has an environmental permit that states the requirements for effluent quality for total phosphorus, total nitrogen, biological and chemical oxygen demand (BOD and COD) and suspended solids (Table 1). There are no limit values for greenhouse gas emissions, but the yearly total emissions are reported.

In 2019 the average influent flow was 290,000 m³ per day. The wastewater temperature varied mainly from 10 to 20 °C. The influent loads, environmental permit limit values for effluent concentrations and removal rates and the treatment results in 2019 are presented in Table 1. The total nitrogen removal after AS was 69% as a yearly average.

On-line measurements, sampling and analysis

The data presented are based on measurements in the AS process and of the total exhaust air of the whole treatment plant. Parameters are mainly measured from all individual AS lines. However, liquid phase N₂O is measured only on AS lines 5 and 9 and until April 2019 NO₂⁻-N data are available only from AS lines 1 and 2. The data presented in Figures 3, 5 and 6 are based on these limitations.

The AS process is monitored with both on-line measurements (Table 2) and laboratory analyses.

The total N₂O emissions of the wastewater treatment process together with CO₂, NO, NO₂, NH₃ and CH₄ have been measured since 2012 using the Gaset CEMS Fourier

transform infrared (FT-IR) system at the only exhaust air pipe where all the air from the underground treatment plant is collected. The measurements represent the total emissions of the process excluding only possible leakages in the above-ground biogas treatment. At the end of January 2017, after mass balance calculations of carbon dioxide production and smoke tests, the sampling point was moved upwards in the exhaust air pipe for a more representative sample.

All the above gas phase and liquid phase on-line measurements, together with wastewater temperature, flows and air flows etc. are recorded in the process control system (Valmet DNA).

Laboratory analyses are carried out twice a week from flow-weighted 24-hour samples collected automatically (Endress + Hauser Liquistation CSF33). Sludge concentrations are analyzed from grab samples. AS effluent NH₄⁺-N, the sum of NO₂⁻-N and NO₃⁻-N (NO_x-N), NO₂⁻-N and alkalinity are measured from individual lines. The laboratory analyses are performed by a certified laboratory (Metropolilab) according to the following standards (NH₄-N ISO 7150:1984, N-tot SFS-EN ISO 11905-1 (C2), NO_x-N SFS-EN ISO 13395/DA, NO₂⁻-N SFS 3029 DA, BOD_{7ATU} SFS-EN ISO1899-1, COD_{Cr} ISO 15705:2002 and alkalinity SFS-EN ISO 9963-1:1996 mod.). Analyzing NO₂⁻-N in AS effluent was started in October 2016 in AS lines 1 and 2 on 25 April 2019 in all treatment lines.

RESULTS AND DISCUSSION

Variations of N₂O emissions and correlation with NO₂⁻

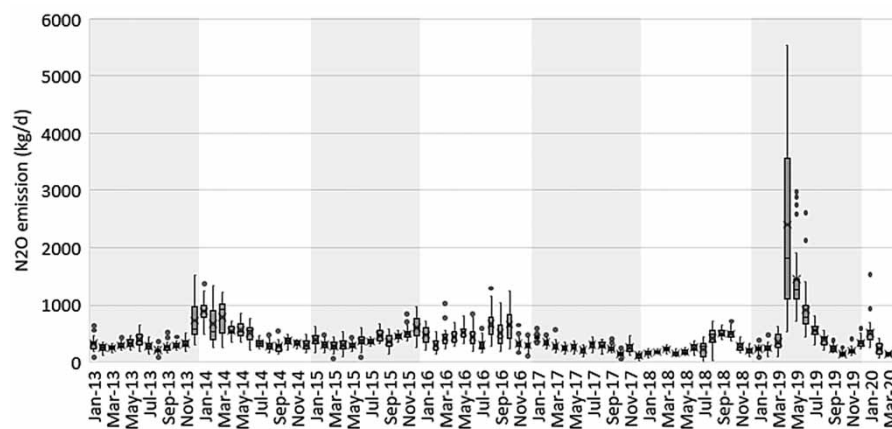
Figure 1 presents the monthly variations in total N₂O emissions (kg/d), calculated from FT-IR measurements from the

Table 1 | Viikinmäki WWTP influent loads, environmental permit limit values and yearly average treatment results in 2019

	Influent concentrations and loads	Environmental permit values	Treatment results
BOD _{7ATU}	250 mg/L	≤10 mg/L	6.2 mg/L
	71,300 kg/d	≥95%	97%
COD _{Cr}	540 mg/L	≤75 mg/L	43 mg/L
	156,000 kg/d	≥85%	92%
Total phosphorus	6.0 mg/L	≤0.30 mg/L	0.19 mg/L
	1,740 kg/d	≥95%	97%
Total nitrogen	49 mg/L	–	4.9 mg/L
	14,200 kg/d	≥80%	90%
Suspended solids	310 mg/L	–	5.7 mg/L
	89,300 kg/d	–	98%

Table 2 | On-line measurements in AS

Position	Measurement		
Last aerated zone, each treatment line	NH ₄ -N	0.1–20 mg (N)/L	Metrohm ADI 2045TI
	Alkalinity	0.08–3 mmol/L	Metrohm ADI 2045TI
	NO _x -N ^a	0.1–100 mg/L	Hach Lange Nitratax plus sc
Mixed AS effluent	Total P	0.01–1 mg (P)/L	Hach Lange Phosphatax sigma
All aerated zones	DO	0–10 mg/L	Hach Lange LCO
Varying zones, lines 5 and 9	Liquid phase N ₂ O ^b	0.01–500 µM	Unisense Wastewater System

^aSum of NO₃-N and NO₂-N.^bTwo probes per line, AS line 9 since April 2016 and AS line 5 since November 2018.**Figure 1** | The monthly variations of the daily average N₂O emissions (kg/d) at the Viikinmäki WWTP since January 2013 as a boxplot. Average values are marked with an X. Horizontal lines indicate the median values, and dots indicate the outliers (values exceeding the interquartile range with more than 50%).

exhaust air starting from the year 2013. The exhaust air flow rate has been measured starting from August 2017, with values varying mainly between 100 and 130 m³/s. An estimated constant air flow of 120 m³/s was used in emission calculations for February 2017 to August 2017 and a 17% reduction of the air flow was used before February 2017, to compensate for the estimated error caused by the placement of the N₂O analyzer sampling point. The data presented in Figure 1 represent an overview of the long-term monitoring. Even though data before and after February 2017 are not completely comparable, the possible error is insignificant in comparison of the magnitude of the peak emissions in 2019.

In April 2019 the N₂O emissions at Viikinmäki WWTP exceeded many times all previous values since the beginning of monitoring (Figure 1). Also, exceptionally high NO₂⁻-N concentrations were observed in several treatment lines, up to 80% of NO_x-N (Figures 2–4). Typical NO₂⁻-N levels since the beginning of measurements in 2016 have been at highest 11% and mainly below 5% of NO_x-N, with concentrations mostly below 1 mg/L (Figure 2(a), 2(c) and 2(d)).

The highest daily average N₂O emissions observed during the peak emission period were 5,540 kg N₂O/d (3,520 kg N₂O-N/d), 20 times higher than the yearly average emissions of 2018. The total yearly emissions, which were 93.6 tn N₂O in 2018 were more than doubled to 227 tn in 2019. Also, nitrogen monoxide (NO), normally under detection limit, could be observed in the exhaust air in April and May 2019, with the highest daily average emission value of 16 kg NO/d.

A comparison of N₂O emissions (kg/d) with NO₂⁻-N, NO_x-N (mg/L) and NO₂⁻-N/NO_x-N (%) in AS effluent is presented in Figure 2.

The NO₂-N values before April 2019 are the average of AS lines 1 and 2. They are considered to be representative for the whole AS process until the beginning of the abnormally high N₂O emissions, based on essentially similar nitrification results between treatment lines. In April 2019, the values from only two treatment lines are deemed to be unrepresentative for the whole AS process (second marked period in Figure 2(a)). In July 2018 there was a two-week period of very poor nitrification due to an unknown

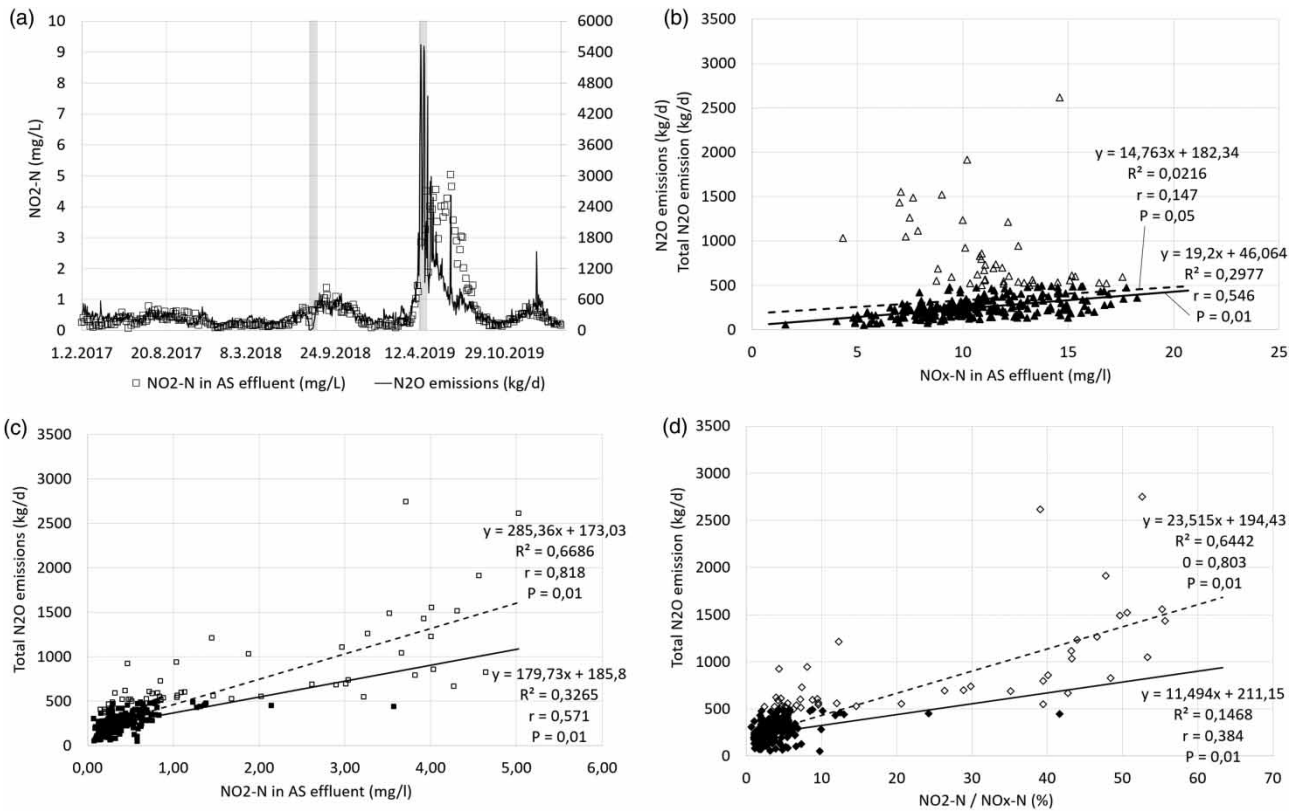


Figure 2 | N₂O emissions from February 2017 to March 2020 and (a) NO₂⁻-N concentrations in AS effluent as a function of time, (b) N₂O emissions vs. AS effluent NO₂⁻-N, (c) N₂O emissions vs. AS effluent NO_x-N and (d) N₂O emissions vs. NO₂⁻-N/NO_x-N (%) in AS effluent. The correlations are presented separately with all N₂O emission values included (all data points and dashed lines, N = 298) and with emissions below 500 kg N₂O/d (filled points only and solid lines, N = 252). Unrepresentative periods, which are not included in data used in parts (b), (c) and (d), are marked with grey background in part (a).

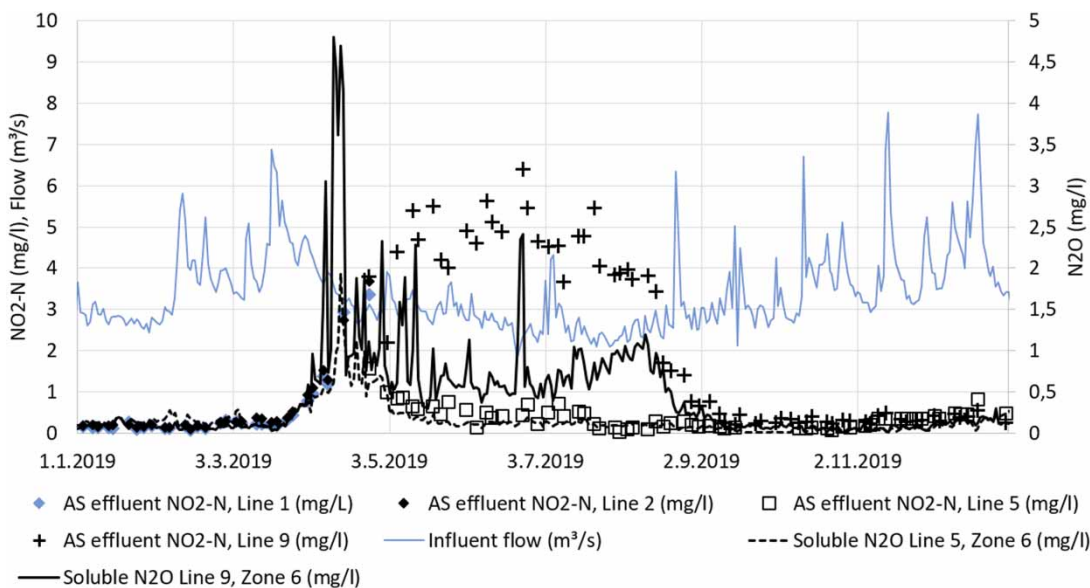


Figure 3 | Plant influent flow, NO₂⁻-N concentration in AS effluent in treatment lines 1, 2, 5, and 9 and soluble N₂O in the last aerated zones in lines 5 and 9.

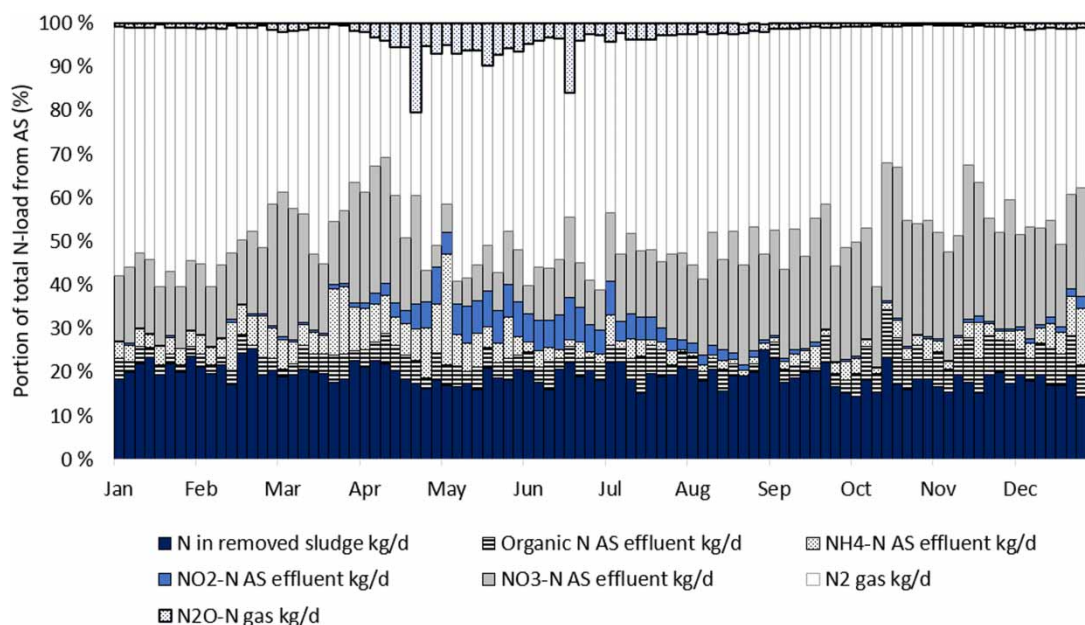


Figure 4 | The measured and calculated fractions of nitrogen in AS, the average of all treatment lines and total exhaust air, during laboratory sampling days in 2019 ($N = 96$).

inhibitory substance and the NO_x-N concentrations were exceptionally low (first marked period in Figure 2(a)).

The NO_x-N concentration in AS effluent correlates well with N₂O emissions (Figure 2(b)) with the abnormal emission values (over 500 kg/d) removed. With all emission values included, the correlation becomes poorer and the values are clearly dispersed. NO₂-N, however, correlated well with and without the over 500 kg/d emissions values (Figure 2(c)). The ratio NO₂-N/NO_x-N (Figure 2(d)) had a somewhat poorer correlation with emissions under 500 kg/d than NO_x-N or NO₂-N concentrations, but when the peak emission values were included, the correlation was strongly increased. The low NO_x-N and NO₂-N concentrations in AS effluent represent mainly high total nitrogen removal, although in some cases, they can also be partly due to lowered ammonia removal together with a dilution of wastewater in peak flow situations.

The liquid phase N₂O concentrations in the last aerated zones and the NO₂⁻-N concentrations in the effluents of AS lines 5 and 9, which are the only AS lines equipped with N₂O probes, and the treatment plant influent flow are presented in Figure 3. The NO₂⁻-N concentrations from AS line 2 until 25 April 2019 are included as there are no NO₂⁻-N data available from lines 5 and 9 before that date.

The AS lines 5 and 9 are both equipped with two N₂O probes, and a clear difference in their liquid phase N₂O could be seen from April to August 2019 (Figure 3).

It can be seen in Figure 3 that after the peak flows both the NO₂⁻-N concentrations in lines 1 and 2 and the liquid phase N₂O concentrations in lines 5 and 9 were increasing. It can be assumed that the NO₂⁻-N concentrations were rising in a similar way in all treatment lines, which is supported by the high NO₂⁻-N values observed after the NO₂⁻-N monitoring was expanded.

After the initially similar rise of N₂O concentrations in treatment lines 5 and 9, high peaks and a deterioration of ammonia removal (Figure 5(a) and 5(b)) could be observed only in line 9. After mid-May the peaks were diminished but the N₂O base level concentration increased in line 9, possibly indicating a shift in the bacterial composition or behavior, before decreasing rapidly in August, together with the NO₂⁻-N concentrations (Figure 3).

Most N₂O emission and concentration peaks could be linked with a higher aerated volume, but the peak in 24.6. (Figures 2(a) and 3) could not. The influent load was lower than usual due to holidays and a low COD/N ratio was suspected to be the cause.

The different fractions of nitrogen in AS effluent and exhaust air during sampling days in 2019 are presented in Figure 4. The organic N in AS effluent represents the difference between the measured values of total nitrogen and NO_x-N and ammonia nitrogen. N₂O in AS effluent is included in the organic N, as there are liquid phase N₂O data only from two AS lines. The amount of nitrogen

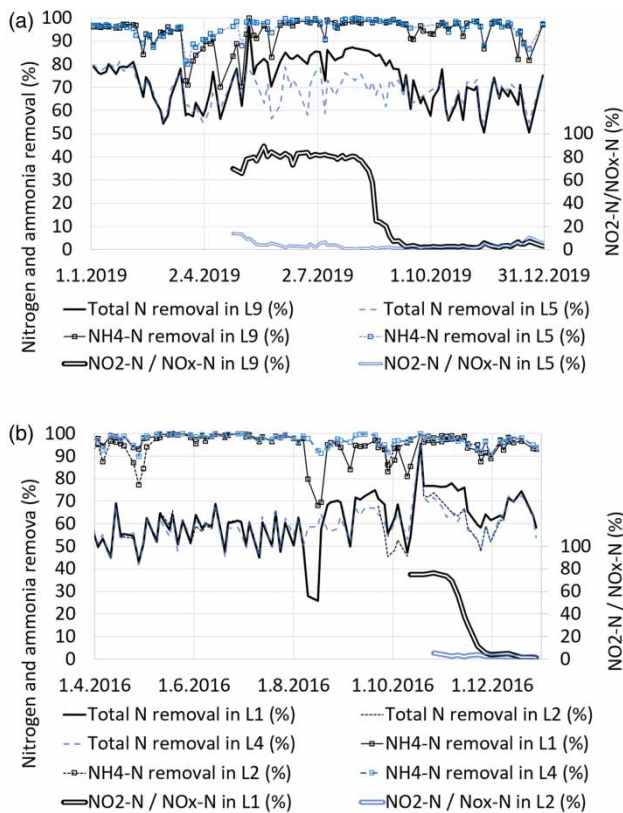


Figure 5 | The portion of NO₂⁻-N in AS effluent and ammonia and total nitrogen removal (a) on AS lines 5 and 9 in 2019 (data available from 25.4.2019) and (b) on lines 1, 2 and 4 in 2016. (N₂O data available from 12.10.2016 on line 1 and 26.10.2016 on line 2.) Line 2 was emptied for maintenance from mid-July to mid-September.

removed in sludge is calculated based on excess sludge removal and the nitrogen concentration of sludge (which is not measured regularly). N₂O gas measured from the exhaust air pipe is assumed to originate from AS, based on earlier research at Viikinmäki WWTP (Heinonen *et al.* 2014; Blomberg *et al.* 2018). Nitrogen gas (N₂) was calculated by subtracting all other nitrogen fractions from the AS influent load. Other gaseous forms of nitrogen (NO, NO₂, NH₃), which may be present in small quantities, are included here in N₂.

The observed total nitrogen removal in AS during the period of increased NO₂⁻ concentrations was high, which is in accordance with a lower consumption of organic carbon in nitrification–denitrification. However, particularly during the highest peak emissions, a considerable portion of the observed nitrogen removal was due to the stripping of N₂O (Figure 4). The highest daily N₂O emission on a sampling day was 4,570 kg N₂O (2,910 kg N₂O-N) on 15 April 2019, equivalent to 20% of the day's AS influent load of 14,100 kg N. The all-time highest daily emission of

5,540 kg N₂O (3,520 kg N₂O-N) took place on the previous day, which was not a sampling day and thus not included in Figure 4.

Two suspected periods of stable shortcut nitrogen removal

Two periods with prolonged nitrite accumulation have been observed at the Viikinmäki WWTP in recent years, suspected to indicate nitrification–denitrification in AS. In 2019 nitrite accumulation was observed on seven out of nine AS lines. At treatment line 9, which was the first one to exhibit elevated concentrations of liquid phase N₂O and the last one to normalize, the suspected nitrification–denitrification with high ammonia removal lasted as long as over three months. A corresponding period of nitrite accumulation was observed also earlier, on only one treatment line in 2016 (Figure 5(a) and 5(b)).

In April 2019 the ammonia removal rate in AS was initially decreased, in all AS lines except 4 and 5, but ammonia removal recovered to mainly well over 95% while up to 80% of the NO_x-N was in the form of NO₂⁻-N (AS line 9 results are shown in Figure 5(a)). Faster recovery of ammonia oxidizing bacteria (AOB) compared to nitrite-oxidizing bacteria (NOB) was also observed by Chen *et al.* (2019), who used heat shocks to initialize nitrification–denitrification in an SBR-process, with both AOB and NOB initially suppressed but AOB recovering faster resulting in NO₂⁻ accumulation.

According to Zhou *et al.* (2011) nitrite accumulation can also be due to inhibition or unbalance of denitrification and a pH- and temperature dependent portion of NO₂⁻ is in the form free nitrous acid (FNA), which can have an inhibitory effect on several microbial processes in concentrations as low as app. 0.02 mg N/L. The initial decrease in ammonia removal as well as the observed high total nitrogen removal rate compared to treatment lines 4 and 5 (Figures 3 and 5) indicate that the process was exhibiting shortcut nitrogen removal. Also, if NO₂⁻ was accumulated in denitrification and not due to NOB inhibition, it should mainly be transformed into NO₃⁻ during aeration and not be seen in the samples.

The NO₂-N levels were high in all treatment lines except 4 and 5, when analyses began. An increase in effluent ammonia could also be observed in all other AS lines except 4 and 5, from 2 to 10 days after line 9 (data not included). When the regular laboratory analyses of NO₂⁻-N from all AS lines were started on 25 April 2019, ratios of NO₂⁻-N to NO_x-N on individual AS lines varying between 58 and 70% were observed with NO₂⁻-N concentrations

mainly 4–6 mg/L. In treatment lines 4 and 5 only a modest and short-term increase of NO₂⁻-N with a maximum NO₂⁻-N to NO_x-N ratio of 13% in both AS lines, as well as an increase in aqueous N₂O in line 5 could be observed, and ammonia removal remained high.

A change in the sludge composition could be observed in all the treatment lines exhibiting nitrification–denitrification, observed as increased turbidity and effluent total phosphorus (Figure 6(a)) and decreased filament and sludge volume indexes (data not included). High turbidity could also be visually observed on line 1 in 2016.

Sludge transfer from lines 4 and 5 to others was started during summer to promote NO₂⁻ removal. In line 9, however, the NO₂⁻-N concentrations began decreasing in late August, just before it was due for sludge transfer, and it was left to recover on its own.

In August 2016 the nitrification rate dropped suddenly in treatment line 1 (Figure 5(b)). NO₂⁻-N analyses from AS effluent in lines 1 and 2 were started in October 2016. It was discovered that in AS line 1 effluent, roughly 75% of NO_x-N was NO₂⁻-N while this was only 5% in line 2 (Figure 5(b)).

The process behavior normalized roughly a month after the start of NO₂⁻-N measurements. When comparing ammonia and total nitrogen removal between treatment lines in 2016 and 2019 (Figure 5) it appears likely that the nitrite accumulation on line 1 in 2016 had begun in August and thus lasted in total almost three months.

There are not enough data to evaluate the effect of NO₂⁻ accumulation on N₂O emissions in 2016 as there are no liquid phase N₂O measurements in line 1. The peak values of total N₂O emissions were considerably lower than in 2019, when seven out of nine AS lines were affected, and there had been peak values also earlier that year (Figure 1). The highest daily N₂O emissions in 2016, however, occurred during NO₂⁻ accumulation in line 1.

Evaluating the impact of process conditions on NO₂⁻ accumulation

The process conditions, such as influent flow, temperature and pH in the AS process during the initiation of the nitrification–denitrification period had no apparent similarities in

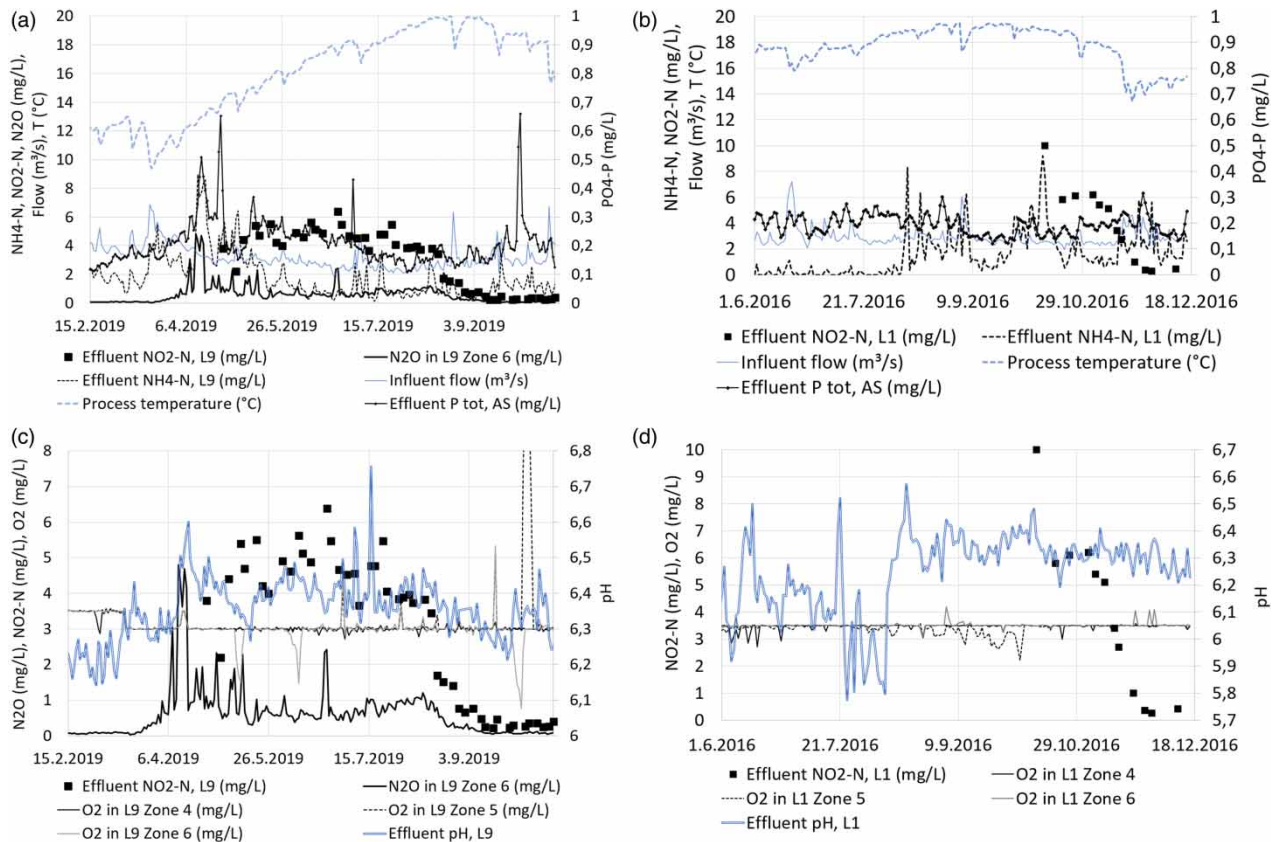


Figure 6 | Liquid phase N₂O in 2019 and NO₂⁻-N in 2019 and 2016 together with different process parameters. All values other than NO₂⁻-N are on-line measurements.

2016 and 2019 (Figure 6). In general, the process conditions at the Viikinmäki WWTP should promote full nitrification.

As FNA is known to have an inhibitory effect on NOB (Zhou *et al.* 2011), it can be speculated if once over a critical level, the accumulated NO₂⁻ and FNA sustained the nitrification–denitrification process via NOB inhibition when NO₂-N was mainly 4–6 mg/L and pH below 6.5. However, the reasons for the initial triggering of the critical accumulation on some but not all treatment lines are not clear. The process conditions are scrutinized in more detail in the following chapters.

Aerated volume and the possible inhibition of AOB and NOB

In normal process conditions, the aerated volume of each AS line – 50%, 67% or 83% of the total volume, equivalent to 3, 4 or 5 aerated zones – is controlled by automation based on the on-line ammonia measurement. The daily average air flows in aeration vary mainly between 6 and 13 nm³/s according to variations in load and nitrification result, with the highest air flows associated mainly to high aerated volume, peak flows and cold influent, and the lowest values to late summer and early autumn with warmer wastewater and high nitrification efficiency. After the high NO₂-N concentrations were observed in 2019, it was noted that ammonia removal was not improved when the aerated volume was increased from 67 to 83% and the N₂O emissions increased significantly (data not included). The maximum aerated volume was manually limited to 67%, to both decrease NO₂-N concentrations in hope to mitigate inhibition by increasing the consumption of NO₂⁻ in the unaerated zones, and to reduce stripping of N₂O. A stricter limitation on the aerated volume to 50% of total volume was also tested on some treatment lines but it resulted in an increase in effluent ammonia. The total sludge age was increased to prevent a decrease in the aerobic sludge age.

Before the sharp increase in N₂O emissions and NO₂-N concentrations in 2019, the measured NO₂-N concentrations were already somewhat elevated, most likely in all treatment lines (Figures 2(a) and 3). When the effluent ammonia of an AS line is increased, the following automated increment of the aerated volume both increases the NO_x concentrations and decreases pH. It can be speculated that when combined with the automated control, initially moderate differences in the nitrification efficiencies and concentrations between AS lines, may have been enough to result in an ultimately completely different process performance.

Dissolved oxygen

Low DO has a role in both promoting nitrification–denitrification – where a range of 1.0–1.5 mg/L has been suggested (Peng & Zhu 2006) – and in N₂O production (Kampschreur *et al.* 2009; Vasilaki *et al.* 2019). Peng *et al.* (2017) observed that in a nitrification–denitrification process, N₂O emissions were linearly dependent on NO₂-N concentrations when DO was <1.5 mg/L but not when DO was >1.5 mg/L.

The measured oxygen concentrations in the constantly aerated zones 4–6 of AS line 9 in 2019 and AS line 1 in 2016 were mainly well over 2.5 mg/L (Figure 6(c) and 6(d)). Temporary low oxygen concentrations can occur at the beginning and end of aerated periods in zones 2 and 3 and also occasionally during peak loads. However, as separate aerated periods in zones 2 and 3 occur mainly one to three times per day and they last for several hours, frequent or long-term DO values below 1.5 mg/L would require a DO measurement error, which is unlikely to happen in several treatment lines simultaneously. Thus, low DO does not appear to be an explanatory factor for either triggering or sustaining the nitrification–denitrification.

Alkalinity and pH

Both low and high pH and the presence of FNA in low pH values and of free ammonia (FA) in high pH values have been linked to NO₂⁻ accumulation in different studies according to Philips *et al.* (2002).

The pH values in the last aerated zones of the AS process vary normally mainly between 6.0 and 6.3 and the daily average alkalinity values are normally above 1 mmol/L. In acidic conditions the portion of FNA is higher and thus the inhibitory effect of NO₂⁻ accumulation is more pronounced (Zhou *et al.* 2011).

In 2016, the pH values temporarily dropped below 6.0 (Figure 6(d)) and the daily average alkalinity to 0.6 mmol/l due to an on-line measurement error which had led to insufficient dosage of calcium hydroxide, and there was a clear temporal connection between the decreased pH and alkalinity and the deterioration of nitrification in treatment line 1.

In 2019, such a connection with decreased pH or alkalinity before the rise in NO₂-N and N₂O levels could not be made (Figure 6(c)).

Impact of side-stream deammonification effluent

The maximum direct impact of the side-stream deammonification process on the N₂O emissions is limited, due to its

size, but a possible connection with the NO₂⁻ accumulation in 2016 has been suspected. During the 2016 NO₂⁻-N accumulation in treatment line 1, the only distinct difference observed between line 1 and other lines was that most of the deammonification process effluent was led via primary settling mainly to AS line 1. At the time, the pilot was in the start-up stage and treating roughly half of its design load. Primary settling should, however, decrease considerably the transfer of bacteria to AS. In 2019 AS line 1 was neither the first nor the last to switch to nitrification–denitrification.

CONCLUSIONS

Two separate incidents of prolonged NO₂⁻ accumulation and suspected nitrification–denitrification were observed in part of the AS lines at the Viikinmäki WWTP, while other lines kept on performing full nitrification in seemingly similar process conditions. At least one of the incidents could be linked with a significant increase in N₂O emissions. Long-term data show a correlation between NO₂⁻-N and N₂O emissions also in normal process conditions but particularly during peak emissions.

It was observed that once initiated, NO₂⁻ accumulation was able to stabilize for a long period in process conditions that normally promoted full nitrification, and it was suspected to be due to NOB inhibition by NO₂⁻ or FNA.

The N₂O emissions observed at the Viikinmäki WWTP indicate a risk of considerable emissions in nitrification–denitrification processes, if they are not properly controlled, which can outweigh the positive environmental impacts of energy and chemical savings. Implementing shortcut nitrogen removal processes should include monitoring the N₂O emissions to avoid adverse environmental impacts.

In addition to measuring gas and liquid phase N₂O, NO₂⁻-N analyses can be used as an indicator of the long-term variations in N₂O emissions. NO₂⁻-N analyses can also reveal abnormal process conditions and provide new insight into the mechanisms of deterioration of nitrification and sludge composition.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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