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Nitrous Oxide Production at a Fully Covered Wastewater Treatment Plant: Results of a Long-Term Online Monitoring Campaign

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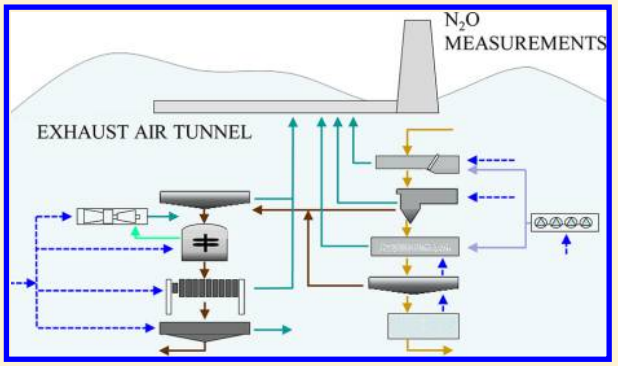
Supporting Information

ABSTRACT: The nitrous oxide emissions of the Viikinmäki wastewater treatment plant were measured in a 12 month online monitoring campaign. The measurements, which were conducted with a continuous gas analyzer, covered all of the unit operations of the advanced wastewater-treatment process. The relation between the nitrous oxide emissions and certain process parameters, such as the wastewater temperature, influent biological oxygen demand, and ammonium nitrogen load, was investigated by applying online data obtained from the process-control system at 1 min intervals. Although seasonal variations in the measured nitrous oxide emissions were remarkable, the measurement data indicated no clear relationship between these emissions and seasonal changes in the wastewater temperature. The diurnal variations of the nitrous oxide emissions did, however, strongly correlate with the alternation of the influent biological oxygen demand and ammonium nitrogen load to the aerated zones of the activated sludge process. Overall, the annual nitrous oxide emissions of 168 g/PE/year and the emission factor of 1.9% of the influent nitrogen load are in the high range of values reported in the literature but in very good agreement with the results of other long-term online monitoring campaigns implemented at full-scale wastewater-treatment plants.



INTRODUCTION

Municipal wastewater treatment plants (WWTPs) are known to be potential sources of greenhouse gas emissions.[1−6] The strongest greenhouse gas (GHG) that is emitted during the wastewater treatment process is nitrous oxide, a stable oxide of nitrogen with the formula N_2O. Because N_2O has an important catalytic role in the destruction of the stratospheric ozone layer and a 100 year global-warming impact that is 298 times as strong as that of carbon dioxide (CO_2), identifying and understanding the factors that trigger N_2O production in wastewater-treatment processes is crucial for mitigating the most severe impacts of climate change.

Nitrous oxide is produced as intermediate-, end-, and side-products of natural and human-induced catabolic nitrogen-conversion processes.[7] In wastewater-treatment processes, N_2O is mainly produced in aerated compartments of the biological treatment process. However, several studies have also observed significant N_2O emissions in the anoxic stage of the activated-sludge process and in secondary clarification after biological treatment.[8−11] In all process stages, the production of nitrous oxide is strongly affected by process operation and conditions. For instance, N_2O production has been observed to increase in the aerobic zones of the activated-sludge process immediately after a preceding anoxic phase.[10,12,13] Thus, biological treatment processes that have intermittent aeration or zones that switch between aerobic and anoxic conditions are likely to have higher N_2O emissions than processes that do not allow for zone switching or that apply simultaneous denitrification and nitrification. On the contrary, N_2O emissions have been observed to be low at wastewater treatment plants that apply influent flow balancing, have a high sludge-recycling rate, a high sludge age, and a large bioreactor volume.[14] Other conditions that have been observed to impact N_2O production increasingly are suboptimal concentrations of dissolved oxygen in nitrifying activated-sludge processes,[13,15−18] carbon-limiting conditions and low C-to-N rations,[19,20] suboptimal pH levels,[21−23] and elevated nitrite and ammonium concentrations.[9,18] More recently, studies have also observed that inorganic carbon,

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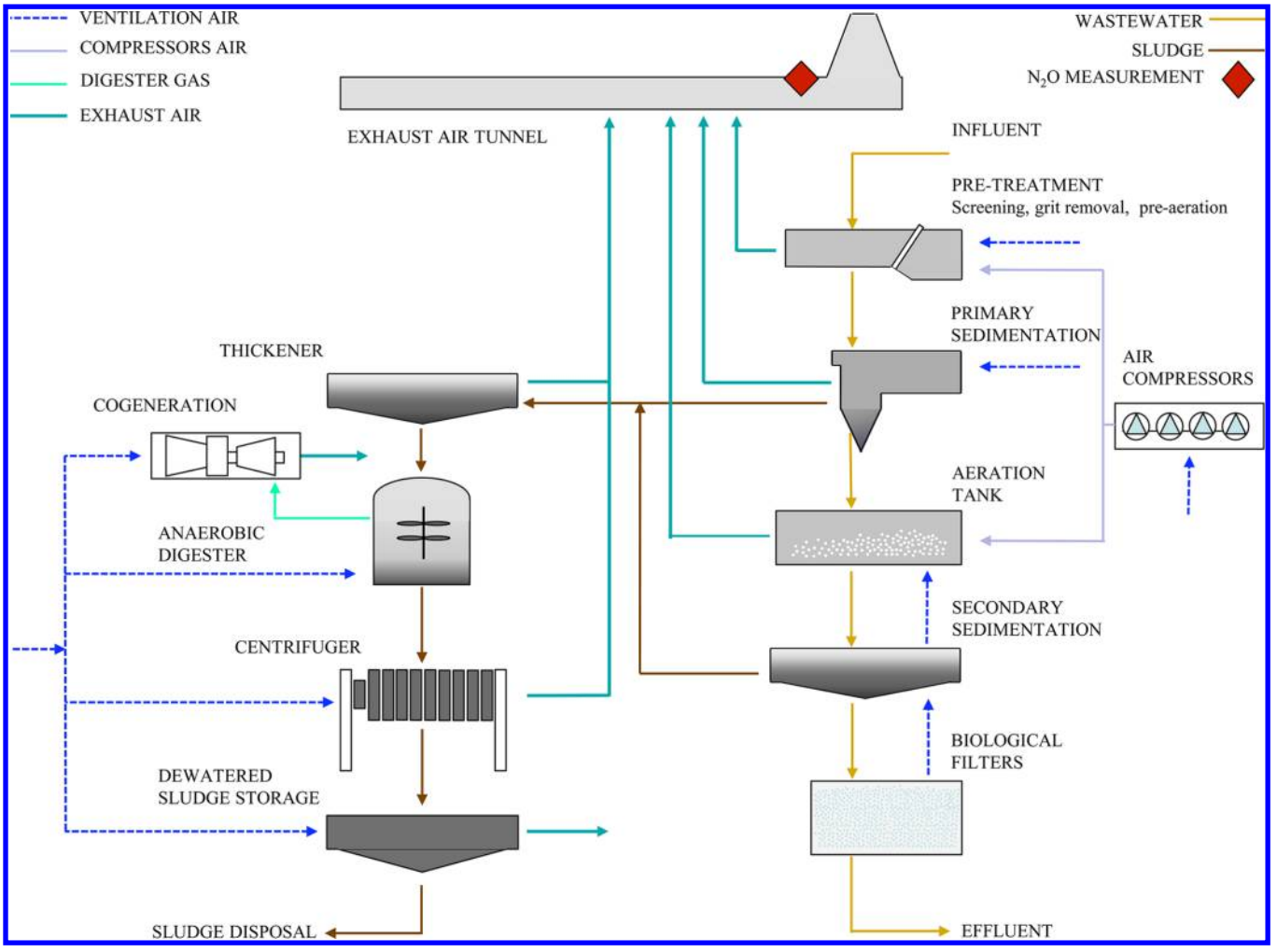

Figure 1. Wastewater-treatment-process diagram of the Viikinmäki WWTP.

when limiting or in excess, increases N_2O production by ammonium oxidizing bacteria.[24−26]

The current method for calculating N_2O emissions from wastewater treatment plants is based on single emission factors that were determined in the early studies on wastewater-related nitrous oxide production.[2,27] According to these studies, treatment processes that do not have biological nitrogen removal generate 3.2 g of N_2O per PE per year,[2] and processes with biological nitrogen removal generate 7.0 g of N_2O per PE per year.[27] However, more recent research on full-scale wastewater treatment plants has revealed a high variability in the measured N_2O emission rates[9,28−30] and, consequently, the use of universal constant emission factors has been questioned.[5,12] Although variability in measured N_2O emissions is most likely to stem from the above-discussed differences in process conditions, the wide range of measured emissions may also be partially explained by the diversity of the applied measurement methods; despite the existence of an EPA endorsed protocol for determining N_2O fluxes from biological wastewater-treatment plants,[31] the measurement procedures of full-scale studies have thus far differed with respect to the length of the measurement campaign and to the sampling approach including discrete or continuous sampling and off-gas or liquid-phase measurement.[9,32] In addition, full-scale measurements have traditionally focused solely on the biological phase of the treatment process even though extensive nitrous oxide production has also been observed in secondary clarification and other stages of the wastewater-treatment process.[5,11] Given these findings and the fact that recent studies have repeatedly proposed that the dynamics of N_2O production in the WWTPs can only be captured through long-term measurements,[10,32] the most reliable insights on diurnal variations and the total volume of N_2O production are most likely achieved with online measurements that cover all unit operations of the wastewater treatment process.

The objective of this study is to make a comprehensive inventory of the total annual nitrous oxide emissions at a full-scale WWTP in Helsinki, Finland and to identify the process parameters that affect nitrous oxide production during wastewater treatment. Previously, the nitrous oxide emissions of a full-scale wastewater treatment process have been measured in the Kralingseveer WWTP in The Netherlands in 2011−2012, but these measurements did not cover secondary sedimentation or the tertiary treatment of wastewater.[29] The present study is the first long-term online monitoring campaign ever implemented at a full-scale wastewater-treatment plant that comprises all of the unit processes of the wastewater-treatment process.

MATERIALS AND METHODS

Field Site Description. The Viikinmäki WWTP, which treats the wastewater of approximately 840 000 inhabitants in

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the Helsinki metropolitan area, is the largest treatment plant in Finland and the Nordic countries. In 2012, it had an average influent flow of 310 000 m^3 d^{-1}, of which approximately 15% had an industrial origin and the remaining 85% consisted of domestic wastewater. The plant is a fully covered underground wastewater treatment plant, and it is situated amid residential districts. The wastewater-treatment process consists of influent pumping, bar screening, grit removal, primary sedimentation, a biological reactor with denitrifying and nitrifying configuration, secondary sedimentation, and denitrifying postfiltration (Figure 1). The process operation is highly automated, meaning that the major part of the process adjustments is executed on the basis of online analysis and measurements.

In each of the activated sludge process lines, the dissolved oxygen in all six zones can be controlled by manipulating the corresponding air-flow rates. The fourth, fifth, and sixth zones are always aerated, whereas the aeration in the initial three zones is progressively switched on only when the ammonia content at the end of the bioreactor exceeds a treatment threshold. The overall number of aerated zones is thus used to meet the removal efficiency defined by the plant management by adjusting the anoxic volume; usually, the first zone is kept nonaerated. The schematic of the activated sludge line and its main process parameters during the research period are reported in Figure S1 and Table S1.

Ventilation is handled by four separate systems (pretreatment, primary sedimentation, activated sludge process + postfilters and sludge storage, and digestion + dewatering), but the ventilation air from all of the systems is directed to the same exhaust air channel (Figure 1); only the air from dewatered sludge storage is not directed into this common air channel. The ventilation is maintained at a constant power, and the design exhaust airflow in the channel is approximately 120 m^3 s^{-1}. The plant-specific environmental permit defines the operation requirements for the Viikinmäki WWTP (Table 1). For the present, none of these requirements concern greenhouse gas emissions.

Table 1. Operational Requirements and Removal Efficiency at The Viikinmäki WWTP

	Viikinmäki environmental permits	EU (91/271 /ETY)	treatment results 2011	treatment results 2012	
Tot-N	≥70	≥70	90	88	%
Tot-P	≥95	≥80	97	96	%
	≤0.3	≤1	0.2	0.23	mg l^{-1}
SS	≤15	≤35	6.7	7.3	mg l^{-1}
$BOD_{7(ATU)}$	≥95	≥70	98	97	%
	≤10	≤30	5.7	6.7	mg l^{-1}
COD_{Cr}	≥80	≥75	92	91	%
	≤75	≤125	40	45	mg l^{-1}

Process Monitoring. *Off-Gas Analyzer Equipment.* The treatment plant's total N_2O emissions were continuously measured via an online Fourier transform Infrared (FT-IR) analyzing unit, the Gasmet CEMS II (Gasmet Technologies Inc.), which was situated in the effluent air channel (Figure 1).

The Gasmet CEMS II system is a multicomponent gas analyzer designed to continuously monitor the pollutant concentrations in gas mixtures. The measuring equipment, which consists of an FT-IR gas analyzer, an industrial computer, and a sampling system, has the capacity to simultaneously measure more than 50 different gas components. The samples are not diluted or dewatered before the spectroscopic analysis. The sample gas was collected from the effluent air channel and pumped into the analyzer through a heated sample line. Normally, all of the parts of the measuring unit, including the sample line, are heated to 180 °C, but because the effluent air from the WWTP is not extremely hot or wet, the temperature was set at 50 °C. All of the analyses were executed relative to the ambient air pressure. Nitrogen gas was used as zero gas for both calibration and gas analysis.

At the Viikinmäki WWTP, the Gasmet CEMS II analyzer was connected to the plant automation system, and the data were stored in the internal database of the treatment plant. The measurement data are available at 1 min intervals. The measurements covered all of the WWTP's unit operations. A total of seven different gas components were analyzed from the effluent air: water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), nitric oxide (NO), nitrogen dioxide (NO_2), and nitrous oxide (N_2O). The measurements dated back to June 2012 (because the Gasmet CEMS II online measurement unit was put into operation at that time) and will continue to operate in the future as part of the WWTP's online operation control system. In this study, the analysis results from the period July 1 2012 to June 30 2013 are examined.

Online Process Parameter Monitoring. The process parameters at the Viikinmäki WWTP were monitored via the online monitoring system of the plant. In particular, suspended solids (SS), nitrate nitrogen (NO_3–N), ammonium nitrogen (NH_4–N), total phosphorus (Tot-P), orthophosphate, alkalinity, pH, conductivity, and mixed liquor SS were taken into account at different plant locations. The wastewater temperature data were collected at 24 h intervals from the online measurement equipment positioned in the effluent wastewater channel.

Laboratory Analysis. In addition to the online process monitoring, the quality of the preclarified effluent was examined via laboratory analysis during two 24 h sampling periods, which were executed under normal process conditions in October 2012 and August 2013. During these sampling periods, a 1 h composite sample was taken of the primary clarified effluent every hour, and the fractions of $BOD_{7(ATU)}$, COD_{Cr}, NH_4–N, total nitrogen (Tot-N), and Tot-P were analyzed according to standard methods in an outsourced laboratory the following day. The results of the laboratory tests were then studied in relation to the effluent air N_2O concentrations. Before the comparative analysis, both of the effluent air N_2O concentrations and the concentrations of the pretreated wastewater components were converted from ppm_v to loads (kg h^{-1}) by using the measured exhaust airflow in the effluent air tunnel.

RESULTS AND DISCUSSION

Total N_2O Emissions from the WWTP. The total annual emissions from the Viikinmäki WWTP were calculated based on the online measurement data, which were collected from the FT-IR analyzer at 1 min intervals. Measured exhaust airflow of 120 m^3 s^{-1} was applied for the emission calculations. The total nitrous oxide emissions were found to be approximately 141 tons per year. Consequently, on average, 1.9% of the annual influent total nitrogen load of about 4700 t was emitted into the atmosphere as nitrous oxide, with the daily average emission

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being 115 t d^{-1} with a standard deviation of 35 t d^{-1}. Of the total greenhouse gas emissions resulting from the Viikinmäki wastewater treatment process, nitrous oxide emissions comprised 86% (i.e., 42 020 t of CO_2 equivalents) and methane emissions approximately 14% (i.e., 6840 t of CO_2 equivalents mainly originating from the sludge treatment process). Fossil carbon dioxide emissions accounted for less than 1% (i.e., 113 tons of CO_2) of the total emissions. The CO_2 equivalents for the total nitrous oxide and methane emission daily averages were 18.7 ± 4.8 t/d and 0.3 ± 0.04 t/d, respectively. The total methane and nitrous oxide emissions were calculated using the 100 year global warming potentials presented in the technical summary of IPCC 2013 report.[4] Gaseous emissions from the dewatered sludge storage tanks (Figure 1) were not included in these calculations because this part of the plant has a separate ventilation air outlet.

The highest emission rate was observed in June 2013. During that time, 2.8% of the total influent nitrogen load was emitted as nitrous oxide. The lowest emission factor of 14.9 gN_2O–N (kg influent N)$^{-1}$, i.e., 1.5% of influent Tot-N, was measured in September 2012. The difference between these extreme values is more than 13 gN_2O–N (kg influent N)$^{-1}$, and the variance in the monthly emission factors is 1.3 gN_2O–N (kg influent N)$^{-1}$ (Table 2).

Table 2. Monthly Nitrous Oxide Emissions and Influent Nitrogen Loads at Viikinmäki WWTP

month	N_2O emission, t month^{-1}	influent N load, t month^{-1}	emission factor, gN_2O–N (kg influent N)$^{-1}$
July 2012	7.9	324.6	15. 5
August 2012	11.3	386.2	18.6
September 2012	9.7	414.7	14.9
October 2012	13.8	408.5	21.5
November 2012	12.0	391.8	19.4
December 2012	12.4	391.8	20.1
January 2013	13.0	404.9	20.4
February 2013	10.2	369.2	17.6
March 2013	9.9	408.6	15.5
April 2013	11.4	423.6	17.6
May 2013	13.2	419.1	20.0
June 2013	15.9	357.2	28.4
Total	140.7 [t year^{-1}]	4700.2 [t year^{-1}]	19.1

Compared to prior research results,[2,9] the total N_2O emissions of 168 g per PE per year were remarkably high at the Viikinmäki WWTP during the 12 month period. Because the process conditions during the monitoring period were typical and the average effluent total nitrogen concentrations were low (5.1 mg l^{-1}), these results undermine the argument that the lowest N_2O emissions are measured from wastewater treatment processes that achieve low effluent nitrogen levels.[14] However, some of the operational features employed during the Viikinmäki wastewater-treatment process, i.e., fluctuating influent flow[14] and intermittent aeration at the activated-sludge process,[14,28,33] have been identified as possible features promoting N_2O production in prior studies.

Although the N_2O emissions measured during this long-term study are high compared to the emission values presented in other recent studies[30,34] and the computational emission factor was more than 50 times higher than the factor presented by the IPCC,[35] these results are in accordance with the outcomes for the long-term online measurement campaign implemented at the Kralingseveer WWTP.[32] The Kralingseveer campaign, which is for the time being the only other full-scale online monitoring campaign ever executed, presented an emission factor of 2.8% for influent N, whereas in this study, an emission factor of 1.9% for influent N was introduced (Table 2). Both emission factors are significantly higher than the factor of 0.035% for influent N proposed by IPCC.[2,35] However, the large differences between the monthly emission rates in both studies indicate that invariable emission factors are not the most relevant method for estimating annual nitrous oxide production at full-scale WWTPs (Table 2). This finding supports prior conclusions regarding the unreliability of the emission estimates based on constant emission factors[36] and highlights a need to develop new dynamic-process models for N_2O emission modeling.[37,38]

In addition to accurately quantifying of the total annual N_2O emissions, the online monitoring campaign at the fully covered Viikinmäki WWTP provided a unique insight into the distribution of the total GHG emissions at a full-scale WWTP. According to these measurements, the total nitrous oxide emissions comprised more than 86%, i.e., 42 040 t of CO_2 equivalents, of the total GHG emissions of the Viikinmäki wastewater treatment process. The results support the Kralingseveer study, which presented a N_2O share of 78.4% of the plant's total GHG emissions.[32] However, contrary to the Viikinmäki measurement campaign, the N_2O emissions from secondary sedimentation were not included in the Kralingseveer measurements. Given the high solubility of N_2O and the

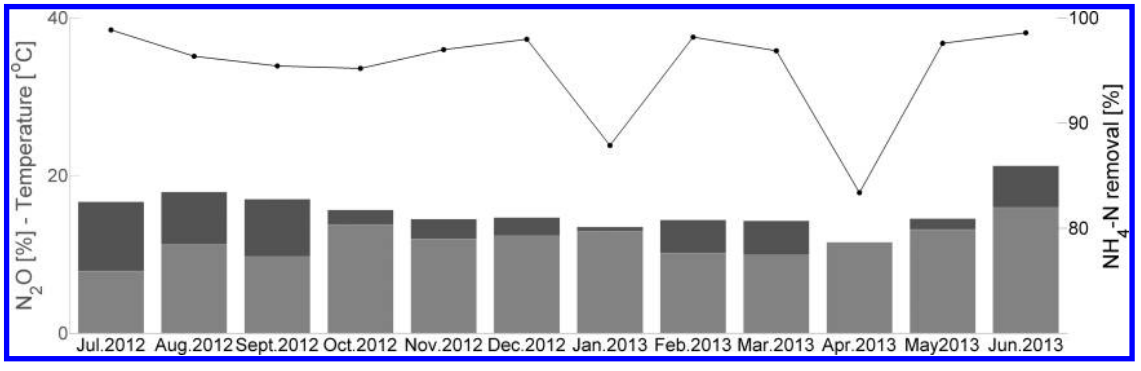

Figure 2. Annual variations in the wastewater temperature and the N_2O production at the Viikinmäki WWTP in July 2012–June 2013: average monthly emissions (light gray bar), average monthly temperature (dark gray bar), and percentage of NH_4–N removal (solid black line).

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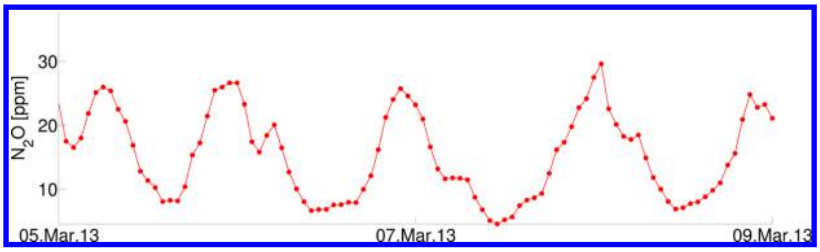

Figure 3. Diurnal variations in the N_2O concentrations in March 2013.

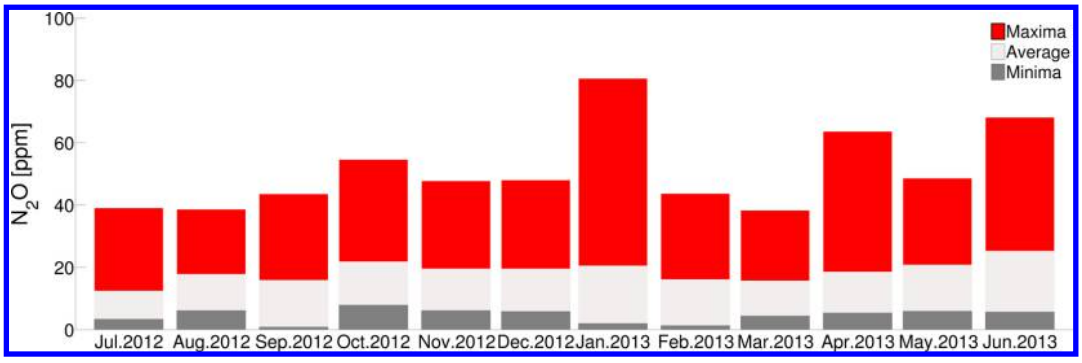

Figure 4. Monthly ranges of the hourly N_2O concentrations.

denitrification taking place in the sedimentation basins, these emissions can be significant. Although similar findings about the significance of N_2O emissions with respect to a WWTP's total GHG emissions have also been presented in other recent studies[30,39] most of the national and international emission estimates are still composed on the basis of the IPCC factor values originally presented by Czepiel et al.[2]

Seasonal Variations. To account for the possible factors behind the strong seasonal variations in N_2O emissions, we examined the effect of the seasonal wastewater quality variation on N_2O production throughout the research period. Figure 2 shows the average monthly variations in terms of wastewater temperature, N_2O emissions, and percentage of NH_4–N removal. The highest monthly emissions were measured in June 2013 (15.9 t month^{-1}), whereas the lowest emissions were measured in July 2012 (7.9 t month^{-1}). The highest monthly average for the wastewater temperature was recorded in June 2013 (21.3 °C). The lowest daily wastewater temperatures were registered during the snowmelt period in April 2013 (8.8 °C). The process was fully nitrifying during the investigated period except for slight drops in January and April 2013. The correlation between N_2O emissions and the wastewater temperature was investigated by determining the Pearson product-moment correlation coefficient, R, and its probability value, p, at a significance level of 0.05 for the daily average values. No significant correlation was found: $R = 0.017$ and $p = 0.373$ with $n = 365$ measurements.

Wastewater temperature is known to be one of the factors decelerating, and even inhibiting, the nitrogen conversion reactions. Within a suitable temperature range for biological activity, reaction rates are known to slow down with decreasing temperature. Nevertheless, each biomass has its own specific temperature dependency. At the Viikinmäki WWTP, the seasonal dynamics in wastewater temperature are extremely strong due to the snow melting season in March–April: The oldest districts in the WWTP's operational area have combined sewers, meaning that during the snow melting period, the temperature of the influent wastewater momentarily drops significantly while the volume of the influent wastewater multiplies. Moreover, the average temperature during the winter season is notably lower than during the summer season (Figure 2). To observe the effects of the seasonal variations of the temperature conditions at the Viikinmäki WWTP on nitrous oxide production, we examined the proportionality between the total N_2O emissions and the effluent-wastewater temperature. With respect to our prior assumptions, the analysis of the 12 month measurement data revealed no correlation between the two variables despite the fact that the seasonal variations in N_2O emissions were somewhat important (Table 2 and Figure 2). Likewise, no correlation was observed when the wastewater temperature dropped significantly in April 2013 or when the wastewater temperature was at its highest in June 2013 (Figure 2). Hence, the changes in wastewater temperature alone were not responsible for determining the N_2O production rate at the Viikinmäki WWTP.

The effect of temperature on N_2O production has also been studied at the Kralingseveer WWTP.[32] A long-term online measuring campaign conducted at the plant there revealed a seasonal dynamic in N_2O production. During the research campaign, the wastewater temperature and the emission rates were found to have a negative correlation with a time lag of 2 to 3 months. The correlation between N_2O emissions and temperature with a time lag of different sludge retention times (1×SRT, 2×ST, 3×SRT,...) was calculated, but no delayed correlation was observed.

Diurnal Variations. In recent studies, the diurnal variations in N_2O production have been associated with changes in DO concentrations,[13,15−17] with changes from anoxia to aerobic conditions[12] and with the dynamics of the nitrate and nitrite concentrations in the activated sludge reactors.[40] At the Viikinmäki WWTP, the diurnal variations in N_2O emissions were compared with the diurnal changes in influent organic and nitrogen loads. Our hypothesis was that these variables would have a strong positive correlation because the influent nutrient load at the Viikinmäki WWTP is also known to follow a regular diurnal pattern.

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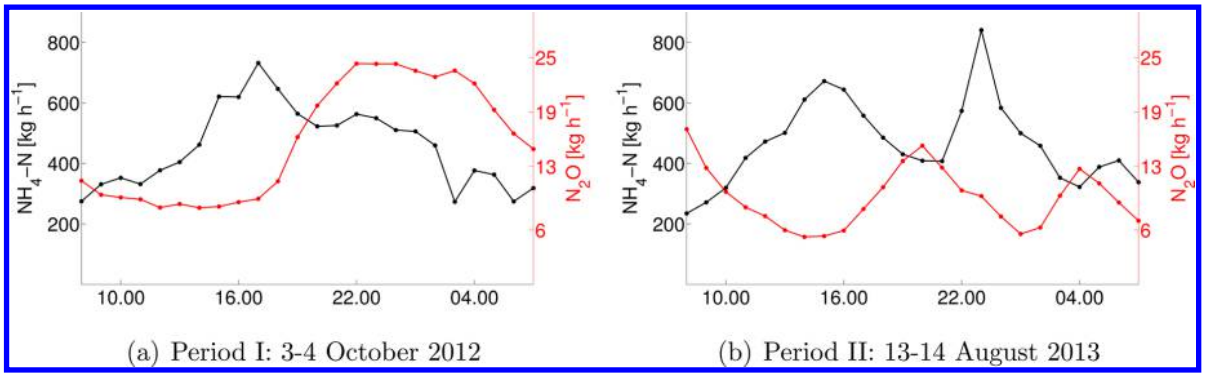

Figure 5. Diurnal variations during a 24 h sampling period in the ammonium nitrogen load (kg h^{-1}) in the activated-sludge process and effluent N_2O emissions (kg h^{-1}) at the Viikinmäki WWTP in Period I (panel a) and Period II (panel b).

The long-term online monitoring campaign revealed regular and strong diurnal variations in the effluent N_2O concentration (Figure 3). It was evidenced that the highest average daily N_2O emissions were related to the highest degree of diurnal variation (Figure 4), being that the highest concentrations were measured invariably at night and the lowest around noontime. The diurnal variations were found to be the greatest in January 2013 (Figure 4), and a significant positive correlation was observed between the average weekly emission and the magnitude in N_2O variation within a day (R = 0.61, p = 0.000, n = 52). The effect of wastewater temperature on the variations in the diurnal N_2O emissions was investigated by applying the Student's t test to the low-temperature data set (below 15.6 °C) and high-temperature data set (above 15.6 °C). No significant difference between the hourly N_2O variations in the two different data sets was found (t test; p = 0.144, n = 52).

To distinguish between the process characteristics that accrue with respect to the hourly differences in N_2O production, we examined the quality of the primary clarifier effluent during two sampling periods in October 2012 (hereafter referred as "Period I") and August 2013 (hereinafter referred as "Period II"). The objective of the comparison was to find out whether a correlation existed between the diurnal variations in the influent nutrient load and the N_2O emissions. To better investigate the interdependence between these process parameters, we conducted a correlation inspection while taking into account the observed time lag. The diurnal dynamic of N_2O production lagged approximately 5 h behind the ammonium nitrogen load during both sampling periods, as shown in Figure 5.

The first sampling period revealed a strong delayed relation between the $BOD_{7(ATU)}$ load and the total N_2O emissions. During the first sampling period in October 2012, the changes in influent $BOD_{7(ATU)}$ load explained approximately 84% of the variation in the total N_2O emissions. During the second sampling period, the same model explained only about 25% of the variation in the total N_2O emissions. However, an interrelationship between the influent nitrogen load (NH_4–N, Tot-N) and the effluent N_2O emissions was noted during both sampling periods.

During both sampling periods, the nitrous oxide production had a delayed correlation with the total nitrogen and ammonium nitrogen loads that was measured from the primary clarified effluent (R = 0.74...0.83, p = 0.00, n = 24 in Figure S2c–e). An increased ammonium nitrogen load in the nitrifying zones of the activated sludge process enhanced the WWTP's overall N_2O production. However, such an interdependence was only visible on an hourly basis when the variations in the monthly emission factors were notable (Table 2), and no correlation between the monthly N_2O emissions and the monthly NH_4–N influent load was observed (R = 0.25, p = 0.007, n = 100). This lack of correlation can be explained by the synergy of different process parameters, which diminish the visible dependence between the influent ammonium nitrogen load and the effluent N_2O emission. For instance, the high N_2O emissions in June 2013 most probably resulted from the extremely low alkalinity (and thus a lack of inorganic carbon) of the wastewater (<1.0 mequiv l^{-1} during that period) in the activated-sludge process because no significant changes in the influent nutrient load were monitored at the time.[41] The level of alkalinity in the process is usually controlled by lime addition to a minimum level of 1.6 mequiv l^{-1}.

It could be hypothesized that increasing the BOD load would increase the competition between AOBs and heterotrophic bacteria. The 5 h time lag between the dynamics of the N_2O emissions and the influent $BOD_{7(ATU)}$ load was equal to the retention time of the anoxic zone during the Viikinmäki denitrification–nitrification process. Thus, the N_2O emissions were, in fact, correlated almost linearly with the load with respect to the aerated, nitrifying zones of the activated-sludge tank in Period I (Figure S2a). However, we repeated the 24 h sampling period in August 2013, and the delayed positive correlation between the N_2O emission and the influent $BOD_{7(ATU)}$ load to the activated-sludge process was unsubstantial (Figure S2b). More test results would be needed to define the significance of the positive correlation between the $BOD_{7(ATU)}$ load and the overall N_2O emissions. On the basis of the two test runs, the correlation seems to occur only occasionally and is strongly affected by the $BOD_{7(ATU)}$-to-NH_4–N ratio, which happened to be relatively stable during the first test period in October 2012 (R = 0.83, p = 0.00, n = 24). The BOD-to-NH_4–N-ratio was approximately 2.5 during Period I and varied between 2.7 and 4 during Period II.

With regard to prior research that has associated diurnal variations with the changes in influent ammonium load,[13,28,42] the findings of this study seem reasonable. However, because the anoxic–aerobic volume of the activated sludge process under study was controlled by the ammonium concentrations in the biologically treated wastewater, there is no clear consensus about whether the enhanced overall nitrous oxide production primarily resulted from the increased ammonium

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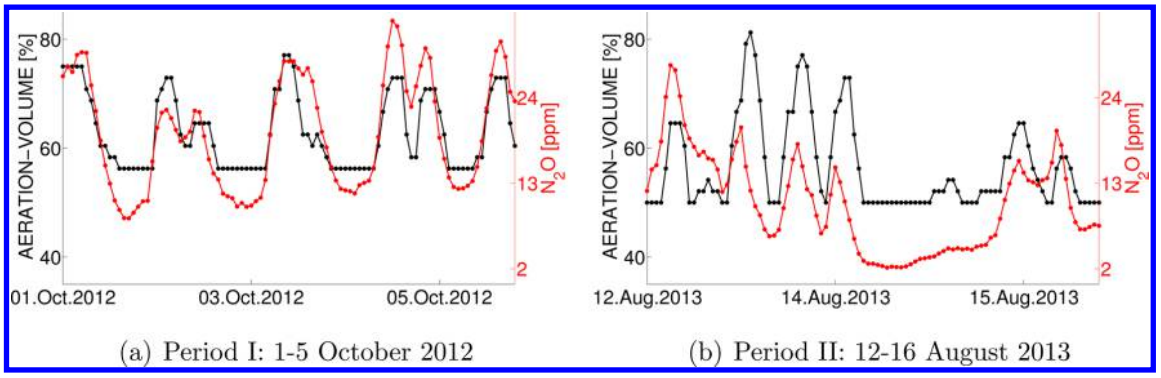

Figure 6. Interdependence between the aerated biological volume and the total nitrous oxide emissions in Period I (panel a) and Period II (panel b).

nitrogen load during the activated-sludge process or from the greater number of nitrifying zones (Figure S1).

According to the long-term online monitoring data, an increase in the number of nitrifying zones seems to result in higher overall nitrous oxide emissions, as shown in Figure 6 for Period I and Period II, with R = 0.40 for the 1 year of continuous data (p = 0.00, n = 8760). Thus, these observations support the theory that most N_2O emissions from the Viikinmäki WWTP are produced in the activated-sludge process by AOBs and possibly via nitrifier denitrification. However, for the examination of the mechanisms responsible for N_2O production in the Viikinmäki activated-sludge process, dynamic process modeling needs to be studied more closely: Further local measurements of gaseous emissions and liquid-phase N_2O concentrations from different reactors are needed. Although a plant-wide online measurement gives very valuable information about the overall N_2O emissions, it is very challenging to localize their source and understand the production mechanisms with this approach.

Regardless of the ultimate factor behind the strong diurnal variation in the measured N_2O emissions, it is evident that the dynamics of the nutrient load to the activated-sludge process promote N_2O production at the Viikinmäki WWTP. This may result partially from the high level of loading during the studied activated-sludge process, which is currently operating at its full capacity. The impact of the loading level can be investigated in the future because the extension of the biological process of the Viikinmäki WWTP was put into operation in 2014. Another possible subject for further research is the effect of flow equalization on the overall N_2O emissions at the Viikinmäki WWTP.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04466.

Schematic of the activated sludge process (Figure S1), main process parameters (Table S1) at the Viikinmäki wastewater treatment plant, and correlation between process variables (Figure S2). (PDF)

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Notes

The authors declare no competing financial interest.

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