Emissions of N₂O, CH₄, and CO₂ from VEAS waste water treatment plant.



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Abstract:

In the IPCC guidelines for national climate gas inventories (Sandmo 2011), the default for estimating N₂O emission from Wastewater Treatment Plants is that N₂O emission is 2% of "processed" nitrogen; i.e. nitrogen removed by through precipitation (sludge) and nitrification + denitrification. Based on previous measurements at an early stage of the development of the VEAS process, it was hypothesized that the performance of the plant is much better than this (i.e. a lower percentage of processed N emitted as N₂O). We tested this by measuring N₂O emissions at various spots within the treatment plant, as well as the concentrations of N₂O in the liquid phase throughout, including the exit water. This was done at 12 occasions throughout a period of 124 days, starting February 2, 2011, thus covering a range of operational conditions regarding water temperature (which is very low in winter) and various loading (high precipitation leads to high water flow with low concentrations of nutrients). Finally we tested the performance of the entire WWTP by sampling the exhaust gas from the entire plant which is collected and exits through a high chimney.

We also included measurements of CO_2 and CH_4 emissions in order to evaluate the performance of the WWTP with respect to all three relevant Green House Gases (GHG).

The results verified that the performance of the VEAS process with respect to N_2O emission is much better than the IPCC guidelines. On the average, the emission of N_2O -N to air from the entire plant (through the chimney) amounts to 0.2% of the processed N. If the N_2O lost as dissolved N_2O in the exit water is included, the percentage increase to 0.3. Single day values vary quite substantially, and the experimental data suggest that the performance of the plant can be improved by optimization of the routines.

Analysis of gas emissions within a single process hall showed that the nitrification reactors (NIT) emit most of the N₂O (average 55 ± 30 (stdev) g N₂O h⁻¹ from NIT), but a significant fraction of the N₂O left the process hall dissolved in the exit water from the denitrification reactor (31 ± 25 g N₂O-N h⁻¹). This single process hall represents 1/12 of the entire plant; thus the estimated emission from all NIT-reactors amount to 660 ±360 N₂O h⁻¹. This is to be compared with the measured N₂O emission from the entire plant based on analysis of the air ventilating through the chimney (460 ±340 g N2O-N h⁻¹). It shows that process hall emission can account for all the N2O measured in the chimney.

The total emissions of CO₂ and CH₄ through the chimney were 803 kg CO₂ h^{-1} (±150) and 2.68 kg CH₄ h^{-1} (±0.66) (std dev). The nitrification+denitrification reactors account for most of this CO₂, but for CH₄ the emission from nitrification + denitrification accounts for only 30%. Thus, there is a significant source of CH₄ emission within the plant in addition to the nitrification and denitrification reactor.

In terms of global warming CO_2 –equivalents, CO_2 emissions is the largest source (803 kg h⁻¹), N₂O is the second (215 kg h⁻¹), and CH₄ is the lowest (54 kg h⁻¹).

Background and introduction: Description of the VEAS WWTP.

TheVEAS-WWTP is built in solid rock. Figure 1 shows a 3D drawing of the entire plant and Figure 2 shows the functional units and flows. Waste water flow = 9000 - 39500 m³ h⁻¹. Chemical characteristics of the wastewater entering the plant: pH 7,4, suspended material 236 mg/l, alkalinity 3,3 meqv/l, total organic Carbon (TOC) 90 mg/l, biological oxygen demand (BOF5) 164 mg/l, Chemical oxygen demand (KOF) 360 mg/l, total-phosphorous (Tot-P) 3,7 mg/l, total-nitrogen (TKN + NOX) 29 mg/l, ammonium 16,6 mg/l (all average values).

Nitrogen is removed from the wastewater through precipitation (33-43% of N removal) and through subsequent nitrification/denitrification (57 - 67 % of total N-removal). The average residence time in the nitrification (NIT) and denitrification (DEN) reactor is 0,3 h and 0.2 h, respectively. The C-source to the nitrification reactor is methanol.

For a more detailed description of the plant, see Sagberg et al. (1998)



Figure 1. Drawing (3D) of the entire plant. Hall 7 (marked) was used to measure gas emissions from nitrification and denitrification reactors.



Figure 2. Flows and reaction cheme for the entire VEAS plant. In total there are 24 nitrification and 24 denitrifiation reactors. The emissions were measured from two reactors in Hall 7 (see Fig 1).

Characteristics and Operation of the nitrification reactor:

Since the nitrification reactor proved to be the most potent source of N_2O , special attention will be given to its operation. The following description is based on Sagberg et al (1998) and Mao et. al. (2008).

Each of the 24 reaction tanks contain $\sim 350m^3$ upflow biofilters (Degremont BIOFOR) consisting of (lightweight) expanded clay aggregates (Leca) pellets. The pellets are 3–5mm in diameter, and have high density (1.24 gmL⁻¹) compared to normal Leca. The pellets are coated with a nitrifying biofilm, built up through several years of continuous flow-through of mechanically purified wastewater rich in ammonium (0.5–2; average 1.2mM), with organic carbon [total organic carbon (TOC)= 35–45mg L_1] and alkalinity (3,1 meqv L_l). The wastewater is injected at the bottom of the reaction tank filled with Leca particles; aeration is secured by air injection with the incoming water; the average residence time of the water is 18 min; and the water-temperature range from 5 to 15 °C (seasonal variation). As the water flows through the reactor (100–180 L s⁻¹, average 160), ~50% of TOC is removed, 30% by heterotrophic respiration and 20% by assimilation/adsorption (adding to the biofilm, which is partly removed by vigorous backwashing every 14 h). The calculated rate of heterotrophic respiration on the filter material during normal operation is 1–2 mmol CO₂-C g⁻¹ carrier material h⁻¹ (based on mass balances for TOC). On the average, 90% of the ammonium is oxidized, resulting in a substantial reduction of pH (near-neutral at inlet, 6.2-7 at outlet). The estimated oxidation rate of ammonium during a normal operation is 0,5-2 mmol N g⁻¹ Leca h⁻¹.

Previous studies of the nitrification reactor:

In a previous study of the nitrification rates and the amounts of nitrifying bacteria on pellets from the nitrification reactor (Mao et al., 2008), we estimated a cell density of ~ 10^9 cells of ammonia oxidizing bacteria (AOB) per g Leca material, based on quantification of the amoA gene (coding for ammonia monooxygenase). Cloning sequencing suggested approximately equal population size of Nitrosospira and Nitrosomonas, wheras the abundance of archaeal ammonia oxidizers was insignificant. The population of ammonia oxidizing bacteria (10^9 g⁻¹) was sufficient to explain the observed nitrification rates. Based on

ammonia oxidation rates *in situ* (i.e. under normal operation of the WWTP), we were also able to estimate the average growth rate of AOB to be 0.001-0.01 h^{-1} . This means that the average residence time of AOB must be 4-40 days, which supports the operators notion (Sagberg *et al.*, 1998) that the backwashing (every 14 hour) removes heterotrophic biofilms but only a marginal fraction of the AOB. On this basis, it was hypothesized that AOB primarily are situated in an inner part of the biofilm (near the surface of the pellet), which is not peeled off by the backwashing. Strong attachment of AOB to surfaces have been demonstrated for soils as well (Aakra et al 2000).

The biofilm also had a diverse community of heterotrophic denitrifying bacteria (cloning-sequencing of nirK), which is thought to create anoxic conditions and contribute to denitrification (which can also be conducted by AOB under oxygen limiting conditions). Considering this crucial role of heterotrophic film formation and its dependence of the backwashing (thin film after washing, increasing gradually through the 14 hours till next backwashing), we were particularly interested in the N₂O emission at various stages between two washing events.

Materials and methods:

For evaluation of the performance (i.e. N2O emission as % of nitrogen removed from the waste water) of the biological treatment (nitrification – denitrification) we measured the nitrogen flow and -removal at each date of emission measurement. The estimated nitrogen flows were calculated from water flow (online flow monitors) and measured total nitrogen concentration (organic + ammonium and nitrate+nitrite) measured at point 1 (in flow), 3 (water into the nitrification reactor) and 8 (exit water), Figure 3. The nitrogen removal in SED is primarily solids (sludge) and NH3/NH4⁺ (the ammonium is stripped after methane fermentation of the sludge), and is included in the total N removal. Total N was analysed as Kieldahl N at VEAS accredited lab.



Figure 3. Drawing of flows and emissions measured within Hall 7: 1 is the water flow into the sedimentation tank, 3 is the water flow to the nitrification reactor (NIT), 6 is the water flow to the denitrification reactor (DEN), and 8 is the exit water. 2 is exit sludge, 4 is air flow into the nitrification reactor and 5 and 7 is the exit air from the nitrification and denitrification reactor, respectively. Gas concentrations in the water were analyzed (by headspace analyses) at point 1, 3, 6 and 8. Emissions were measured by analyzing exit air (through hoods, see below) at point 5 and 7.

Net emissions (CH₄, CO₂ and N₂O) at point 5 and 7 were estimated based on measured concentrations in exit air through hoods (collecting gas from 2 reaction chambers for NIT and DEN), measured concentrations in the hall air.

For point 5, the existing ventilation system was used; we sampled directly from the exit channels which collects the exit air from the two NIT reactors. The exit air is a mixture of the air flow through NIT (air blown in, point 4) and a significant flow of air from the hall (the hoods cover the chambers, but are not gas tight; fans secure low pressure in hoods so that a significant amount of air from the hall flows through the

narrow slits between the hoods and the surface). Emission estimates are based on the measured amounts in exit air, corrected for the amounts of N_2O through hall-air entering through the slit (Figure 4).



Fig 4. Sampling of nitrification reactor (NIT)

At point 7, the hoods collect gas flow from the reactor (mass flow by ebullition of N_2 and N_2O , CO_2 etc) + large amounts of hall-air. The estimated mass flow of gas flow from the reactor was insignificant compared to the amount of gas entering the hood from the hall. As for point 5, the emissions were estimated from flow (through the hood exit channel), and concentrations measured in hall-air and in the exit channel.



Fig 5: Sampling from denitrification reactor (DEN)

Gas measurements:

All gas samples (from hoods and headspace) were analysed by GC, in principle as described by Molstad et al (2007), but with a traditional GC equipped with Electron capture detector for determination of N_2O , Flame Ionization detector for CH₄ and Thermal Conductivity detector for CO₂.

Headspace analysis:

Water samples were taken with a 60 mL syringe equipped with a 3-way valve. A volume of 20 mL was taken, and 20 ml air (from the hall) was drawn into the syringe, which was then closed and shaken vigorously (by hand) for 2 min. The gas phase was then pushed through a needle mounted on one of the outlet of the 3-way valve into an evacuated 12 mL serum flask (with butyl rubber septum) to reach a pressure of ~ 1.5 bar. These gas samples were then analysed by GC (Molstad et al., 2007), and the amount of dissolved CH_4 and N_2O was calculated, assuming equilibrium between headspace and liquid, contribution from hall air was subtracted (determined each day).

Calculations:

Nitrous oxide (N₂O):

<u>Gas in liquid</u> was measured by headspace analysis after equilibrating 20 ml liquid with air taken from the process hall. The temperature of the water after sampling and vigorous shaking (to obtain equilibrium) was ~ 15 °C, and the amounts of gas (N₂O) originally in the liquid was estimated based on solubility at 15 °C, subtracting the amounts of gas in the air of the process hall (which was also measured at each time of samping).

1 ppmv N2O in headspace = 1.51 nmol N₂O in whole flask (liquid+ gas phase)

= 42.3 ng N_2 O-N in whole flask.

A fraction of this derives from the air drawn from the process hall, and should be subtracted: 1 ppmv in 20 mL hall-air contains 0.85 nmol $N_2O = 23.7$ ng N_2O -N.

Thus, a measured conc of 1 ppmv in headspace and 1 ppmv in hall air gives 42.3-23.7 = 18.6 ng N₂O-N in the 20 mL liquid sample.

 $\Rightarrow \text{ The amount of } N_2O-N \text{ in the 20 mL liquid sample is } W=C_{headsp}*42.3-C_{hall}*23,7, \text{ where } C_{headsp} \text{ is measured conc (ppmv) in headspace and } C_{hall} \text{ is measured conc (ppmv) in the hall air.}$

The amounts in g N₂O-N pr m³ is $C_{\text{liquid}} = W*10^{-9}*10^{3}/0.02$ for obvious reasons.

Gas in gas samples from process points:

The temperature of the gas at the point where gas flow was measured was approximately 20° C, and the estimated concentration of N₂O was calculated accordingly:

1 L at 20 $^{\circ}$ C = 0.041 mol N₂O = 1,165 g N₂O-N

 $1\text{ppmv} = 1.165*10^{-6}*10^{3} = 1.165*10^{-3}$ g N₂O-N/m³ (again for obvious reasons)

But the concentrations measured are in a mixture of two gas-flows: one from the hall (F_{hall}) and one from the source (F_{source}) => the amount of N contributed by the source (in F_{total} = F_{source} + F_{hall}). The calculated concentration that is "due" to the source is :

$$\dot{C}_{source} = C_{source measured} - C_{hall} * F_{hall} / F_{total}$$

In the nitrification reactor, a small amount of N_2O is also entering the system with the flow of sparging air into the system. Hence the equation for NIT is :

$$\dot{C}$$
 source = $C_{source measured}$ - $C_{hall}*F_{hall}/F_{total}$ - $C_{amb}*F_{sparge}/F_{total}$

where C_{amb} is the ambient concentration of N_2O in the atmosphere and F_{sparge} is the flow of sparging air.

Gas in samples from the chimney (collective)

The calculation is equivalent to that above (for gases from point sources), but simpler:

we assume ambient concentration in the air drawn into the WWTP (treatment plant), which is 0.35 ppmv for N₂O, 1.84 ppmv for CH₄, and 361 ppmv for CO₂

Methane (CH₄):

<u>CH₄ in the liquid</u> : Equivalent calculations were done for methane. In this case we are interested in g CH₄. The solubility of methane is 5.4% of that for N₂O, and the ambient CH₄ concentration in the atmosphere is 1.84 ppmv. Otherwise, the calculations follow the same scheme as for N₂O

1 ppmv CH₄ in headspace = 0.87 nmol CH₄ in whole flask (liquid+ gas phase)

= 14 ng CH₄ in whole flask.

A fraction of this derives from the air drawn from the process hall, and should be subtracted: 1 ppmv in 20 mL hall-air contains 0.84 nmol $CH_4 = 13.4$ ng CH_4 .

Thus, a measured concentration of 10 ppmv in headspace and 2 ppmv in hall air gives $W = 10*14-2*13.4 = 113.2 \text{ ng CH}_4$ in the 20 mL liquid sample.

 $\Rightarrow \text{ The amount of CH}_4 \text{ in the 20 mL liquid sample is } W = C_{headsp} * 14 - C_{hall} * 13.4, \text{ where } C_{headsp} \text{ is } measured \text{ conc (ppmv) in headspace and } C_{hall} \text{ is measured conc (ppmv) in the hall air.}$

The amounts in g CH₄ pr m³ is $C_{\text{liquid}} = W*10^{-9}*10^{3}/0.02$

<u>CH₄ in gas samples</u>: 1 L at 20 °C = 0.041 mol CH₄ = 0.67 g CH₄ 1ppmv = $0.65*10^{-6}*10^{3} = 0.67*10^{-3}$ g CH₄/m³

Gas in samples from the chimney (collective)

As for N_2O , the ambient CH_4 (i.e. concentration in the atmosphere) was subtracted.

Carbon dioxide (CO₂)

Due to uncertainties regarding pH at different points in the process, the calculation of transport of dissolved (+dissociated) CO_2 has not been estimated in detail. But emissions to the atmosphere follows the same scheme as for CH_4 and N_2O . Ambient concentrations are ~360 ppmv).

1 L at 20 °C = 0.041 mol CO₂ = 1,8 g CO2 1ppmv = $0.65*10^{-6}*10^{3} = 0.67*10^{-3}$ g CH₄/m³

Results.

Analysis within the system: gas flows with water and emission to the atmosphere from nitrification and denitrification reactors (Hall 7).

The measured gas concentrations and estimated emissions and flows for each single time of measurements (from February 2 til June 6, 2011) are all listed in Tables A1-A3 (Appendix).

Figure 6 shows the average flows and emissions of the three gases (with standard deviation in parenthesis). These averages include some measurements when the operation was suboptimal (low airflow to NIT, low methanol to DEN), which apparently resulted in higher emissions. This calls for more systematic investigations of operation-effects on emissions.



Figure 6. Gas flows (with water) and emissions (to atmosphere) within the system based on measured concentrations (and flow) in Hall 7 (2 NIT and 2 DEN reactors). The figure shows average values for the period Febr 2 till June 6 2011 (raw data in Table A1-3, appendix). Flow with water are shown as horizontal arrows, emissions to the atmosphere as vertical arrows. Individual figures are shown for each gas; the top figure shows the names of the flows and emissions which will be used in the rest of the report.

In the following, we will show some more detailed plotting and analyses of some essential variables. Fig 7 demonstrates the large variability of N₂O emission from NIT. It also shows that a substantial fraction of the N₂O produced leaves the nitrification reactor with the water flow (potentially to be reduced in DEN). Fig 8 shows the CH₄ data for NIT, demonstrating that the CH₄ emitted from NIT is not produced there, but enters the reactor as dissolved CH₄ from SED. Fig 9 shows the CO₂ emission from NIT and DEN. As explained in the figure legend, the low CO₂-emission from DEN reflects a combination of slow transport (still water, marginal ebullition) and possibly high pH.



Figure 7: N_2O flows from the nitrification reactor (sum for two reactor chambers). Average values for each date are shown by lines, single measurements as single dots. The emission to the gas phase (E(NIT)is the measured emission through the hood (corrected for N_2O in air from the process hall, and ambient N_2O in the process (sparging) air, see mm). The flow of N_2O leaving the nitrification tank with the exit water (F(NIT-DEN) is entering the denitrification tank (subsequent step). Despite the high flow of sparging air through the system, a significant fraction of the N_2O in the nitrification tank is not emitted to air.



Figure 8: CH₄ flows in and out from the nitrification reactor (sum for two reactor chambers). In-flow with the water (from SED) is shown as single black squares (F(SED-NIT)). Flow out of the reactor to air is shown in blue (emission to air, E(NIT)) and red (flow with exit-water, F(NIT-DEN)). Average values for out-flow each date are shown by lines, single measurements as single dots. The emission to the gas phase (blue colour) is the measured emission through the hood (corrected for CH₄ in air from the process hall, see mm). The flow of CH₄ leaving the nitrification tank with the water (F(NIT-DEN), red colour)) is entering the denitrification tank (subsequent step). In contrast to N₂O, the sparging effectively removes most of the CH₄, reflecting the low solubility of CH₄ compared to that of N₂O. Thus, most of the CH₄ in NIT is emitted to the atmosphere. The flow of methane into the system (F(SED-NIT)) is largely matching the output, The outflow (E(NIT)+F(NIT-DEN)) was correlated with the in-flow of methane (F(SED-NIT)) ($r^2=0,5$). Thus there is little evidence for CH₄ production within NIT.



Figure 9. CO_2 emission (NB kg CO_2 h⁻¹) from nitrification reactor (E(NIT), blue) and Denitrification reactor (E(NIT), red). Average values for each date are shown by lines, single measurements by dots. The low emission from DEN is due to marginal transport (the water is still, and ebullition of N₂ is probably inefficient to transport significant amounts of CO_2 out of the system). Thus, most of the CO_2 is probably leaving the system with the exit water.

Correlations: CH₄ emission correlated with CH₄-concentrations in the exit water both for the NIT reactor (r=0.49) and DEN (r=0.81). N2O emission also correlated with the N₂O concentration in the exit water, both for NIT (r=0.77) and DEN (r= 0.89). None of these correlations are particularly surprising.

Measurements of exit air from the entire plant:

The concentrations in the chimney for various sampling times are plotted in Figure 10.



Fig 10 Concentrations of CO₂, CH₄ and N_2O in exhaust air from the entire plant. The values are plotted as log_{10} values of concentrations in ppbv (μ L m⁻³), thus a value of 3 is equivalent to 1000 ppbv, or 1 ppmv. The concentrations of the gases were closely correlated (r^2 was 0.70 for CO₂ against N_2O , 0.81 for CO₂ against CH₄ and 0.77 for CH₄ against N_2O). The average concentration ratio [CO₂]/[CH₄] was 121 (stdev= 13, min=97, max=139). The average concentration ratio [CH₄]/[N_2O] was 11.3 (stdev= 5.7, min=5.7, max=16.2). The measured air flow in the chimney was $332*10^3$ m³ h⁻¹ (stdev = 30, min= 293, max=374, all in 10^3 m³ h⁻¹). Based on the measured air flow and concentrations (minus that in ambient air), the total emission from the entire plant was calculated. The result is shown in Figure 11.



Fig 11 Emission of CO, CH_4 and N_2O from the entire plant, log_{10} values of emissions in g h⁻¹ (NB: the unit for N_2O is g N_2O not N_2O -N).

Based on the measured concentrations in the chimney, we calculated average emissions of the three gases for entire plant, shown in Table 1. The emissions expressed in CO2 equivalents (i.e. global warming CO_2 equivalents) are shown at the bottom line.

Table 1. Estimated emissions of the three gases in kg h^{-1} , as measured in the exhaust chimney (standard deviations, and min/max). The bottom line shows the emissions expressed in CO₂-equivalents (i.e. global warming CO₂ equivalents, using a factor of 20 and 300 for CH₄ and N₂O, respectively).

Units	CO2	N2O-N *	CH4	N2O *
average kg/h	803	0,46	2,68	0,72
stdev	150	0,34	0,66	0,53
max	1061	1,04	3,75	1,63
min	552	0,16	1,80	0,24
kg CO2-equivalents h-1	803	215	54	215

 $*N_2O$ emissions are expressed both as kg N_2O -N (as a biogeochemist would do) and as kg N_2O (as an atmospheric chemist would).

Can the emissions from the process hall account for the concentrations in the chimney?

The estimated emissions of N₂O from the entire plant (0,72 \pm 0,53 kg N₂O h-1) is in reasonable agreement with the emission from the nitrification and denitrification reactors: the measurements were done for 2 chambers of a total number of 24 in the entire plants. The total N₂O emissions to air from these two chambers was 55 \pm 28 g N₂O-N h⁻¹ (standard dev), which amounts to 86 \pm 44 g N₂O h⁻¹. From the 24 reaction chambers (24 NIT and 24 DEN) we should thus expect 1.04 \pm 0.5 kg N₂O h⁻¹, which shows that the emissions from the nitrification and denitrification reactors as measured inside the plants can account for allthe N₂O measured in the chimney.

For CO₂, we also find that the emissions measured from NIT+DEN (avg 56 kg CO2 h-1 for two chambers, stdev= 17) can account for most of the CO₂ emission measured in the chimney: for 24 chambers we get an estimated emission of 672 ± 204 kg CO₂ h-1.

In contrast, the emissions of CH₄ from the nitrification and denitrification reactors added up to the entire plants (i.e. from all 24 reactor chambers) is much lower than the emissions from the entire plant. The emission from two chambers were 68.7 g CH₄ h (stdev = 35), which adds up to 824 \pm 204 g CH₄ h-1, which is only 30 % of that measured in the chimney. There is evidently another strong source of CH4 in the plant.

Emission of N₂O-N as % of total N removal:

The average rate of N-removal in the entire VEAS plant is 220 kg N h⁻¹ (stdev=95). The average rate of N₂O emission through the chimney is 0.46 kg N₂O-N h⁻¹, which is 0.2 % of the nitrogen removal. If we include the N₂O in the exit water from DEN (56% of direct emissions from NIT+DEN, Fig 6), the emission of N₂O-N increase to ~0,3% of N-removal. The fate of the N₂O in the exit water is uncertain however. In theory, a significant fraction of the N₂O in the exit water can be reduced en route from DEN to the bottom of the fjord. This is in fact quite plausible considering the residence time in the transport tube compared to that in the denitrification reactor: the average residence time in the denitrification reactor is only 0,2 h, but the transport of the water to its exit at the bottom of the fiord takes 0.3-1.2 h. It appears likely that a significant fraction of the N₂O is reduced during transport to the fiord.

Identification of operational conditions that enhance N₂O emissions:

The results for single dates (Appendix 2) indicate that low airflow through the nitrification reactor results in high N_2O production in this compartment, primarily as N2O transport with exit water to the denitrification tank (not as higher emission to the atmosphere). The results for low methanol dosage to the denitrificaton tank are variable. More systematic investigations by deliberate change of operational conditions are needed to identify operations that may systematically enhance or reduce emissions. The importance of management on N_2O emissions was underscored in a recent literature study by Westling (2011), who found that the emissions of N_2O -N as a fraction of the N-removal varied grossly between treatment plants.

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Appendix: primary data.

Appendix 1: Primary data on N2O.

Appendix 2: Calculated N₂O flows and emissions at each point in DEN and NIT reactors Hall 7 (see Fig 3 for codes). The last three columns are 1) total N₂O output (emission from NIT+ DEN and flow with exit water from DEN) 2) total N removal in DEN+NIT (i.e. nitrogen removed through nitrification and denitrification, estimated from chemical determination of total N in water in and water out), and 3) the N₂O-N output as % of N-removal

Appendix 3: primary CH4 data, Hall 7

Appendix 4: Primary CO2-data Hall 7

Appendix 5: primary data Chimney.

Appendix 6: Calculated emissions based on chimney concentrations and flow

Appendix 7: operational descriptions at the time of sampling/emission measurements (in Norwegian).

Appendix table 1. Primary data N₂O.

Pimary data N2O

date	1 SANDFAN G	3 SED	5 NIT emissio n	6 NIT exit- water	7 DEN emission	8 DEN exit- water	9 luft hall	Flow 5 (air flow)	Flow 7 (air flow)	Flow 4 (prosess air)	Flow 6 (water flow)	temp, water (oC)	primær betingelse	sekundær betingelse
date	ppm N2O	ppm N2O headsp ace	ppm N2O	ppm N2O headspac e	ppm N2O	ppm N2O headspac e	ppm N2O	m3/h	m3/h	m3/h	l/s	°C		
2.2.		8,76	33,20	21,60	1,76	2,64	1,85	2410	1220	2150	210	8,8	tykt vann	normal
8.2.		2,76	32,34	28,04	0,92	1,06	0,89	2350	992	1885	171	7,9	før vask	normal
11.2.		3,41	13,73	23,40	1,74	4,27	2,73	1980	1120	1810	200	7,8	etter vask	normal
15.2.		2,90	15,71	30,19	2,11	2,58	2,28	2540	1030	991	261	7,4	lav metanol	avvik
15.2.		2,83	17,06	32,95	2,14	2,57	2,40	2540	1030	991	261	7,4	lav metanol	avvik
15.2.		1,95	26,33	31,74	1,29	1,77	1,34	2650	1020	1800	171	7,5	nok metanol	normal
15.2.		1,87	19,73	31,27	1,28	1,72	1,33	2650	1020	1800	171	7,5	nok metanol	normal
18.2.		4,33	47,97	40,01	1,83	2,30	1,69	2550	1140	1108	201	7,7	lav luft	avvik
18.2.		4,88	32,50	32,65	2,37	2,98	2,23	2460	1140	1798	218	7,7	nok luft	normal
18.2.			30,66					2460	1140	1798	218	7,7	nok luft	normal
18.2.			33,80					2460	1140	1798	218	7,7	nok luft	normal
4.4.		0,94	3,50	3,49	1,00	4,16	0,61	2564	1043	1713	473	6	tynt vann	normal
4.4.		0,95	3,57	3,46	1,01	4,45	0,62	2564	1043	1713	473	6	tynt vann	normal
7.4.		1,52	3,66	na	0,92	3,03	0,73	2722	1114	1410	502	6,1	tynt vann	normal
7.4.		na	3,71	3,94	0,94	3,26	0,72	2722	1114	1410	502	6,1	tynt vann	normal
7.4.		1,40	3,75	3,95	0,98	3,20	0,72	2722	1114	1410	502	6,1	tynt vann	normal
12.5.	0,73	4,67	16,15	12,08	1,54	4,21	1,08	2780	1150	1780	295	12,1	før vask	normal
12.5.	0,71	4,74	16,12	12,89	1,52	4,36	1,11	2780	1150	1780	295	12,1	før vask	normal
13.5.	1,78	3,81	23,57	14,83	1,99	5,71	1,64	2720	1060	1790	305	12,1	etter vask	normal
13.5.	1,74	3,93	23,59		2,00	5,63	1,79	2720	1060	1790	305	12,1	etter vask	normal
1.6.	3,01	3,18	15,43	10,75	2,83	8,65	1,45	2670	1100	1660	319	12,2	nok metanol	normal
1.6.	2,95	3,56	15,22	10,60	2,87	7,96	1,51	2670	1100	1660	319	12,2	nok metanol	normal
1.6.	1,66	3,21	17,29	11,84	2,55	47,10	1,19	2730	1040	1630	313	12,2	lav metanol	avvik
1.6.	1,73	3,28	17,10	11,80	5,32	45,72	1,21	2730	1040	1630	313	12,2	lav metanol	avvik
6.6.	2,62	3,59	15,74	13,65	2,12	17,90	1,12	2660	1130	1725	259	13,2	nok luft	normal
6.6.	2,77	2,87	15,56	13,26	1,97	17,71	1,08	2660	1130	1725	259	13,2	nok luft	normal
6.6.	2,69	3,44	16,36	13,43	2,27	17,63	1,00	2660	1130	1725	259	13,2	nok luft	normal
6.6.	1,16	1,80	21,21	25,15	4,86	39,49	1,04	2300	1140	1160	235	13,2	lav luft	avvik
6.6.	1,16	1,86	20,69	24,49	4,90	39,17	1,05	2300	1140	1160	235	13,2	lav luft	avvik
6.6.	1,17	1,76	20,70	24,37	4,82	38,98	1,22	2300	1140	1160	235	13,2	lav luft	avvik

date	Flow 6 (water flow)	temp, water (oC)	notes on conditions	1 SED liquid inflow	3 SED liquid outflow	5 NIT emis- sion	6 NIT liquid outflow	7 DEN emis- sion	8 DEN liquid outflow	tot N2O out (5+7+8)	tot N- removal	% N2O - N
date	l/s	°C		g N2O- N/h	g N2O- N/h	g N2O-N/h	g N2O- N/h	g N2O- N/h	g N2O- N/h	g N2O- N/h	g N/h	%
2.2.	210	8,8	High TOC		12,36	92,65	32,88	-0,13	2,57	95,09	30540	0,30
8.2.	171	7,9			2,95	88,06	35,86	0,03	0,73	88,82	17450	0,50
11.2.	200	7,8			2,87	31,12	33,30	-1,30	4,17	34,00	22035	0,14
15.2.	261	7,4	Methanol low		3,23	42,39	57,45	-0,20	2,58	44,77	23103	0,18
15.2.	261	7,4	Methanol low		2,96	46,14	62,82	-0,31	2,43	48,26	23103	0,20
15.2.	171	7,5			1,57	79,95	40,35	-0,06	1,33	81,22	15675	0,50
15.2.	171	7,5			1,47	59,61	39,75	-0,06	1,27	60,82	15675	0,37
18.2.	201	7,7	Air low		5,18	139,68	59,78	0,18	2,07	141,93	16678	0,84
18.2.	218	7,7			6,03	91,43	52,12	0,19	2,87	94,49	35133	0,26
18.2.	218	7,7				87,88						
18.2.	218	7,7				96,87						
4.4.	473	6	low TOC		2,15	9,84	11,34	0,47	13,76	24,06	11478	0,19
4.4.	473	6	low TOC		2,17	10,06	11,21	0,48	14,76	25,30	11478	0,20
7.4.	502	6,1	low TOC		4,24	10,47		0,24			12553	
7.4.	502	6,1	low TOC			10,67	13,52	0,29	10,92	21,88	12553	0,15
7.4.	502	6,1	low TOC		3,80	10,78	13,55	0,33	10,67	21,78	12553	0,15
12.5.	295	12,1		0,27	9,13	51,05	25,76	0,61	8,09	59,75	25390	0,23
12.5.	295	12,1		0,19	9,25	50,91	27,54	0,55	8,39	59,85	25390	0,23
13.5.	305	12,1		1,99	6,70	72,90	32,30	0,42	11,13	84,45	36813	0,22
13.5.	305	12,1		1,71	6,80	72,81		0,27	10,74	83,82	36813	0,22
1.6.	319	12,2		5,32	5,75	46,28	24,13	1,76	19,03	67,07	16018	0,40
1.6.	319	12,2		5,12	6,58	45,57	23,69	1,74	17,28	64,59	16018	0,39
1.6.	313	12,2	Methanol low	2,35	6,06	53,45	26,62	1,65	110,64	165,74	16018	1,02
1.6.	313	12,2	Methanol low	2,50	6,20	52,82	26,50	4,98	107,33	165,13	16018	1,02
6.6.	259	13,2		3,94	5,84	47,55	25,68	1,32	34,07	82,94	26800	0,30
6.6.	259	13,2		4,26	4,46	47,03	24,95	1,16	33,72	81,92	26800	0,30
6.6.	259	13,2		4,20	5,67	49,61	25,37	1,67	33,66	84,95	26800	0,31
6.6.	235	13,2	Air low	1,04	2,18	55,45	43,97	5,08	69,62	130,15	17233	0,74
6.6.	235	13,2	Air low	1,03	2,28	54,05	42,77	5,11	69,03	128,19	17233	0,73
6.6.	235	13,2	Air low	0,87	1,93	53,85	42,39	4,78	68,52	127,14	17233	0,72

Appendix 2.

Appendix 3. Primary CH₄ data (hall 7, DEN+NIT)

date	1 SANDFANG	3 SED	5 NIT emission	6 NIT exit-water	7 DEN emission	8 DEN exit- water	9 luft hall
	ppm CH4	ppm CH4	ppm CH4	ppm CH4	ppm CH4	ppm CH4	ppm CH4
2.2.		145,38	53,47	13,10	20,15	22,11	12,23
8.2.		144,10	39,13	9,20	16,26	13,35	6,24
11.2.		113,55	22,05	11,69	18,73	18,58	13,41
15.2.		127,89	27,59	12,08	17,43	17,99	10,74
15.2.		124,77	27,76	12,42	17,72	18,40	7,57
15.2.		147,36	27,31	9,68	15,73	17,92	7,52
15.2.		147,49	27,63	9,73	16,12	16,67	10,85
18.2.		123,29	41,20	10,73	12,96	19,33	9,07
18.2.		133,10	55,92	12,13	14,16	18,39	9,02
18.2.			55,43				
18.2.			56,21				
4.4.		23,50	12,69	5,14	5,86	6,42	3,78
4.4.		23,24	12,74	5,23	5,92	7,02	3,80
				mislykket			
7.4.		34,51	22,41	prøve	12,84	13,15	11,11
7 4		mislykket	22.00	12.00	10 10	12.07	11.01
7.4.		prøve	22,68	13,06	13,13	13,87	11,01
7.4.	60.02	30,60	22,94	13,15	13,41	13,57	10,87
12.5.	69,93	118,64	70,67	15,01	29,50	32,62	10,15
12.5.	69,39	120,90	/1,10	15,94	29,14	33,95	9,80
							2,28
13 5	7/ 32	1/11.08	75.02	17.86	30.65	27.10	12,35
13.5.	75 5/	154 66	7/ 69	17,00	30,05	25.80	12,50
1.6	46.89	53 33	39.90	13.12	15.03	14 48	8 92
1.6	42 79	68 48	39.40	12.46	15,03	13.61	8.81
1.6	34.28	56,98	35.92	11.80	14.62	15.81	7.66
1.6.	40.93	59,21	35.29	12,57	15.70	14.95	7.85
6.6	87.23	127.99	30.17	12.97	22.91	17.00	8.53
6.6.	94.60	95.67	29.73	13.88	20.32	17.06	7,53
6.6	88.66	120.65	31.29	13.29	22.38	17.07	8.11
6.6.	57.74	84.68	42.37	19.56 20.99 16.44		16.44	7,34
6.6.	60.02	109.66	41,16	19.68	21,70	16.03	7,24
6.6.	63,44	89,82	40,85	19,02	22,25	16,17	7,60

Appendix 4 Primary data CO₂, Hall 7

dato	1 SANDFANG	3 SED	5 NIT emission	6 NIT exit- water	7 DEN emission	8 DEN exit- water	9 luft hall
	ppm CO2	ppm CO2	ppm CO2	ppm CO2	ppm CO2	ppm CO2	ppm CO2
2.2.		3785	14315	9729	1997	9061	1834
8.2.		2863	12400	9677	1245	9062	935
11.2.		2777	8143	9269	1841	9412	1930
15.2.		2158	11086	11053	1659	9834	1516
15.2.		3306	13494	9741	2044	9873	1587
15.2.			12882				
15.2.			13385				
18.2.		3789	10213	10683	2390	9968	1823
18.2.		3835	10313	10874	2431	10176	1916
18.2.		4078	12166	11172	1653	8339	1109
18.2.		2258	11876	10948	1618	7809	1188
4.4.		1441	8070	6633	1343	6426	882
4.4.		1373	8407	6499	1320	7083	987
7.4.		2303	7058	mislykket prøve	1266	6544	1006
7.4.		mislykket prøve	7108	7224	1313	7213	936
7.4.		2125	7147	7291	1338	7511	890
12.5.	4010	4036	16503	11231	2110	11415	1234
12.5.	4378	4032	16520	12175	2046	11637	1115
							464
							513
13.5.	3054	3898	17020	12569	2216	11848	1530
13.5.	2776	4055	17000		2335	11193	1579
1.6.	4211	4382	17027	11116	1950	10907	1401
1.6.	4244	4916	16860	10653	2070	10114	1744
1.6.	2518	4141	14656	11284	1646	11444	1733
1.6.	2725	4225	14385	11433	3860	10919	1346
6.6.	8920	5476	13328	11809	1809	12650	1062
6.6.	9648	4131	13168	11293	1581	12594	940
6.6.	9340	5143	14007	11440	1830	11961	934
6.6.	4213	4638	11817	15651	2224	11895	974
6.6.	4804	5138	11400	15313	2166	12178	1036
6.6.	4261	4660	11397	15134	2225	11950	1338

dato	klokkeslett		prøvenr	CO2	N2O	CH4
				ppm	Ppm	ppm
9.1.11 13:30	13:00	serie 1	1	1558	0,936	11,72
9.1.11 13:30			2	1624	0,925	12,12
9.1.11 13:30			3	1560	0,938	11,99
9.1.11 13:30			4	1524	0,915	11,77
9.1.11 13:30			5	1599	0,928	11,87
9.1.11 13:30			6	1578	0,947	11,83
06.09.11 10:00	10:00		7	1606	0,772	12,17
06.09.11 10:00			8	1655	0,750	12,05
06.09.11 10:00			9	1544	0,756	11,95
06.09.11 10:00			10	1664	0,759	11,93
06.09.11 10:00			11	1670	0,778	12,35
06.09.11 10:00			12	1610	0,760	12,29
06.09.11 10:00			13	1638	0,772	12,52
06.09.11 10:00			14	1607	0,763	12,06
06.09.11 10:00			15	1557	0,767	12,11
21.09.11 10:00	10:00	serie 2	1	1420	0,974	10,95
21.09.11 10:00			2	1422	0,964	11,70
21.09.11 10:00			3	1439	0,985	11,27
21.09.11 15:25	15:25		5	1403	1,292	13,06
21.09.11 15:25			6	1415	1,307	13,37
21.09.11 15:25			7	1441	1,328	12,92
27.09.11 9:40	09:40		9	1945	1,984	20,10
27.09.11 9:40			10	2003	2,028	20,32
27.09.11 9:40			11	1889	1,948	19,18
27.09.11 13:05	13:05		13	1977	2,308	17,01
27.09.11 13:05			14	1997	2,343	16,88
27.09.11 13:05			15	1974	2,299	17,10
27.09.11 15:30	15:30		17	1881	2,699	16,75
27.09.11 15:30			18	1885	2,713	16,17
27.09.11 15:30			19	1879	2,733	15,83
27.09.11 18:20	18:20		21	2073	3,347	19,23
27.09.11 18:20			22	2063	3,337	18,92
27.09.11 18:20			23	1994	3,259	19,70

Appendix 5 Primary data, Chimney

Appendix 6. Estimated emissions based on air flow and gas concentrations in chimney (ambient concentrations of the three gases subtracted)

	emissions, kg h-1			
date and time	CO2	N2O-N	CH4	N2O (whole molecule)
01.09.2011	810.08	0.26	2.40	0.41
01.09.2011	854,41	0,26	2,50	0,40
01.09.2011	811,15	0,26	2,47	0,41
01.09.2011	786,88	0,25	2,41	0,39
01.09.2011	837,87	0,26	2,44	0,40
01.09.2011	823,25	0,26	2,43	0,42
06.09.2011	731,39	0,16	2,18	0,26
06.09.2011	760,01	0,16	2,16	0,24
06.09.2011	694,94	0,16	2,13	0,25
06.09.2011	765,54	0,16	2,13	0,25
06.09.2011	768,60	0,17	2,22	0,26
06.09.2011	733,54	0,16	2,21	0,25
06.09.2011	750,15	0,16	2,26	0,26
06.09.2011	732,16	0,16	2,16	0,25
06.09.2011	702,52	0,16	2,17	0,25
21.09.2011	582,73	0,23	1,80	0,35
21.09.2011	584,12	0,22	1,95	0,35
21.09.2011	593,66	0,23	1,86	0,36
21.09.2011	552,25	0,33	2,14	0,51
21.09.2011	558,36	0,33	2,20	0,52
21.09.2011	572,37	0,34	2,12	0,53
27.09.2011	880,38	0,59	3,70	0,93
27.09.2011	912,38	0,61	3,75	0,95
27.09.2011	849,01	0,58	3,51	0,91
27.09.2011	1047,73	0,82	3,57	1,29
27.09.2011	1060,56	0,84	3,54	1,32
27.09.2011	1045,54	0,82	3,60	1,29
27.09.2011	1004,78	1,01	3,58	1,58
27.09.2011	1007,58	1,01	3,44	1,59
27.09.2011	1003,96	1,02	3,35	1,60
27.09.2011	913,38	1,04	3,38	1,63
27.09.2011	908,11	1,03	3,32	1,62
27.09.2011	871,57	1,01	3,47	1,58

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Runde		1	1	1	1	1	1	1	2	2	3	3	4	4	4	4
SerieID:		А	с	D	E	F	G,M	н, к	B, N	O, P, R	S, T	U,W	X,Y	Ø,Å	AA, BB, EE	CC, DD, FF
Dato:		02.feb	08.feb	11.feb	18.feb	18.feb	16.feb	15.feb	04.apr	07.apr	12.mai	13.mai	01.jun	01.jun	06.jun	06.jun
Tilstand		Vann	Vask	Vask	Oksygen	Oksygen	Metanol	Metanol	Vann	Vann	Vask	Vask	Metanol	Metanol	Oksygen	Oksygen
Beskrivelse		tykt vann	Rett før vask	Rett etter vask	Lav lufttilførsel	Tilstrekkelig lufttilførsel	Lav metanoldos ering	vanlig metanoldos ering	snøsmelting, tynt vann	snøsmelting, tynt vann	Rett før vask	Rett etter vask	Vanlig metanoldos ering	Lav metanoldos ering	Lav lufttilførsel	Tilstrekkelig lufttilførsel
Kriterier		vannmengde 2000 I/s ammonium inn over 20 mg/l	se tabell vedlegg	se tabell vedlegg	under 5 mg/l O2 i DEN-tank	over 7 mg/l O2 i DEN- tank	nitrat ut over 3 mg/l	nitrat ut under 1,5 mg/l	vannmengde 7000 l/s ammonium inn under 5 mg/l	vannmengde 7000 l/s ammonium inn under 5 mg/l	se tabell vedlegg	se tabell vedlegg	nitrat ut under 1,5 mg/I	nitrat ut over 3 mg/l	under 5 mg/l O2 i DEN- tank	over 7 mg/l O2 i DEN- tank
Ammonium inn NIT 8	mg/l	25,2	26,9	22,4	24,8	24,8	24	24,8	8,9	6,4	17,7	18,6	13,1	12,4	19,3	19,8
Ammonium ut NIT 8	mg/l	11,6	19,8	3,1	5,35	5,6	4,6	2,8	0,7	0,9	7,6	6	1,25	0,83	7,6	10,1
рН		7,17	7,31				7,14		7,34	7,16						
nitrat inn sed 4	mg/l	1,62	2,43	2,18	0,97	0,98	1,05	0,99	14,18	13,5	0,82	0,94	1,13	1,2	1,58	1,58
nitrat inn, DEN- tank 8	mg/l	13,1	14,2	13,7	15,6	13,9	14,5	18,3	8,3	7,7	11,8	12,8	11,7	10,3	12,1	11,6
nitrat ut, DEN 8	mg/l	0,8	1,4	2,1	1	1,6	3,9	1,4	3,4	2,2	1,6	1,7	1	4	0,8	0,8
metanol-dosering DEN 7	l/h	96	61	84	101	100	82	92	122	131	120	135	58	40	94	79
metanol-dosering DEN 8	l/h	58	47	55	61	58	46	64	98	105	68	74	78	54	63	55
turbiditet, SED 7	FTU	25,6	20	25	45	42	32	17	14	15	22	22	12	18	12	13
oksygen DEN-tank 8	mg/l	9,9		9	9,4	9,3	9,8	10,6	8,9	8,4	8,2	8,4	8,9	8,9	8,5	8,5
orto-P DEN-tank 8	mg/l	0,27	0,22	0,25	0,24	0,26	2	0,3	0,07	0,1	0,55	0,47	0,01	0,01	0,05	0,05
vann-mengde inn, MTU	l/s	1990	1550	1800	1925	2075	1745	1840	5722	6916	2684	2660	3322	4350	3140	2530
vann-mengdeDEN 71	l/s	104	85	105	98	108	130	86	219	251	147	153	168	157	130	118
vann-mengde DEN 74	l/s	106	86	95	102	110	131	86	218	251	146	152	151	156	129	117
luft-mengde NIT 71	m³/h	1067	944	906	217	900	991	900	855	708	893	895	830	815	862	208
luft-mengde NIT 74	m³/h	1086	941	904	891	898	i vask	900	858	702	890	898	831	816	863	950
vann-mengde SED7	l/s	494	325	328	338	372	438	308	721	853	568	584	498	491	525	488
vann-mengde SED 8	l/s	453	306	324	335	357	441	285	731	844	536	571	495	530	524	480
slam SED 7	I/s	9,27	8,7	9,17	9,81	10,97	10,29	7,03	6,47	4,13	10,94	7,75	11,14	11,14	11,17	?

Runde	SerielD:	Dato:	Tilstand	Beskrivelse	NIT 71	NIT 74	DEN 71	DEN 74
1	С	08.feb	Vask	Rett før vask	24	24	24	24
1	D	11.feb	Vask	Rett etter vask	0,5	0	2,5	3,5
3	S, T	12.mai	Vask	Rett før vask	12	14	6	20
3	U,W	13.mai	Vask	Rett etter vask	3,5	1	1,3	2