MEASUREMENT OF GREENHOUSE GASES (CH_4, N_2O, CO_2) IN MUNICIPAL WASTEWATER TREATMENT PLANTS

Introduction

Wastewater treatment plants can emit relevant amounts of greenhouse gases. Process emissions of methane (CH_4) and nitrous oxide (N_2O) are often the most important greenhouse gas sources in wastewater treatment plants. CH_4 is mainly produced and emitted through leakage in anaerobic process stages (anaerobic sludge treatment). Therefore, monitoring of methane emission requires monitoring approaches for diffuse emission sources, such as the tracer gas method or the drone flux measurement. N_2O originates from biological nitrogen removal in the biological treatment and is largely released to the atmosphere during aeration of the sewage. Hence, methods to monitor emissions from point sources (flux hood method, e.g Figure 1) are optimal for quantification. Typically, a small share (0-2%) of the treated nitrogen is emitted as N_2O. In a few cases, emission factors of up to 10% have been reported. Due to the high greenhouse gas potential of N_2O (273 gCO_2-e/gN_2O for a 100-year timescale), small amounts of N_2O have a substantial impact on the carbon footprint of wastewater treatment. In Switzerland, N_2O from wastewater treatment plants cause roughly 1% of the countrywide greenhouse emissions.

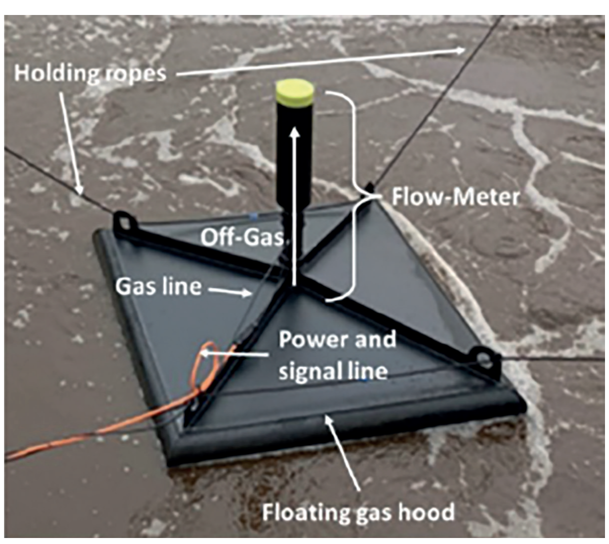

Figure 1: off-gas collection and flow measurements on a full-scale wastewater treatment plant in Switzerland (upwater, 2023)

N_2O is produced through multiple pathways in nitrification and denitrification. During mainstream wastewater treatment, N_2O is primarily produced biotically (Figure 2) and to a minor extent abiotically. N_2O formation is rather complex since multiple organisms are known to possess formation pathways. Ammonium oxidizing bacteria (AOB) are known to perform at least two pathways for N_2O production. In heterotrophic denitrification, N_2O is an obligate by-product but is fully degraded given that process conditions are set correctly. Heterotrophic denitrification is therefore an important and the only biological N_2O sink in

Municipal wastewater treatment plant

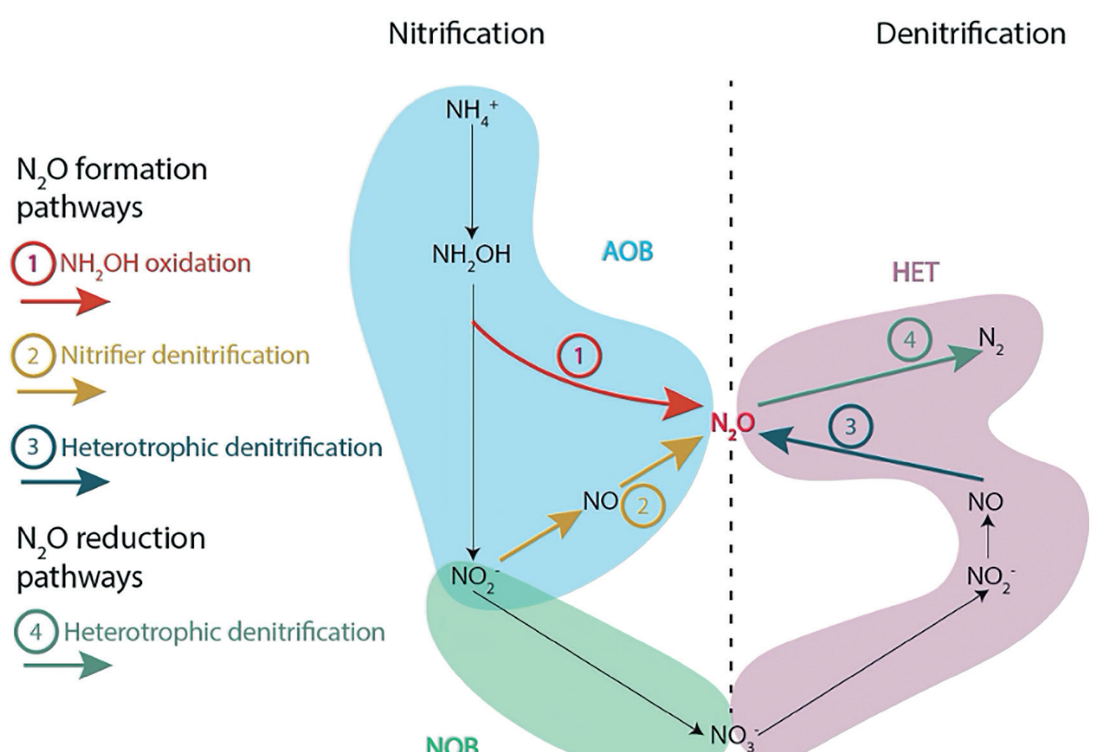

Figure 2: N_2O formation during biological nitrogen removal in the wastewater treatment (Gruber 2021)

wastewater treatment. Other minimization strategies involve optimization of the aeration strategy in the biological treatment and an adapted nitrogen load management.

N_2O emissions typically exhibit large diurnal and seasonal variations. Hence, long-term on-line monitoring approaches are required to properly estimate the N_2O emission factor und test mitigation strategies. Off-gas monitoring systems are most suitable to measure the emissions given the low maintenance costs and the high spatial and temporal resolution. Additionally, monitoring of process emissions allows quantification of the oxygen transfer in biological treatment process enabling substantial process optimization and energy savings. However, off-gas monitoring is generally not established on wastewater treatment plants, due to the missing commercial suppliers and the relatively high investment costs.

In Switzerland, a research project on N_2O emissions from wastewater treatment plants led by Eawag (Swiss Federal Institute of Aquatic Science and Technology) resulted in a versatile monitoring solution and a Spin-off company (upwater AG) offering off-gas monitoring systems and a monitoring campaign service. The technology developed has been successfully applied in 20 one-year monitoring campaigns. Here, the monitoring systems and results from a monitoring campaign are presented.

Monitoring system

The monitoring system developed by Eawag and upwater ("Notos") consist of floating gas hoods for off-gas sample collection equipped with a flow measurement (Figure 1) and a central monitoring station for concentration measurement (Figure 3). The emissions are calculated using the following formula:

$$L_{N_2O-N} = c_{N_2O-N,offgas} \cdot Q_{Air} = \frac{N_2O_{measured}}{10^6} \cdot Q_{Air} \cdot \frac{p_N}{R * T_N} \cdot M_N \qquad (1)$$

$L_{N_2O\text{-}N}$	[gN/h]	Emitted N_2O load per time interval
$C_{N_2O\text{-}N,offgas}$	[gN/Nm³]	N_2O concentration in the off-gas
Q_{Air}	[Nm³/h]	Measured air flow rate in the aeration tank, in standard cubic meters per hour
N_2O measured	[ppmv]	measured N_2O concentration in the off-gas
p_N	[Pa]	standard pressure: 1013.25 hPa
T_N	[K]	standard temperature: 298 K
R	[J/mole/K]	universal gas constant: 8.314 J/mole/K
M_N	[gN/mole]	molar mass of N_2O-N: 28 gN/mole

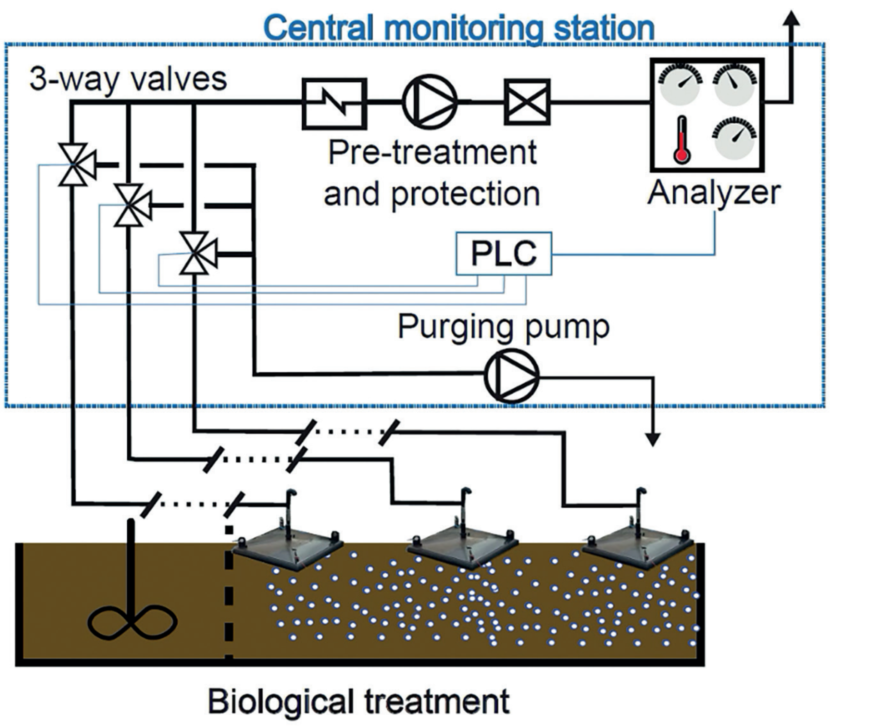

Figure 3: "Notos" monitoring system (Gruber 2021)

For concentration measurement, a NDIR gas analyzer is used for multiple sampling points. Fast response time and a low drift are important features of such a sensor. N_2O concentrations in full-scale monitoring campaigns are typically between 0 and 300 ppm. However, concentrations of up to 3000 ppm can be detected during high emission phases on some plants. A fully automatized multiplexing system using 3-way valves connected with up to 14 off-gas hoods provides high spatial resolution as well as automatic calibration of the system. The central monitoring station is equipped with a liquid removal system as a pre-treatment to protect the sensor. The continuous purging of the sample lines allows short measurement intervals (<1 min).

Gas Analyser

The gas analysis is carried out using NDIR technology (INFRA.sens®) in the spectral range of 3-5µm (Figure 4). The INFRA.sens® uses the absorption bands for methane at 3.4µm, for carbon dioxide at 4.3µm and for nitrous oxide at 4.5µm. The basic photometric setup is shown in Figure 5. The radiation source is a modulating black body radiator (IR-Source), which can be modulated in the frequency range of 1-10Hz. To achieve the highest possible resolution, a 250mm long sample cell is used, which is coated with a special gold layer. The gold layer has a high reflectivity and leads to a high signal level at the detector side. The IR detector is located on the opposite side and consists of 4 elements. Interference filters are used to filter out the gas-specific spectral components for the respective detectors. The Interference filters have a very narrow bandwidth and an efficient blocking grade. This results to a very high selectivity and negligible cross interference to other gas components. A reference measurement in a spectral region without absorption due to the gas concentration ensures long-term stable measurement results.

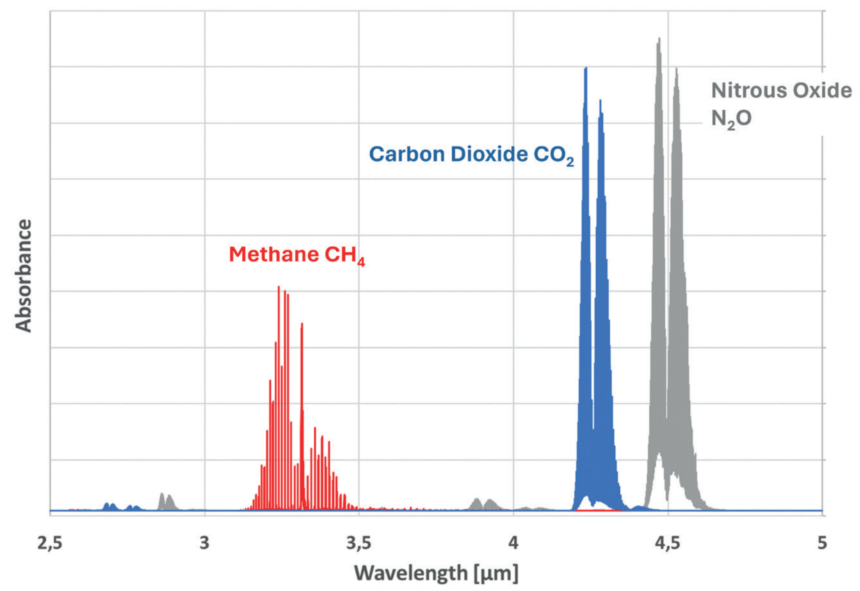

Figure 4 : Infrared Absorption Spectrum of Methane, Carbon dioxide and Nitrous oxide

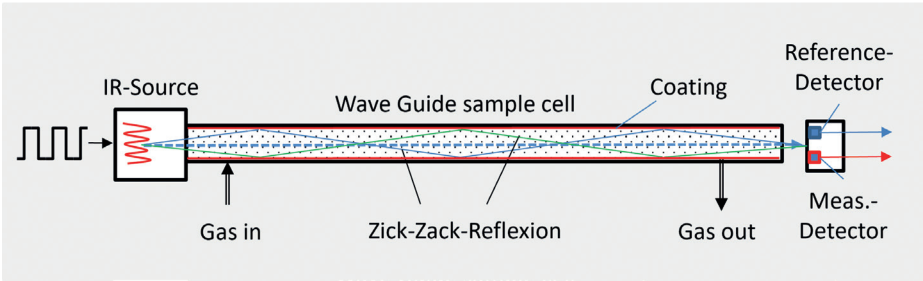

Figure 5 :Principal design of the INFRA.sens® gas sensor module

The complete signal processing takes place in an electronic evaluation unit (Base board), which is located below the optical bench as shown in Figure 6. The data transfer is managed by an RS232 Interface. CAN-Interface and MODBUS (option) are also available.

The sample cell is thermostatted at 50°C to prevent condensation inside the sample cell. Since the emitter and the detector are also heated by this thermostatisation, the temperature error of these components has also been eliminated. The entire setup is integrated in a sheet metal housing, which is insulated on the inside to block external temperature influences. The gas analyzer is specified for an ambient temperature of 5-45°C. The warm-up time is less than 45 minutes.

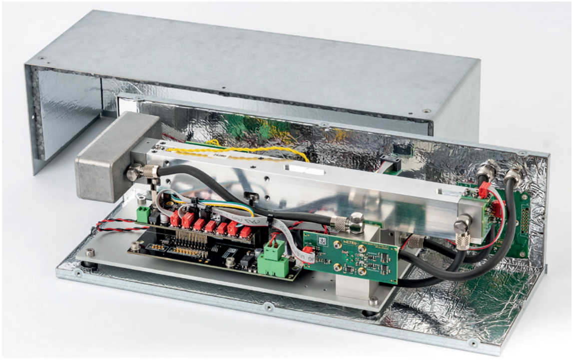

Figure 6: INFRA.sens® Module (CH_4, CO_2, N_2O and O_2) integrated into a sheet metal housing with temperature-controlled environment (Thermobox)

Oxygen Measurement

In addition, there is also an electrochemical (EC) oxygen sensor (galvanic fuel cell) in this setup to measure the oxygen concentration in the gas mixture. The O2.sens[D] has a range of 0-100Vol.% O_2 and is very selective for Oxygen, even in the presence of other gases at high concentrations. Compared to physical gas sensors the lifetime of electrochemical gas sensors is limited due to the chemical reactions within the sensor. The lifetime is measured in Vol.%·h. Typical sensor lifetime is >500.000Vol.%·h. In the presence of 10-20Vol.% oxygen the calculated lifetime is approx. 3-6 years. The O_2.sens[D] is able to communicate with the INFRA.sens electronics (Base board) via I²C interface. Compared to a standard millivolt data transfer the I²C interface is very rugged and less sensitive against electromagnetic interference (EMI).

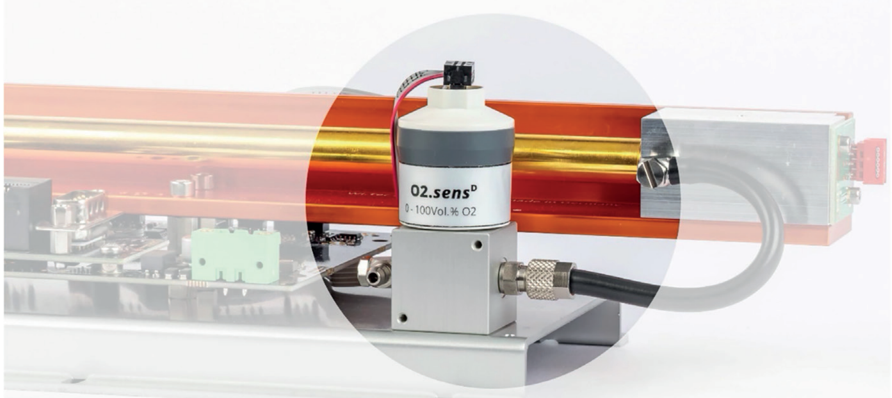

Figure 7. Electrochemical Oxygen gas sensor (O_2.sens[D]) integrated into a standard INFRA.sens® module.

General features

Table 1: Gas analysis specifications

Ranges	0-100ppm N_2O 0-500ppm N_2O 0-2000ppm N_2O 0-1000ppm CH_4 0-5Vol.% CO_2 0-20 Vol.% O_2
Gas flow	0.1-1.5 l/min.
Dimensions	318mmx120mmx75mm (INFRA.sens®) 345mmx125mmx103mm (Thermobox)
Weight	app. 720g
Lifetime	>40 000h (NDIR) >500.000Vol.%·h (EC)
Warm-up time	<1min. (initial) (full specification with heater after 60 minutes)
Response time t90	1.5s-15s (NDIR) <5s (EC)
Detection limit	<1ppm N_2O <10ppm CH_4 < 0.01 Vol.% CO_2 <0.1 Vol.% O_2
Linearity error	<1% F.S.
Supply voltage	15-30 VDC
Power consumption	<2W (with Heater < 30W)
Output signal	RS232, Modbus or CANbus
Operating temperature	5-45°C
Air pressure	300-1200 hPa (mbar)
Ambient Humidity	<95% rel. Humidity

Monitoring campaign

The strong seasonal and diurnal emission variation can be seen in a one-year monitoring campaign at a Swiss wastewater treatment plant (Figure 8). The short-term dynamics are strongly influenced by rain events which are indicated by temperature drops. Typically, rain events substantially decrease N_2O emissions due to dilution of the wastewater. The emissions reach their maximum during the strong wastewater temperature increase between spring and summer. The maximum concentration at this plant was 350 ppm. The emission peak phase can probably be linked to a change in the composition of the microbial community with strong impacts on the accumulation of nitrogen compounds leading to N_2O formation. Mitigation strategies at this plant mainly involve reduction of air flow in the biological treatment and optimization of denitrification. Thanks to the monitoring campaign substantial energy savings could be achieved by monitoring oxygen transfer and adapting the aeration system and strategy accordingly.

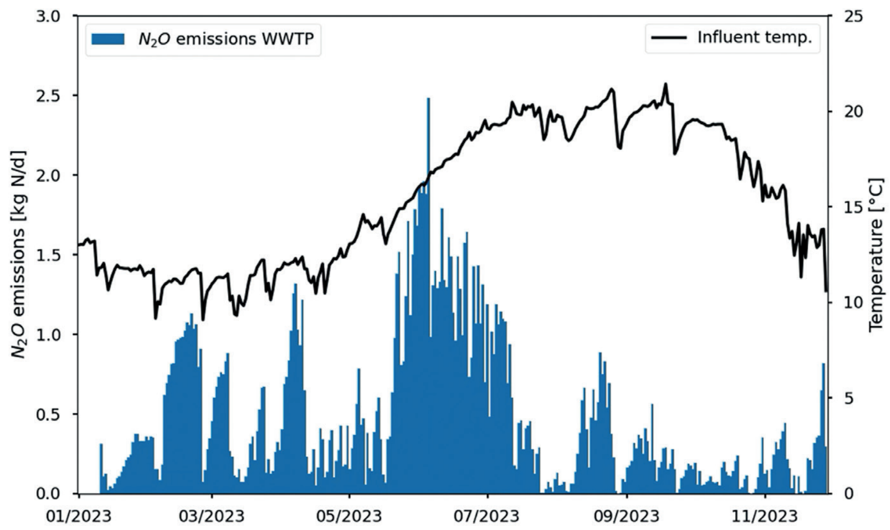

Figure 8: N_2O emissions and temperature during a one-year monitoring campaign on a Swiss wastewater treatment plant (updater 2024)

Conclusion

N_2O is an important source of greenhouse gases from wastewater treatment. Due to the substantial spatial and temporal variation of the emissions, long-term on-line monitoring approaches with a high spatial resolution is required for emission quantification and mitigation strategies. The "Notos" off-gas monitoring system has been demonstrated to be applicable in a wastewater treatment environment over long-term. The system is based on an accurate multi-channel NDIR gas analyser (INFRA.sens®) integrated into a fully automated monitoring system. The stability and accuracy of the NDIR technology used was impressively demonstrated in various series of measurements. Continuous use over a maintenance period of several months is therefore possible without any problems. In the future, wastewater treatment plants are expected to monitor N_2O emissions to reduce the carbon footprint and foster the full potential of off-gas monitoring systems for energy savings.

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Chlorine generation – a simple and reliable solution

Euro-Gas' GazCal Gas Generator provides a simple and effective solution for generating Chlorine (Cl2) gas. The GazCal Gas Generator overcomes the traditional difficulties associated with handling Chlorine gas cylinders, such as problematic accuracy and erratic shelf life.

The rugged, portable and battery-operated tool is designed for use in a wide range of industries, including the water treatment sector, where personnel face the challenges of testing and calibration. The GazCal comes in a robust and compact carrying case and allows for rapid testing and calibration with negligible warm-up time. This simple-to-use device can be operated by anyone, requiring only the necessary PPM level to be set via the unit's dial-up digital display.

The GazCal generates Cl2 levels ranging from 0.5 – 20 ppm and is also suitable for use as a surrogate for the cross-calibration of O3, ClO2, COCl2, HF and F2. Its design overcomes the problem of short shelf life. The cell life is only used up when the unit is in operation, while traditional cylinders can simply die out before 6 months. The generator can last for up to a decade, often without the need to change the cell and requiring only a yearly recertification of calibration.

The GazCal cell can operate for up to 500 parts per million (ppm) hours, which is equivalent to a continuous usage of 100 hours at a concentration level of 5ppm. This extended lifespan allows for a minimum of 400 calibrations to be conducted. The device includes a cell life indicator that displays the remaining life of the generating cell, enabling operators to plan ahead. Installing a new generating cell is a simple process once the current cell has been depleted. Although the GazCal generator may have a higher initial cost compared to a small cylinder, it is a more cost-effective option in the long run.

Also, unlike gas cylinders, which only attain one specific concentration per cylinder purchased, the GazCal is entirely adjustable between the 0.5ppm to 20.0ppm range and in 0.1ppm steps. The GazCal produces many different concentration levels from one device. In addition, low concentrations of Cl2 are efficiently produced with the GazCal, even 1ppm and 2ppm levels, whereas it is extremely problematic to achieve cylinder stability at low concentration levels.

More information online: ilmt.co/PL/67K6

For More Info, email: 60049pr@reply-direct.com