

# Development of an extended ASM3 model for predicting N<sub>2</sub>O emissions in a full-scale wastewater treatment plant

K. Blomberg, P. Kosse, A. Mikola, A. Kuokkanen, T. Fred, M. Heinonen, M. Mulas, M. Lübken, M. Wichern, R. Vahala

An Activated Sludge Model #3 (ASM3)-based pseudo-mechanistic model describing nitrous oxide (N<sub>2</sub>O) production was created in this work in order to provide more insight into the dynamics of N<sub>2</sub>O production, consumption and emissions at a full-scale wastewater treatment plant (WWTP). N<sub>2</sub>O emissions at the studied WWTP are monitored plant-wide with FT-IR analyser. Additionally, the stripping of N<sub>2</sub>O was

included by applying a K<sub>L</sub>a based approach, which has not been widely considered before. The objective was to extend the existing ASM3-based model of the plant and assess how well the full-scale emissions could be predicted with the selected model. Validity and applicability were tested by comparison of simulation results with comprehensive online data.

The ASM3-based model in this study was created stepwise

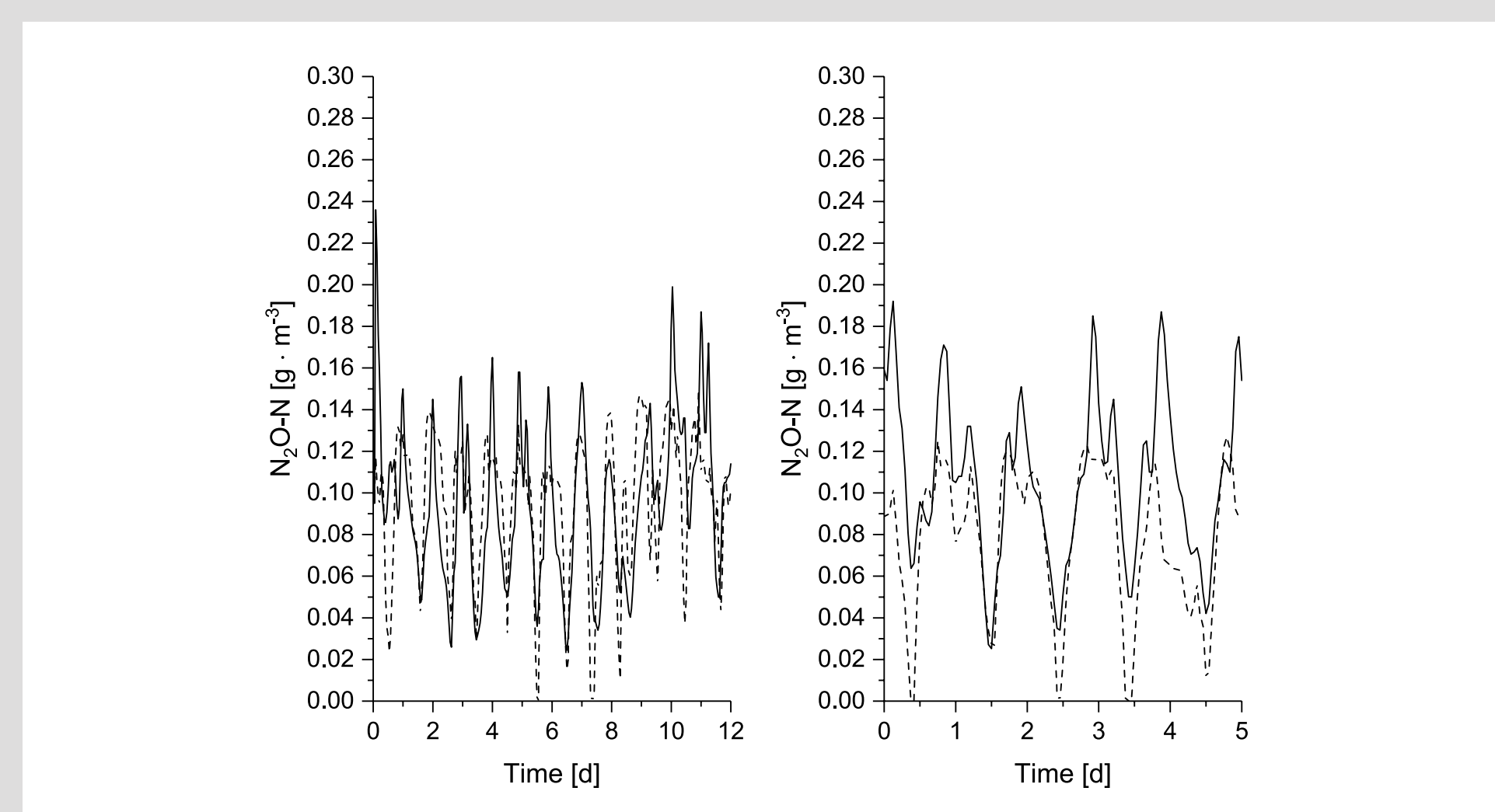
1. Extension of the original nitrogen conversion processes in ASM3 into two-step nitrification and two-step denitrification reactions
2. Extension of denitrification into four-step denitrification
3. Implementation of the hydroxylamine (NH<sub>2</sub>OH) pathway
4. Implementation of N<sub>2</sub>O stripping by applying a K<sub>L</sub>a based approach

The model was calibrated and validated using FT-IR data from the Viikinmäki WWTP (Fig. 1), which is the largest treatment facility in the Nordic countries with its population equivalent of 1 100 000.

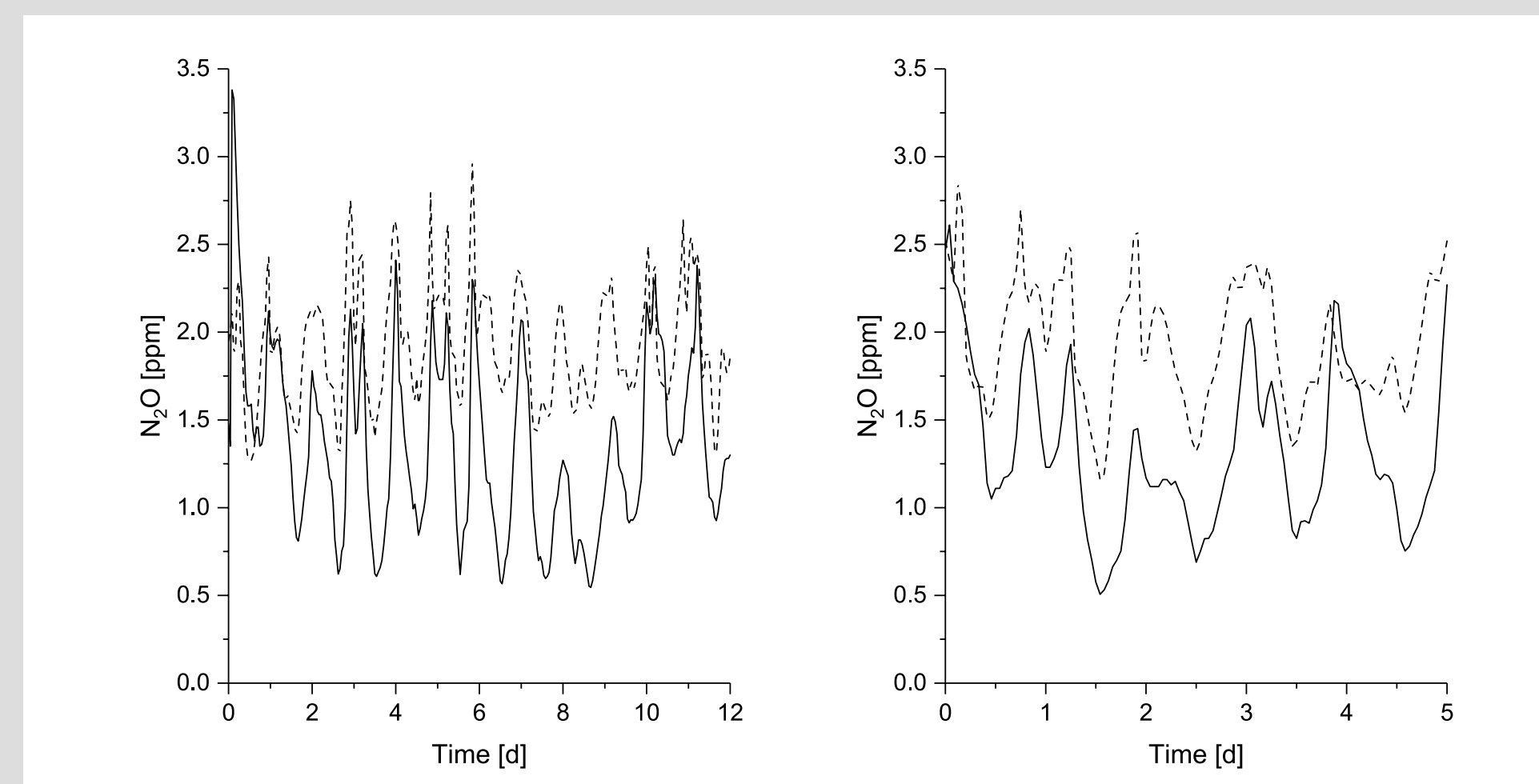


**Fig. 1** Continuous emission monitoring at the bedrock wastewater treatment plant Helsinki Viikinmäki, Finland. Picture shows the denitrifying post-filtration unit. The underground area covers an area of 14 hectares, the above ground 3 hectares. Source: Sanna Alku, Helsinki Regions Environmental Services Authority (HSY).

The fully extended ASM3-based model was able to capture the measured N<sub>2</sub>O variation in both liquid and gaseous phases at the plant (Fig. 2 & Fig. 3). The average liquid phase N<sub>2</sub>O concentration in the fourth aerated Zone was 0.04 g N<sub>2</sub>O-N m<sup>-3</sup> and 0.03 g N<sub>2</sub>O-N m<sup>-3</sup> and in the sixth aerated Zone 0.09 g N<sub>2</sub>O-N m<sup>-3</sup> and 0.11 g N<sub>2</sub>O-N m<sup>-3</sup> during the calibration and validation period, respectively.



**Fig. 2** Modelled (dashed line) and measured (solid line) N<sub>2</sub>O-N concentration in the liquid in the sixth continuously aerated zone during calibration (left) and validation (right).



**Fig. 3** Modelled (dashed line) and measured (solid line) N<sub>2</sub>O emissions during calibration (left) and validation (right).

The results show that an ASM3-based model can be successfully extended and applied in modelling N<sub>2</sub>O production at a full-scale WWTP as the model was able to produce not only the measured N<sub>2</sub>O production but also the comprehensive online monitoring data collected at the plant. This work also introduces the N<sub>2</sub>O stripping into the process dynamics, which had been lacking from the previous suggested models.



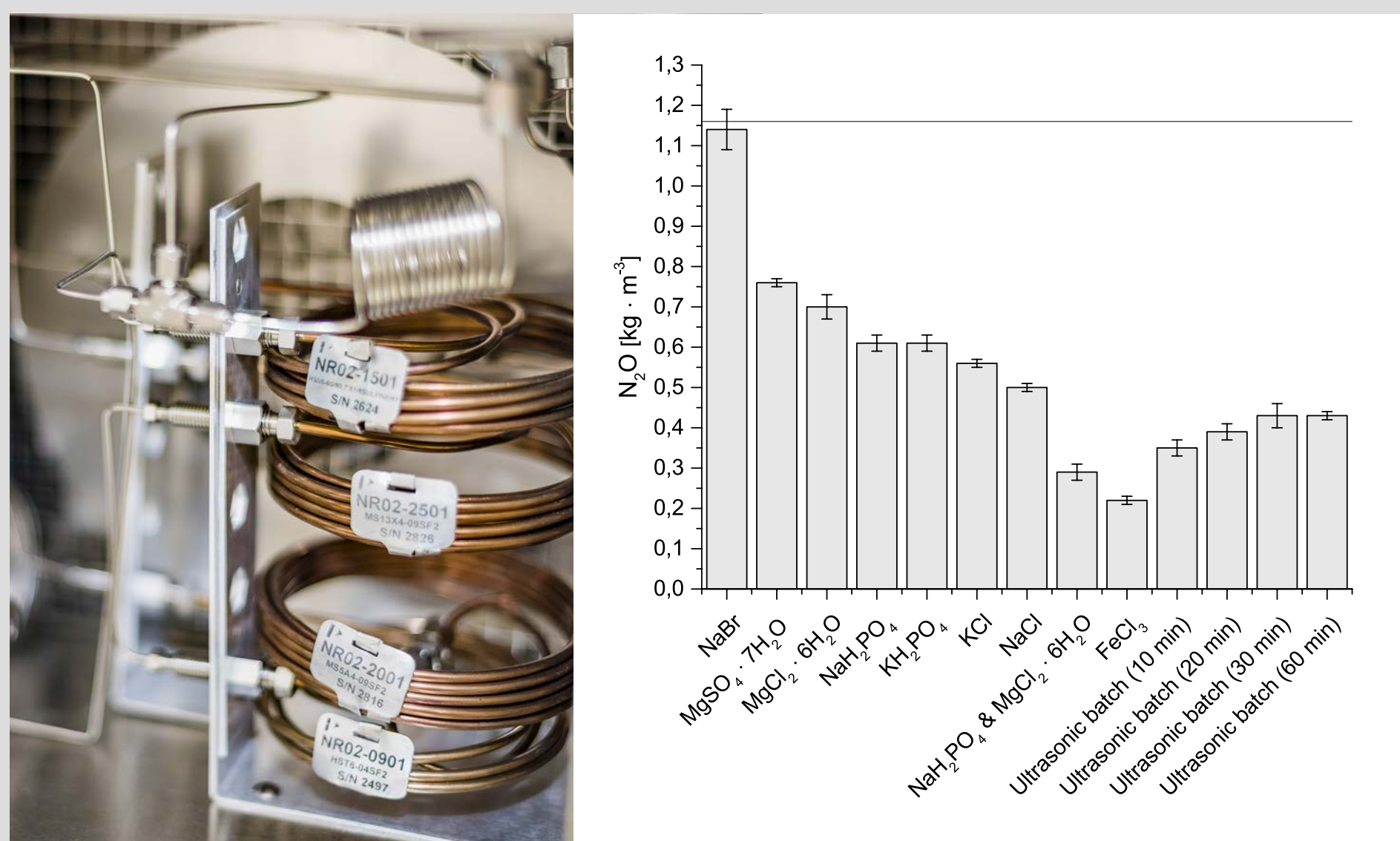
# Quantification of nitrous oxide in wastewater based on salt-induced stripping

P. Kosse, M. Lübken, T. C. Schmidt, M. Wichern

Monitoring nitrous oxide ( $N_2O$ ) emissions from wastewater treatment plants has attracted much attention in recent years demanding accurate and rapid quantification methods. A salt-assisted methodology is proposed by which  $N_2O$  is chemically stripped out from wastewater and quantified by gas chromatography (GC-TCD) subsequently. Eight different inorganic salts have been evaluated, likewise the application

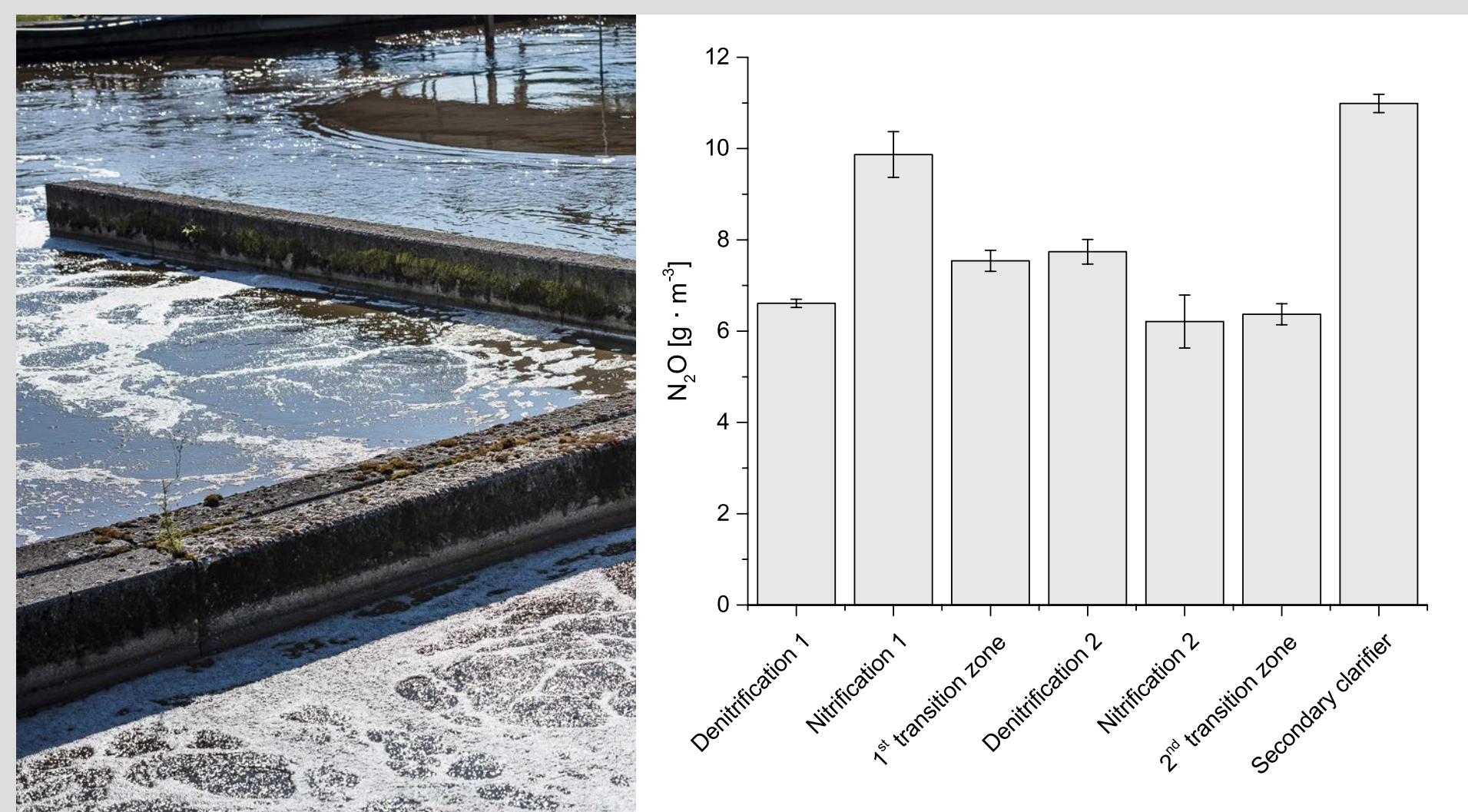
of ultrasound. By addition of sodium bromide (NaBr) the best recovery rate of about 98 % ( $= 1.14 \pm 0.05 \text{ kg m}^{-3}$ )  $N_2O$  from a saturated stock solution ( $1.16 \text{ kg m}^{-3}$ , 295.85 K and 1 atm) was achieved. Practical applicability of the method has been demonstrated by applying NaBr to grab samples from a municipal wastewater treatment plant.

The solubility of  $N_2O$  in the liquid phase is determined by three factors: temperature, environmental pressure above the liquid phase and the salinity. Taking advantage on the latter one forms the basis for the salt-assisted stripping methodology. When  $N_2O$  becomes dissolved a hydration shell surrounding the gas molecules is formed. This effect is mainly driven by dipole-dipole interactions between  $H_2O$  and  $N_2O$  molecules. Dipole-dipole interactions are weak forces compared to ion-dipole ones, hence the addition of inorganic salts will cause  $N_2O$  to strip out. Once it has transferred from the liquid phase into the gas phase it can easily be quantified using gas chromatography.



**Fig. 1**  $N_2O$  recovery concentrations [kg m<sup>-3</sup>] after applying inorganic salts (chemical approach) and an ultrasonic bath (physical approach) for stripping. The maximum possible recovery concentration was 1.16 kg m<sup>-3</sup> based on water temperature. Picture: Rubin 2/2017, © Damian Gorczany.

From all of the tested inorganic salts NaBr showed the best stripping effect (Fig. 1). When applying NaBr,  $1.14 \pm 0.05 \text{ kg m}^{-3}$  could be recovered, which is equal to 98 % of the total possible recover concentration that was  $1.16 \text{ kg m}^{-3}$  at 295.85 K and 1 atm. At WWTP level  $N_2O$  could be reliably measured by the proposed analytical procedure (Fig. 2). The highest  $N_2O$  concentration was found in the secondary clarifier with  $10.99 \pm 0.20 \text{ g m}^{-3}$ . Besides,  $N_2O$  could be quantified in the activated sludge process with up to  $9.87 \pm 0.50 \text{ g m}^{-3}$  yielding  $7.75 \text{ g } N_2O \text{ PE}^{-1} \text{ a}^{-1}$  specifically for the investigated WWTP.



**Fig. 2** Results from validating the practical applicability of NaBr for  $N_2O$  stripping. Picture: Rubin 2/2017, © Damian Gorczany.

- The salting-out approach is a feasible, rapid and accurate method to quantify  $N_2O$  where it is actually produced – in the liquid phase.
- In combination with established gas chromatographic methods for  $N_2O$  quantification, it offers a feasible alternative to existing monitoring devices such as optical online sensors.
- Salt-induced stripping in combination with gas chromatography is an approach that can easily be applied to access liquid  $N_2O$  concentrations at wastewater treatment plants in dependency of hydraulic retention times (HRT), or at various treatment units at any point of time, as well as in dependency of diurnal and annual variations.
- Due to the complete stripping of  $N_2O$  the method is not prone to matrix effects and the diurnal variation of wastewater.
- In contrast to similar, established approaches such as headspace analysis, the proposed method does not rely on air-water partitioning coefficients that are currently not available for  $N_2O$  and wastewater.
- It is likely that the current method will even work for other greenhouse gases of concern with lower solubilities than  $N_2O$ , such as methane ( $CH_4$ ) and for other matrices such as sewage sludge.

